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FINAL TECHNICAL REPORT

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ABSTRACT

The electronic interactions responsible for the observed electronically induced phase transformations in several important classes of materials were investigated theoretically in close collaboration with experimental programs at other institutions. These include destruction of superconductivity and onset of a normal magnetic state at low temperatures in ternary rare-earth superconducting compounds and the possible occurrence of a new mixed phase, the origin of the phase transition to the superconducting phase in the Chevrel compounds, the possibility of excitonic superconductivity in CuCl_2 , the origin of phonon anomalies in Pd and Pt metals, electronically driven phonon instabilities and the formation of charge density waves in layered transition metal dichalcogenides

I. INTRODUCTION

This Final Technical Report under AFOSR Grant No. 76-2948 covers a highly prolific period of solid research accomplishments marked especially by their forefront and innovative character. New theoretical/computational methods were developed and applied to the study of electronically driven phase transitions in a wide variety of materials. To report in detail on all these accomplishments would require a massive tome. Since four interim annual technical reports have already been submitted, this Report will summarize progress and accomplishments achieved on several projects in this last year.

The high level of productivity is seen from the appended total list of publications for the entire period - numbering some 50 publications in all. This is but one measure of the accomplishments and recognition achieved. It does not include the numerous invited (and contributed) papers presented at national and international conferences, invited seminars and colloquia presented at universities and national labs, international conferences and seminars which the PI helped to organize (often as chairman or co-chairman), service on national and international scientific committees, etc.

II. RESEARCH OBJECTIVES

The aims and purposes of this research were to (i) develop sophisticated theoretical and computational methods which would (ii) permit the accurate theoretical determination of the electronic structure of complex systems and the origin of their electronically driven phase transitions. It is widely recognized that the many important and increasingly complex properties of such materials require the most developed form of the quantum theory of matter. Unique information derived from such studies is increasingly attracting the interest of material scientists seeking solutions and/or understanding of phenomena (including some in the more classical metallurgical domain) thought previously to be too complex for first principles theoretical treatment.

III. METHODS AND APPROACH

The newly discovered exotic phenomena in complex materials such as the rare-earth ternary superconductors have challenged the traditional understanding acquired from approximate theoretical treatments within the quantum theory of matter. This challenge has been met by recent developments of the energy band method which have made it an increasingly powerful, sophisticated, and successful tool of the solid state physicist. The success of the energy band approach is based on the work of Hohenberg, Kohn and Sham in developing the local density functional formalism for investigating various ground state properties of solids. Aside from providing a rigorous basis and justification of the single particle energy band description, it has led to accurate tractable computational schemes for describing them from first principles.

Because of the importance of charge transfer between different atom species, meaningful results are possible only if carried out self-consistently. For magnetic systems, local spin density functional theory carried out as self-consistent spin-polarized energy band calculations (different potentials for different spins) are obviously necessary. Both self-consistency (which requires iterative procedures to obtain convergence) and spin polarization make these calculations enormously more complicated and time consuming and so have been carried out, using traditional methods, only on simple systems.

Our work has been at the forefront of these developments in the local density theory-energy band approach. Several novel schemes, such as the self-consistent linear combination of atomic orbitals (LCAO) method and the self-consistent linearized augmented plane wave (APW) and the self-consistent spin-polarized linear muffin tin orbital (LMTO) methods are now among the basic methods we have developed and are using in our fundamental theoretical studies of both bulk solids and surfaces. The examples described later under progress indicate some

of the richness and variety of properties and phenomena which are being and can be studied today. Comparisons with experiment provide today such a demanding test of the predictions of one-electron theory that our work has the additional virtue in permitting, by the comparison with experiment, 'accurate determinations of the relative magnitude and importance of many-body effects in real solids.

IV. SCIENTIFIC SIGNIFICANCE OR IMPACT ON TECHNOLOGY

The important phenomena of phase transitions, superconductivity and magnetism in the complex systems being investigated are highly exciting from the scientific point of view. In addition, these materials are also important technologically in that they have potential device applications, and so the theoretical knowledge obtained from the underlying physical phenomena may have important technological consequences. To give one example, the Chevrel phase ternary molybdenum chalcogenides are examples of compounds with remarkable physical properties. Not only do they present the highest superconducting transition temperatures found for any ternary system so far ($\sim 14\text{K}$), but they also have critical magnetic fields ($\sim 600\text{ kG}$) which are by far the highest ones ever observed. This latter property has created the main interest in these materials because they could be suitable for certain technological applications such as the production of very high magnetic fields. Some of their properties are related to their unusual phonon spectrum or to the extreme pressure sensitivity of their transition temperatures and others to the occurrence of lattice instabilities at low temperatures which are often believed to be closely related to superconductivity in general. Hence the additional excitement caused by the observation that the addition of magnetic impurities like Eu causes a large increase in the critical field. Most recently, major interest has focussed on the magnetic behavior at low temperatures and its influence on superconductivity including (i) the possible coexistence of superconductivity and magnetic order at low temperatures and (ii) the observation of reentrant magnetism from the superconducting state back to the normal state at low temperatures. Our own work has given the first understanding of the complex

phenomena associated with the origin of magnetism and/or superconductivity in these materials and appears to explain the very high upper critical fields observed in these systems.

V. RECENT PROGRESS ACHIEVED

A. High Field Superconductivity of Chevrel Phase Compounds

The properties of the Chevrel phase compounds, particularly SnMo_6S_8 and EuMo_6S_8 , are of great scientific and technological interest because of their unusual high magnetic field properties including the enhancement of the upper critical field H_{c2} observed when Eu is added to SnMo_6S_8 . For example, up to a Eu concentration of 0.5, T_c is hardly changed with the depression occurring abruptly only at high concentration. This behavior is contrary to observations on all other materials with the addition of a local magnetic moment and the theory of Abrikosov and Gor'kov.

We have carried out self-consistent LMO energy band calculations for these compounds including all electrons in all 15 atoms per unit cell. As a result of these unique studies, we have demonstrated that superconductivity is due to the high Mo d-band density of states at the Fermi energy resulting from the unusual large charge transfer of Mo electrons to the chalcogens. There is also a large charge transfer from the metal site to the cluster giving Eu essentially no occupied conduction bands and for Eu a typically divalent isomer shift in very good agreement with the experiments of Dunlap, et al. Furthermore, we find, also in close agreement with their spin lattice relaxation rate measurements, that the conduction electron density of states, and hence $[JN(E_F)]$,

is reduced by an order of magnitude from its metallic state value. This results in a very weak coupling of the 4f electrons to the conduction electrons and hence only a very weak Ruderman-Kittel interaction which leaves the dominant magnetic interaction to be the weak dipole interaction surmised by Redi and Anderson.

B. Isostructural Phase Transition in fcc La and High Superconducting Transition Temperature

Fcc La shows, at low temperature under pressure, an apparently isostructural phase transition at ~ 53 kbars. The importance of understanding this transition is related to the importance of the observed high superconducting transition temperature, T_c , and its unusually large pressure derivative, dT_c/dp . This latter observation has raised wide speculation that a new pairing mechanism involving f electrons was operative.

We have been carrying out extensive studies, as proposed last year, of the electronic structure and properties of fcc La at ambient and high pressures by means of a self-consistent relativistic LAPW study of the band structure of fcc La at three values of the lattice constant. An important feature of this approach, especially in view of the care which is necessary when treating f states, is that few restrictions (i.e. constraints) are built in; for example, the charge density, and the resulting self-consistent potential, are allowed a general (i.e., non-muffin-tin) form, and important relativistic effects are included either exactly (mass-velocity and Darwin terms) or non-perturbatively (spin-orbit interaction).

We find that the f bands lie ~ 2 -2.5 eV above the Fermi level and are ~ 1 eV wide, resulting in a very small (0.05 electrons) localized f occupation. Under pressure the f bands rise and broaden appreciably, resulting in only a slight increase in f occupation. The rigid-muffin-tin approximation for the electron-phonon interaction, λ , overestimates the superconducting transition temperature T_c by 40%, but we find that the drastic increase in T_c under pressure can be attributed primarily to changes in the electronic stiffness. Structural transitions which occur at 25 kbar and 53 kbar may be related to changes in Fermi surface topology which we find to occur approximately at these pressures. Indeed, the theoretically observed behavior of the bands under pressure strongly suggests a Lifshitz-Dagens structural instability due to a strongly d-f hybridized band crossing E_F in both pressure ranges.

C. Origin and Nature of the α - γ Phase Transition in Cerium

As discussed in our proposal last year, cerium metal has a number of unusual but not yet well understood properties which are thought to arise from the nature and character of its 4f electrons. These unique properties, which include a phase diagram with at least five solid phases, the occurrence of antiferromagnetism at low pressures and superconductivity in the high pressure phases, have stimulated much experimental and theoretical work. Theoretical efforts have been mainly concerned with model investigations of the isostructural α - γ transition. This work has emphasized the local character of the 4f states while describing the band structure by relatively crude models.

We have undertaken relativistic, self-consistent linearized augmented plane wave (LAPW) band structure calculations for fcc cerium at various values of the lattice constant equal to or greater than that of α -cerium in order to study the isostructural α - γ phase transition which occurs under pressure

In contradiction to the 4f electron promotional model of the transition, the results yield essentially one 4f electron to be occupied in each phase but with the 4f wave function somewhat less localized, and therefore more bandlike, in the "collapsed" α phase. A singly occupied 4f state is shown to be consistent with the available experimental data. The weaker bonding of the 4f electrons, compared to that of the 6s-5d valence electrons, accounts for α -cerium appearing to have 3.5-3.7 bonding electrons. Our calculation of the superconducting transition temperature, T_c , suggests that a small spin fluctuation contribution detrimental to superconductivity is necessary to account for the very low value of T_c in α -Ce.

D. Surface Phase Transitions in W(001)

The unusual phase transition of the (001) surface of tungsten metal has been investigated using results of our self-consistent calculation for the tungsten (001) surface, obtained by means of our recently developed self-consistent linearized-augmented-plane-wave (LAPW) method for thin films. Above $T_c \simeq 300\text{K}$ the ideal (1x1) surfaces are observed, and the reconstructed c(2x2) and c(2.2x2.2) superlattices are observed for W and Mo, respectively, below T_c .

Our work has centered on the generally accepted view, which we have developed, that instabilities in the electronic ground state with respect to a spatially inhomogeneous perturbation are associated with sharp structure in the electronic generalized susceptibility function. In bulk systems, such structure has been related to the existence of parallel pieces of Fermi surfaces (nesting features) and is responsible for the occurrence of spin density waves in chromium metal and spiral spin structures in the rare-earth metals. Using

our self-consistent results for W(100) we have calculated the layer-projected generalized susceptibility function to detect such incipient instabilities. We find that electronic surface states or surface resonance states near the Fermi energy appear to drive the phase transition through a surface phonon softening and a gapping of the two-dimensional Fermi surface. This provides, for the first time, theoretical evidence that the phase transition may indeed be electronically driven — in agreement with the earlier proposal of P.W. Anderson (Nobel Laureate) and Tosatti.

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Relativistic electron densities and isomer shifts in transition-metal ions*

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Relative isomer shifts of 3d, 4d, and 5d ions are obtained by calculation of atomic electron charge densities, using numerical Hartree-Fock and multiconfiguration Dirac-Fock theory, with exact exchange, to describe the ionic systems. The relativistic calculations, for both point and finite nucleus models, are compared with results obtained from the nonrelativistic calculations augmented by one-electron relativistic corrections. The relativistic charge densities and experimental isomer shifts are employed to deduce estimates of changes in mean square nuclear radii.

I. INTRODUCTION

With the discovery of the Mössbauer effect, it was widely recognized that the measurement of isomer shifts had great potential for becoming an important tool for the study of both nuclear and electronic properties of atoms in various environments.^{1,2} The isomer shift provides a measure of the product of the difference of mean-square radii of two nuclear isomers and the difference in electron density in the region of the nucleus, between two isomeric atoms in different chemical environments. Whereas these quantities are impossible to measure by themselves, isomer-shift measurements coupled with independent information about either the isomeric radii or the electronic densities provides knowledge of the other. Thus, in principle, a measurement of the isomer shift between two ions in different environments, and an accurate calculation of the electronic charge densities would allow one to deduce the change in nuclear isomeric radii. Unfortunately, the enormous difficulties involved in determining theoretically either electron or nuclear densities has left the promised potential largely unfulfilled.

In the face of the greater difficulties inherent in the state of nuclear theory, some progress has been made in this field by assuming, as a first crude approximation, that the electronic charge difference between several ions in different chemical environments may be ascribed to a change in ionicity.^{3,4} Thus, Hartree-Fock calculations have been performed, on various charge states of an atom⁵ and the resultant electron charge densities

at the nucleus are then used to estimate relative isomer shifts. Implicit in this procedure is the assumption that the difference in nuclear radii is the same for the various ionic states. Using these calibrations, comparison with experimental isomer shifts then provides estimates of other effects due to the chemical environment, such as ligand bonding and electron correlations.

The isomer shift S_{AB} between a source B and an absorber A is given by the well-known expression^{2,6,7}

$$S_{AB} = (2\pi c/3E_\gamma) Z e^2 [|\psi_A(0)|^2 - |\psi_B(0)|^2] \delta \langle r^2 \rangle, \quad (1)$$

where E_γ is the γ -ray energy, Z is the nuclear charge, $e|\psi_A(0)|^2$ and $e|\psi_B(0)|^2$ are the electron charge densities at the nuclei of the source and the absorber, respectively, and $\delta \langle r^2 \rangle$ is the change in mean-square nuclear-charge radius between isomers. For a given pair of isomers, $\delta \langle r^2 \rangle$ is constant, and $|\psi_A(0)|^2 - |\psi_B(0)|^2$ measures the change in electronic charge densities as the ions are placed in different compounds. Implicit in this formulation are the assumptions that the electron density is constant over the nuclear volume and that the change in electronic state (ψ_A to ψ_B) does not affect the nuclear densities. Thus, the calculated values of S_{AB} for various charge states of the same isomers yield the dependence of isomer shift on changes in atomic electron density; the differences between measured and calculated S_{AB} allow one to deduce the additional effects of the chemical environment.

This paper reports results of a study of the rela-

ELECTRONIC STRUCTURE, FIELD-INDUCED MAGNETIZATION DENSITY AND NEUTRON MAGNETIC FORM FACTOR OF PALLADIUM[†]

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The magnetic field induced magnetization density and neutron magnetic form factor of Pd metal is obtained from an *ab initio* APW energy band study of its electronic structure and properties. The magnetization consists of the spin density calculated for states on the Fermi surface and a much smaller orbital contribution. The solid state wavefunctions are found to yield a spatial localization of the spin density which is greater than that of the very contracted Hartree–Fock density of the free Pd²⁺ ion. The theoretical magnetic form factor, which is dominated by the contribution of the fifth band, is found to be in excellent agreement with the measurements of Cable, Wollan, Felcher, Brun and Hornfieldt.

1. Introduction

The transition metals have been studied more extensively than have other metal groups in the periodic table. Their electronic structure and properties have been measured using a variety of experimental methods which yield both macroscopic information (e.g. magnetization, magnetic susceptibility and specific heat) and microscopic information (e.g. de Haas–van Alphen, magnetoresistance, optical reflectivity, photoemission) which have been related directly to the electronic band structure. By contrast, there are few experiments which yield direct information about the nature of wavefunctions in these metals. The determination of the neutron magnetic form factor in magnetically ordered systems which gives the Fourier transform of the magnetization density is perhaps the one

outstanding exception. While theory has been successful, in most cases, in yielding an adequate account of the energy dependent properties, it has had distinctly poorer success in explaining observed form factors because of the greater theoretical (and computational) problem associated with treating magnetically ordered systems. [In ferromagnets, one must include the exchange interactions between all Bloch electrons (which results in so-called spin polarized bands) which are treated only approximately by spin polarized band calculations and obtain the magnetization density as the difference between spin-up and spin-down band magnetization densities each obtained as sums over all occupied (spin) states.] The magnetic form factor studies [1–3] have found that for the 3d transition metal ferromagnets the spin densities are considerably contracted spatially and are well represented by those for the Hartree–Fock ions in the +2 ionization state [4]. By contrast, the spin densities obtained from band-structure calculations yield form factors which are not in as good agreement with experiment [5–8].

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Role of matrix elements in the theoretical determination of generalized susceptibilities in metals*

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The role of matrix elements in the calculation of the generalized susceptibilities $\chi(\vec{q})$ of metals is discussed using the results of an augmented-plane-wave energy-band calculation for the eigenvalues and eigenfunctions of Sc metal. The inclusion of the oscillator strength matrix elements is found to significantly alter the structure obtained for $\chi(\vec{q})$ in the constant-matrix-element approximation. The effect of local-field corrections on the phonon anomaly in Sc and the observed magnetic ordering of dilute rare-earth Sc alloys are described; in the latter case, a crude estimate of this effect is found to restore a (broad) peak in $\chi(\vec{q})$ at $\vec{q} \approx [0, 0, 0.5(\pi/c)]$, in good agreement with experiment.

I. INTRODUCTION

The generalized susceptibility function which measures the response of the system to an external probe is central to the understanding of many physical phenomena in solids. Although the calculations of these response functions are rather involved, the considerable refinement in the computational techniques which has been achieved in recent years makes accurate *ab initio* studies possible. The greater realization that (except perhaps for very simple metals) the true response function of a real solid is quite unlike the frequently used free-electron Lindhard function has led to attempts to include the real band-structure effects^{1,2} into the calculations. In the random-phase approximation (RPA), the dynamic, i.e., wave-vector and frequency dependent, electron-electron dielectric function is written

$$\epsilon(\vec{q}, \omega) = 1 + (4\pi e^2 / \Omega q^2) \chi(\vec{q}, \omega), \quad (1)$$

where Ω is the crystal volume and

$$\chi(\vec{q}, \omega) = \chi_1(\vec{q}, \omega) + i\chi_2(\vec{q}, \omega) \quad (2)$$

$$= - \sum_{kk'} \frac{n_k - n_{k'}}{E_k - E_{k'} + \hbar\omega + i0} \times \langle \psi_k | e^{-i\vec{q} \cdot \vec{r}} | \psi_{k'} \rangle \langle \psi_{k'} | e^{i\vec{q} \cdot \vec{r}} | \psi_k \rangle. \quad (3)$$

Here E_k is the Bloch energy of the state k with Bloch function ψ_k and occupation number n_k ; k includes both the band index and the wave vector $\vec{k}$ which is restricted to the first Brillouin zone. The oscillator-strength matrix element

$$M_{kk'}(\vec{q}) = \langle \psi_k | e^{-i\vec{q} \cdot \vec{r}} | \psi_{k'} \rangle, \quad (4)$$

imposes the restriction $\vec{k}' = \vec{k} + \vec{q} + \vec{G}$, where $\vec{G}$ is a reciprocal-lattice vector; ω denotes the frequency of the external field, and $\chi(\vec{q}, \omega)$ is the bare sus-

ceptibility of the solid, i.e., the effects due to local fields are not included. The zeros of $\epsilon_1(\vec{q}, \omega) = \text{Re}[\epsilon(\vec{q}, \omega)]$ determine the plasmon dispersion relation and $\epsilon_2(\vec{q}, \omega) = \text{Im}[\epsilon(\vec{q}, \omega)]$ is related to many properties including the dynamic form factor $S(\vec{q}, \omega)$, the optical conductivity, and the optical reflectivity.³

The static response function $\chi(\vec{q})$, i.e., the response function for $\omega = 0$ is itself of very great interest because of its possible role in causing electronically driven instabilities which are manifested as spin-density waves, charge-density waves, or in structural phase transformations. From Eq. (3) we can write down the expression for $\chi(\vec{q})$:

$$\begin{aligned} \chi(\vec{q}) &= \chi(\vec{q}, \omega = 0) \\ &= - \sum_{kk'} \frac{n_k - n_{k'}}{E_k - E_{k'}} |M_{kk'}(\vec{q})|^2 \\ &= -2 \sum_{kk'} \frac{n_k(1 - n_{k'})}{E_k - E_{k'}} |M_{kk'}(\vec{q})|^2. \end{aligned} \quad (5)$$

It has been argued that due to the "nesting" features, i.e., the existence of flat and parallel areas of the Fermi surface, the denominator in Eq. (5), will tend to be vanishingly small, giving rise to a large peak in $\chi(\vec{q})$ at the nesting wave vector. Such a large peak in $\chi(\vec{q})$ coupled with exchange enhancement effects in, for instance, paramagnetic chromium,^{4,5} has been thought to be the main reason for driving the paramagnetic phase unstable with respect to an antiferromagnetic phase, and has since been used by a number of workers to account for various other instabilities related to Fermi-surface geometry. The occurrence of anomalies in phonon spectra of metals has also been related in a similar way to

Electronic structure and properties of EuO and EuS in the molecular-cluster approximation*

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Molecular-cluster models are developed to describe ground-state properties of EuO and EuS in the Hartree-Fock-Slater one-electron approximation. Spin-polarized $(\text{EuX})^{0+}$ complexes are examined using both neutral- and ionic-model potentials which incorporate a part of the effect of the crystalline environment. Self-consistent calculations are made for $(\text{EuO}_6)^{0+}$. From the charge and spin densities, the transferred hyperfine field at the O site in EuO is found to be -8 ± 2 kG and a small solid-state bonding effect is predicted for the neutron magnetic form factor. The pressure dependence of the charge density at the Eu nucleus in EuS is determined as a function of bond length in the $(\text{EuS}_6)^{0+}$ cluster and used to obtain from the experimental data an isomer-shift calibration constant $\alpha = -0.48 \text{ a.u. mm/sec}$. The one-electron energy levels of the $(\text{EuO}_6)^{0+}$ cluster are found to be in good agreement with the augmented-plane-wave results of Cho when both calculations are performed with similar model potentials. The extension to self-consistency leads to significant energy-level rearrangement which indicates the importance of final-state relaxation and Coulomb correlation effects in the interpretation of experimental spectra.

I. INTRODUCTION

The europium chalcogenides EuX ($X = \text{O}, \text{S}, \text{Se}, \text{and Te}$), an important class of magnetic semiconductors, have magnetic ordering properties which vary from ferromagnetic (EuO) to antiferromagnetic (EuTe), and exhibit a red shift in their optical spectra with increasing magnetic order. Insulators in the pure state, they become semiconducting when doped with rare-earth impurities, and show large negative magnetoresistances near their transition temperatures. A review of the experimental properties and of the theoretical interpretations has been given by Methfessel and Mattis.¹ The general picture which has emerged is one of magnetic moments localized on Eu^{2+} ions with a high-spin configuration $(4f^7)(4f^7)^0$. These moments are coupled by an antiferromagnetic 180° superexchange interaction, acting through the X^{2-} ligand ions, and by a ferromagnetic exchange which depends on the covalent mixing of Eu $4f$ orbitals with the unoccupied $5d$ orbitals on nearest-neighbor Eu sites. Now most rare earths are trivalent yielding, in their respective monochalcogenides, two electrons to the ligand ion, and one to the conduction band, so that the compounds are metallic. Added as impurities to the insulating Eu chalcogenides, rare-earth ions populate the conduction band with a fraction of their third valence electrons. Since the conduction band is involved in magnetic ordering (as shown by the magneto-optical red shift, and as expected from the nature of the ferromagnetic interaction), the phenomena associated with the magnetic phase transition are modified and the negative magnetoresistance effects are obtained. More detailed elucidation of these effects has been attempted in terms

of both impurity and energy-band models,¹ but no complete theory can be said to have been found.

The spin-polarized one-electron theory has been quite successfully applied in interpreting magnetic properties, optical data, and photoemission spectra of lighter materials, notably the $3d$ metals and their compounds. While the limitations of such a model are evident, for example, in their inability to predict correctly multiplet splittings observed, it is clearly worthwhile to investigate their applicability to open-shell rare-earth systems.

This paper describes the results of theoretical molecular-cluster calculations for EuO and EuS in the Hartree-Fock-Slater (HFS) approximation. Both model-potential and self-consistent studies are undertaken to better understand the role of "localized" $4f$ electrons in the bonding and magnetic interactions of rare-earth compounds. Several ground-state properties of these systems, notably charge and spin densities, are used to determine such experimental properties as neutron magnetic form factors and transferred hyperfine fields. Results for the pressure dependence of the electron density at the Eu nucleus in EuS are used in conjunction with the experimental Mössbauer isomer-shift data of Kalvius *et al.*² to determine α , the isomer-shift calibration constant, for ^{151}Eu .

As is well known, parametrized band-structure models^{3,4} have been presented which are compatible with a one-electron interpretation of optical, x-ray, photoemission, and magnetic data for the europium chalcogenides. Thus, the applicability of the one-electron HFS model to the description of some of these excited-state properties is also tested in this work, with special attention to $4f$

Combined Fourier Transform and Discrete Variational Method Approach to the Self-Consistent Solution of the Electronic Band Structure Problem within the Local Density Formalism

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Abstract

This novel approach combines a discrete variational treatment of all potential terms arising from the superposition of the spherical overlapping atomic charge densities with a rapidly convergent Fourier series representation of all multicenter nonspherical potential terms. The basis set consists of the exact numerical atomic valence orbitals, augmented by charge transfer states, virtual atomic states, and single analytic Slater orbitals for increased variational flexibility. The initial potential is a non-muffin-tin overlapping atomic potential including nongradient local density exchange and correlation terms. Full self-consistency is obtained by a procedure that combines an iterative scheme within the superposition model with a self-consistent optimization of the Fourier components of the nonspherical charge density terms. Ground-state properties such as structure factors and cohesive energy are computed. The results for diamond show very good agreement with experiment. Comparison of the results with the Hartree-Fock calculation is discussed.

1. Introduction

It is now widely recognized that energy band theory has become a powerful and sophisticated method for studying a wide spectrum of solid-state properties. The proliferation of energy band schemes and their application to increasingly diverse problems attests to the current popularity of band theory. Increasingly too, however, its very success in describing a host of sophisticated new solid-state experiments has led to a "tide of rising expectations" which the various existing computational energy band schemes (such as APW, OPW, KKR, etc.) have been hard pressed to satisfy. In addition to challenging experiments performed on important materials having complex crystallographic structures, these new experiments have demanded not only theoretical descriptions of high-resolution eigenvalue phenomena, but also detailed and precise solid-state wave functions with which to determine the expectation values of different observable operators. Such a demanding test of the predictions of one-electron theory has the additional virtue in permitting, by their comparison with experiment, accurate determinations of the relative magnitude and importance of many-body effects in real solids.

In this paper we describe a new approach to the fully self-consistent solution of the one-particle equations in a periodic solid within the local density functional formalism [1]. It is specifically designed and developed to incorporate special features with which to overcome difficulties encountered by other methods. Specifically, as will be shown

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Band-Structure Contributions to X-Ray Emission and Absorption Spectra and Edges in Magnesium*

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The soft-x-ray $L_{2,3}$ emission and absorption spectra of Mg metal have been determined by means of high-resolution *ab initio* augmented-plane-wave calculations. The inclusion of transition-matrix elements calculated from the augmented-plane-wave wave functions changes the sharp structure found in the joint density of states, yields an $L_{2,3}$ emission spectrum in good agreement with experiment, and indicates that band-structure effects play an important role in the observed x-ray threshold shape.

Despite both intensive and extensive efforts, the theoretical understanding of x-ray emission and absorption edges in metals is still a subject of controversy and disagreement mainly because of the differing roles assigned to band-structure (one-electron) and conduction-electron-core-hole, final-state interaction (many-body) effects.^{1,2} In the simple metals Li, Be, Na, Mg, and Al the shapes of the observed threshold edges in both emission and absorption fail to exhibit the sharp step-function edges expected to be characteristic of free-electron metals. Instead, experimentally determined edges are either sharp and peaked at

threshold (e.g., the $L_{2,3}$ edges of Na, Mg, and Al) or broad and rounded (e.g., the K edges of Li, Be, Mg, and Al) over energies ≈ 1 eV. Since these features and especially the sharply peaked nature of the $L_{2,3}$ edges do not seem explicable in a one-electron theory based on the free-electron model, many-body models were developed by Mahan³ and Nozières and de Dominicis⁴ in which the conduction-electron-core-hole interactions play a central role. These theories predict threshold edges whose shapes are characterized by threshold exponents α_0 (for $L_{2,3}$ edges) and α_1 (for K edges); for photoemission the asymmetry

Direct Correlation of Phonon Anomalies in NbC with Fermi-Surface-Induced Maxima in Generalized Susceptibilities*

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The generalized susceptibility of NbC, determined from its augmented plane wave energy band structure (with constant matrix elements), shows large maxima, arising in large part from Fermi surface "nesting," to occur at precisely those $\vec{q}$ values at which soft modes have been found in the phonon acoustic branches by Smith. These maxima can be represented by a warped cube of dimension $\sim 1.2(2\pi/a)$ in momentum space, in striking agreement with the soft mode surface proposed by Weber.

Long known for their remarkable properties such as high melting points and ultrahardness, the transition-metal carbides and nitrides are considered an important class of materials because of the occurrence of high superconducting transition temperatures, T_c . The systematic neutron-scattering determinations of phonon dispersion curves $\omega(\vec{q})$ in the carbides of the transition-metal IV and V series by Smith and Gläser¹ revealed the existence of soft phonons and led to attempts to correlate these soft-phonon modes to the high T_c values. Such a direct correlation between lattice instabilities and high T_c 's is becoming more accepted; an important problem is the theoretical understanding of the origin of phonon-mode softening in superconductors. While rigorous formulations of dynamical matrix theory have been proposed, such as the work of Sinha,² based on the augmented plane-wave (APW) method, no *ab initio* calculational predictions of phonon spectra have been reported. A phenomenological model theory utilizing the modified shell and supercell model has been employed, particularly

for NbC, by Weber, Bilz, and Schröder.³ Weber⁴ was able to show that the introduction of the supercell interactions, which describe the d - d metal interaction, is essential for obtaining the observed dips in $\omega(\vec{q})$. An important result was obtained by Mostoller⁵ when he showed that the general shapes of the dispersion curves, but not the phonon anomalies, could be obtained using a free-electron dielectric screening function and describing the electron-ion interaction in a pseudopotential representation. More recently, Sinha and Harmon⁶ were able to reproduce the longitudinal branches of the phonon dispersion curves in Nb and NbC by using a local pseudopotential to represent the electron-ion interaction. In this work, which necessarily introduced other approximations, the dielectric screening matrix was expressed in terms of several parameters which were determined by fitting the calculated longitudinal modes to the experimental values. While noting the possible importance of structure in the diagonal d -band part of the susceptibility function, Sinha and Harmon⁶ assumed $\chi(\vec{q})$ to be $\vec{q}$ in-

ELECTRONICALLY DRIVEN PHONON ANOMALIES IN TRANSITION METAL CARBIDES*

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Large maxima in the generalized susceptibility of $\chi(q)$ of TaC calculated from its APW band structure are found to correlate very well with observed soft phonon modes. Such maxima are not found for HfC where phonon anomalies are not observed.

Systematic neutron scattering determinations of phonon dispersion curves $\omega(q)$ in the carbides of the transition metal IV and V series by Smith and Glaser [1] revealed the existence of soft phonons and led to attempts to correlate these phonon anomalies to their observed high superconducting transition temperatures, T_c . By contrast, phonon anomalies are not observed in low T_c (< 0.05 K) compounds such as HfC and ZrC. Theoretical efforts to understand phonon dispersion curves of the transition metal carbides have been based either on phenomenological models [2-4] or parameterized theories [5,6] as *ab initio* calculations of the dynamical matrix within a microscopic formulation are still not available. We have recently reported [7] that a detailed *ab initio* study of the generalized susceptibility, $\chi(q)$, of NbC, determined from its augmented plane wave (APW) energy band structure, shows large maxima arising (in part) from Fermi surface "nesting", to occur at precisely those q values at which minima (soft modes) have been found in the phonon acoustic branches by Smith [1]. These maxima can be represented by a warped cube of dimension $\sim 1.2 (2\pi/a)$ in momentum space, in striking agreement

with the soft mode surface, proposed phenomenologically by Weber [3].

In this letter, we report results of similar investigations of TaC which is isoelectronic to NbC, has a $T_c = 10.35$ K (vs 11.1 K for NbC) and also shows strong phonon anomalies. As in NbC we find large maxima in $\chi(q)$ at precisely those q values at which the soft modes have been observed [1]. By contrast, the calculated $\chi(q)$ for HfC (based on a rigid band shift of E_F in the TaC band structure) shows no maxima and hence no phonon softening - again in agreement with experiment.

It has long been known that the screening of a phonon mode with wave vector q can be strongly enhanced by a large scattering of the conduction electrons across "nesting" portions of the Fermi surface, spanned by the vector q . Thus, the generalized function $\chi(q)$ plays an important role in the lattice dynamics of the system, and, under certain simplifying assumptions, it can be shown that if χ becomes large, the renormalized phonon frequencies (due to electron-phonon interaction) can become small and consequently, soft phonon modes (or lattice instabilities) can be expected. In the constant matrix element approximation, $\chi(q)$ is defined as:

$$\chi(q) = - \sum_{n, n'} (f_k^n - f_{k+q}^{n'}) / (E_k^n - E_{k+q}^{n'}), \quad (1)$$

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U GENERALIZED SUSCEPTIBILITIES AND ELECTRONICALLY DRIVEN PHONON ANOMALIES
IN TRANSITION METAL CARBIDES*

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ABSTRACT

Large maxima in the generalized susceptibility, $\chi(\vec{q})$ of NbC and TaC calculated from their APW band structures are found to correlate very well with soft phonon modes observed by Smith. Such maxima are not found for ZrC and HfC where phonon anomalies are not observed.

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THEORETICAL DETERMINATIONS OF MAGNETIZATION DENSITIES AND
NEUTRON MAGNETIC FORM FACTORS IN METALS*

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ABSTRACT

Whereas a variety of experimental methods yield information which has been related directly to the electronic band structure, there are few experiments which yield direct information about the nature of wavefunctions in metals. Perhaps the one outstanding exception is the determination of the neutron magnetic form factor which gives the Fourier transform of the magnetization density. In the past few years, accurate neutron experiments have shown the inadequacy of the commonly used free atom/ion Hartree-Fock form factors. This paper describes recent advances in high resolution energy band studies of APW wavefunctions, magnetization densities, and neutron form factors in metals. Illustrative results obtained in our Laboratory for several important transition and rare-earth metal systems are presented and compared with experiments carried out at ORNL, ANL, and Ames Laboratory. Unlike the case of the ferromagnetic metals, we find very good agreement with experiment for the paramagnetic metals studied to date.

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ROLE OF BAND STRUCTURE ON THE X-RAY EDGE-SHAPE IN Na METAL^{*}

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Marked structure found in an APW study of both the density of states and transition matrix elements contributing to the emission, absorption spectra of Na emphasizes the need for including band structure effects in all X-ray edge analyses.

Sodium metal has been widely assumed to be the prototype of a free-electron metal, because its $L_{2,3}$ emission spectrum [1] is free-electron-like, its Fermi surface is spherical, its effective mass is nearly equal to the free-electron mass, and its optical properties are well described by a Drude model. Here we report augmented plane wave (APW) band structure calculations which are consistent with the above-mentioned free electron properties of Na, but which produce significant and qualitative deviations from the free electron picture of sodium's $L_{2,3}$ absorption edge. Our calculations reveal marked structure in both the conduction band density of states and in the core-conduction band dipole matrix elements; they indicate that at least part of what had once been thought to be a many-body threshold anomaly at the $L_{2,3}$ X-ray absorption edge of Na may be a band structure effect; and they call into question all X-ray edge analyses which do not account for band structure effects.

In the one-electron approximation the intensity $I(E)$ for the emission or absorption of X-rays of energy E is given by

$$I(E) = c \int d\mathbf{k} |\langle \psi_c | \nabla | \psi_k \rangle|^2 \delta(E - E_k + E_c) \quad (1)$$

$$= c \int \frac{dS_k}{|\nabla_k E_k|} |\langle \psi_c | \nabla | \psi_k \rangle|^2.$$

Here ψ_k and E_k are, respectively, the Bloch wavefunction and the Bloch energy of an electron with wave vector $\mathbf{k}$ and band index n . ψ_c and E_c are the core function and the core energy of the optical electron (2p state for the $L_{2,3}$ spectrum of Na), and c is a constant of proportionality. The integral in eq. (1) is over a constant energy surface $E = E_k - E_c$ in $\mathbf{k}$ -space. For the emission spectrum, all the energy states E_k are occupied and for the absorption spectrum, the states are unoccupied.

Note from eq. (1) that in the constant transition matrix element (TME) approximation, the intensity depends on the partial density of states (DOS) because of the dipole selection rule and *not* on the total DOS. In fig. 1 we show the partial DOS for Na obtained from our APW calculation. The free-electron DOS is shown in fig. 2 for comparison. We notice that the APW total DOS and the partial DOS are significantly different from their counterparts in the free-electron model, especially at energies above the Fermi energy, E_F . In particular, we find structure in the APW DOS which is absent in the free-electron DOS. The positions of the peaks in our s and d DOS correlate very well with those observed in the $L_{2,3}$ absorption spectra.

From figs. 1 and 2, it is clear that only in the free-electron approximation and neglecting dipole selection rules completely, can one say that the X-ray intensity ought to be parabolic. One notices that the inclusion of dipole selection rules, even for a free-electron

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BAND THEORY OF K-EDGE TRANSITIONS IN Li^*

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APW band calculations of the soft X-ray K absorption and emission spectra of Li are used to discuss the extent to which various conflicting theories and measurements of absorption, emission, electron-energy-loss, and photoemission can be reconciled.

The K X-ray emission and absorption edges of Li, although intensely studied for almost half a century, remain the subject of both experimental and theoretical controversy. Experimentally, a consensus has yet to be reached on (i) whether the high energy emission threshold and the low energy absorption edge are very broad [1-4] (~ 0.4 eV), broad [4, 5] (~ 0.2 eV), or sharp (~ 0.05 eV) [6]; (ii) whether [7] or not [3] absorption and emission edges overlap; (iii) whether [2, 8] or not [3, 9] the edge breadths exhibit more temperature dependence than a Fermi factor; (iv) whether the maximum of the emission spectrum is at threshold or $\approx \frac{1}{2}$ eV below [4, 5] (v) whether [6] or not [3] the absorption spectrum has a relative maximum $\approx \frac{1}{2}$ eV above threshold; (vi) the importance of impurities in shaping the edges [5], and (vii) the quantitative shape of X-ray photoemission lines [8, 10]. Theoretically, there are still debates on the relative importances of (i) band structure effects [11, 12] (ii) Auger broadening, [13], (iii) phonon broadening, [11, 14], (iv) electron-hole scattering resonances [16, 17] and (v) the Nozières-de Dominicis many-body effect [18]. In this paper we report augmented plane wave (APW) band structure calculations for Li, and indicate the extent to which they constrain the

possible interpretations of the K edge spectra of Li. Since similar calculations of the $\text{L}_{2,3}$ X-ray spectra of Mg successfully described the spectral positions of all the observed structures, and produced spectral shapes in excellent semi-quantitative agreement with the data [19], we have considerable confidence in the method's ability to predict semi-quantitatively the shapes of the K emission and absorption spectra of Li.

The X-ray emission or absorption intensity $I(E)$ is given in the one-electron approximation by

$$I(E) \propto \sum_n \int d^3k |\langle \psi_c | \nabla | \psi_{nk} \rangle|^2 \delta(E - E_{nk} + E_c) \quad (1)$$

where ψ_{nk} and E_{nk} are the Bloch function and energy respectively of a conduction electron in band n with wavevector k ; ψ_c is a 1s Herman-Skillman atomic core function of energy E_c , and E_{nk} is restricted to occupied (empty) conduction states for emission (absorption). We have evaluated eq. (1) using eigenvalues and wave functions found at 285 non-equivalent points k in the irreducible 1/48th portion of the Brillouin zone, using the accurate tetrahedron method [20, 21]. This method gives us an advantage over earlier calculations which were limited by histogram techniques. The warped-muffin-tin version of the APW method was employed, permitting the potential to vary in the interstitial region. The potential was computed assuming a lattice constant = 6.5971 au, a superposition of

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Role of electronic structure on observed phonon anomalies of transition-metal carbides*

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The possible role of electronic structure on observed phonon anomalies in high-temperature superconducting transition-metal carbides is studied by means of accurate *ab initio* calculations of the conduction electron response function. From augmented-plane-wave determinations of the electronic band structure, density of states, and Fermi surface of NbC and TaC, the wave-vector-dependent generalized susceptibility, $\chi(\vec{q})$, is calculated in the constant-matrix-element approximation. For both NbC and TaC, $\chi(\vec{q})$ has strong maxima at precisely those $\vec{q}$ values at which soft modes were observed by Smith and Glaser. Maxima in $\chi(\vec{q})$ are predicted for other directions. The locus of these $\vec{q}_{\text{max}}$ values can be represented by a warped cube of dimension $\sim 1.2(2\pi/a)$ in momentum space—in striking agreement with the soft-mode surface proposed phenomenologically by Weber. In sharp contrast, the $\chi(\vec{q})$ calculated for both ZrC and HfC—for which no phonon anomalies have been observed—fall off in all symmetry directions away from the zone center. In agreement with Phillips, we thus interpret the phonon anomalies in the transition-metal carbides as due to an "overscreening" effect resulting from an anomalous increase of the response function of the conduction electrons.

I. INTRODUCTION

The transition-metal carbides and nitrides of the transition-metal IV, V, and VI series owe their wide commercial use to their remarkable physical properties, essentially their great hardness and high melting points—properties usually related to the existence of covalent bonds between the metal and ligand atoms. Aside from their interesting physical properties, the transition-metal carbides (and nitrides) under study are good metallic conductors with conductivities comparable to those of the parent transition metal. The 9 and 10 valence-electron compounds are superconductors with high superconducting transition temperature T_c ($T_c = 11.1$ K for NbC, 10.35 K for TaC, and 16.8 K for NbN), while the 8 valence-electron compounds like ZrC and HfC have a low $T_c \leq 0.05$ K. An empirical correlation between the occurrence of high T_c and the presence of phonon softening in the phonon spectra of the transition-metal carbides (TMC) was pointed out by Smith and Gläser,¹ and Smith² after a systematic study of the phonon dispersion curves of the TMC by coherent inelastic neutron scattering. Such a correlation between phonon anomalies and high values of T_c has been also observed for a large number of *d*-electron superconducting compounds or alloys, e.g., the well-known Nb-Mo system for which Powell *et al.*³ showed that the low- T_c alloy Nb_{0.25}Mo_{0.75} ($T_c \approx 0.04$ K) no longer possesses any phonon anomaly. The A-15 superconductors like V₃Si and Nb₃Sn also display a correlation between high values of T_c and

the occurrence of a low-temperature structural phase transformation⁴ (from the cubic to tetragonal phase), or the existence of anomalous mode softening for the nontransforming compounds. However, even though instability or anomalous phonon softening in many systems appear to be correlated with the occurrence of a high T_c , there also exist some counter examples.⁵ Quantitative relations between these experimental facts are more difficult to draw from first-principles calculations. However, in the existing model theories, such as the strong-coupling theory,⁶ the occurrence of soft phonon modes reflected in the variation of the second moment of the phonon frequency, $\langle \omega^2 \rangle$ (defined in Ref. 6), does not appear to be sufficient to explain the variation of the electron-phonon coupling constant λ which essentially determines T_c .⁷⁻⁹

Since the two physical phenomena, phonon mode softening and high T_c , occur concomitantly in the TMC, it is very important to understand the origin of the phonon anomalies in these materials. In this work, we examine the role played by the response function of the conduction electrons in the occurrence of soft phonon modes, namely, we calculated from first principles the wave-number-dependent generalized susceptibility function $\chi(\vec{q})$ in the constant-matrix-element approximation for the 9 and 8 valence-electron TMC: NbC, TaC, and ZrC, HfC. We find an anomalous increase in the susceptibility of the 8 valence-electron TMC at exactly the $\vec{q}$ values where the anomalies in the phonon spectrum are observed experimentally. By studying the response function along symmetry

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DIRECT CORRELATION OF OBSERVED PHONON ANOMALIES AND MAXIMA IN THE
GENERALIZED SUSCEPTIBILITIES OF TRANSITION METAL CARBIDES*

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The generalized susceptibility, $\chi(\vec{q})$, of both NbC and TaC determined from APW energy band calculations show large maxima to occur at precisely those $q_{\max}$ values at which soft phonon modes were observed by Smith. Maxima in $\chi(\vec{q})$ are predicted for other directions. The locus of these $q_{\max}$ values can be represented by a warped cube of dimension $\sim 1.2(2\pi/a)$ in momentum space - in striking agreement with the soft mode surface proposed phenomenologically by Weber. In sharp contrast, the $\chi(\vec{q})$ calculated for both ZrC

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Local Density Formalism Approach to Cohesive Properties of Solids: Diamond, BN, and LiF

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Abstract

Predictions of the local density formalism approach to cohesive properties of covalently bonded solids (diamond and cubic BN) and prototype ionic system (LiF) are described using results of our recently developed fully self-consistent numerical basis set LCAO-DVM approach. Comparisons with restricted Hartree-Fock results and experiments for cohesive energies and equilibrium lattice constants are presented. Some of the principal bonding mechanisms in these crystals are discussed in terms of the contributions of local exchange and correlation to the binding and the charge redistribution relative to the noninteracting atoms.

1. Introduction

Despite the manifold successes of energy band theory in describing a wide spectrum of solid state properties, the *ab initio* determination of cohesive energies and equilibrium lattice constants remains as a relatively unexplored and underdeveloped field of study. Thus, there has developed considerable interest in the application of the local density formalism (LDF) [1, 2] for the study of the ground state electronic properties of molecules and solids. Investigations of the cohesive properties of small molecules [3-5], metals [6], and rare-gas solids [7] have elucidated the possibilities of obtaining a reasonably accurate description of binding energies and equilibrium geometries by incorporating exchange and correlation effects directly into a one-body potential. Similar studies on compounds, ionic insulators, and covalent semiconductors are beset with the difficulties of having to consider the full (nonmuffin-tin) crystal potential and to explicitly account for charge redistribution and hybridization processes by means of a fully self-consistent treatment. Such effects cannot be conveniently treated within the standard Augmented Plane-Wave (APW) or Kohn-Korringa-Rostoker (KKR) techniques previously used for such studies.

We have recently developed [8, 9] the fully self-consistent numerical basis set linear combination of atomic orbitals (LCAO) discrete variational method (DVM) for treating ground and excited state properties of solids in the LDF approximation. This scheme permits the treatment of general (i.e., analytic or numerical) basis functions and crystal potentials, and the determination of fully self-consistent solutions of the LDF one-particle equations without restricting the iterative path to a superposition of spherical charge densities [4] or to muffin-tin models [6, 7]. We have demonstrated a rapid convergence of the self-consistent (SC) cycle when the treatment of the full crystal charge density is suitably apportioned between real-space and Fourier-transformed recipro-

Generalized electronic susceptibility and charge-density waves in 1T-TaS₂ and 1T-TaSe₂[†]H. W. Myron* and J. Rath[‡]

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Generalized susceptibilities, $\chi^0(\vec{q})$, have been obtained for the 1T polymorphs of both TaS₂ and TaSe₂ from their Korringa-Kohn-Rostoker band structures. Peaks are found which correspond to the charge-density-wave (CDW) nesting vectors found by Wilson, Di Salvo, and Mahajan and appear to confirm the role of electronically driven instabilities as the origin of the observed CDW in these metals.

I. INTRODUCTION

The recent discovery^{1,2} of charge-density waves (CDW) in the layered dichalcogenides has stimulated great interest in the subject of electronically induced instabilities in metals first discussed in the pioneering work of Overhauser.³ Along with spin-density waves and phase transformations, CDW are thought to be manifestations of these instabilities which result from a divergence in the generalized static electronic susceptibility, $\chi(\vec{q})$. In the approximation of linear-response theory,³ $\chi^0(\vec{q})$ may be written

$$\chi(\vec{q}) = \chi^0(\vec{q}) / [1 - I(\vec{q})\chi^0(\vec{q})], \quad (1)$$

where $I(\vec{q})$ is the electron-electron interaction and $\chi^0(\vec{q})$ (the bare susceptibility) is defined as

$$\chi^0(\vec{q}) = \sum_{n,n',\vec{k}} \frac{|M_{n,n'}(\vec{k}, \vec{k}+\vec{q})|^2 f_{n,\vec{k}} (1 - f_{n',\vec{k}+\vec{q}})}{E_{n',\vec{k}+\vec{q}} - E_{n,\vec{k}}}. \quad (2)$$

Fermi surface "nesting," i.e., the existence of large parallel pieces of Fermi surface, leads to a divergence in $\chi^0(\vec{q})$ and possibly to a divergence in $\chi(\vec{q})$ itself, depending on the value of $I(\vec{q})$.

Electron-diffraction studies^{1,2} have revealed that the previously observed³ anomalous electromagnetic properties of the group-VB layered transition-metal dichalcogenides may be related to the formation at some temperature of CDW's and their accompanying periodic lattice distortions. This anomalous behavior has been associated with a nearly two-dimensional Fermi surface supporting a CDW formation which, in turn, introduces a periodic lattice distortion generally incommensurate with the lattice.^{1,2} The amplitude of these incommensurate waves grows from a high-temperature (below 550 K in 1T-TaSe₂) down as far as the first-order transition temperature which represents the point of conversion (or "lock-in") to a commensurate geometry.² In the absence of any

firm theoretical calculations of $\chi(\vec{q})$ on these materials, Wilson *et al.*¹ and Williams *et al.*² made use of the augmented-plane-wave results of Mattheiss⁷ on 1T-TaS₂ available to them, generated a Fermi surface, and interpreted the electron diffraction and resistivity data observed for 1T-TaSe₂. This Fermi surface is nearly two-dimensional in the basal plane ($k_z = 0$) with its walls parallel to the ΓA direction.

This paper reports results of detailed *ab initio* studies of $\chi^0(\vec{q})$ for the 1T polymorphs of both TaS₂ and TaSe₂ derived from their Korringa-Kohn-Rostoker (KKR) band structures⁸ and full Brillouin-zone Fermi surfaces. As was found earlier,⁸ the Fermi surface for both the disulfide and the diselenide are very similar, having cross sections which are approximately constant in planes that are perpendicular to the z axis and have large sections which can be nested by approximately the same wave-vector parallel to the ΓM direction. However, the response function of the system contains not only information about Fermi-surface (FS) features ("nesting") but also about band-structure effects for states just above and below the Fermi energy ("volume effects"). Although previous discussions have emphasized FS nesting features, we find that both contribute substantially to the important structure found in $\chi^0(\vec{q})$. Accurate calculations of $\chi^0(\vec{q})$ for both systems show major peaks to occur at those $\vec{q}$ values corresponding to the CDW vectors found by Wilson *et al.*¹ The theoretically obtained maxima in $\chi^0(\vec{q})$ appear to provide a detailed confirmation of the role of electronically driven instabilities as the origin of the observed CDW in these metals.

II. BAND STRUCTURE AND FERMI SURFACE

The energy-band structure of both 1T-TaS₂ and 1T-TaSe₂, determined by the KKR method in the

Self-consistent numerical-basis-set linear-combination-of-atomic-orbitals model for the study of solids in the local density formalism

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A new approach to the fully self-consistent solution of the one-particle equations in a periodic solid within the Hohenberg-Kohn-Sham local-density-functional formalism is presented. The method is based on systematic extensions of non-self-consistent real-space techniques of Ellis, Painter, and collaborators and the self-consistent reciprocal-space methodologies of Chaney, Lin, Lafon, and co-workers. Specifically, our approach combines a discrete variational treatment of all potential terms (Coulomb, exchange, and correlation) arising from the superposition of spherical atomlike overlapping charge densities, with a rapidly convergent three-dimensional Fourier series representation of all the multicenter potential terms that are not expressible by a superposition model. The basis set consists of the exact numerical valence orbitals obtained from a direct solution of the local-density atomic one-particle equations and (for increased variational freedom) virtual numerical atomic orbitals, charge-transfer (ion-pair) orbitals, and "free" Slater one-site functions. The initial crystal potential consists of a non-muffin-tin superposition potential, including nongradient free-electron correlation terms calculated beyond the random-phase approximation. The usual multicenter integrations encountered in the linear-combination-of-atomic-orbitals tight-binding formalism are avoided by calculating all the Hamiltonian and other matrix elements between Bloch states by three-dimensional numerical Diophantine integration. In the first stage of self-consistency, the atomic superposition potential and the corresponding numerical basis orbitals are modified simultaneously and nonlinearly by varying (iteratively) the atomic occupation numbers (on the basis of computed Brillouin-zone averaged band populations) so as to minimize the deviation, $\Delta\rho(\vec{r})$, between the band charge density and the superposition charge density. This step produces the "best" atomic configuration within the superposition model for the crystal charge density and tends to remove all the sharp "localized" features in the function $\Delta\rho(\vec{r})$ by allowing for intra-atomic charge redistribution to take place. In the second stage, the three-dimensional multicenter Poisson equation associated with $\Delta\rho(\vec{r})$ through a Fourier series representation of $\Delta\rho(\vec{r})$ is solved and solutions of the band problem are found using a self-consistent criterion on the Fourier coefficients of $\Delta\rho(\vec{r})$. The calculated observables include the total crystal ground-state energy, equilibrium lattice constants, electronic pressure, x-ray scattering factors, and directional Compton profile. The efficiency and reliability of the method is illustrated by means of results obtained for some ground-state properties of diamond; comparisons are made with the predictions of other methods.

1. INTRODUCTION

The current popularity of energy-band theory stems from its successful application to the study of increasingly diverse problems in solid-state physics. Recent new sophisticated experiments on both traditional materials and those having complex crystallographic structures have demanded, however, not only theoretical descriptions of phenomena related to the one-electron *eigenvalue* but also detailed and precise *wave functions* with which to determine the expectation values of different observable operators. Such a demanding test of the predictions of one-electron theory has the additional virtue in permitting, by their comparison with experiment, accurate determinations of the relative magnitude and importance of many-body effects in real solids. Thus, there has developed considerable interest in applying the Hohenberg-Kohn-Sham^{1,2} local-density-functional (LDF) formalism to the investigation of various ground-state properties of solids, despite the usual difficulties of solving the associated one-

particle equation characterized by a multicenter nonspherical potential. A variety of well-known approximations have been introduced in order to reduce the complexity of the problem. For example, the various forms of orthogonalized-plane-wave (OPW) techniques^{3,4} suffer from serious convergence difficulties when applied to solids containing first-row atoms with no *p* states in the atomic cores. Recent studies with extended sets of orthogonalized plane waves⁵ have indicated errors in the eigenvalues of the order of up to a few volts due to poor convergence in calculations employing several hundreds of OPW's. The muffin-tin approximations applied to augmented-plane-wave (APW) calculations^{6,7} have been recently criticized as introducing errors of up to a rydberg in the potential in diamond⁸ and other covalent structures,⁹ and overestimating the binding energy in some covalently bonded molecules by as much as (100–300)%.¹⁰ Recent LCAO (linear orbitals)-type calculations^{11–13} have overcome the difficulty of treating non-muffin-tin potentials and have demonstrated that efficient convergence with respect

Ground-state electronic properties of diamond in the local-density formalism*

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We use our previously reported method for solving self-consistently the local-density one-particle equations in a numerical-basis-set linear combination of atomic orbitals expansion to study the ground-state charge density, x-ray structure factors, directional Compton profile, total energy, cohesive energy, equilibrium lattice constant, and behavior of one-electron properties under pressure of diamond. Good agreement is obtained with available experiment data. The results are compared with those obtained by the restricted Hartree-Fock model: the role of electron exchange and correlation on the binding mechanism, the charge density, and the momentum density is discussed.

I. INTRODUCTION

The local density functional (LDF) formalism of Hohenberg, Kohn, and Sham,^{1,2} and its recent extension as a local spin-density functional formalism,³ form the basis of a new approach to the study of electronic structure in that the effects of exchange and correlation are incorporated directly into a charge-density-dependent potential term that is determined self-consistently from the solution of an effective one-particle equation. Applications of the LDF formalism to atoms^{4,5} and molecules⁶ have yielded encouraging results. Similar applications for solids are complicated by (i) the need to consider both the short-range and the long-range multicenter crystal potential having nonspherical components, (ii) the difficulties in obtaining full self-consistency in a periodic system, and (iii) the need to provide a basis set with sufficient variational flexibility. Hence, theoretical studies of ground-state electronic properties of solids in the LDF formalism have been mainly limited to muffin-tin models for the potential,^{7,8} non-self-consistent schemes,⁹ treatments of simplified jellium models¹⁰ or spherical cellular schemes.^{11,12}

We have recently proposed^{13,14} a general self-consistent method for solving the LDF formalism one-particle equation for realistic solids using a numerical-basis-set LCAO (linear combination of atomic orbitals) expansion and retaining all nonspherical parts of the crystal potential. We have demonstrated a rapid convergence of the self-consistent (SC) cycle when the treatment of the full crystal charge density is suitably apportioned between real-space and Fourier-transformed reciprocal-space parts and have indicated the large degree of variational flexibility offered by a nonlinearly optimized (exact) numerical atomic-like basis set. We have shown that all multicenter interactions as well as the nonconstant parts of the crystal potential are efficiently treated by

a three-dimensional Diophantine integration scheme.

The purpose of this paper is to illustrate the applicability of our method to real systems by studying the ground-state electronic properties of diamond. Diamond has been long considered as a prototype for covalently bonded insulators¹⁵ and a great deal of experimental work has been done on its ground-state properties, including cohesive energy,¹⁶ lattice-constant studies,¹⁷ x-ray scattering factors,^{18,19} charge density,¹³ and directional Compton profile.^{20,21} In addition, theoretical studies on its ground-state properties within the restricted Hartree-Fock (RHF) model are available²²⁻²⁵ so comparison with the predictions of the LDF formalism is possible. Although the *eigenvalue spectrum* (band structure) of the local exchange Hamiltonian for diamond has been studied previously by a variety of first-principles techniques [augmented plane waves (APW),^{26,27} orthogonalized plane waves (OPW),²⁸⁻³⁰ pseudopotential OPW,³¹ LCAO,³²⁻³⁵ and cellular methods¹¹], the ground-state observables related to the ground-state crystal charge density have received much less attention. While our method was shown¹³ to accurately reproduce the band structure of diamond as obtained by other techniques^{32,33} (when correlation and self-consistency is omitted so as to be compatible with the previously published band-structure models and the full nonspherical components of the potential are retained in both calculations), we do not consider this as a stringent test since the LDF formalism in its "standard" form does not make any claim on the physical significance of the band eigenvalues nor are these eigenvalues sensitive enough to the details of the basis set and potential.¹⁶ In what follows we present our results for the x-ray scattering factors, charge density, directional Compton profile, total energy, and equilibrium lattice constant and discuss the role of exchange

Self-consistent numerical-basis-set linear-combination-of-atomic-orbitals investigation of the electronic structure and properties of TiS_2 [†]

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A fully-self-consistent numerical-basis-set linear-combination-of-atomic-orbitals calculation of the electronic structure of TiS_2 is reported using the method described previously. The calculated band structure differs considerably from those previously obtained by non-self-consistent muffin-tin models. Comparison with experiment shows that the calculated optical properties for energies below 16 eV and the various characteristics of the valence and conduction bands agree very well with optical-absorption and electron-energy-loss data as well as with photoemission, x-ray absorption, and appearance-potential spectra. A small indirect gap (0.2–0.3 eV) occurs at the points *M* and *L* in the Brillouin zone with a larger direct gap (0.8 eV) at Γ . We suggest that the characteristic semi-metallic large *g* value observed experimentally originates from a near coincidence of the band gap with the enhanced spin-orbit splitting which is consistent with the soft-x-ray data and our band model. The bonding mechanism in TiS_2 is discussed in detail: it is shown by a direct calculation of the self-consistent charge density and the transverse effective charge that the system is predominantly covalent with small static ionic character and large dynamic ionicity. In contrast with muffin-tin *X α* models, the bonding is found to be largely due to Ti 4*s*4*p* to S 3*p* bonds and a much weaker Ti 3*d* to S 3*p* bond. The effects of muffin-tin approximation and self-consistency are discussed in detail. Extrapolation of these results to the case of TiSe_2 is made and the possible origin of its charge-density wave is discussed.

I. INTRODUCTION

The renewed experimental and theoretical interest in the layered transition-metal dichalcogenides has brought about in the last few years much greater understanding of their unusual anisotropic optical and transport properties,¹ and, more recently, those properties associated with the observation of charge-density waves² in some of these systems. Perhaps an outstanding exception is 1T- TiS_2 for which the available information is still in a state of flux and conflict. For example, while optical experiments³ have suggested that TiS_2 is a semiconductor with a gap of about 1–2 eV, recent temperature-dependent resistivity measurements on high-purity stoichiometric samples^{4,5} demonstrated a semimetallic behavior and a remarkable temperature-dependent electrical resistivity proportional to T^2 from at least 10–400 K. Similarly, the theoretical description has had its difficulties. An early non-self-consistent Korringa-Kohn-Rostoker (KKR) calculation in the muffin-tin (MT) approximation⁶ showed a fundamental gap of 2.0 eV at Γ and a smaller indirect gap of 1.4 eV between Γ and *L*. Further, while some of the calculated interband transition energies in the MT-KKR model could be reconciled with the observed data only after a rigid shift of about 1.4 eV was introduced in the theoretical transition energies, an empirical non-self-consistent tight-binding model^{7,8} with pa-

rameters chosen to fit these observed optical transitions yields (a) a valence-band width about a factor of 2 too small (relative to the x-ray photoemission data^{9–11}) and (b) a similar underestimation of the *d*-conduction-band width (compared with the observed appearance-potential spectra¹²). Similar contradictions occur in the various one-electron models derived to explain absorption mechanisms in TiS_2 : while the semiempirical (optical data) model of Murray *et al.*⁷ suggests the occurrence of a nonoverlapping metal *d* band in the gap formed between the bonding and antibonding metal-nonmetal *s-p* bands (σ - σ^* gap), the crystal-field model of Husiman *et al.*,¹³ suggests that the metal *d* band appears in the valence-band continuum. By contrast, x-ray photoemission of Williams and Shepherd¹⁰ places the lower part of the *d* band in partial overlap with the valence band, while a second component of this band appears in the antibonding σ^* region.

In this paper, we present the results of an *ab initio* theoretical study of the electronic properties of TiS_2 using our self-consistent numerical-basis-set linear-combination-of-atomic-orbitals (LCAO) method.^{14,15} This method uses an accurate non-linearly optimized (exact) atomic basis set for all core, valence, and some virtual states of the atoms appearing in the unit cell. All interaction and overlap integrals are evaluated accurately using a three-dimensional numerical Diophantine integra-

ELECTRONIC STRUCTURE AND PROPERTIES OF THE ACTINIDES*

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(Invited paper)

We review the present state of understanding of the electronic structure and physical properties of actinide metals and intermetallic compounds as derived from relativistic APW energy band studies of some of the light (Th, U, Np, and Pu) and heavy (Am, Bk, and Cm) metals, the intermetallics URh₃ and UIr₃, and (NaCl structure compounds such as) UC. Emphasis is placed on the importance of Coulomb correlation and the role of actinide-actinide separation in determining the itinerancy (as in the light metals) or localization (as in the heavy metals) of the 5f electrons and in turn their resulting magnetic and other properties. The UX₃ systems considered are significant because the uranium sites are sufficiently separated to fall in the local moment/orbital range of the Hill superconductivity/magnetism plot but show no magnetic ordering. Comparisons to recent optical, de Haas-van Alphen and other data are given when available. The contrasting cases of the transition and rare-earth systems make it clear that the 5f electrons are a unique species which offer exciting challenges to both experimentalists and theorists.

1. Introduction

The last two decades have witnessed remarkable advances in our understanding of the electronic structure and properties of a wide range of materials. Sparked by the introduction and use of highly sophisticated experimental techniques, a mass of experimental knowledge has emerged which challenged previous (and oftentimes simplified) theoretical models and brought about a more unified view of electronic structure and behavior. First the noble metals, then the important transition metals and their compounds and, most recently, the rare-earths have each enjoyed a period of research which resulted in a high degree of sophisticated understanding previously thought unlikely. Such a period has only recently arrived for actinide research—called, for many reasons and only somewhat euphemistically, the “last frontier” in the study of the electronic structure of materials. Until recently, the difficulties of obtaining samples of sufficient purity and overcoming problems associated with their radioactive nature have resulted in slow progress and limited understanding. In the last decade the more intensive experimental efforts have fos-

tered intensive theoretical study of the basic phenomena and have given rise to a more unified understanding of their electronic properties [1].

That the actinides enjoy their own unique position among the elements, arises from an unusual set of circumstances. In the transition metals the s and d valence electrons form the conduction bands which are responsible for their electric, magnetic, and optical properties. The rare-earths are unique in that their 4f electrons are so highly localized that whereas they determine the various exotic magnetic structures and properties of their metals, they have little effect on other chemical and physical behavior which arises from the transition metal-like structure of their 5d and 6s valence electrons. The 5f electrons in the actinide elements are not as well localized as the 4f's in the rare-earths and have energies which are close to those of the 6d and 7s electrons. This produces the unusual condition of a strong “competition” in actinide solids between the 5f electrons and the 6d and 7s electrons in determining their electronic structure and properties. The contrast between the results on the actinides and those on transition and rare-earth metals makes clear that the 5f electrons are a species of their own [1], with interesting and complex properties that present great theoretical challenges.

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DEFECT STATE MODEL FOR LOCALIZED EXCITATIONS IN LiF*

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We find that a defect state treatment of localized excitations in LiF within the local density functional formalism accounts remarkably well for the observed experimental (core plus optical gap) excitations - in contrast to the failure of the one-electron band model. We show that when electron relaxation, self-interaction and charge polarization effects are taken into account by treating the excitation as a localized point defect, the improved band model predicts the correct excitation and interband states.

Despite extensive investigations, the nature of the fundamental optical gap and core excitations in ionic solids -- of which LiF is considered the prototype -- remains as a challenge to experimentalists and theorists alike. Theoretically, two basic models have been extensively applied: the restricted Hartree-Fock (HF) model [1] and the local density (LD) model [2-3]. With the recent advances in linear combination of atomic orbitals (LCAO) techniques, the more conventional non-self-consistent muffin-tin schemes were abandoned in favor of the more sophisticated extended basis set self-consistent (non-muffin-tin) LCAO methods for both models. Their applications have, however, yielded mixed results: (i) local exchange calculations [3] with an exchange coefficient α close to 1.0 could reproduce the optical gap but an extended Gaussian basis ($\alpha = 1$) study [2] gave calculated one-electron energies substantially lower than experiment in the interband region [4] and yielded the suggestion that the observed spectra both in the optical gap region (11-12 eV) and in the Li-K excitation region, (60-62 eV) be reinterpreted as Bloch-type interband transitions instead of as bound excitons - in marked contradiction with recent experiments [4-8]. (ii) restricted HF calculations [1] revealed a pronounced disagreement of the one-electron eigenvalue differences with experimental transition energies in the whole spectral region and indicated that electron correlation, electron-hole interactions and relaxation corrections (calculated

using a simplified atomic model) are necessary to bring the results into agreement with experiment. It was further stated by these authors [1] that the local exchange model is inadequate for describing excitations in these materials.

We report results which show that a proper treatment of localized excitations in the LD model accounts remarkably well for all the observed experimental data in contrast to the failures of the one-electron band model. Our method goes beyond the conventional band model by considering excitation processes as transitions involving point-defect states in a solid and uses *total (statistical) energy* differences between separately calculated ground and excited states rather than *one-electron* energy differences of a ground state calculation to evaluate the relevant excitation energies. Specifically, this is done by our "small periodic cluster" (SPC) model [9] in which we perform a fully self-consistent band structure calculation but with a large crystallographic unit cell (8-16) atoms) containing a locally excited atom at its center instead of the usual (perfect crystal) primitive cell. The model allows for explicit electron-relaxation effects, self-interaction corrections (for the non-existence of Koopmans' theorem in the local density model even in the unrelaxed limit), charge polarization correction and correlation (treated in the free-electron approximation) effects.

Our starting point is the self-consistent (SC) band structure obtained by solving the one-particle LD functional Hamiltonian with a free-electron exchange potential (using $\alpha = 2/3$) and the electron correlation potential of Singwi et al. [10]. Our LCAO basis set con-

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Ground- and excited-state properties of LiF in the local-density formalism*

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The band structure, charge density, x-ray scattering factor (and their behavior under pressure), equilibrium lattice constant, and cohesive energy of the prototype ionic solid LiF were determined using our recently developed self-consistent numerical basis set (non-muffin-tin) linear-combination-of-atomic-orbitals method, within the local-density formalism (LDF). The details of the bonding and the effects of exchange and correlation on the electronic structure are discussed with reference to the conventional picture of ionic bonding. Remarkably good agreement is found with the observed data for the ground-state properties of the system. Contrary to the results of previous band studies, the conventional band-structure approach to excitation energies (i.e., identifying them with the band eigenvalue differences) is found to fail completely in accounting for the observed data in the entire x-ray and optical spectral region when fully self-consistent solutions of the LDF one-particle equation with no further approximation to the crystal potential are obtained. It is found that in the presence of some spatial localization of the initial or final crystal states, the spurious self-interaction terms, as well as the polarization and orbital relaxation self-energy effects are of a similar order of magnitude as the Koopmans-like interband terms. In order to treat these effects within the LDF self-consistently, we describe the excitation processes as transitions involving point-defect-like states in the solid calculated by a supercell method in which the excitation energies are determined as total-energy differences between (separately calculated) excited- and ground-state configurations. The excited state is represented as a superlattice of locally excited sites using large (8- and 64-atom) unit cells, each containing a single excited site. We find, in the self-consistency limit, that a small but finite degree of spatial localization of the excited states exists even for valence excitations, inducing thereby self-interaction as well as self-energy relaxation and polarization effects. The LDF model is found to account very well for both interband and exciton transitions over the entire spectral region (12-695 eV) and to yield definite predictions regarding the exciton bandwidths and series limits.

I. INTRODUCTION

The study of the ground-state electronic properties of molecules and solids in the local-density formalism (LDF)¹⁻³ has recently attracted considerable attention. Investigations of the cohesive properties of small molecules,⁴⁻⁶ metals,⁷⁻⁹ and rare-gas solids¹⁰ have elucidated the possibilities of obtaining a reasonably accurate description of binding energies and equilibrium geometries by incorporating exchange and correlation effects directly into a one-body potential. Similar studies on compounds, ionic insulators, and covalent semiconductors are beset with the difficulties of having to consider the full (non-muffin-tin) crystal potential and to explicitly account for charge redistribution and hybridization processes by means of a fully self-consistent treatment. We have recently developed^{10,11} the fully self-consistent numerical-basis-set linear combination of atomic orbitals (LCAO) discrete variational method. This scheme permits the treatment of general (analytic or numerical) basis functions and crystal potentials and

the determination of fully self-consistent solutions of the LDF one-particle equation without restricting the iterative path to muffin-tin charge densities¹² or to superposition models.¹³ Applications of this approach include the study of the ground-state properties of diamond,¹⁴ boron nitride,¹⁵ titanium disulfide,¹⁶ cadmium sulphid, and LiAl.

The present study extends our treatment to ionic solids, for which LiF has been chosen as a prototype. We first consider the description of ground-state properties of the system, such as the band structure, charge density, x-ray scattering factors, cohesive energy, equilibrium lattice constant, and behavior under pressure, and compare the predictions of the LDF model with both experimental data and with available restricted Hartree-Fock (HF) results.¹⁷ We then consider the excited-state properties of the system by first using the standard band approach to excitation energies (i.e., viewing them as differences in the band eigenvalues between unoccupied and occupied bands). Contrary to what has been previously suggested,¹⁶⁻¹⁸ we find that, whereas this approach

Theoretical Determinations of Spin Densities

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Abstract

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This paper describes and discusses some aspects of the present status of theoretical determinations of spin (and charge) densities in atoms, molecular clusters, and solids. Selected results of recently completed calculations are used to illustrate "state of the art" methodology and accomplishments.

1. Introduction

In this paper, I will review several aspects of the present status of theoretical determinations of spin (and charge) densities, obviously of high interest to the Conference, by means of examples which will give a flavor of recent developments in atoms, molecular clusters and solids. Because of space limitations and for sound pedagogical reasons, the examples given will be limited to those investigations which have been carried out in my group. A more detailed description of theoretical methods and results is given elsewhere [1]. Emphasis will be placed on neutron magnetic form factor studies as these give directly, through the Fourier transform, the magnetization densities. On the other hand, hyperfine interaction measurements, which provide information about both charge and spin distributions, should not be overlooked by the active researcher.

For this discussion, it is convenient to write the charge density $\rho_c(\mathbf{r})$ and spin density $\rho_s(\mathbf{r})$

$$\begin{aligned}\rho_c(\mathbf{r}) &= \rho_{c\uparrow}(\mathbf{r}) + \rho_{c\downarrow}(\mathbf{r}) \\ \rho_s(\mathbf{r}) &= \rho_{s\uparrow}(\mathbf{r}) - \rho_{s\downarrow}(\mathbf{r})\end{aligned}\quad (1)$$

where $\rho_{c\sigma}(\mathbf{r})$ and $\rho_{s\sigma}(\mathbf{r})$ are respectively the charge and spin density for an electron of given spin orientation, $\sigma (= \uparrow \text{ or } \downarrow)$. For generality, I have written $\rho_{c\sigma}(\mathbf{r}) = \rho_{s\sigma}(\mathbf{r})$ although if a single calculation were done, then the equality would hold. As is well known unlike the case of neutrons or X-rays, the limitation of the hyperfine measurements as a probe is that they measure the value of ρ_c and ρ_s only at one point, namely, at the position of the nucleus: the isomer shift measures the total charge density at the nucleus, $\rho_c(0)$; for a magnetic hyperfine measurement in which core polarization effects are dominant, the relevant quantity is the net spin density at the nucleus.

The state of theory will be the subject of the remainder of my talk. Because of its great success in explaining a variety of phenomena in solids, there arose great unrealistic expectations that theory could and would give detailed answers to the questions raised by the experimentalists. Instead, progress has been slow because of the difficulties inherent in treating an interacting many-body system which cannot be solved selectively for the particular information needed by the experimentalist. Fortunately, a number of developments in the last five years show

great promise for more rapid progress to be made in the future, and hence, one can therefore be somewhat more optimistic about the degree of theoretical support that can be provided.

2. Free atoms/ions: relativistic Dirac-Fock studies

As has been the case for some time, theory is in good shape for treating free atoms and ions, thanks to the highly successful self-consistent-field models. The newest results, dealing with isomer shifts, isotope shifts, core polarization and neutron magnetic form factors have been obtained from fully relativistic Dirac-Fock (DF) calculations. Here we can mention only some examples of this work. Free atom results are particularly useful for complex materials for which *ab initio* calculations, of the molecular cluster and solid state types to be described, later are clearly impossible.

2.1. Relativistic restricted Dirac-Fock results

Recent efforts in obtaining accurate free ion charge densities have centered on calculations using numerical Hartree-Fock or Dirac-Fock theories (with exact exchange) or their approximate counterparts, Hartree-Fock-Slater and Dirac-Fock-Slater theories (when the Slater free-electron exchange is used). A systematic study of relativistic electron densities and isomer shifts in 3d, 4d, and 5d ions has been made recently [2] using the numerical self-consistent field program of Desclaux [3]. Both multiconfiguration D-F (for both point and finite nuclei) and H-F calculations of the changes in $\rho(0)$ were performed (with $\Delta r/r$ assumed constant) for each set of ions, thus obtaining relative values of the isomer shift S_{AB} in a consistent approximation. They then compared S_{AB} values with experimental isomer shifts in order to separate the nonrelativistic and relativistic atomic contributions to the isomer shift from those contributions due to the chemical environment. In each of the cases considered, these workers [2] calculated the ionic ground states. For the Hartree-Fock problem, this was the single-configuration Hund's rule ground state in Russell-Saunders coupling. However, the relativistic single particle wavefunctions are eigenfunctions of the total angular momentum, but not of the separate spin and orbital angular momenta; thus, the Dirac-Fock calculations are performed in *j-j* coupling. However, the total wavefunction is not a single *j-j* configuration but rather a linear combination of *j-j* configurations of total angular momentum $J = L + S$. This multiconfiguration Dirac-Fock wavefunction formally approximates as closely as possible the $(L + S)$ Hartree-Fock wavefunction.

Dirac-Fock calculations have been performed by Desclaux and Freeman [4] for the divalent and trivalent ions of the rare-earths. The importance of relativistic effects in the rare-earths has been demonstrated in a dramatic way by means of

Electronic structure and lattice instability of metallic VO_2 [†]

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A first-principles energy-band study of the metallic rutile phase of VO_2 using a general crystal potential and an expansion of the Bloch functions in a linear combination of atomic orbitals is reported. The results are compared with previous work and experimental optical, x-ray absorption and emission, and x-ray photoelectron spectroscopy data. We obtain a large density of states at the Fermi energy; the Fermi surface is found to be determined by the two lowest d bands, at the bottom of the " π " manifold which is split by the orthorhombic field; the lowest-band Fermi surface possesses some nesting features corresponding to a nesting vector $\vec{q} = \Gamma R$. A calculation of the generalized susceptibility in the constant-matrix-element approximation shows the existence of a maximum at the zone boundary R . We suggest that the formation of a charge-density wave with wave vector $\vec{q} = \Gamma R$ accompanied by a periodic lattice distortion is thus possible; the subsequent condensation of phonons at the point R could then explain the crystallographic phase transition observed at $T = 339$ K.

I. INTRODUCTION

Vanadium dioxide undergoes a crystallographic phase transformation at $T_c = 339 \pm 1$ K from the monoclinic distorted rutile structure to the tetragonal rutile structure which is accompanied by an abrupt jump in the metallic conductivity^{1,2} [from 10^{-2} to 10^4 ($\Omega \text{ cm}$)⁻¹] and a jump in the magnetic susceptibility³ [from 6.5×10^{-5} to 6.7×10^{-4} emu/mole]. This semiconductor to metallic phase transformation has been studied very extensively both experimentally and theoretically.⁴ Unlike V_2O_5 and other transition-metal compounds known as "Mott-Hubbard insulators" which show antiferromagnetic ordering in the low-temperature phase, VO_2 remains paramagnetic below T_c and no long-range magnetic order is observed either in magnetic susceptibility,⁵ Mössbauer,⁶ or nuclear-magnetic-resonance experiments.⁷ The semiconducting monoclinic phase of VO_2 is characterized by a pairing of the vanadium atoms along the c axis resulting in a doubling of the unit-cell size; along the c axis one finds alternatively short and long metal-metal distances^{3,7}; at the same time, each vanadium "pair" is tilted with respect to the c axis, the vanadium atoms being no longer at the center of the distorted ligand octahedron. It is also worth noting the large further distortion of the octahedral geometry in the low-temperature phase, with an important shortening of some of the V-O bonds.⁸ This pairing of the vanadium atoms can explain the lack of localized moments and account for the magnetic properties and possibly some of the electrical properties of the semiconducting phase, as the

electrons may now be trapped in homopolar bonds.¹⁰ This picture has been also useful in accounting for some features of the magnetic behavior¹¹ of the alloy $\text{V}_{1-x}\text{Nb}_x\text{O}_2$ with $x \leq 0.5$.

A. Electronic structure models

These structural peculiarities led Goodenough¹² to propose a model of the electronic structure which can explain some properties of the metallic and semiconducting phases. This model is based on molecular orbital theory in conjunction with crystal field and chemical bonding ideas. In the metallic state, the interaction of cations along the c axis gives rise to a narrow d band which is overlapped by a wider π^* band formed by antibonding vanadium d and oxygen p_z states. In the low-temperature phase, the crystal distortion is thought to be responsible for three effects: (i) the π^* band rises above the Fermi level due to a stronger vanadium d -oxygen p_z interaction, resulting from the shortening of the distance of the vanadium to one oxygen atom; (ii) the d band splits due to the pairing of V atoms along the c axis; (iii) the lowest part of the d band is filled and separated by a small gap from the upper part, thereby accounting for the semiconducting properties of the compound.

The essential features of the electronic structure of the metallic phase of VO_2 proposed by Goodenough¹² have been confirmed by the band-structure calculation of Caruthers *et al.*,¹³ using the combined augmented-plane-wave-linear-combination-of-atomic-orbitals (APW-LCAO) inter-

Electronic Structure and Reentrant Magnetism in Superconducting ErRh_4B_4

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Results of *ab initio* self-consistent energy-band calculations on the full 18-atom/unit-cell ternary alloys MRh_4B_4 ($M = \text{Y}$, Er and Ho) are reported and used to discuss their superconducting and magnetic properties—including the observation of reentrant magnetism in the normal state at $T < 0.9$ K in ErRh_4B_4 .

The recent discovery¹ of reentrant magnetism (at $T = 0.9$ K) accompanying a transition to a normal metallic state in ErRh_4B_4 , a ternary rare-earth superconductor with $T_c^s = 8.7$ K, has generated considerable interest in the origin of this new phenomenon. It has also raised important questions regarding our understanding of magnetism and superconductivity and the nature of their possible coexistence. This Letter reports results of *ab initio* self-consistent (SC) energy-band calculations carried out on three of these MRh_4B_4 systems, with $M = \text{Er}$, Y (an 11.3-K superconductor), and Ho (a ferromagnet below 6.6 K), in their paramagnetic states. Very similar total and orbital (l) angular momentum decomposed atomic densities of states (DOS) are found for the three systems investigated. The peak in the total DOS at the Fermi energy arises from the $4d$ states at the Rh site and appears to be responsible for the superconductivity of the Y and Er systems. The lower $5d$ DOS at the rare-earth site could give rise to magnetic ordering via the $4f$ - $5d$ (on the rare-earth site) Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction in HoRh_4B_4 (at a temperature above its otherwise possible superconducting-transition temperature T_c^s) and at a temperature well below the observed T_c^s in ErRh_4B_4 .

In this new group of ternary borides, MRh_4B_4 , Matthias *et al.*² originally reported the existence of either ferromagnetism ($M = \text{Gd}$, Tb , Dy , and Ho) or superconductivity ($M = \text{Y}$, Nd , Sm , Th , Er , Tm , and Lu), with transition temperatures rang-

ing from ~ 2.5 to ~ 12 K and noted the unexplained switchover from magnetism to superconductivity in going from Ho to Er . The later discovery of a transition from superconductivity to magnetism¹ in the same system upon lowering the temperature of the sample was surprising. For our studies we therefore chose $M = \text{Ho}$ and Er , and also Y (which has no $4f$ electrons), and a T_c^s which is almost exactly equal to that of the Lu alloy (which has a full $4f$ shell).

The band calculations for the full 18-atom unit-cell structures were performed self-consistently using the linear muffin-tin orbital (LMTO) method and other related methods.³ The calculational scheme is essentially the same as the one used earlier for a number of A-15 compounds⁴ but extended to cover also ternary systems. The LMTO method³ is a computationally rapid and efficient method for obtaining insight into the major physical aspects of energy-band structure. By using the logarithmic derivative as a parameter, the usual energy dependence of the elements in the eigenvalue matrices can be neglected to a good approximation. Moreover, by replacing the Wigner-Seitz-cell integrations by integration over overlapping Wigner-Seitz spheres, the matrix elements are very easily set up. All this makes the LMTO method much more rapid than the augmented-plane-wave and Kohn-Korringa-Rostoker methods, without much sacrifice of accuracy.

The potential contained the Hedin-Lundqvist

CONDUCTION ELECTRON POLARIZATION, MAGNETIZATION DENSITIES AND NEUTRON MAGNETIC FORM FACTORS IN METALS*

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The problem of setting up "itinerant" and "localized" descriptions of 3d, 4f and 5f electron states is discussed. Recent band-theory predictions of conduction-electron polarization, magnetization density and the neutron magnetic form factor for various metals are described. Comparisons of theory with experiment show good agreement, and confirm our ideas on the range of validity of the energy-band description.

1. Introduction

A few years ago, if we had been asked what are the criteria of "itinerant-electron magnetism" (the title of this conference), most of us would have responded with a discussion in terms of the spatial extent of the wave function, or (in the case of magnetic carriers) the extension of the spin density distribution. A comparison between theories based on atomic wave functions (as representative of the localized limit) and free-electron wave functions (as representative of the other extreme) would have been included. However, with the accumulation of a mass of data—on the experimental side notably from neutron magnetic scattering investigations, and on the theoretical side notably from energy band studies of transition and rare-earth metals—it became gradually recognised that this simple picture of "itinerant" and "localized" states was unsatisfactory. In recent years, a more sophisticated and more correct description has been developed which instead focuses on the degree of extension or localization in energy of the state in question. Simply put, whether a localized or itinerant description is to be used depends on which of two competing terms is dominant—Coulomb correlation, and the effective band width arising from the overlap of d or f orbitals on neighbouring atoms and their hybridization with orbitals of differing angular momentum character. In the intermediate case where neither effect can be neglected, in-

teresting, complex and unusual properties result—as in the actinides [1].

With the foregoing as the stated theme of this paper, I will consider several aspects of the band model which are important for an accurate one-particle description of magnetization densities in metals. Outstanding among these is the consideration that *eigenvalues* are not as sensitive as *wave functions* to the approximate potential used in the calculation, so that energy bands by themselves are less likely to provide detailed explanations of electronic interactions in solids than are studies where the wave function is an essential element. Thus the investigation of phenomena requiring wave functions for their description may well be the key to assessing the limits of the single-particle model and to understanding the role of many-body effects in metals. It is for this reason that so much significance attaches to the recent developments in band-theory technique which nowadays allow us to make meaningful and detailed comparisons with experiment involving the wave functions.

However, whereas a variety of experimental methods yield information that has been related to the electronic *band structure*, there are few kinds of experiment which yield direct information about the *wave functions* in metals. Perhaps the one outstanding exception is the determination of the neutron magnetic form factor, which gives the Fourier transform of the magnetization density. Over the past few years, accurate neutron-scattering experiments have shown up the inadequacy of the commonly-used free atom and free ion Hartree-Fock form fac-

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ELECTRONICALLY DRIVEN PHONON ANOMALIES AND PHASE TRANSFORMATIONS *

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We have studied the possible role of electronic structure on observed phonon anomalies and phase transformations by means of accurate calculations of the generalized response function, $\chi(\vec{q})$, for non-interacting conduction electrons. Both Fermi surface "nesting" (parallel sections of Fermi surface) and so-called "volume" effects (parallel electron-hole bands crossing the E_F) are included using results of energy band calculations and our recently developed analytic tetrahedron linear energy method. Correlations of the positions of phonon anomalies and/or the occurrence of phase transformations with large maxima in $\chi(\vec{q})$ are found and provide strong evidence that they arise from an electronically driven divergence in $\chi(\vec{q})$: (1) In Ti-TaS_2 and Ti-TaSe_2 , large peaks in $\chi(\vec{q})$ are found at the observed q values along ΓM corresponding to the CDW. (2) In both Pd and Pt metals, a large peak is found at precisely that q value along $[110]$ for which large Kohn anomalies have been found. An additional peak is found along $[111]$ which predicts the occurrence of a Kohn anomaly in this direction (but which is stronger in Pd than in Pt). (3) Large peaks in $\chi(\vec{q})$ are found for both NbC and TaC at precisely those q values at which soft modes were observed by Smith and Glaser. Maxima in $\chi(\vec{q})$ are predicted for other directions. The locus of these q_{max} values can be represented by a warped cube of dimension $\sim 1.2 (2\pi/a)$ in momentum space - in striking agreement with the soft mode surface proposed phenomenologically by Weber. No such peaks are found for ZrC and HfC, for which no phonon anomalies have been observed. (4) For the tetragonal rutile phase of VO_2 , we find a large maximum in $\chi(\vec{q})$ at the zone boundary R. This suggests the possible formation of a CDW with $q=\Gamma\text{R}$. The subsequent condensation of phonons at R could then explain the crystallographic (metal to semiconducting) phase transition at $T=340$. Recent x-ray diffuse scattering measurements by Terauchi and Cohen of Northwestern confirm these predictions; their results show a lattice instability near the metal-insulator transition to occur at the R point.

1. INTRODUCTION

Recent theoretical and experimental developments have called attention to the central role played by the generalized susceptibility function $\chi(\vec{q})$ in the understanding of many physical phenomena in solids. Since $\chi(\vec{q})$ measures the response of the system to an external (generally spatially in-

homogeneous) perturbation, emphasis has been placed on possible anomalous behaviour which may result from an instability in the conduction electron gas as a result of a divergence in this response function. In linear-response theory

$$\chi(\vec{q}) = \chi(\vec{q}) / (1 - I(\vec{q})\chi(\vec{q})) \quad (1)$$

where $I(\vec{q})$ is the electron-electron inter-

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Electronic structure and proton spin-lattice relaxation in PdH

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We report a detailed augmented-plane-wave energy-band study and wave-function analysis of stoichiometric PdH which shows that, even though the Fermi surface of PdH is qualitatively similar to that of silver, the simple "proton model" is not valid. Instead, the screening of the proton in PdH is found to be larger than in an isolated H atom due, in part, to the formation of a H-Pd bonding band below the bottom of the *d*-band complex. This result, which is in qualitative agreement with Switendick's earlier calculation, is confirmed by ultraviolet photoemission experiments. A partial density-of-states (DOS) analysis in the energy range spanned by the six valence and conduction bands reveals the quantitative details of the bonding mechanism between the Pd and H constituents. At the Fermi energy, the high Pd *d* to H *s* DOS ratio ~ 10.3 is found to be far higher than expected in silver, despite the fact that the Fermi-surface geometry is similar. The field-induced conduction-electron spin density at the proton site is evaluated from the wave functions at the Fermi energy. The calculated value of the spin-lattice relaxation rate arising from the contact term in the hyperfine interaction is found to be in good agreement with the experimental value of Wiley *et al.*

I. INTRODUCTION

The metal-hydrogen systems have received wide attention due, in part, to the large number of their technical applications.^{1,2} They are also important for the tests they provide of several theories. The study of the behavior of a proton in a simple metal was started with the pioneering work of Friedel,³ and later extended by several authors.⁴ It is now well established that the screening of a proton in an electron gas is not well described by linear screening theories, because the perturbation introduced by a proton is simply too strong and nonlinear screening effects are very important.⁴ These theories essentially treat the proton as an isolated impurity in an electron gas, and are based upon a self-consistent solution of the Schrödinger equation using the Hohenberg-Kohn-Sham⁵ local-density-functional formalism; they are expected to give interesting results only for the so-called "simple metals" which are known to absorb an extremely small quantity of hydrogen. While electron-gas models provide useful information about variation in the screening with variation of the average interelectronic distance, their quantitative predictions must be treated with caution, as the jellium model is recognized⁶ to be a quite crude representation because even the so-called simple metals show substantial departures in their Fermi-surface properties, etc., from that of an electron gas.

Since the transition metals like Pd can absorb a large amount of hydrogen, the proton cannot be treated as a dilute impurity. Thus, for these *d*-electron systems one would not expect to obtain meaningful results from electron-gas theories. To

describe properly the electronic structure of transition-metal hydrides, alternative methods, like the augmented-plane-wave (APW) band-structure method, have been used by Switendick⁷ and other authors.^{8,9} Theoretical studies have also been made of nonstoichiometric compounds, using either the supercell method⁷ (with an assumed rigid order of the vacancies) or the virtual-crystal approximation.⁹ Recently, the electronic structure of disordered substoichiometric PdH_x compounds has been obtained using the average-*t*-matrix approximation,¹⁰ and the coherent-potential approximation.¹¹

Among the transition-metal hydrides, the PdH_x system is of particular interest because (i) the superconducting transition temperature¹² T_c increases with increasing values of *x* (for $x \geq 0.8$) and (ii) the reverse isotope effect¹³ on T_c (observed when H is replaced by deuterium) is a challenging problem for both theorists and experimentalists. Miller and Satterthwaite¹⁴ proposed a qualitative explanation of (ii) based upon changes in the electronic structure which arise from differences in the zero-point motion amplitudes of the two isotopes, leading to a stronger bonding of the hydrogen atom (compared to D) to the palladium atom. An alternative explanation, given by Ganguly,¹⁵ proposes that the anharmonicity due to a large zero-point motion amplitude of the protons leads to a different electron-phonon coupling and to a reduction of the electron-phonon coupling constant λ when D is replaced by H. This theory assumes that the electronic properties of PdH and PdD are identical (e.g., same density of states at the Fermi energy...). The importance of anharmonic effects in the electron-phonon interaction is

RE-ENTRANT MAGNETISM IN RARE-EARTH SUPERCONDUCTING TERNARY COMPOUNDS *

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Superconductivity and magnetism in the new group of rare-earth ternary borides, MRh_4B_4 , has been reported recently by Matthias et al. Particularly striking has been their observation of re-entrant magnetism accompanying the return to a normal state at low temperatures ($T = 0.9$ K) in the superconductor ErRh_4B_4 which has a superconducting transition temperature of 8.5 K. We discuss the origin of superconductivity and magnetism in these systems using results of *ab initio* self-consistent LMTO energy band calculations for the alloys $M = \text{Y}$, Er and Ho .

1. Introduction

There has developed, in recent years, great interest in the electronic structure and properties of ternary compounds. A key motivation has been the hope that higher superconducting transition temperatures, T_c , and higher critical field materials could be obtained. For the Chevrel phases, with general formula $\text{M}_x\text{Mo}_6\text{S}_8$ (where M is a metal and x a number near 1), there are a number of metallic elements which cause the compound to be superconducting. Surprisingly, Fischer and collaborators [1] at Geneva and Rennes found that the paramagnetic rare-earth metals also formed superconductors whereas earlier the addition of paramagnetic rare-earth impurities was always found to lower T_c . Recently, Matthias et al. [2] reported that in a new group of ternary borides, MRh_4B_4 , either ferromagnetism ($M = \text{Gd}$, Tb , Dy ,

Ho) or superconductivity ($M = \text{Y}$, Nd , Sm , Th , Er , Tm and Lu) existed. In table 1 we list the transition temperatures of some of the rare-earth compounds. We see a sharp break from magnetism (T_c^m) and superconductivity (T_c^s) in going from Ho to Er . Of considerable interest has been the later discovery [3] of re-entrant magnetism (at $T = 0.9$ K) accompanying a transition to a normal metallic state in ErRh_4B_4 , a rare-earth superconductor with $T_c^s = 8.7$ K; this has also generated considerable excitement as to the origin of this new phenomenon. It has also raised important questions regarding our understanding of magnetism and superconductivity and the nature of their possible coexistence.

In this paper, we discuss the origin of these phenomena using results of *ab initio* self-consistent energy band calculations carried out on three of these MRh_4B_4 systems, with $M = \text{Er}$, Y (an 11.3 K superconductor) or Ho (a ferromagnet below 6.6 K) in their paramagnetic states. Very similar total and orbital (l) angular momentum decomposed atomic densities of states (DOS) were found for the three

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CHAPTER 4

CALCULATION OF CHARGE AND SPIN DENSITIES
IN SOLIDS *

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1. Introduction

Ch. 2 has given a review of the theory of the isomer shift and some basic features of electron densities as determined theoretically for free atoms or ions. In this chapter, we describe in some detail the present state of our theoretical abilities to determine electron densities in condensed matter. It is apparent at once that numerous approximations have to be made to reduce a many-body, many-center problem to a tractable form. The great variety of more or less severe approximations which have been applied in reducing the many electron problem has led to a literature with a rich vocabulary and confusing terminology. One purpose of this review is to try to clarify the differences and similarities between various methods, and to assess the state of theoretical and computational development in predicting the wavefunction-dependent properties. In order to explore the range of validity of several models, we discuss a selected number of experimental results where comparisons can be made.

We begin by discussing the highly successful self-consistent-field models for treating free atoms and ions. The effects of spin and symmetry restrictions on the single determinant wavefunction and approximations to the Hartree-Fock exchange operator are surveyed. The importance of relativistic and finite-nuclear-size phenomena for determining quantitative results for electron densities near the nucleus is stressed.

Free atom/ion models have an obviously limited utility in molecules and solids, due to chemical bonding and electron delocalization. Perturbed atom, and finally, fully variational molecular orbital theories represent one response to these limitations. It is apparent that self-consistent molecular cluster models can (within a one-electron framework) represent a satisfactory generalization of the free atom/ion scheme for localized properties. We discuss the encouraging progress which has been made in recent years, and find indications that first-principles MO calculations may soon prove to be more useful than extrapolating atomic results.

The delocalized Bloch wavefunction approach for periodic solids has now reached a fairly high state of development, particularly for metals. We display

Ab initio self-consistent study of the electronic structure and properties of cubic boron nitride*Alex Zunger[†] and A. J. Freeman

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We present the results of a first-principles fully self-consistent study of the electronic properties of cubic boron nitride in the local-density formalism using our previously published numerical-basis-set linear combination of atomic orbitals scheme. The resulting band structure shows considerable disagreement with previously published orthogonalized-plane-wave, augmented-plane-wave, and pseudopotential studies. A detailed study of the ground-state properties of the system, such as x-ray scattering factors, cohesive energy, equilibrium lattice constant, and their behavior under pressure, yields very good agreement with available experimental data. Reasonably good agreement is obtained for excited state properties determined by optical and x-ray absorption measurements. The bonding characteristics in this prototype of III-V compounds are discussed in detail and compared with results of our previous study of its isoelectronic homopolar analog, diamond, and with studies on the hexagonal graphitelike modification of BN.

I. INTRODUCTION

The extraordinary properties of cubic boron nitride have been the subject of intense experimental investigations since its discovery in 1957 by Wentorf.¹ The simplest III-V compound, it is isoelectronic and isostructural with diamond. Its hardness matches that of diamond² while its effective ionic charge is the highest of all known III-V compounds.^{3,4} Like carbon, BN crystallizes in two forms, a cubic zinc-blende and an hexagonal (graphite-like) structure. These properties make a comparative study of these compounds particularly interesting. We have previously studied the electronic properties of diamond^{5,8} in the local-density formalism (LDF)^{7,8} using our first-principles self-consistent numerical-basis-set linear combination of atomic orbitals (LCAO) method.^{9,10} In particular, we have investigated the band structure, charge distribution (as measured by x-ray scattering factors), cohesive energy, equilibrium lattice constant, behavior under pressure, and the bonding characteristics induced by the various electron exchange and correlation potentials pertaining to the local-density formalism. In this study, we extend our investigation to the isoelectronic cubic boron nitride in an attempt both to understand the electronic structure features in the heteropolar zinc-blende system and to test further the applicability of the LDF to quantitative descriptions of covalent-ionic systems.

The crystal structure of cubic boron nitride has been established by Wentorf¹ (lattice constant $a = 3.615 \pm 0.001$ Å at 25 °C). Its optical properties in the infrared region have been studied by Gielisse *et al.*³ and recently by Chrenko¹¹ who has also investigated its ultraviolet absorption spectra. Some preliminary results have also been published by Phillip

and Taft¹² and Halperin and Katzir.¹³ The spectra of the core levels have been studied by means of x-ray emission spectroscopy.¹⁴⁻¹⁶ The distribution of electrons in the ground state recently has been studied by Weiss¹⁷ by means of x-ray crystallography.

Theoretical studies¹³⁻²⁷ of the electronic structure of cubic BN include the work of Kleinman and Phillips¹⁸ using a pseudopotential technique in which the heteropolar antisymmetric potential (which vanishes in the homopolar diamond case),¹⁹ is treated as a small perturbation on the previously computed diamond potential. Hamstreet and Fong²⁰ have indicated that since the basic pseudopotential cancellation in crystals like BN made up of first-row atoms is incomplete due to the lack of p character in the core states, a nonlocal correction to the pseudopotential is necessary. Adjusting empirically their local and nonlocal pseudopotential parameters, they obtained a band structure that differs substantially from that of Kleinman and Phillips.¹⁸ In a subsequent orthogonalized-plane-wave (OPW) study, Bassani and Yoshimine²² have similarly faced a plane-wave convergence difficulty due to the lack of pseudopotential cancellation for crystal states having p symmetry. (Their model employs atomic *Hartree-Fock* charge densities to represent the crystalline density and the crystal exchange potential is linearized with respect to the single-site potentials). Wiff and Keown²³ and Keown²⁴ have calculated the band structure of BN using the augmented-plane-wave (APW) method with a muffin-tin crystal potential in which the boron and nitrogen potentials were obtained by linearly scaling the carbon potential and adding a constant Madelung term (with effective charge chosen empirically to yield a gap of 8.8 eV)¹ to account for the partial ionic character of the system.

Local-density self-consistent energy-band structure of cubic CdS

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Self-consistent *ab initio* studies of the electronic-energy-band structure of cubic CdS are reported within the local-density-functional (LDF) formalism. All electrons are included using our previously reported linear-combination-of-atomic-orbitals method in a numerical basis representation. In the first set of calculations we employ the same lattice constant, exchange (only) potential, and computational parameters as were used by Stukel *et al.* in their early self-consistent orthogonalized-plane-wave (SCOPW) investigation so that a direct comparison of results can be made and the validity of the SCOPW approach for covalently bonded 4d systems can be assessed. In the second set of calculations, the Stukel *et al.* computational restrictions are relaxed, a more accurate lattice parameter is employed, and the Kohn-Sham exchange and the Singwi *et al.* correlation potential are used to obtain the local-density formalism solutions to the band problem, including variation of the band structure and related properties with pressure (change of lattice constant). Comparison with optical and x-ray and uv photoemission experiments for excitations of both the *s-p* and metal *d* bands in the 5–19 eV region indicate very good agreement. The direct gap at Γ is, however, found to be 0.5 eV (25%) too small, a discrepancy similar to that previously found in nonempirical studies for other heteropolar insulators (e.g., Ne and LiF). This is traced to the neglect of the different orbital relaxation at the Γ_{25} and Γ_1 band edges and to the noncancellation of the self-interaction terms characteristic of the local-density potential. Simple atomic total-energy models for these effects are shown to bring this gap into good agreement with experiment. It is concluded that a first-principles (parameter-free) exchange and correlation LDF model describes very well the main electronic-structure features of the system.

I. INTRODUCTION

There now exists vast literature comprising experimental and theoretical investigations of the electronic structure and related properties of the important II-VI compounds. Of obvious importance for understanding and interpreting many of the observed properties of these materials is a detailed knowledge of their underlying electronic band structures. In this regard, recent optical and photoemission experiments have played an important role in elucidating key features of the band structure over an increasingly large range of energies above the fundamental band gap.

On the theoretical side, pioneering *ab initio* energy-band studies¹⁻³ were carried out for many of these materials using the non-muffin-tin self-consistent orthogonalized-plane-wave (SCOPW) method. This technique has been applied in recent years to the study of the electronic structure of a large number of semiconductors and semimetals, and has resulted in a considerable gain in insight into the systematics of both the III-V and III-VI compounds as well as in a better understanding of the photoemission, high-pressure, and optical data for these materials. At that time, the only popular alternative method was the non-self-consistent empirical pseudopotential approach^{4,7} which completely avoided the specification of the microscopic potential in the solid (i.e., the nature of the Coulomb exchange and correlation fields) by pa-

rametrizing empirically the first few Fourier components of an unspecified crystal potential. Although this phenomenological approach has produced a great deal of information on the variation of the gaps in II-VI compounds and the origin of the important band-structure critical points in the Brillouin zone, no meaningful comparison of the adequacy of the SCOPW approach, as well as that of the underlying exchange models, could be made. More-recent developments in semiempirical non-local (non-self-consistent) pseudopotential theory³ have improved considerably the agreement between the calculated band structure and x-ray and uv photoemission data by introducing a few additional disposable parameters to describe the geometry of the angular-momentum-dependent model pseudopotential terms. Although a successful parametrization scheme, little could be learned regarding the microscopic nature of the elementary interactions which lead to this success. Further, due to the independence of the parametrized model potential on its associated variational wave function, questions such as self-consistency and the nature of the crystal dissociation products [which are well-defined local-density-functional (LDF) atoms in both linear-combination-of-atomic-orbitals (LCAO) and SCOPW models] have remained largely unresolved and have inhibited a meaningful comparison with first-principles models based on well-understood (but less successful) crystal potentials. Subsequent studies on the convergence properties

Band structure and lattice instability of TiSe_2

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The energy band structure of TiSe_2 , determined in the local-density approach yields a semimetal (band overlap 0.20 ± 0.05 eV) with holes at Γ and electron pockets only at L . The dimensions of the electron pocket indicate the presence of $(7-8) \times 10^{20}$ carriers/cm³ in excellent agreement with both transport and angular-resolved photoemission data. The observed charge-density wave is attributed to characteristic "volume" effects, i.e., nesting of parallel electron-hole bands at E_F separated by the Γ - L zone-boundary wave vector.

The nature and unusual properties of the electronic state of TiS_2 and TiSe_2 have become the subject of intense interest and study. The question as to whether TiS_2 (and TiSe_2) is a semiconductor or a semimetal is still not resolved and the closely coupled question of the origin of the unusual T^2 temperature dependence of its resistivity is still not understood. The recent observation^{1,2} of a $2a_c \times 2c_0$ lattice instability in TiSe_2 at temperatures below 202°K, coupled with its semimetallic conductivity above this temperature in the most nearly stoichiometric crystals ($\sim 10^{20}$ – 10^{21} carriers/cm³), has served to intensify interest and speculation as to its electronic structure. Of particular concern has been the mechanism with which to explain the origin of its charge-density wave (CDW) and the failure to observe such an instability in TiS_2 . Theory has not added enlightenment. The early non-self-consistent Korringa-Kohn-Rostoker (KKR) muffin-tin band calculation³ for TiS_2 (TiSe_2) gave a fundamental gap of 2.0 eV (1.2 eV) at Γ and a smaller indirect gap of 1.4 eV (0.5 eV) between Γ and L ; similar semiconducting characteristics have been predicted by empirical tight-binding studies.⁴

Recently, our fully-self-consistent numerical basis set linear combination of atomic orbitals (LCAO) general (non-muffin-tin) potential calculation for TiS_2 ,⁵ showed good agreement with optical properties for energies below 16 eV. Contrary to previous expectations, a small indirect gap (0.2–0.3 eV) was found to occur at the points L and M in the Brillouin zone, with a larger direct gap (0.8 eV) at Γ . (A recent comprehensive analysis of transport, magnetic susceptibility, Hall effect, resistivity, Seebeck, etc.,⁶ data yielded a gap of 0.2–0.5 eV, in agreement with our predictions.) Since extrapolation of our results for TiS_2 to the case of TiSe_2 is crude at best, and since muffin-

tin³ or semiempirical models⁴ are not able to resolve these questions, we undertook an *ab initio* study of the electronic band structure of TiSe_2 in order to understand its various measured properties. Of direct interest was to compare with the first angle-resolved photoemission studies of Bachrach *et al.*,⁷ which showed conduction-band overlap of the valence band along the Γ - M direction by at least 0.5 eV.

The band structure was calculated in the local-density functional (LDF) approach, using our previously published numerical basis set LCAO discrete variational method.^{5,8} We find that TiSe_2 is a semimetal with an indirect negative gap (0.20 eV) between Γ and L ; contrary to some previous expectations,² no electron pocket was found at M . The dimensions of the electron pocket at L (0.20 LH , 0.25 LA , and 0.5 LM) indicate the presence of $(7-8) \times 10^{20}$ conduction-band carriers/cm³ in the perfect crystal. This is in very good agreement with the independently reported transport¹ and angle-resolved photoemission experiments.⁷

In our calculations, the linear basis set consisted of Ti 1s to 4p orbitals and Se 1s to 4d orbitals, obtained as accurate self-consistent (numerical) solutions to the corresponding single-site LDF one-particle equations. About 3500–4000 Diophantine integration points per unit cell, together with a cutoff distance of 27 a.u. for the direct space lattice sums, were needed (as was the inclusion of the Se 4d and Ti 4p virtual orbitals) in order to obtain a numerical accuracy of 2–3 mRy in the band eigenvalues for energies below $\epsilon_F + 7$ eV. The initial crystal potential was constructed from an overlapping superposition charge density made up from atomic Ti 3d²4s² and Se 4s²4p⁴ solutions of the LDF equations. The potential included the local exchange $\rho^{1/3}$ (with a 2/3 coefficient) and the nongradient correlation contribution.¹⁰ All

Structurally Induced Semimetal-to-Semiconductor Transition in 1T-TiSe₂Alex Zunger^(a) and A. J. Freeman*Department of Physics and Astronomy and Materials Research Center, Northwestern University,
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We show that observed changes in the nature of the conducting state of 1T-TiSe₂ in going from the normal semimetallic state to the charge-density-wave semiconducting state can be successfully modeled by variation of a single structural parameter, z , which modulates the Ti-Se bond length. These *ab initio* band-structure results lead to a number of interesting experimental consequences.

Current interest in charge-density-wave (CDW) phenomena in metals, especially the layered dichalcogenides of the transition series, remains high, particularly, as regards their origin and the physical properties which accompany the transition to the CDW state.¹⁻⁴ Recent advances in *ab initio* band-structure theory avoid the approximations underlying the more conventional approaches to the one-electron problem (e.g., muffin-tin approximations, lack of self-consistency, shortcomings in the basis-set representations, etc.), and have been found to describe accurately the properties of the normal state of these compounds. In particular, the nature of the conducting state of TiS₂^{5,6} and TiSe₂⁷ (semiconductor and semimetal, respectively), which had been highly controversial for some time,⁸ has now been correctly predicted; even more strikingly, these calculations were able to predict the dimensions of the electron and hole pockets in TiSe₂,⁷ in excellent agreement both with transport measurements⁷ and with recent angle-resolved photoemission data.⁹ Similar studies on TiS₂⁵ and VSe₂¹⁰ were used to analyze successfully a wealth of experimental data, including x-ray and uv photoemission, optical reflectivity, infrared effective charge, appearance-potential spectra, and transport properties, and have provided a coherent microscopic picture of the chemical bonding in these systems.

Questions pertaining to the electronic properties of the CDW state, however, remain largely unresolved. Although the basic phenomena involving phonon-mediated interactions between the electron and hole pieces of the Fermi surface (FS) have been phenomenologically understood for some time on the basis of simple momentum-conserving geometrical FS models, a theoretical description of the underlying changes in the electronic structure of the CDW state is still lacking. This has a simple practical reason. Unlike the unit cell of the normal phase, which contains a

tractable number of atoms, the CDW state is extremely complex (e.g., in TiSe₂ it contains 24 atoms and 128 of its 720 electrons are in valence states) and so cannot be treated by the present generation one-electron methods with an accuracy comparable to the relevant band overlaps and band gaps (0.1–0.2 eV).¹¹ In particular, the large number of internal structural degrees of freedom in the CDW phase, makes it practically impossible to establish a direct correlation between the structural deformations accompanying the CDW formation and the pertinent electronic properties.

We have isolated a simple structural variable in 1T-TiSe₂ that allows the electronic response to the observed complex pattern of lattice distortions in the CDW state to be modeled in a simple and direct way. This simple structural degree of freedom is the internal crystal parameter¹² z that modulates the Ti-Se bond length and determines the height of the Se atoms above the metal-layer planes. The simplicity of the model permits a detailed study of the electronic response to such structural deformations and provides a direct characterization of the conducting states of the material in terms of its electronic structure. Among other results, variations of this parameter in a first-principles energy-band calculation are found to transform the system from a semimetallic state to a semiconducting-like state characteristic of the CDW phase. The results of these energy-band studies lead to a number of interesting, and possibly important, experimental consequences, including the effect of pressure on the conduction properties and the prediction of the absence of a surface superlattice due to atomic relaxation at the surface.

The band calculations were performed with use of the numerical-basis-set linear combination of atomic orbitals (LCAO) method described previously^{5,12}; briefly, it consists of a first-principles LCAO approach to the local-density-functional

Evidence for Possible Electronic Contributions to the W(001) Surface Phase Transition

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The calculated surface generalized susceptibility, determined from *ab initio* self-consistent thin-film energy bands for the unreconstructed phase of W(001), displays a prominent peak at $\bar{M}$ when matrix elements and local-field corrections are included and supports proposed charge-density-wave interpretations of the observed reconstruction to the $c(2 \times 2)$ phase. These results are consistent with the Debe and King parallel-shift model and the suggestion that W(001)- $c(2 \times 2)$ -H at room temperature represents an impurity-stabilized substrate reconstruction.

Surface-structural phase transitions are becoming a subject of intense experimental and theoretical investigation. A prototypical example is given in the low-energy-electron-diffraction (LEED) studies of the tungsten^{1,2} (001) surface which show a temperature-dependent phase transition to a $(\sqrt{2} \times \sqrt{2})R45^\circ$ or $c(2 \times 2)$ structure when the temperature is lowered below about 300 K. This transformation seems to be of second order and is reversible on varying only the temperature. [A similar transition has been observed on Mo(001).³] Recent investigations^{1,2} conclude that

chemisorbed impurities (hydrogen in particular) need not be present on the surface when the $c(2 \times 2)$ structure is observed, thus implying that the transition is characteristic of the clean surface.

Felter, Barker, and Estrup¹ and Debe and King² have suggested that relatively small periodic distortions could account for the phase transition, and they have noted that this is compatible with a charge-density-wave (CDW) mechanism as in the layered transition-metal dichalcogenides. A LEED intensity analysis³ for W(001) at 100–140 K supports a model proposed by Debe and King¹ in-

Electronic structure of 1T-VSe₂

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A first-principles self-consistent (non-muffin-tin) band-structure calculations on 1T-VSe₂ is used to analyze some of the transport and optical properties. The material appears to be metallic with characteristic overlaps between the metal *d*-based and nonmetal *p*-based bands. These overlaps are found to be sensitively modulated both by the change of the (anomalously high) *c/a* ratio and by the sandwich height parameter *z* (determining the V-Se bond length). This leads to a number of interesting predictions regarding the electronic structural changes associated with the charge-density-wave instability.

I. INTRODUCTION

The origin of charge-density waves (CDW) and their relation to the observed anomalous behavior of the layered transition-metal dichalcogenides continues to be of great theoretical and experimental interest. Of the various dichalcogenides, the 1T family of the group-VI compounds may be among the most interesting for study because of the wide variety of phase transitions and associated anomalous properties which they exhibit.^{1,2} For the 1T-TaS₂ and 1T-TaSe₂ systems the Korringa-Kohn-Rostoker (KKR) energy-band calculations of Myron and Freeman³ gave Fermi surfaces which are very similar for both systems, having cross sections which are approximately constant in planes that are perpendicular to the *z* axis and which can be nested by approximately the same wave vector parallel to the ΓM direction. Using the energy-band structure and three-dimensional Fermi surface, Myron *et al.*⁴ calculated accurately the generalized susceptibility $\chi(\vec{q})$, which arises from both Fermi-surface nesting and band-structure effects for bands just above and below the Fermi energy E_F . Maxima were found at those $\vec{q}$ values which correspond to the CDW nesting vectors found by Wilson *et al.*² Recently, Woolley and Wexler⁵ determined the band structure and Fermi surface of 1T-TaS₂, -TaSe₂, and -VSe₂ using the layer method for band calculations in a so-called double muffin-tin approximation to the potential.

In our recent local-density self-consistent (SC) non-muffin-tin investigations of the electronic structure and properties of the group-IVB materials 1T-TiS₂⁶ and -TiSe₂,⁷ we found profound changes to occur relative to the results of the early non-self-consistent muffin-tin KKR results

obtained previously.⁸ Whereas the muffin-tin KKR results gave a semiconductor with a fundamental gap of 2.0 and 1.2 eV at Γ and a smaller indirect gap of 1.4 and ~0.5 eV between Γ and *L* for TiS₂ and TiSe₂, respectively, our self-consistent numerical basis linear combination of atomic orbitals (LCAO) method reduced the calculated direct gap in TiS₂ to 0.8 eV and the indirect gap between 0.2 and 0.3 eV. For TiSe₂, our SC-LCAO results showed it to be a semimetal with an indirect overlap of 0.2 eV between Γ and *L*—in agreement with transport⁹ and angle-resolved photoemission¹⁰ experiments. These results appear to confirm the validity of the local density functional energy-band approach for describing the electronic structure of the layered dichalcogenides.

In addition to the standard energy-band study of TiSe₂, we also investigated¹¹ the effect of internal structural changes—specifically, the effect of varying (i) the so-called sandwich height parameter *z*, which determines the vertical positions of the Se atoms above and below the metal plane, and (ii) the *c/a* ratio on the electronic structure. We found that the observed changes in the nature of the conducting state in going from the normal semimetallic to the charge-density-wave semiconducting state can be successfully modeled by variation of a single structural parameter *z*. Among other results, variations of this parameter in the energy-band calculations are found to transform the system from a semimetal to a semiconducting-like state characteristic of the CDW phase and to lead to a number of possibly important experimental consequences, including the effect of pressure and intercalation on the conducting properties.

As a consequence of this work on the group-IVB

Electronic band structure, optical properties, and generalized susceptibility of NbO_2

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The electronic structure of the high-temperature rutile phase of NbO_2 is studied by the linearized-augmented-plane-wave method. Potentials constructed by superposition of neutral-atom and ionic-charge densities are used to explore variability of the electronic band structure. A rigid-band scheme is shown to accurately describe optical absorption of the rutile phase of NbO_2 , stabilized by the addition of 20 at. % Ti as measured by Raccah *et al.* Differences between the band results for rutile NbO_2 and the optical absorption measurements on the low-temperature body-centered tetragonal phase of NbO_2 are attributed to band splittings induced by lattice distortion which occur at the phase transition. The static-electron response function $\chi(\vec{q})$ is calculated in the constant-matrix-elements approximation. In contrast to the case of isoelectronic VO_2 , no Fermi-surface nesting features are observed, and $\chi(\vec{q})$ is found to be structureless in the vicinity of the point $P = (1/4, 1/4, 1/2)$ which has been associated with a possible soft-mode phonon instability responsible for the lattice transformation.

I. INTRODUCTION

Niobium dioxide shows a structural phase transformation (rutile to body-centered tetragonal) around 810°C accompanied by rapid changes in resistivity and magnetic susceptibility. The high-temperature rutile phase is metallic, while the distorted phase is found to be semiconducting.¹⁻⁴ The transition is less abrupt than in the isoelectronic compound VO_2 and has been characterized as second order by neutron-diffraction studies.⁵ It is possible to prepare good single crystals of NbO_2 in contrast to the first transition series compounds, so this system provides a good testing ground for comparing theories of electron-phonon interactions and electronically driven transitions with experiment. In addition, pseudobinary compounds such as $\text{Ti}_x\text{Nb}_{1-x}\text{O}_2$ are found useful in studying effects of d -electron occupancy on electrical, optical, magnetic, and structural properties.⁶⁻⁹

Neutron and x-ray studies have provided accurate values for atomic positions in both phases of NbO_2 . The low-temperature distorted phase is understood to be essentially equivalent to a dimerization of the metal-atom chains found along the rutile c axis, analogous to the famous Peierls distortion. In the case of VO_2 , x-ray diffuse scattering measurements by Terauchi and Cohen¹⁰ confirm the existence of soft phonon modes centered at the point $R = (\frac{1}{2}, 0, \frac{1}{2})$ of the Brillouin zone as predicted

by a band-structure study.¹¹ However, the mechanism of the phase transition in NbO_2 is less clear^{5,12,13} and neutron-scattering experiments have failed to detect low-frequency soft-mode phonon branches¹³ particularly at the wave vector $P = (\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ thought to be associated with the static lattice distortion.

In this paper we study the electronic band structure and the generalized susceptibility $\chi(\vec{q})$ in order to assess the possible role of electronic instabilities in the observed structural phase transformation. Since, as is well known, first-principles calculations on such systems of rather low symmetry are difficult, some calibration against experiment must be made prior to estimating the validity of the theoretically determined electronic response functions. Thus it is especially important for our work that Lu *et al.*¹⁴ have made extensive optical reflectance measurements on single-crystal NbO_2 and $\text{Ti}_x\text{Nb}_{1-x}\text{O}_2$ and have derived the associated absorption function $\epsilon_2(\omega)$. These data provide the basis for a detailed comparison between theoretical band structures and experiment.

For the band studies we use the recently developed linearized-augmented-plane-wave (LAPW) method of Koelling and Arbmán.¹⁵ As discussed in Sec. II, this method has proven to provide an efficient and accurate approach for complex structures. Using a rigid-band scheme, the results of our calculations are found to describe accurately the optical absorption¹⁴ of the rutile phase

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LOCAL DENSITY APPROACH TO BULK AND SURFACE CHARGE DENSITIES*

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I. INTRODUCTION

As is clear from some of the other lectures given at this Institute, the current popularity of energy band theory stems from its successful application to the study of increasingly diverse problems in solid state physics. Recent new sophisticated experiments on both traditional materials and those having complex crystallographic structures have demanded, however, not only theoretical descriptions of eigenvalue phenomena but also detailed and precise wave functions with which to determine not only charge and spin densities but also the expectation values of different observable operators. Such a demanding test of the predictions of one-electron theory has the additional virtue of permitting, by their comparison with experiment, accurate determinations of the relative magnitude and importance of many-body effects in real solids. Thus, as emphasized by Norman March, there has developed considerable interest in applying the Hohenberg-Kohn-Sham (1,2) local density functional (LDF) formalism, and its recent extension as a local spin density functional (LSDF) formalism (3), to the investigation of various ground state properties of solids despite the usual difficulties of solving the associated one-particle equation characterized by a multi-center non-spherical potential.

Applications of the LDF formalism to atoms (4,5) and molecules (6) have yielded encouraging results. Similar applications for solids are complicated by (i) the need to consider both the short range and the long range multicenter crystal potential having non-spherical components, (ii) the difficulties in obtaining full self-consistency in a periodic system and (iii) the need to provide a basis set with sufficient variational flexibility. Hence, theoretical

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The observation of magnetism and superconductivity in both the ternary rare-earth rhodium borides (MRh_2B_4) and the Chevrel phase ternaries $\text{M}_x\text{Mo}_6\text{S}_8$ (with x close to 1) and most recently (i) the discovery of re-entrant magnetism accompanying a transition to a normal metallic state at $T < T_c$ (the superconducting transition temperature) and (ii) the coexistence of magnetism and superconductivity have generated considerable excitement as to the origin of these phenomena. We discuss the origin of magnetism and superconductivity in the MRh_2B_4 compounds and re-entrant magnetism in ErRh_2B_4 using the results of *ab initio* self-consistent LMT0 energy band calculations. The total and separate l -decomposed contributions to the density of states (DOS) arising from the two M, eight Rh and eight B atoms per unit cell are used to estimate their various contributions to magnetic ordering (via the 4f-5d RKKY interaction) and/or superconductivity (using a Gaspari-Gyorffy model to obtain the electronic contributions to λ , the electron-phonon coupling parameter, and McMillan strong coupling theory to obtain T_c). Comparisons are made with recent experimental results and several experimental speculations about the re-entrant magnetism state are presented including the possibility of a mixed (ferromagnetic and superconducting) state.

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INTRODUCTION

The discovery [1,2] of magnetism and superconductivity in rare-earth ternary compounds has brought together the study of these seemingly opposing collective phenomena. In particular, the observations of re-entrant magnetism in ErRh_2B_4 and $\text{Ho}_{1.2}\text{Mo}_6\text{S}_8$ and most recently the coexistence of antiferromagnetism and superconductivity in several of the Chevrel ternaries have raised questions regarding these phenomena and our fundamental understanding of the interactions leading to magnetism and superconductivity.

In the ternary boride MRh_2B_4 compounds (with M = a rare-earth metal) Matthias *et al.* [1] found that either ferromagnetism (M = Gd, Tb, Dy, and Ho) or superconductivity (M = Y, Nd, Sm, Er, Tm, and Lu) existed at temperatures $T < 12$ K. Table I gives both the magnetic transition temperatures (T_m^0) and the superconducting transition temperatures (T_c^0). The behavior shown in Table I is in sharp contrast to that observed in the ternary Chevrel phase compounds $\text{M}_x\text{Mo}_6\text{S}_8$ and $\text{M}_x\text{Mo}_6\text{Se}_8$ where each rare-earth compound was found to be superconducting except for Ce and Eu. The sharp break in properties between the M = Ho and Er boride compounds is of especially great interest—with magnetism for Ho ($T_m^0 = 6.56$ K) and superconductivity for Er ($T_c^0 = 8.7$ K), even though the effective magnetic moments of both RE ions ($10.6 \mu_B$ for Ho and $9.6 \mu_B$ for Er) differ by only a small amount (~10%). Surprisingly, ErRh_2B_4 , which becomes superconducting at 8.7, was found to become magnetic at $T = 0.9$ K with the return of the system to a normal conducting state ("re-entrant magnetism" in a superconductor).

We have been studying the origin of these phenomena using results of *ab initio* self-consistent band structure calculations carried out on five of these ternary borides, notably M = Y (which has no 4f electrons), Gd (with the largest total spin),

Ho, Er, and Lu (which has a closed 4f shell). We are particularly concerned with the competing mechanisms for producing magnetism and superconductivity in the rare-earth systems. However, only a qualitative understanding is at present possible because our band calculations are for the paramagnetic states.

The magnetic and superconducting interactions are included in the sense of perturbation theory. A more complete—and much more difficult—theory would solve the basic Hamiltonian with both magnetic and superconducting interactions included simultaneously. Such a treatment would provide a unified view of the phenomena of magnetism and superconductivity. Here we consider not only phenomena in which the magnetic interactions inhibit superconductivity, but also those in which the superconducting ordering prevents the onset of magnetism. This discussion leads to the suggestion of a possible new experiment and the occurrence of a mixed (magnetism and superconductivity) state for ErRh_2B_4 .

METHOD

Since some details of our energy band calculations [4] have been given elsewhere, and due to space limitations, we note here only that the calculations were done self-consistently for the full 18 atoms per unit cell using the Linear Muffin Tin Orbital (LMT0) and related methods with a potential that contained the Hedin-Lundquist treatment for exchange and correlation in the relativistic Dirac equation but without spin-orbit coupling.

RESULTS

Since the basic energy structures are

GENERALIZED SUSCEPTIBILITIES AND PHONON ANOMALIES IN Pd and Pt METALS *

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The generalized susceptibility, $\chi(q)$, in Pd and Pt for q along the $[100]$, $[110]$, $[111]$, and $[120]$ directions was determined from their APW and RAPW energy band structures, respectively, using the analytic tetrahedron linear energy scheme of Rath and Freeman. The band structures were previously found to yield Fermi surface radii, temperature dependencies of the static magnetic susceptibility, $\chi(T)$, resistivity, and a spin lattice relaxation, $T_1 T$, in very good agreement with experiment. In the $\chi(q)$ calculations, we used 2048 tetrahedra in 1.48th irreducible BZ and the energy eigenvalues for bands 4, 5, and 6 which cross the Fermi energy as fitted to a Fourier series representation. The intraband parts of $\chi(q)$ at $q = 0$ for both metals are found to agree with the density of states at the Fermi energy to within 0.5%. Our results show that the dominant contribution to χ_{intra} arises from the dominant band 5 whose "jungle-gym" FS has strong nesting features; the main peak for Pd occurs at the same q value ($= 0.65\pi/a$) for q along the $[0q0]$, $[q, q, 0]$, and $[q, q, q]$ directions. The locus of this main peak is a square in the $(0, 0, 1)$ plane. The maximum of χ_{intra} for q along the $[110]$ and $[111]$ directions are 23% and 13%, respectively, higher than the value of $\chi(q)$ at $q = 0$. For q along the $[010]$ and $[120]$ directions, the peak is, however, lower than the value of χ_{intra} at $q = 0$. Hence, while phonon anomalies are predicted for the $[110]$ and $[111]$ directions, no anomaly is predicted for either the $[100]$ or $[120]$ direction. The predicted q value for the $[110]$ anomaly, $q = 0.65\pi/a$ is close to the experimental value of $\sim 0.7\pi/a$. Although there may be a hint of an anomaly at $0.56\pi/a$ in the measurements, a more detailed investigation of this region is called for. For platinum, χ_{intra} for q along the $[010]$, $[110]$ and $[111]$ directions has main peaks which occur at $q = 0.68\pi/a$, $0.75\pi/a$, and $0.85\pi/a$, respectively. Here too, this main peak comes from the nesting of the jungle-gym Fermi surface which is not, however, as flat as that of palladium. Anomalies are predicted (although weaker in Pt than in Pd) along $[110]$ and $[111]$ but not along $[100]$ and $[120]$. The $[110]$ anomaly is close to the measured q value ($\sim 0.7-0.8\pi/a$). Also in agreement with experiment, we predict a weaker $[110]$ anomaly for Pt than for Pd. In both Pd and Pt, weaker anomalies are predicted for the $[111]$ direction than for the $[110]$ direction.

1. Introduction

The role of electronic structure in determining phonon anomalies in metals has become a subject of intense interest. Strong impetus for these investigations has been given by the correlation of spin den-

sity waves, charge density waves (CDW) and phonon anomalies with maxima in the generalized susceptibility, $\chi(q)$, for the non-interacting conduction electrons. Some time ago, Kohn [1] showed that for a free-electron gas, the existence of a sharp Fermi surface leads to non-analyticities in the phonon dispersion relations (now known as "Kohn anomalies") which occur at phonon momentum values equal to twice the momentum of the electrons at the Fermi surface. Subsequently, Taylor [2] treated the effect of various radii of curvature of a single band Fermi surface, Afanasev and Kagan [3] gave a more detailed discussion for the case of a flat Fermi surface, and

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Electronic band structure and properties of α -U (*)

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Résumé. — Utilisant une version relativiste de la méthode LAPW, nous présentons des résultats d'une étude détaillée de la structure de bande électronique ainsi que de quelques propriétés physiques de l'uranium dans la phase orthorhombique. Les densités d'états totales et partielles sont utilisées pour discuter les résultats de photo-émission de Veal et Lam. Les surfaces de Fermi des bandes prédominantes 6 et 7 présentent une symétrie élevée ainsi que quelques particularités topologiques (*nesting*) qui peuvent être comparées aux mesures actuelles d'effet dHvA d'Arko et Schirber. Le calcul du facteur de forme neutronique en présence d'un champ magnétique est en bon accord avec les mesures de Maglic *et al.*

Abstract. — We present some results of a detailed study of the electronic band structure and some physical properties of orthorhombic uranium using a relativistic version of the LAPW method. Total and projected (by orbital angular momentum) densities of states are used to discuss the photo-emission data of Veal and Lam. The Fermi surfaces of the dominant 6th and 7th bands are found to have high symmetry (and some nesting features) of interest to dHvA measurements being pursued by Arko and Schirber. The theoretical magnetic field induced neutron form factor is found to be in good agreement with the measurements of Maglic *et al.*

The anomalous physical properties of α -U have made it a subject of great interest for experimental and theoretical study. Unfortunately, its complex structure (orthorhombic with 4 atoms/unit cell) and the resulting lack of symmetry have made its theoretical study by conventional energy band methods exceptionally difficult and costly. Thus, while we were able to study the light and heavy actinide metals [1] in their cubic (high temperature) structures, the study of α -U awaited development of a computational scheme which was not only rapid and efficient but which avoided the so-called *asymptote problem* which plagued our earlier efforts.

In this paper we report some results of our relativistic energy band studies on α -U using a relativistic version of the linearized augmented plane wave method [2-3] (LAPW). This scheme has been successfully applied to the study of some actinide compounds, notably UGe, [4], UIr, [2], and URh, [5]. We have determined the energy band structure, density of states (DOS), orbital angular momentum projected DOS (for use in analysing the XPS experiments of Veal and Lam [6], detailed Fermi surface cross-sections in close collaboration with the work of Arko and Schirber [7] reported elsewhere at this conference), wavefunctions and magnetic field induced spin densities, neutron magnetic form factors (in close collaboration with and to understand the measurements of Maglic *et*

al. [8]), and generalized susceptibilities, $\chi(q)$ (for investigating possible electronically driven phonon anomalies and charge density waves). Because of space limitations we are able only to give a brief indication of this extensive work here. A full report is being prepared for publication elsewhere.

The three lattice parameters and the atomic positional parameter, u , were obtained by extrapolating the temperature dependent X-ray measurements of Barrett *et al.* [9] to the temperatures assuming that the system was cooled under pressure in order to avoid the anomalies associated with transitions at $T < 43$ K. Using these parameters ($a = 5.360$ Å, $b = 11.086$ Å, $c = 9.328$ Å, and $\mu = 0.102$) our model warped muffin tin potential was constructed in the standard overlapping charge density model using the Kohn-Sham-Gaspar ($\alpha = 2/3$) exchange. In our calculation we use the $f^1 d^3 s^1$ configuration. Different estimates including a pseudo-self-consistent model (as was used earlier for UGe₂) to determine an improved choice of configuration, indicate that a configuration in which roughly 0.25 to 0.5 electron are transferred from the f to the d levels is more appropriate. The calculated band structure was fitted with a Fourier series and used in our determinations of the Fermi surface, DOS and $\chi(q)$.

Figure 1 shows the $l = 3$ angular momentum projected DOS. We see a good deal of structure in the total DOS (not shown) arising from the lower symmetry and the hybridized set of s , p , d , and f bands. There is a rapidly increasing total DOS just above E_F

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Electronic Structure and Magnetism of CuNi Coherent Modulated Structures

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The electronic and magnetic properties of a coherent modulated structure consisting of three atomic layers each of Cu and Ni perpendicular to $[111]$ were determined from *ab initio* self-consistent spin-polarized energy-band calculations. We predict a substantial reduction in spin magnetization and contact hyperfine fields H_n at the Ni layers (in contrast with enhancements reported earlier from ferromagnetic resonance measurements), charge ($0.1e$) and spin ($\sim 0.01\mu_B$) transfer to the Cu sites, and large H_n at the Cu nuclei.

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Considerable interest has been aroused by the observation of greatly enhanced elastic properties of short-wavelength composition-modulated bimetallic films¹ and especially by the significantly larger magnetization density of a short-wavelength (30 Å) CuNi thin composition-modulated film² compared to that of pure Ni as deduced from ferromagnetic resonance experiments. White and Herring³ have proposed that the anomalously large magnetization value is indicative of a complex magnetization distribution, including negative regions, which can substantially increase ferromagnetic resonance frequencies.

In this Letter, we present the first theoretical determination of the electronic structure and magnetic properties of a realistic layered coherent modulated structure (CMS). *Ab initio* self-consistent, semirelativistic, spin-polarized linear muffin-tin orbital (LMTO) energy-band calculations have been carried out on a 50-50-composition CMS consisting of three atomic layers each of Cu and Ni modulated along the $[111]$ direction.² We find no evidence for a complex magnetization distribution. Instead, the spin magnetization of the Ni layers is reduced relative to that of pure Ni: The central Ni layer moment is $0.50\mu_B$ whereas that of the interface Ni layers is $0.37\mu_B$. The large reduction of the "interface" Ni layer moments is consistent with the magnetically dead layers reported earlier for Ni layers deposited on a Cu substrate.⁴ The calculated core-polarization hyperfine fields, H_n , at the Ni sites also show a reduction proportional to that found for the spin magnetization. The small Cu magnetic moments ($\sim 0.01\mu_B$) result in large H_n values which

are substantially larger than any Knight shifts observed for Cu.

Our CMS, shown in Fig. 1, has six atoms per unit cell and four inequivalent layers denoted as "bulk"-like for the central Cu and Ni and "interface" for the remaining Cu and Ni. Since depositions of a metal A on a metal B result in a lattice constant for the initial layer which is between that of A and B, we form our CuNi structure with

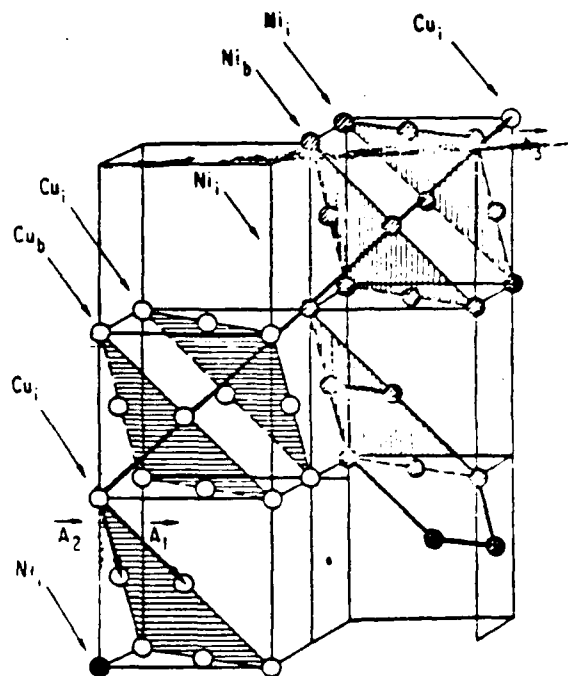


FIG. 1. CuNi CMS modulated along $[111]$ (without local strain). $\bar{A}_1$, $\bar{A}_2$, and $\bar{A}_3$ define the six-atom unit cell; *i* and *b* denote "interface" and "bulk."

ELECTRONIC STRUCTURE OF SURFACES, SURFACE MAGNETISM AND SURFACE PHASE TRANSITIONS *

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Abstract.— We describe and discuss several recent developments in the study of surface phenomena in this rapidly developing area of research which is becoming of great interest to the Mössbauer spectroscopist.

The study of surface phenomena has added a new and important area of research which has yet to be exploited fully by the Mössbauer spectroscopist. As discussed at the Conference, this is particularly true as regards transition metals where recent advances in experimental and theoretical methods for studying bulk and surface properties have increased our knowledge about these phenomena but have also raised important questions about our fundamental understanding in a dramatic way. Here I will mention two areas, surface magnetism and surface phase transitions, which are particularly important examples of recent developments in this fast growing field.

A. Surface States, Surface Magnetization and Electron Spin Polarization in Ferromagnetic Transition Metals.

A striking example of some of the conflicting results is the contradictory conclusions about the validity of the Stoner-Wolfarth-Slater band theory of ferromagnetism drawn from electron spin polarization experiments [1]. The possibly important role of surface phenomena in reconciling these difficulties has been recognized in recent years and theoretical efforts at describing the electronic structure of surfaces have intensified. These investigations share the common problem with bulk studies of treating localized d electrons along with the itinerant s-p electrons. For bulk systems, considerable progress has been made in the last few years in this direction [2].

Similarly, sophisticated theoretical methods are being developed for accurately determining the electronic structure of transition metal surfaces. These use the bulk energy band methods in the local density formalism as extended to the case of a thin film [3-15]. As in bulk systems, a number of thin film studies for transition metals has shown that self-consistency plays an essential role [6-12,15].

I discuss in detail the work which we [9-12] have carried out on ferromagnetic transition metal films using our recent extension of the local spin density functional formalism to thin films. These are the first spin polarized ab initio self-consistent energy band studies of ferromagnetic transition metal films that are thick enough [9-layers for Ni(001) and 7 layers for Fe(001)] to accurately determine the energy dispersion and spatial character of the surface states and their effects on the surface spin polarization layer by layer spin and charge distributions and layer projected density of states.

One striking feature of the results is the Friedel type oscillation induced by the surface discontinuity in the layer spin magnetic density - but not in the charge density. A result of particular interest here is the prediction of a decrease (by 20%) in the surface layer magnetic moment in Ni and a larger increase in the case of Fe. There is no evidence for magnetically 'dead' layers.

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Local Density Functional Approach to the Isostructural
 γ - α Transition in Cerium Using the Self-Consistent
Linearized Augmented Plane Wave Method

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MAGNETIC INTERACTIONS IN CHEVREL PHASE TERNARY COMPOUNDS

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We report detailed results of ab-initio self-consistent LMTO energy band studies of several Chevrel phase ternaries, EuMo_6S_8 and SnMo_6S_8 . In these unique calculations, all electrons of the full 15 atoms/unit cell are treated explicitly with a self-consistent Hedin-Lundqvist exchange and correlation potential in the relativistic Dirac equation but without spin-orbit coupling. As in our earlier work on the rare-earth ternary borides, the total and separate (by atom) l -decomposed contributions to the density of states (which show the Eu atoms to be magnetically isolated) are used to discuss their magnetic and superconducting properties.

The discovery that the ternary compounds of the rhodium borides, MRh_4B_4 , and the Chevrel phase molybdenum chalcogenides, MMo_6S_8 (or Se_8), exhibit (i) superconductivity and/or magnetism including (ii) the co-existence of the two and (iii) re-entrant magnetism in several important systems has generated great interest in the origin of these phenomena both experimentally and theoretically. Experiments on these systems have far outstripped theoretical understanding and have generated numerous unsolved questions.

In the case of the rare-earth ternary rhodium borides our self-consistent LMTO energy band studies have provided a qualitative understanding of the underlying electronic structure and some of the basic phenomena observed [1]. These results were also used to predict [1, 2] a possible mixed state in ErRh_4B_4 at temperatures above the re-entrant magnetism temperature—a state which may have been seen in the magnetization vs. magnetic field measurements of Ott et al. [3]. The complexity of the crystal structure of the Chevrel phase ternaries have made difficult even non-self-consistent energy band studies. Instead, early studies were carried out with approximate molecular cluster-tight binding [4] and (limited basis set) localized orbital methods [5]. We here report results ab initio self-consistent LMTO energy band studies of several of the MMo_6X_8 compounds ($\text{M} = \text{Eu}$ and Sn) which include all electrons and all 15 atoms in the unit cell.

The band calculations have been performed by use of the Linear Muffin Tin Orbital (LMTO) method [6]. The scheme of calculation is essentially the same as has been used for calculations on A15 compounds [7] and ternary borides [1].

The crystal structure data of Marezio et al. [8] on PbMo_6S_8 has been used in all our Chevrel phase

calculations, but without distortion of the Mo-octahedron and with a rhombohedral angle of 90° . Further, if one considers spherical symmetric potentials around each site, this leaves only 4 types of atoms in the structure, whereas including the distortion would make most of the 15 atoms per cell inequivalent. In this simplified structure there is one Sn site, six equivalent Mo sites, but two types of S-sites.

The potential used the Hedin-Lundqvist treatment of exchange and correlation. The charge densities from the core states as well as from partly occupied f -states were recalculated in each iteration by using the actual MT-potential. The basis set included s , p and d states for all atoms, while in the three-centre terms in the LMTO matrices $l_{\text{max}} \leq 3$. This results in an eigenvalue problem of dimension 135×135 . The sharp structure in the total DOS shown in fig. 1 for EuMo_6S_8 arises from the very flat nature of the energy band structure. Very similar results were also found for SnMo_6S_8 which is a superconductor. These flat bands yield high electron velocities at E_F and appear to explain the unusually high upper critical fields, H_{c2} , found in these superconductors. We see that there is considerable structure in the total DOS, particularly around E_F , which arises from the Mo-4d electrons. From a partial DOS calculation [cf. table 1], we find that there is a high 4d DOS at E_F which is favorable for superconductivity. There is a distinct gap in the DOS just above E_F which falls in the middle of the Mo- d bands and a smaller band gap between the Mo- d and S- p states as was also inferred or seen in the earlier calculations [4, 5]. As for most other high T_c compounds, the Fermi level falls just 2 electrons below the middle of the bonding-antibonding "gap" of the metal d -states. (This explains why the ternaries $\text{Mo}_2\text{Re}_4\text{S}_8$, which have 2 more electrons per cluster, are semiconductors.) Usually for Mo compounds, the d bands are oc-

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Magnetism and superconductivity in C15 compounds from self-consistent band calculations

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All-atom—all-electron self-consistent semirelativistic linear muffin-tin orbital energy-band studies are reported for TiBe_2 , ZrZn_2 (at ambient and high pressures), the high- T_c superconductor ZrV_2 , and the ultralow- T_c superconductor YAl_2 . Total and partial (by atom type and l values) density of states, Stoner-like parameters, electron-phonon coupling parameter λ and superconducting transition temperatures T_c (determined within the rigid muffin-tin approximation and McMillan's strong coupling theory with and without paramagnon contributions), and their behavior under applied pressure are used to discuss the origin of their observed magnetism and/or superconductivity. From an analysis of the results, we suggest possible high- T_c superconductivity at high pressure for ZrZn_2 , and its unlikely occurrence for TiBe_2 unless dominant soft phonon modes exist.

I. INTRODUCTION

The cubic Laves or C15 compounds of type MgCu_2 exhibit a number of interesting phenomena including (i) the much studied weak ferromagnetism¹⁻³ in ZrZn_2 and (ii) correlations between high superconducting transition temperatures T_c and lattice instabilities¹⁰⁻¹⁷ ZrV_2 and HfV_2 , which are well known in the more familiar A15 and rocksalt transition-metal compounds. Interest in superconductivity and itinerant magnetism in the C15's has recently been revitalized following the report of itinerant antiferromagnetism in TiBe_2 by Matthias *et al.*¹⁸ This discovery followed the expectation raised by the theoretical proposal of Enz and Matthias¹⁹ that the itinerant ferromagnetism of ZrZn_2 arises from inhibited " p -state" pairing. In this view, the Cooper pair interaction is thought to be repulsive at short distances (s state) due to a dominant soft phonon, leaving only p and high pair states to be attractive. Thus, the s -state repulsion would contribute to the Stoner factor sufficiently to tip the balance toward magnetism and to prevent the occurrence of p -state superconductivity. They further predict that above a critical pressure at which the magnetism is destroyed in ZrZn_2 , p -state pairing superconductivity would appear and in TiBe_2 would coexist with any antiferromagnetic ordering.

Although extensively studied experimentally, only approximate model calculations^{8,9} have been performed for the electronic band structure of ZrZn_2 treated as a diamond lattice of zirconium atoms with the zinc atoms entirely neglected. No energy-band

studies have been made of TiBe_2 (or the high- T_c superconductors). Thus, it has not been possible to assess the possible electronic contributions to either a more conventional approach to superconductivity and/or magnetism or to the inhibited p -state pairing idea. This paper reports the first all-atom—all-electron, self-consistent semirelativistic energy-band calculations for TiBe_2 , ZrZn_2 (at ambient and high pressures), the high- T_c superconductor ZrV_2 , and the ultralow- T_c superconductor YAl_2 . Total and partial (by atom type and l values) density of states (DOS), calculated Stoner-like parameters to study the conditions for magnetism, electron-phonon coupling parameters λ , and T_c values and their behavior under pressure are presented and used to provide a qualitative understanding of these phenomena including the possibility of superconductivity in ZrZn_2 and TiBe_2 with the application of pressure without invoking p -state pairing.

II. METHOD

The energy-band structures were determined self-consistently using the linear muffin-tin-orbital (LMTO) method.²⁰ The C15 (AB_2) structure is a very closely packed structure with 71% of the volume filled by touching spheres and the site symmetry is high for the two constituents. This makes the C15 structure especially suitable to study with the LMTO band method using spherically symmetric potentials. The basis set included s , p , and d orbitals ($l_{\text{max}} = 2$) for each site, while the three-center terms included l

Rare-Earth Magnetic Isolation and Superconductivity of the Chevrel-Phase Compounds

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Results of *ab initio* self-consistent linear muffin-tin orbital energy-band studies for EuMo_6S_8 , GdMo_6S_8 , SnMo_6S_8 , and SnMo_6Se_8 , including all electrons in all 15 atoms/unit cell are reported. The large charge transfer from both the Eu, Gd, and Sn sites and from the Mo sites to the chalcogens is shown to be the driving mechanism with which to explain their unusual magnetic and superconducting properties.

The unusual magnetic and superconducting properties of the ternary molybdenum chalcogenides have attracted a great amount of experimen-

tal and theoretical interest.¹ These Chevrel-phase compounds, with general formula $M_x\text{Mo}_6\text{S}_8$ (or Se_8) and x between 1 and 4, occur for a large

SELF-CONSISTENT ELECTRONIC BAND STRUCTURE OF
CHEVREL PHASE COMPOUNDS¹

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As described elsewhere in these proceedings, the Chevrel phase molybdenum chalcogenides, MMo_6S_8 (or Se_8), exhibit a number of unusual properties including high T_c superconductivity and the highest upper critical fields, H_{c2} , known. They also exhibit magnetism and its coexistence with superconductivity and the phenomenon of re-entrant magnetism at low temperatures (see, for example, Fischer, 1978, and references cited therein).

From the theoretical side, the complexity of the crystal structures has made difficult even non-self-consistent energy band studies of the Chevrel phase ternaries. Instead, early studies were carried out with approximate molecular cluster-tight binding (Mattheiss and Fong, 1977; Andersen et al., 1978)

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THEORETICAL EVIDENCE FOR AN
ELECTRONICALLY DRIVEN ISOSTRUCTURAL
PHASE TRANSITION IN FCC LANTHANUM¹

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I. INTRODUCTION

The observation in lanthanum of a high superconducting transition temperature, T_c , and its large pressure derivative, dT_c/dp , has led to wide speculation that a pairing mechanism involving *f* electrons is responsible. Under pressure, T_c rises sharply from 6K at ambient pressure and saturates at a value of nearly 13K around 200 kbar. In addition, at 53 kbar and low temperature, a phase transition occurs which is

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Self-consistent linearized augmented-plane-wave study of the electronic structure and superconductivity of fcc lanthanum under pressure

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We report the results of a linearized augmented-plane-wave calculation of the electronic structure of fcc La at three lattice constants corresponding to ambient pressure, 50, and 120 kbars. The Kohn-Sham-Gaspar approximation for exchange and correlation is used and the potential is allowed a fully non-muffin-tin form. The f bands lie ~ 2 – 2.5 eV above the Fermi level and are ~ 1 eV wide, resulting in a very small (0.05 electrons) localized f occupation. Under pressure the f bands rise and broaden appreciably, resulting in only a slight increase in f occupation. The rigid-muffin-tin approximation for the electron-phonon interaction λ overestimates the superconducting transition temperature T_c by 40%, but we find that the drastic increase in T_c under pressure can be attributed primarily to changes in the electronic stiffness η . Structural transitions which occur at 25 and 53 kbars may be related to changes in Fermi-surface topology which we find to occur approximately at these pressures.

I. INTRODUCTION

The observation in lanthanum¹ of a high superconducting transition temperature T_c and its large pressure derivative dT_c/dP has led to wide speculation that a pairing mechanism involving f electrons is responsible. Under pressure, T_c rises sharply from 6 K at ambient pressure and saturates at a value of nearly 13 K around 200 kbars, as shown in Fig. 1. Two separate questions arise: (i) Why is La a high- T_c superconductor at all, since the isoelectronic elements Sc and Y are not good superconductors? (ii) What is the cause of the large pressure derivative, $dT_c/dP \approx 1$ K/10 kbar, which is among the largest known for superconductors?

From Fig. 1, the slope dT_c/dP is seen to show structure at 25 and 53 kbars. In addition, Balster and Wittig¹ have measured a concomitant anomaly in the low-temperature electrical resistivity at 53 kbar. As La is known² to be fcc at room temperature in a wide pressure range around 53 kbar, they have proposed that these anomalies arise from an isostructural (fcc — fcc) phase transition which terminates at a critical point below room temperature. Especially considering the decrease in dT_c/dP by a factor of 4 (Ref. 1) at this transition, this revives questions concerning the complex interrelation of lattice instability, phonon softening, and high-temperature superconductivity.

The superconductivity of La was attributed by Kondo³ and many others^{4–5} to f -electron mecha-

nisms of various kinds, with the large pressure derivative of T_c resulting from variation with pressure of the energy of the f state. The explanation in terms of f -electron states lying above, but very close to, the Fermi level E_F was also supported by other peculiarities observed in La. The temperature dependence of the magnetic susceptibility⁶ was interpreted to be due to an effective localized moment of one-half Bohr magneton, and the Knight shift, also normally temperature independent, was found⁷ to increase by 20% in cooling from room temperature to 1.5 K. The linear specific-heat coefficient⁸ was found to be very large and the thermal-expansion coefficient⁹ was found to be negative in certain temperature regions. These phenomena all seemed to suggest the occurrence of significant $4f$ -electron character in La, and it has been argued¹⁰ that La must be a “ $4f$ -band” metal. In addition, the low melting point of La had led Matthias *et al.*¹¹ to postulate an f -electron concentration of 0.7 electrons/atom.

However, the development of reliable tunnel junctions led to the unambiguous assignment of La as a relatively strong-coupling d -electron superconductor,^{12–15} with electron-phonon coupling constant $\lambda \approx 0.8$ – 0.9 . While this partially accounts for the large electronic specific heat, which is enhanced by the factor $(1 + \lambda)$, it still leaves the possibility that the pressure enhancement of T_c is related to f character in the electronic structure. Ratto, Coqblin, and Galleani⁵ have attributed

APPENDIX C

Lectures and Seminars presented by Arthur J. Freeman , 1979

Theory Colloquium, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Feb. 7, 1979. Talk: "Local Density Approach to Bulk Solids and Surfaces".

Physics Department Colloquium, Louisiana State University, Baton Rouge, Louisiana, Feb. 8, 1979, Talk: "Electronic Structure of Bulk Solids, Surfaces and Chemisorption".

Seminar, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, Feb. 2, 1979, "Re-entrant Magnetism in Rare-earth Superconducting Compounds".

Physics Department Colloquium, University of Illinois at Chicago Circle, Chicago, Illinois, Feb. 21, 1979, Talk: "Electronic Structure of Bulk Solids, Surfaces and Chemisorption".

Symposium on Muon Spin Rotation and Associated Problems, April 12-14, 1979, Dogashima, Japan, Invited Paper: "Muon Hyperfine Anomalies".

Talks given at the Institute of Physics, Peking, People's Republic of China, April 17, 1979, "Local Density Theory of Electronic Structure of Solids"; April 18, 1979, "Reentrant Magnetism in Rare-earth Superconducting Ternary Compounds"; April 19, 1979, "Surface States and Surface Magnetism in Ferromagnetic Transition Metals".

Talks given at the University of Nanking, Nanking, People's Republic of China, April 23, 1979, "Local Density Theory of Electronic Structure of Bulk and Surfaces"; April 24, 1979, "Reentrant Magnetism in Rare-earth Superconducting Ternary Compounds".

Talks given at Fudan University, Shanghai, People's Republic of China, April 25, 1979, "Local Density Theory of Electronic Structure of Bulk and Surfaces"; April 26, 1979, "Reentrant Magnetism in Rare-earth Superconducting Ternary Compounds".

Talks given at Hangchow University, Hangchow, People's Republic of China, April 27, 1979, "Local Density Theory of Electronic Structure of Bulk and Surfaces".

American Physical Society Meeting, Chicago, Illinois, March 19-23, 1979, Leader of group session "Band Theory of Metals".

Int. Conf. on Layered Materials and Intercalates, University of Nijmegen, The Netherlands, Aug. 28-31, 1979, Member of the Organizing Committee and Chairman of the 2nd plenary session.

ICM'79, Munich, Germany, Sept. 3-7, 1979, Talks: "Magnetic Interactions in Chevrel Phase Ternary Compounds" and "Surface States, Surface Magnetization and Electron Spin Polarization in Ferromagnetic 3d Metals"; Member Int. Program Committee; Organizer, Chairman and Invited Speaker at Panel Symposium on Surfaces and Magnetism; Speaker at Closing Plenary Panel "Trends In Magnetism".

Int. Conf. on Mössbauer Spectroscopy", Portoroz, Yugoslavia, Sept. 10-14, 1979, Invited paper: "Electronic Structure of Surfaces, Surface Magnetism and Surface Phase Transitions" (with C. S. Wang, H. Krakauer and M. Posternak); Chairman and Organizer of Panel on Surfaces.

Talk at ETH, Zürich, Switzerland, Sept. 17, 1979, Physics Department Colloquium, "Surface Magnetism in Ferromagnetic 3d Metals".

American Physical Society Talks Presented, March 1979, Chicago, Illinois

"Near Infra-red Luminescence from CuCl" (with G.K. Wong, J. Bajaj and C.W. Chu).

"Infra-red Absorption in CuCl" (with F. Wagner, Jr., M. Weinert and C.W. Chu).

"Self-Consistent Electronic Structure of Ternary Chevrel Phase Compounds",
(with T. Jarlborg).

"Electronic Structure of CuCl" (with C.S. Wang, T. Jarlborg and M. Weinert).

"Electronic Structure of Cu- and Ag-Halides" (with T. Jarlborg).

"Isostructural Phase Transitions and Superconductivity in fcc La" (with
W.E. Pickett and D.D. Koelling).

"Local Density Functional Study of the α - γ Isostructural Phase Transition
in Cerium" (with W.E. Pickett and D. D. Koelling).

Lectures and Seminars Presented - 1980

Physics Department Colloquium, University of Indiana, Bloomington, Indiana, February 12, 1980: "Magnetism and Superconductivity in Ternary Rare-earth Compounds"

Sanibel Symposia, Palm Coast, Florida, March 4-20, 1980: "Electronic Structure of High Temperature Superconductors; C-15's and Chevrel Phase Compounds"

International Symposium on the Physics of Actinides and Related 4f Materials, Zurich, Switzerland, April 9-11, 1980.

Invited papers:

"f-Electrons in Solids: Electronic Structure and Properties of Actinides and Rare-Earths" (Opening talk)

"f-electron Bonding, Electronic Structure and Phase Transitions"

Chairman of Panel Session: "Localized vs Itinerant f-electrons"

International Conference on Physics of Magnetic Materials, Jaszowiec, Poland, April 12-20, 1980. "Magnetism of Surfaces, Interfaces and Modulated Structures" (invited paper); Organized and Chaired Symposium on Trends in Magnetism.

Colloquium Physics Department, ETH, Zurich, Switzerland, April 23, 1980, "Magnetism and Superconductivity of the Chevrel Phase Compounds"

Colloquium Physics Department, University of Basel, Basel, Switzerland, April 28, 1980, "Magnetism Surfaces, Interfaces and Modulated Structures"

Colloquium Physics Department, ETH, Zurich, Switzerland, April 29, 1980, "Surface States and Electronically Driven Surface Phase Transitions"

Colloquium Physics Department, University of Geneva, Geneva, Switzerland, May 2, 1980, "Magnetism and Superconductivity of Chevrel Phase Compounds"

International Conference on Ordering in Two Dimensions, Lake Geneva, Wisconsin, May 28-30, 1980 "Generalized Susceptibilities and Electronically Driven Surface Phase Transitions (invited paper given by H. Krakauer)

V International Conference on Hyperfine Interactions, Berlin, West Germany, July 21-25, 1980, "Magnetism of Surfaces, Interfaces and Modulated Structures" (Invited talk) (unable to attend due to illness of son)

Yamada Conference IV on Physics and Chemistry of Layered Materials, Sendai, Japan, September 8-10, 1980, "Electronic Band Structure of Transition Metal Dichalcogenides and Artificial Layered Coherent Modulated Structures" (Invited paper) (unable to attend due to illness of son)

International Conference on Ternary Superconductors, Lake Geneva Wisconsin, September 24-26, 1980 "Spin Polarization and High Critical Fields in Chevrel Compounds" (Invited talk)

Talks presented at the American Physical Society Meeting in New York, 24-28 March 1980

Invited talks

"Magnetic Isolation and Superconductivity in Rare-Earth Chevrel Compounds"
T. Jarlborg

"Surface Resonances, Generalized Susceptibilities and Electronically Driven
Surface Phase Transitions"
H. Krakauer

Other talks

"Self-Consistent Electronic Structure of Coherent Metal Superlattices: Cu-Ni"
(with T. Jarlborg)

"Magnetism/Superconductivity in Cl_5 Compounds from Self-consistent LMO
Band Calculations"
(with T. Jarlborg)

"Hyperfine Anomalies in Muonic Atoms From Breit Interactions and Unrestricted
Dirac-Fock Solutions"
(with J.V. Mallow, J.P. Desclaux and M. Weinert)

"Self-consistent Electronic Structure of the Contracted Tungsten (001)
Surface"
(with M. Posternak and H. Krakauer)

"Self-consistent Electronic Structure of $\text{A}'(111)$ Films and Chemisorption
Bonding of Oxygen on $\text{A}'(111)$ "
(with D.-S. Wang, H. Krakauer and M. Posternak)