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CORRELATION AND COLLECTIVE MODES IN NARROW BAND MATERIALS.(U)
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Correlation and collective modes have been studied for systems with quite localized valence or conduction bands. In particular this research has been concerned with localized electron-hole states and how they contribute with other excitations to the dynamical response of the system. The most important aspect studied has been the effect of excitons or exciton-like states on superconducting properties. Initially the system studied has been Cu_2O for which a simplified tight-binding model was used. The results showed that an

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cont→ effective attractive interaction between electrons due to the local field produced by interacting electron-hole pairs was possible. Under the appropriate conditions this interaction could lead to a superconducting state. The contribution of the localized excitation structure and plasmon modes to the electronic loss spectra was also analyzed. Here the effect of the primary electron energy on the plasmon peak position was shown to be significant.

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I. Research Objective

The overall objective of this research is to study correlation and collective modes for systems with quite localized valence or conduction bands. For these systems one must often consider the effects of excitation structure and localized collective modes to understand the interaction with optical or electronic probes or large scale correlated states such as superconductivity. In certain cases one must consider these effects to understand even ground states properties, such as for narrow band insulators. In particular this research has been concerned with localized electron - hole states and excitonic modes and how they contribute with other excitations to the dynamical response of the system.

During the preceding year we have completed studies of interband excitations and surface and bulk plasmon modes and their contributions to the electron energy loss spectra of TiO and FeO. These studies were important for understanding the structure of the loss spectra, which can be a very precise probe of surface electronic structure and the effects of adsorption.

We have also begun studies of mechanisms for superconductivity which are alternatives to the phonon-coupling mechanism. Among these new mechanisms are coupling via plasmons or excitons. The excitonic mechanism is especially promising for narrow band systems, and we have started investigations of Cu_2O to ascertain whether excitonic effects can cause an attractive, non-local dynamical response. This work may lead to an explanation of some unusual experimental results for this and other systems.

In conjunction with these investigation of particular effects for specific systems, we have continued a program of developing computer codes useful in the study of localized systems. These include band structure codes and cluster codes for studying well-localized structures at the surface or in the bulk. With the band structure codes, we have expanded the number of lattice symmetries available

to include the rocksalt structure appropriate for transition metal monoxides. With the cluster codes, we have added new features to improve convergence and to simulate better the bulk environment for clusters representing defects in the solid.

In the following sections, we will discuss how we proceeded toward our objectives. We will also discuss some of the future work we will do in this area.

II. Localized Effects in Superconducting Systems

A. Alternative Coupling Mechanisms

From time to time some researches have proposed and others have looked for other mechanisms besides the basic phonon mechanism for obtaining the effective attractive interaction between electrons. The search was motivated in part by the enormous benefit which would accrue from finding a superconducting state which persisted even up to liquid nitrogen temperatures (around 70°K). The highest critical temperature yet found is in the range of 25-30°K.

Bardeen, Cooper and Schrieffer[1] showed that superconductivity arises from an effective attractive interaction between quasi-particles near the Fermi surface of a degenerate electron system. In their work and in most subsequent work, the effective interaction is assumed to be a constant over frequency up to a cut-off frequency beyond which it is zero. However, the effective interaction need not be constant and it need not be due to phonon coupling alone. Some worker have considered additional mechanisms such as plasmons or excitons and have also considered a dynamic, momentum-dependent interaction. It has been speculated that plasmon[2] or exciton[3,4] coupling can greatly increase the critical temperature T_c. Different structures such as layered metal-oxide-semiconductor systems or thin films have also been considered as candidates for enhanced T_c.

An electron-hole plasmon mechanism was shown by Pashitkii[5] to give an attractive coupling for model semiconductor or semi-metal systems with appreciably different conduction and hole electron masses. Later Tanaka[2] showed that the electron plasmons alone would support the attractive coupling for semiconductors in both two- and three- dimensional systems. However, Kelly and Hanke[6] did a careful calculation for Si(111)- SiO_2 in a MOS system where they considered a coupled electron-phonon and electron-plasmon mechanism. They solved the weak-coupling superconductivity equations for a number of carrier densities but found only very slight enhancements of T_c due to plasmons at low carrier densities. No enhancement of T_c which could be attributed to plasmon coupling has been seen experimentally.

Other coupling mechanisms have been considered which are related to the plasmon or excitonic mechanisms. An acoustic plasmon mode which can be due to interacting electrons and holes as in the Pashitskii model[5] or to the interaction between heavy d and light s electrons has been suggested. Calculations for transition metals using the latter interaction show that the enhancement of T_c is minor[7]. Another model involves an electron heavy hole mechanism where the electron pairing arises from the exchange of virtual bosons associated with vibrations of the hole lattice.[8] Here, again, more complete calculations show that the enhancement of T_c would be small [9].

The excitonic mechanism of superconductivity has been considered before[3], but the most recent model is due to Allender Bray and Bardeen (ABB).[4] They chose to consider excitons in a semiconductor where they are well-defined excitations. A metal in intimate contact with the semiconductor provided free carries which interacted by way of the excitons. The authors chose a narrow-gap semiconductor to treat within their model since the valence electrons can, in many cases, be considered as if in a free electron metal with the gaps introduced by perturbation theory. The model calculations were made to second order in the electron-exciton coupling and revealed an attractive local polarization field due to the exciton coupling. Under certain very favorable conditions the model predicted a value of T_c at room temperature or above. However,a later calculation by Bardeen[10] indicated a much smaller enhancement of T_c was likely.

Inkson and Anderson later came out with a rebuttal to the ABB arguments.[11] They showed that the use of second-order perturbation theory could lead to double counting of the exciton response and that one should use the complete inverse dielectric function ε^{-1} for the semiconductor. Their calculations using a long-wavelength model dielectric function for silicon and indium antimonide showed no enchancement due to excitons, as was also the case with later, more detailed calculations for Ge using pseudopotential energy band structure and wavefunctions.[12] ABB countered[13] that the Inkson and Anderson approach was valid for the systems they considered, but that the ABB model was for different systems. ABB said that excitonic effects were more likely in systems where excitonic excitations were

strong and local field effects, which Inkson and Anderson had neglected, were important.

There is some experimental evidence which may support the ABB contention. Researchers have postulated a similar excitonic-superconductivity mechanism is responsible for recent observations of near-perfect diamagnetism in temperature-quenched CuCl and pressure-quenched CdS at temperatures up to 300°K[14]. Measurements by Lockhart etal [15] have established the existence of an anomalously weak electric field outside the surface of copper. Below 4.5°K a phase transition occurs and the electric field drops from the expected value to near zero. A thermal oxide some 20 Å thick covers the Cu surface, and the perfect shielding most likely occurs in that region. The most likely explanation of the shielding is that the surface electrons couple and form a Bose condensate.[16] It is also possible that this phase is superconducting. Other experiments indicate that an exciton gas formed in Cu_2O by laser excitation obeys Bose-Einstein statistics.[17] Since Cu_2O is a semiconducting material with strong excitonic effects of the type considered by ABB, the anomalous behavior may be due to their mechanism.

B. Excitonic Effects

The usual effective interaction constant for superconductivity is written

$$N(0)V = \mu - \lambda \qquad (1)$$

where N(0) is the density of states at the Fermi level of one spin, μ is the density of states times an averaged screened Coulomb interaction and λ is the attractive coupling constant. The effective interaction may be written

$$V(\vec{q},\omega) = 4\pi e^2/q^2\varepsilon(\vec{q},\omega)$$

for wavevector $\vec{q}$ and frequency ω where ε is the total dielectric function containing both electronic and ionic polarizabilities. Now stability requires that $\varepsilon(\vec{q},o) \geq 0$ so by Eq.(1) $\lambda < \mu$ at least at $\omega = 0$. However it is known that λ can be much larger than μ in many cases. Cohen and Anderson[18] have resolved this contradiction by pointing out that the stability requirement applies only to the ionic interaction and that the polarization fields seen by the ions and the

electrons are different, the difference being that the electrons see the ionic self-polarization. When ionic local field effects are included[18], one gets $\lambda \propto \Omega_p^2/\omega_{ph}^2$ where Ω_p is the ionic plasma frequency and ω_{ph} is a phonon frequency. Now λ can be larger than μ, and since the McMillan result for T_c is [19]

$$T_c \propto \exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu(1+.62\lambda)}\right] \tag{2}$$

one can have higher transition temperatures.

Allender, Bray and Bardeen[4] postulated that a similar local field arose for the exciton mechanism and that for a semiconductor, $\lambda_{ex} \propto \omega_p^2/\omega_g^2$ where ω_p is the plasmon energy and ω_g is the gap energy. They derived λ_{ex} for a narrow gap semiconductor and showed that in favorable cases with their model, one could get $\lambda_{ex} \geq \mu$ and substantial increases in T_c.

As was stated in Sec. II. A, the main objection of Inkson and Anderson[11] to the ABB model was that one should use the complete inverse dielectric function ε^{-1} rather than perturbation theory to calculate λ_{ex}. They also said that the exciton and other excitations are poles of the dielectric function, but are zeroes of the interaction because that involves $1/\varepsilon$. Thus they argued that excitons should not be important to the effective interaction and backed this contention up with model calculations of ε^{-1} for Si and In Sb.[11] One can show, however, that this last argument of Inkson and Anderson is not true in all cases. To see this we consider a system with an insulating ground state in the Wannier representation. The local Wannier functions and energies are related to their counterparts in the Bloch-representation by

$$u_n(\vec{r}-\vec{R}_\ell) = N^{-\frac{1}{2}} \sum_\kappa e^{i\vec{\kappa}\cdot\vec{R}_\ell}\, \psi_{n\kappa}(\vec{r})$$

$$E_n(\vec{R}_\ell) = N^{-\frac{1}{2}} \sum_\kappa e^{i\vec{\kappa}\cdot\vec{R}_\ell}\, E_{n\kappa}.$$

Since this transformation is unitary, the ground state of a one-electron system could be written as a determinant of Wannier functions. This state could include the self-consistent band structure in a one-electron formulation. The polarizability

between the non-interacting electron-hole pair is then

$$N^{o}_{12,34}(\omega) = \frac{2}{N}\delta_{1,4}\,\delta_{2,3}\,\frac{(f_{n_1} - f_{n_2})}{E_1 - E_2 - \omega - i0} \tag{3}$$

$$1 = n_1, \ell_1, \text{ etc....}$$

where f_n is the occupation number for band n. Thus we have states 1 and 2 as a particle and hole or vice-versa, and the poles of N^o are just the excitation energies between occupied and unoccupied bands. Since the dielectric matrix is

$$\underline{\varepsilon}(\omega) = \underline{1} - \underline{V}\,\underline{N}^{o}(\omega) \tag{4}$$

the poles of $\underline{N}^o$ are also the poles of $\underline{\varepsilon}$.

Hanke and Sham[20] have shown how to include particle-hole interactions in this matrix notations. Their formula for the polarizability is

$$\underline{N} = \underline{N}^{o}\,(1+\tfrac{1}{2}\underline{V}^{x}\underline{N}^{o})^{-1} \tag{5}$$

where $\underline{V}^x$ is the matrix of exchange interactions between the particles and holes. The sum of all polarizations is then

$$\underline{S} = \underline{N}\left[1 - \underline{V}\,\underline{N}\right]^{-1} \tag{6}$$

and the total inverses dielectric function is

$$\underline{\varepsilon}^{-1}(\omega) = 1 + \underline{V}\,\underline{S}(\omega). \tag{7}$$

Note that if $\underline{N} \to \infty$, $\underline{S} \to -\underline{V}^{-1}$ and $\underline{\varepsilon}^{-1} \to 0$.

Now if long-range screening is sizable, as is the case in many metals, then $\underline{V}$ will dominate $\underline{V}^x$ since the complete exchange term should be screened (i.e., $\underline{\varepsilon}^{-1}\,\underline{V}^x$), and the resulting poles of $\underline{\varepsilon}^{-1}$ will be just the plasmon poles. On the other hand, in insulating systems and in many semiconductors, the $\underline{V}^x$ term is important and screening is not complete. Then the pole structure will be different.

To investigate the pole structure when $\underline{V}^x$ is important, let us consider the simple case in which diagonal elements of $\underline{V}^x$ and $\underline{V}$ are dominant. Thus we have

$$V = V_{ph,ph}$$

$$V^{x} = V_{pp,hh}$$

where p(h) refer to particle (hole) states, and p and h can be on different sites. Now if we rewrite $\underline{S}$ in Eq. (6) as

$$\underline{S}(\omega) = \left[\underline{N}^{o}(\omega)^{-1} - (\underline{V} - \tfrac{1}{2} \underline{V}^{x}) \right]^{-1},$$

then since all matrices are now diagonal, the poles in S are simply

$$\omega = E_p - E_h - V_{pp,hh} + 2 V_{ph,ph} \qquad (8)$$

after summing over all spin states. This is just the singlet excitation energy from state h to state p in first order. Thus in this case, the poles of $\underline{\varepsilon}^{-1}(\omega)$ are just <u>shifted</u> from the poles of $\underline{N}^{o}$, but they still correspond to excitation energies. This result is not too surprising when one recalls that formally $\underline{\varepsilon}^{-1}$ must give the entire one-particle excitation spectrum, including plasmon and particle -hole excitations[21].

C. <u>A Tight - Binding Approach to Calculations of Excitation Structure</u>

The above example shows that there are cases where the contention of Inkson and Anderson does not apply and particle - hole excitations are important. Indeed there are many systems besides insulators where this is true. Of interest in this work are the transition metals and also Cu. As one proceeds across the transition metal series, the d-bands became narrower and particle-hole excitations become quite important so that, for example, Ni has a complicated electron energy loss spectrum. This is true for transition metal compounds as well, and Cu_2O has, of course, strong exciton contributions in the loss spectrum. In most of these cases the strongest excitations are localized, and local field effects and symmetry-breaking due to creation of the hole are significant. Thus one must include off-diagonal matrix elements in any formulation of $\underline{\varepsilon}^{-1}$. This is a completely different situation than the one considered by Inkson and Anderson who showed that off-diagonal elements were not important in their case[11]. No one has considered in detail the contributions of the off-diagonal elements of $\underline{\varepsilon}^{-1}$ to the effective interaction.

We wish a model for local field effects which takes into account the ground state band structure of our system. However, most calculations of $\underline{\varepsilon}^{-1}$ which include band structure effects are based on orbitals derived from the Bloch states of the band structure. These calculations are quite complicated and expensive which is one reason why no detailed studies of local field effects have been made. Furthermore, these calculations can only be made for a limited number of perfect crystals, and we would want a formulation that could study trends in several systems so that we could find the best candidates for an excitonic mechanism. What we need is a parametrized model with which we could derive most of the components of the excitation spectrum so that its results would be believable and which is simple enough to apply to a lot of different structures and compositions.

A simple approach to this problem is the tight-binding theory used to study the electronic structure of transition metal alloys. This theory has given results for the density of states in Cu-Ni alloys[22] across the whole range of compositions which are consistent with photoemission and other experimental results, and the method has also been used to give detailed information on surface segregation in transition metal systems.[23] A similar approach has already been used by Onodera and Toyozowa[24] in their important study of excitons in mixed ionic crystals. The theory should be useful especially for systems with narrow d-bands, and it evidently has the capability of handling complicated mixtures of components.

The d-electrons in the tight-binding approach are described by the usual Hamiltonian

$$H = \sum_i \varepsilon_i c_i^+ c_i + \sum_{i \neq j} t_{ij} c_i^+ c_j \qquad (9)$$

Where ε_i includes all intra-atomic Coulomb interactions on site i and t_{ij} is the hopping integral describing transitions between states i and j. In the resulting densities of states the ε_i terms determine the positions of the bands and the t_{ij} terms determine the widths. One can generalize this formalism straightforwardly to multiple bands.

We have used a continued-fraction formulation of the tight-binding theory to calculate the Green's function and electronic density of states. In the continued-fraction method, the local electronic Green's function is [25]

$$G_{ii}(\omega) = (\omega - \varepsilon_i - \Delta_i)^{-1} \tag{10}$$

where the self-energy terms are

$$\Delta_i = \sum_{j\neq i} \frac{t_{ij}t_{ji}}{\omega-\varepsilon_j - \Delta_j^i} + O(t^3),$$

$$\Delta_j^i = \sum_{l\neq j,i} \frac{t_{jl}t_{lj}}{\omega - \varepsilon_l - \Delta_l^{ij}} + O(t^3) \tag{11}$$

and so on. Typically, one truncates the hierarchy by requiring $\Delta_l^{ij} = \Delta_j^i$. The density of states is then derived from

$$D_i(\omega) = -\frac{1}{\pi} \text{ Im } G_{ii}(\omega). \tag{12}$$

The result in the spectral representation is then

$$G_{ii}(\omega) = \int \frac{D_i(\mu)\, d\mu}{\omega - \mu}\ , \tag{13}$$

where the usual pole structure is understood.

Now we may use the results for G_{ii} to calculate an excitation spectrum. Using G_{ii} from Eq. (13) we arrive at the result for the non-interacting polarizability

$$N^0_{ij,ij} = \frac{2}{N}(f_i - f_j)\int\frac{A_i(\upsilon)A_j(\mu)}{\upsilon - \mu - \omega}\, d\upsilon d\mu. \tag{14}$$

Using Eqs.(3) and (4), we can then compute the matrix $\underline{S}$ with the electron-hole Coulomb and exchange interaction integrals given by

$$\underline{V} - \frac{1}{2}\underline{V}^x = u_{ij,kl} - \frac{1}{2}u^x_{ij,kl}\ . \tag{15}$$

The choice of parameters in Eq. (15) determines the excitation structure. As an example, we consider again the diagonal interaction $(u - \frac{1}{2}u^x)_{ij,kl} = -x$. Then, as before, the imaginary part of the sum of all polarizations is

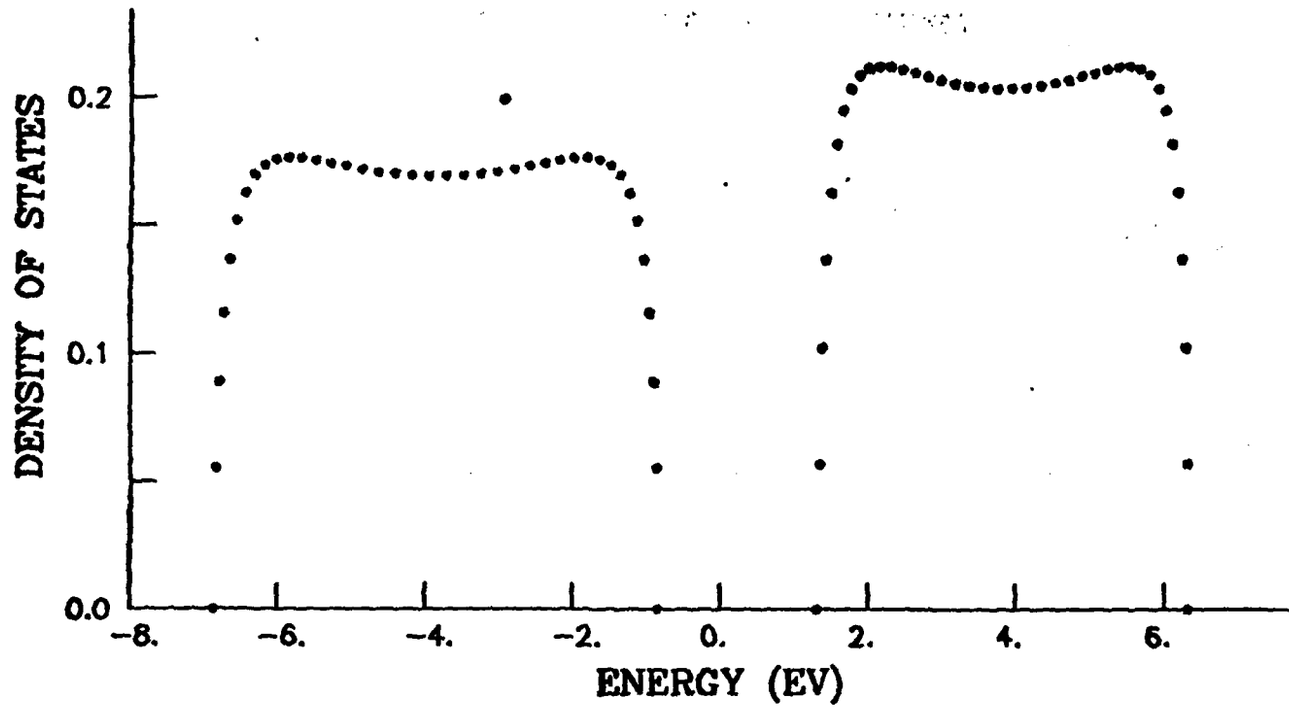

Fig.1a Topmost valence and lowest conduction band densities of states for Cu_2O. The widths are the calculated widths (Ref.25), and the gap is the experimental gap of 2.17 eV.

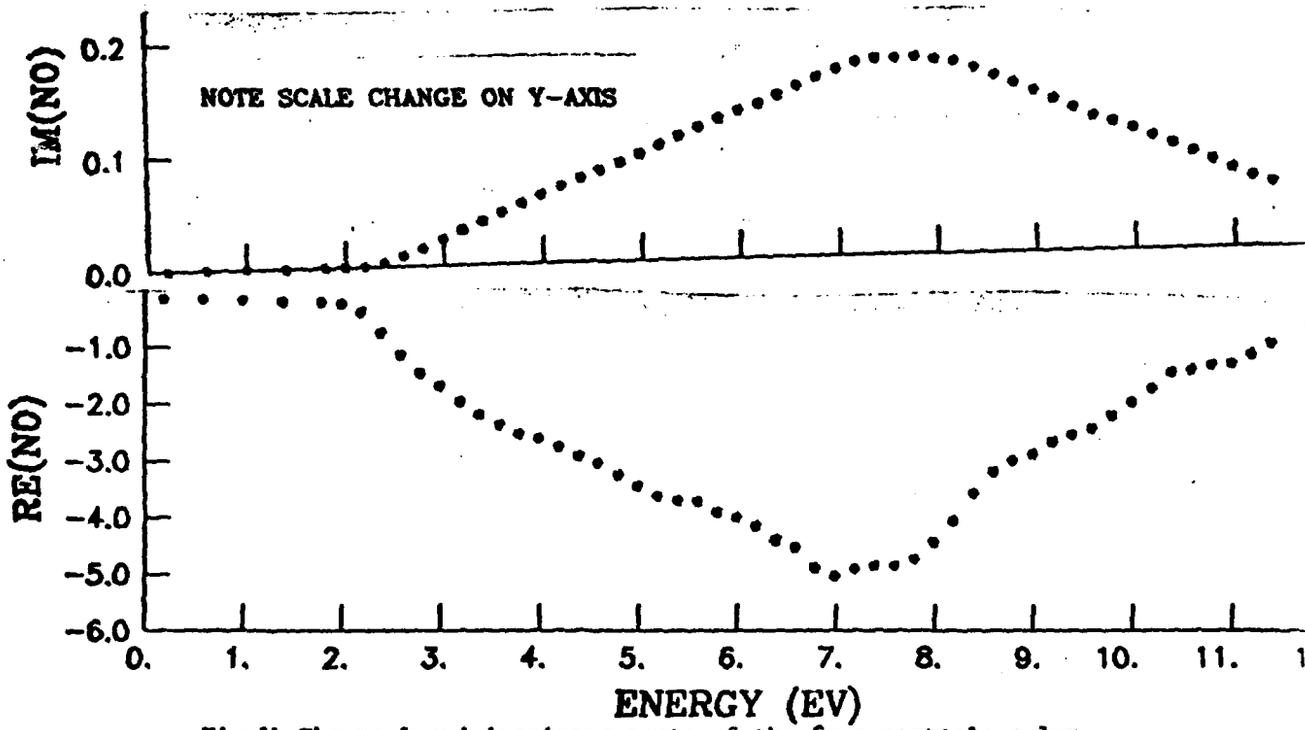

Fig.1b The real and imaginary parts of the free particle polarization N^{o}. Note that $N^{o''}$ is zero below 2.17 eV.

$$\text{Im } S(\omega) = \frac{N^{0''}(\omega)}{[1 + xN^{0'}(\omega)]^2 + [xN^{0''}(\omega)]^2} \quad . \tag{16}$$

If x is zero, the excitation spectrum, given by Im(S(ω)), is just the convolution of electron and hole states. If x is within the appropriate range such that

$$N^{0'}(\omega_x) = -\frac{1}{x} ,$$

$$N^{0''}(\omega_x) = 0 ,$$

then an isolated pole <u>in the band gap</u> results. This is an exciton.

For our initial calculations, we have chosen a simplified exciton interaction. As in the example in <u>Sec. II. B</u>, we choose

$$\underline{V} - \tfrac{1}{2}\underline{V}^x = (u_{ij,ij} - \tfrac{1}{2}u^x_{ij,\,ij})\,\delta_{ij,k\ell} \tag{17}$$

$$= u - \tfrac{1}{2}u^x$$

Then the matrix $\underline{S}$ given in Eq. (6) is diagonal, and we get

$$S(\omega) = \frac{N^0(\omega)}{1-(u - \tfrac{1}{2}u^x)N^0(\omega)} \tag{18}$$

Now to study the attractive part of the local field effect, we must look at

$$\text{Re}\{\varepsilon^{-1}(\omega)\} = 1 + u\ \text{Re}\{S(\omega)\}. \tag{19}$$

From Eq. (9) we get

$$\text{Re}\{S\} = N^{0'}\frac{\left[1-(u - \tfrac{1}{2}u^x)N^{0'}\right] - (u - \tfrac{1}{2}u^x)(N^{0''})^2}{D}, \tag{20}$$

where

$$N^0 = N^{0'} + iN^{0''}$$

$$D = \left[1-(u - \tfrac{1}{2}u^x)N_o'\right]^2 + \left[(u - \tfrac{1}{2}u^x)N_o''\right]^2,$$

and we have suppressed the ω dependence. Since u^x in our case will be considerably larger than u, we have $(u - \tfrac{1}{2}u^x) < 0$; and thus Re{S} will be less than zero only for $N^0 \leq (u - \tfrac{1}{2}u^x)^{-1} < 0$. Therefore as u^x becomes larger, we have a larger frequency range over which Re{S} <0. The form of Eqs. (19) and (20) and the relative sizes of the parameters involved, dictate that $N^{0''}$ must be small (preferably

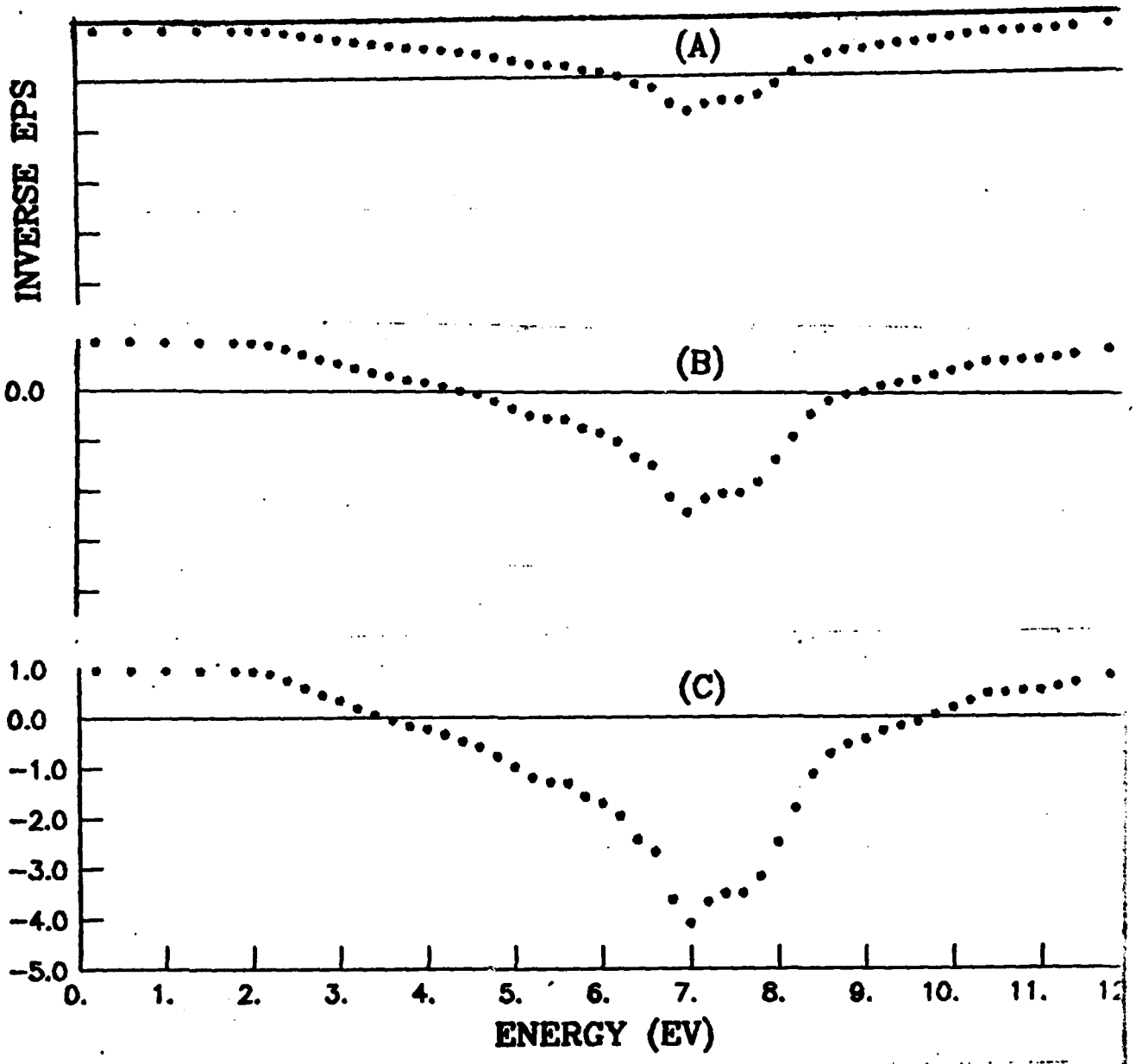

Fig.2 $Re\{\varepsilon^{-1}\}$ with $u-1/2u^x$ set at the value appropriate for the n=1 exciton line of the yellow series ($u-1/2u^x$ = .14 eV) and with (A) u = .1 eV, (B) u = .2 eV, (C) u = .3 eV.

zero) for $R\{\epsilon^{-1}\} < 0$. Therefore true excitons in the band gap will dominate the attractive interaction. However, note that all these restrictions may not apply to the case when $(V - \frac{1}{2} V^x)$ is a matrix.

Our initial calculations were for Cu_2O. The lowest conduction band and highest valence band are both formed from the Cu 3d orbitals according to band structure calculations[26]. The exciton spectrum is quite rich, but we choose here only the initial (n = 1) line of the yellow series[27]. The calculated densities of states for the valence and conduction bands are shown in Fig. 1. These have the widths and relative positions of the actual bands. In Fig. 2 we depict the results for $Re\{\epsilon^{-1}\}$ for a range of values of $u - \frac{1}{2} u^x$ appropriate to the exciton series. As might be expected, $Re\{\epsilon^{-1}\}$ becomes more negative as we increase the size of u and u^x.

We are now extending this method to realistic valence and conduction band densities of states. We are also including the rest of the d-electron interaction integrals so that we have a full matrix formulation. The result should be a believable picture of the exciton contribution to the dielectric response of the system. We are also going to repeat these calculations with the parameters appropriate for CuCl and CdS systems.

III. Development of Calculation Methods

A. Molecular Cluster Methods

We have implemented two methods for calculating the self-consistent electronic structure of molecular clusters, ab-initio Hartree Fock and linear-combination-of-atomic-orbitals-Xα(LCAOXα). These methods give a detailed description of local electronic structure, and the self-consistency allows a description of electronic rearrangement even for changes in complicated geometries. In the present case the methods are useful for studying the effects of localized defects or bound electron-hole pairs on the optical absorption. The cluster approach can also be used to study the contribution of localized excitations to the dynamical response of our bulk systems.

Although we have done several calculations with the Hartree-Fock method, we will use our Xα codes more extensively in the future. One reason is that the UHF code is much more expensive than the Xα code for a given system owing to the difference between the detailed non-local exchange calculation and the local density formulation. Another reason is that the Xα method usually gives accurate results when compared with experiment, at least for ground state properties. The Xα method we use is due to Dunlap et al.[28] and has the advantage over multiple-scattering formulations that it does not use the muffin-tim approximation. The molecular orbitals are in the form of linear combinations of Gaussian orbitals making easier the calculation of matrix elements for system properties. The code can compute integrals for angular momentum up through f and g so that one can study 4d transition metals and even rare earths. However, one would have to add relativistic effects in these cases.

We have modified the codes to better approximate the bulk environment. To do this we employ two methods. One is to remove unpaired valence electrons and replace them with a compensating sphere of charge in which the cluster is inscribed. The other method is to include the interactions with the ions outside the cluster

by adding Madelung terms. Both methods should be useful for semiconductor systems like Cu_2O.

B. Band Structure Methods

We have implemented Xα codes which use an LCAO basis and thus are compatible with our cluster methods. The codes were developed by Wang and Callaway[29] and include d- and f- functions so they can be used on transition metal systems. However, the programs were originally written only for simple, body-centered and face-centered cubic structures with one atom per unit cell. We have now extended them to rocksalt structures so that we can look at transition metal oxides. In the future we will extend them to more general cubic structures with two atoms per unit cell so that, for example, we can look at CuCℓ. The band structure codes are also spin-unrestricted, as are the cluster codes, and we can therefore study spin polarization effects which are important in some transition metal systems.

With the results of the band structure calculations, we can look at such things as optical properties and use the band wavefunctions and matrix elements as a basis for studies of the excitation structure. We may also use the results as a starting point to obtain better parameters for our tight-binding calculations. And eventually we will use the results to provide a detailed environmental potential in a more complete bulk embedding model for our cluster calculations.

IV. Electron Energy Loss Structure of Clean and Oxidized Titanium

In this section we report the completion of our work on analyzing contributions of interband transitions and plasmons to the excitation spectra of transition metals.

There is a qualitative disagreement among the experimental loss spectra, and in addition the results have been given different interpretations so that very different energies for plasmons and interband transitions have been reported. The discrepancies in measurements on transition metals make it unclear whether the plasmon energy position is given by free-electron theory or whether, for example, effects due to the periodic lattice potential are important.

The characteristic loss structure measurements fall into two classes: measurements of losses suffered by electrons with energies of many kilovolts as they are transmitted through thin films and measurements of losses suffered by electrons with energies around 100eV as they are reflected from the material. The former experiments are dominated by electrons which do not undergo elastic scattering while the latter are more highly resolved but contain electrons which have been elastically scattered at least once. A typical reflection spectrum for clean Ti is shown in the lowest curve (E_p = 200eV) of Fig. 3. The transmission spectrum differs in that the main peak is shifted several volts higher in energy.[30] A similar situation occurs when we compare measurements we have made on Fe/FeO systems with transmission experiments. To clear up the confusion and also to provide a basis for use of EELS as a surface analysis tool, we made several measurements of the loss spectra for Ti systems.

The analysis of the clean and oxidized Ti data in Figs. 3 and 4 was given in our last report. In summary, for the clean Ti spectra in Fig. 3, the peak around 5eV is a surface plasmon which very quickly diminishes with oxygen coverage or increasing primary energy. The broad main peak is the bulk plasmon with secondary surface and bulk excitations in its tail. The peaks at about 42eV,

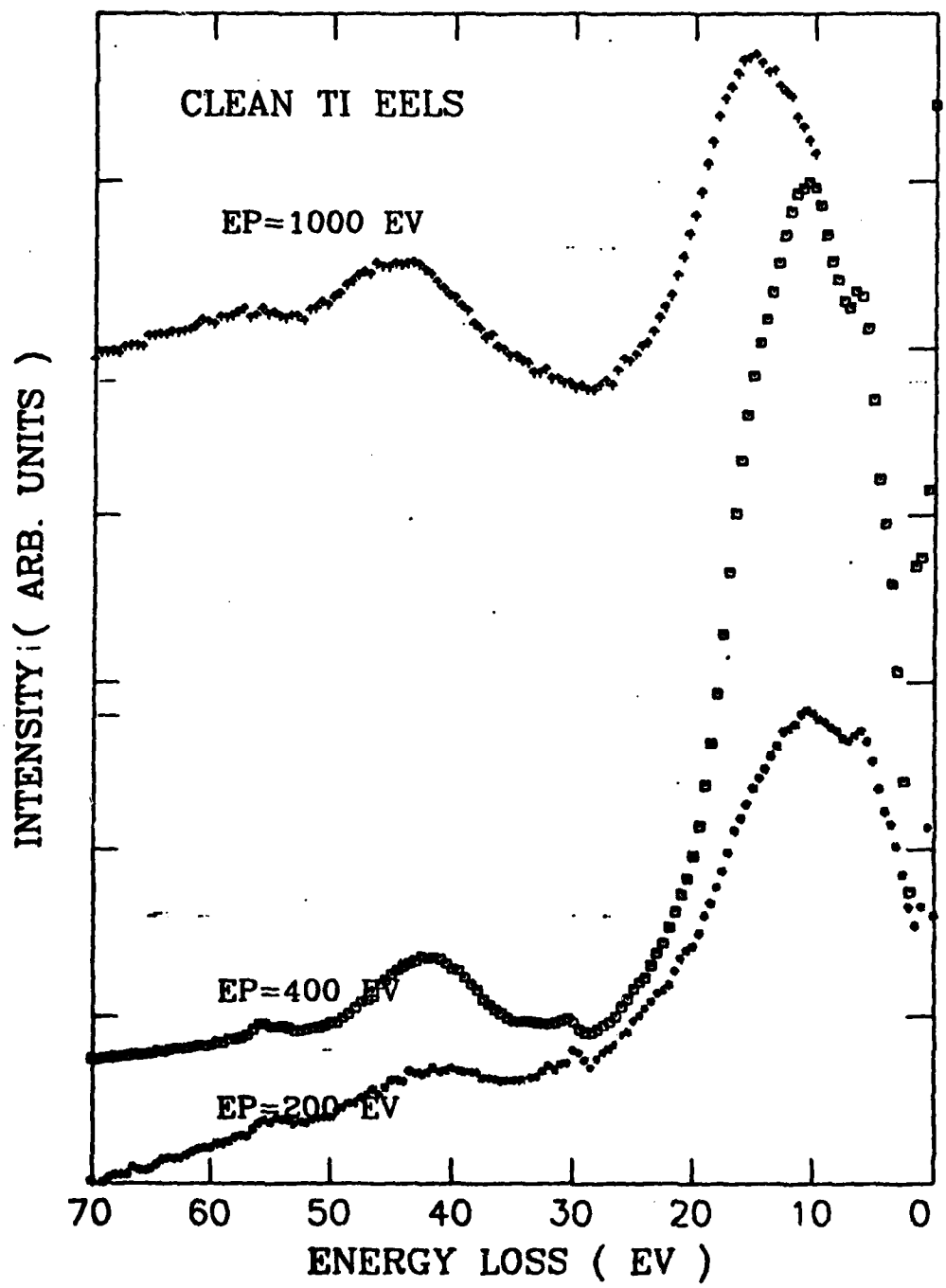

Fig.3 A comparison of clean Ti loss spectra for different primary energies.

which increases in intensity relative to the main peak as primary energy increases, is mysterious. It is in the wrong position for an interband excitation and does not behave like a collective mode. It may be due to a collective excitation triggered by an excited Ti3p electron. For the oxidized Ti spectra in Fig. 4, the lower curve shows the surface peak greatly reduced and the plasmon peak shifted to somewhat lower energy. The O2s peak is now prominent at about 20eV, and the broad 42eV peak persists. The upper curve for EP=1000eV shows a significantly different spectrum with a broadened plasmon peak now shifted to overlap the O2s peak. If the shifting were to continue for higher primary energies, the spectrum would look much like the transmission spectrum.[30] The shifting of the bulk plasmon peak with primary energy is seen both in the clean and oxidized systems and is also seen for other materials.

What could cause the movement of the plasmon peak to higher energies as the incident energy is increased in the reflection experiments and also could cause the difference between the positions of the plasmon peak in the reflection and transmission experiments? A possible explanation of this movement is that it is caused by plasmon dispersion. The RPA formula for dispersion is

$$\omega_q = \omega_p\{1 + \frac{3}{10} + \left(\frac{qv_f^o}{\omega_p}\right)^2 + \ldots\}$$

so that non-zero momentum transfer would always result in a positive energy shift. Now in the transmission experiments,[30] the acceptance angle of the detector is 5 mrad. so that for incident energies of 35 keV the momentum spread for the electrons transmitted in the forward direction is well below the Fermi momentum. However, if there is enough scattering of the electrons within the sample, a significant number of the electrons undergoing plasmon losses and then entering the detector would transfer considerable momentum to the plasmons. We have applied to the electrons a model derived for multiple scattering of ions in a screened Coulomb region[31] and have found that the electron beam does spread enough to allow a significant number of large momentum plasmon losses to be detected.

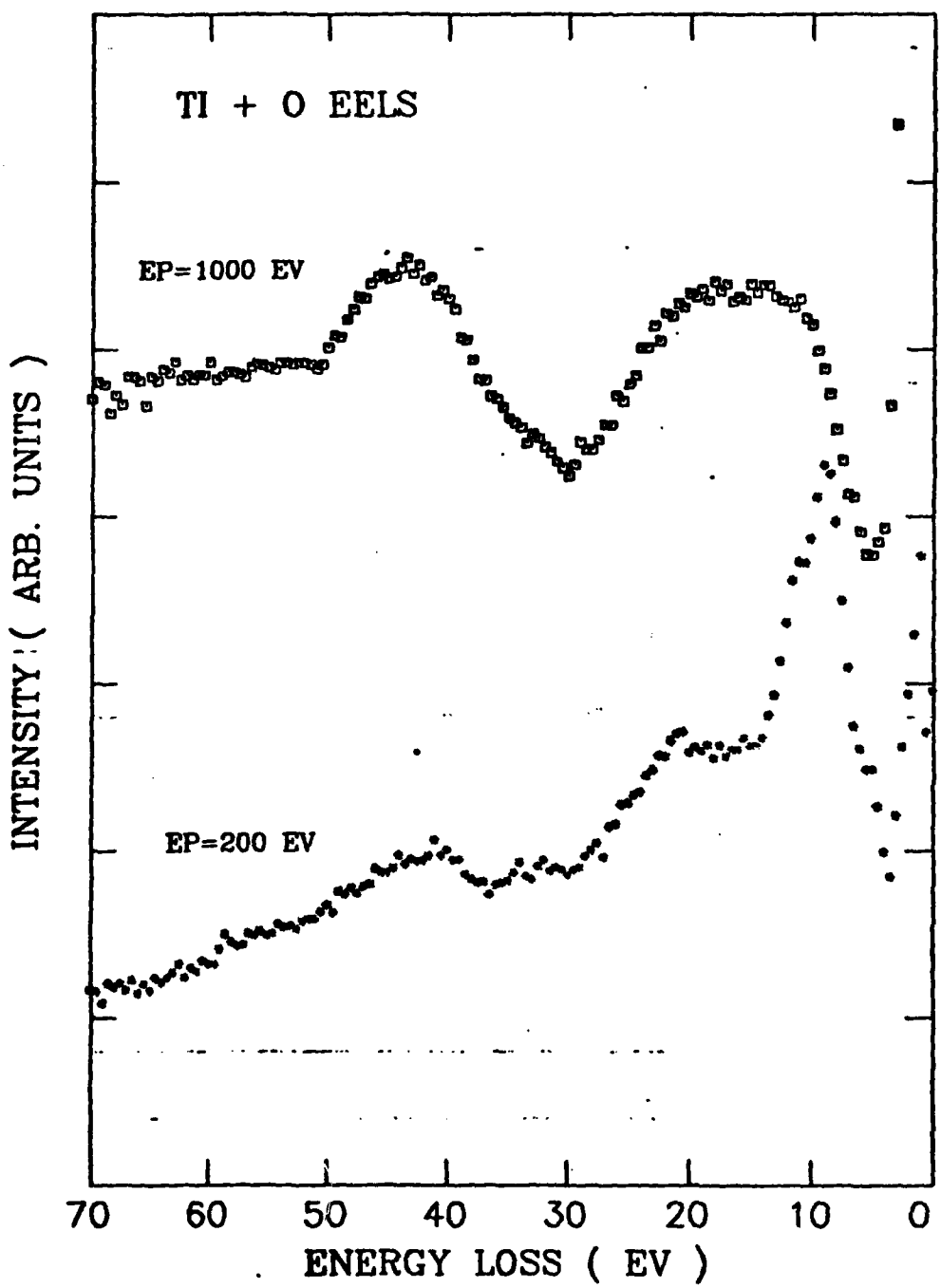

Fig.4 Loss spectra of final oxidized surface for EP=200 eV and EP=1000 eV.

This effect would cause a shift to higher energy and a broadening of the plasmon peak. A similar effect would also take place in the reflection experiments since as the incident energy increased the electrons would penetrate deeper into the sample and be scattered more. This would explain the dependence of the plasmon peak position on incident energy.

There are evidently no measurements of the plasmon dispersion for Ti, but measurements for Al indicate a dispersion of as much as 13 eV.[32] If a plasmon dispersion of several eV with a moderate increase in peak width is possible for Ti, this effect could explain the discrepancy between the transmission and reflection measurements. In that case the reflection peak would be closer to the true zero-momentum volume plasmon energy. Before any definite conclusion can be reached, however, one must do a calculation with a more realistic model of electron scattering.

These results resolve some of the conflicts between transmission and reflection loss spectra. They also reveal that care must be exercised in taking and analyzing the data. In particular for a reactive surface such as that of Ti, oxygen adsorption can greatly change the appearance of the spectrum. Our analysis provides a basis for understanding the origins of the peaks in the spectra, how they change as conditions are varied, and especially what happens to the surface peak.

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VI. Publications and Presentations

The following paper has been presented:

1. "Characteristic Energy Loss Spectra of Clean and Oxidized Ti Surfaces", with K. O. Legg; March 1981 meeting of the APS, Phoenix Az.

The following papers are being prepared for publication:

1. "Optical Constants of TiO_2", to be published in the Handbook of Optical Constants.
2. "Local Fields due to Excitons and Their Effect on Superconductivity".

VII. Personnel

The following personnel have been partially compensated by funds provided in this grant for conducting research during the period October 1, 1980 to September 30, 1981.

Dr. Martin W. Ribarsky - Research Scientist and Principal Investigator.

Mr. David Luedtke - Ph.D candidate.

VIII. Interactions

We had the following interactions in connection with this research during the period October 1, 1980 to September 30, 1981:

1. With Dr. C. S. Wang at the University of Maryland on the modification and use of LCAO-Xα band structure codes developed by her.
2. With Dr. Brett Dunlap of N.R.L. about using and modifying LCAO-Xα cluster codes he has developed.


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