

AD-A131 516

CORRELATION AND COLLECTIVE MODES IN NARROW BAND
MATERIALS(U) GEORGIA INST OF TECH ATLANTA SCHOOL OF
PHYSICS M W RIBARSKY 25 MAY 83 AFOSR-TR-83-0631

1/1

UNCLASSIFIED

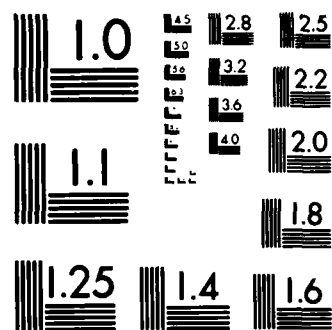
AFOSR-80-0023

F/G 20/12 NL

END

FILED

100



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 83-0631	2. GOVT ACCESSION NO. AD-A131516	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "Correlation and Collective Modes in Narrow Band Materials"		5. TYPE OF REPORT & PERIOD COVERED Interim 1982 Oct. 1, 1981 to Sept. 30, 1982
7. AUTHOR(s) Martin W. Ribarsky		6. PERFORMING ORG. REPORT NUMBER
1. PERFORMING ORGANIZATION NAME AND ADDRESS Georgia Institute of Technology School of Physics Atlanta, Georgia 30332		8. CONTRACT OR GRANT NUMBER(s) AFOSR-80-0023
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research Bolling AFB, Building 410 Washington, D. C. 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2301/A8
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE May 25, 1983
		13. NUMBER OF PAGES 28
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
DISTRIBUTION STATEMENT (of this Report) Approved for public release; Distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Transition metals, copper, correlation, excitons, dielectric response, interband excitation, optical spectra, energy loss spectra.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) 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. Important aspects studied have been the effects of exciton or exciton-like states on superconducting properties, electron energy loss spectra and optical spectra. Initially the system studied has been CuCl for which a tight-binding model was used. The results show that strong effects due to localized excitations		

DD FORM 1 JAN 73 1473

83 08 08 043

UNCLASSIFIED

over

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD A 131 516

DTIC FILE COPY

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

continued

of d-band electrons greatly affect the dynamical response and the effective electron interaction. The exciton resonance in the dynamical response is necessary to obtain the appropriate attractive effective electron interaction for superconductivity. The strong localization effects also will affect the loss spectra and optical spectra. Further calculations are planned for CuCl and also for CdS and Cu₂O.



A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Table of Contents

I. Research Objectives	1
II. Localization in Narrow Band Materials	3
A. General Background	3
III. Tight-Binding Calculations of Electronic Response	6
A. Dielectric Screening Including Local Field Effects	6
B. Exchange Effects	9
C. Calculation for CuCl	10
IV. References	23
V. Publications and Presentations	25

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)
NOTICE OF TRANSMITTAL TO DTIC

This technical report has been reviewed and is
approved for public release IAW AFR 190-12.
Distribution is unlimited.

MATTHEW J. KERPER

Chief, Technical Information Division

I. Research Objectives

The overall objective of this work is to study correlation and collective modes for systems with quite localized valence or conduction bands. For these systems one must consider the effects of localized excitations and collective modes to understand large scale correlated states such as superconductivity or the interaction of the system with optical or electronic probes. In certain cases, such as for narrow-band insulators, one must consider these effects to understand even ground state properties. 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.

The effect of strongly localized excitations on the superconducting properties of a material can be significant. We are most concerned with the effect on the superconducting mechanism itself. For systems such as oxidized Cu or CuCl, there are some experimental indications that the usual phonon-coupling mechanism is augmented or even dominated by an exciton-coupling mechanism. We have developed some models to describe the excitation structure in terms of excitons alone and with these have studied local field effects on the dynamical response. Our objective is to discover whether excitons can cause an attractive response.

The effect of localized excitations on the response to optical or electronic probes is known to be significant. Our exciton models have already successfully explained the optical absorption due to intrinsic excitons in several materials. Our objective here is to provide a detailed description of the effects of local field corrections and umklapp scattering terms on the dielectric response of these materials. Using the same models to describe the collective modes,

such as superconductivity, and dynamical properties of narrow band materials, we can arrive at a consistent description of these systems.

Eventually the models we set up will lead to a clear picture of what should be found in looking for a superconducting state in narrow band materials. Our ultimate objective is to predict new systems which will have optimized properties such as high superconducting transition temperatures. To this end we are developing more detailed descriptions of our test systems to give a full picture of the excitonic and other excitation structures. We can build this valuable information in detail into our more flexible models and thus improve our ability to predict behavior.

II. Localization in Narrow Band Materials

A. General Background

The existence of localized valence bands and localized excitations in narrow band materials renders the usual band-theoretic approach inadequate to describe many properties in these systems. In some cases the usual methods may suffice to describe typical properties of a material, but unexpected new effects may exist which require a detailed description of the microscopic environment of the electron or ion in order to be understood at all. This is evidently the case for the excitonic mechanism of superconductivity in certain narrow band systems. Sometimes even basic electronic properties such as whether a material is an insulator or conductor are not correctly predicted by band theory alone. This is the case for Mott insulators such as TiO which have such narrow d-bands that electrons are restrained from hopping from atom to atom, even though empty d-states are available. Here one must include the localized repulsive interaction between an electron which already occupies an atomic site and one which hops there to get the insulating state. Even some systems which are well-described by the usual methods, such as band theory, may have certain properties which require adding the effects of localization. One example is the optical properties of Si whose electron energy distributions and band gaps are well-described by band theory. Hanke and Sham¹ have shown that local field effects due to electron-hole interactions determine the size and position of the main peak in the optical absorption spectrum.

The effects of excitons in many narrow band systems are well established. Indeed for one system of interest in this research, Cu_2O , some of the earliest and most extensive work on the optical absorption spectra of intrinsic excitons has been done.² The kinetics and thermodynamics of excitons have been measured,

and new states including electron-hole liquids and possibly even Bose-Einstein condensations³ have been observed. At high exciton densities it is predicted that screening by near-by carriers ionizes the exciton gas into an electron-hole plasma and a metal-insulator transition known as a Mott transition occurs. Much work is being done to find this effect experimentally.

Superconductivity in narrow band systems and especially in d- and f-band metals has some markedly different properties than in simple metals. Magnetic and superconducting states, for example, can coexist in some materials. The description of the properties of these materials has been a real challenge for theorists, and in some cases a strong-coupling theory is needed in place of the usual BCS equations. Certain transition metal compounds, especially Al₅-type structures, have the highest known transition temperatures as well as high critical fields.

From time to time researchers have searched for mechanisms besides the basic phonon mechanism for obtaining superconductivity. The possibility of discovering a superconductor with a significantly higher transition temperature motivated their search. Plasmons and excitons in novel structures such as layered metal-oxide-semiconductor systems or thin films have been suggested as possible new superconducting states. Later, experimental studies of some of these systems proved negative, and further theoretical calculations for others indicated that the enhancement effect due to plasmon or exciton coupling would be minor.

More recently some intriguing results have come to light which suggest that the exciton mechanism, especially, may be active in certain narrow band systems. Researchers have postulated that an excitonic-superconductivity mechanism is responsible for observation of near-perfect diamagnetism in

temperature-quenched CuCl and pressure-quenched CdS at temperatures up to 300°K.⁴ Quite recently Collins et al.⁵ have presented calculations connecting conductivity anomalies in CuCl and CdS with an excitonic superconductivity mechanism based on the presence of impurities. This work shows that when the X and Γ points are made nearly degenerate by hydrostatic pressure, there may exist a region of attractive electron-electron interaction between electrons in the conduction bands supplied by impurities. Calculations based on the Eliashberg strong-coupling equations indicate that this exciton-coupled state may be superconducting. Measurements by Lockhart et al.⁶ 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. The most likely explanation of the shielding is that electrons couple with holes in the surface oxide formed and produce a Bose condensate.⁷ It is also possible that this phase is superconducting.

III. Tight-Binding Calculations of Electronic Response

In this section we discuss flexible and economical models we have developed which are formulated in a way that effectively deals with narrow valence bands. The work in this section is condensed from research papers which will be submitted shortly for publication.

A. Dielectric Screening Including Local Field Effects

We have recently developed a tight-binding formulation that enables one to make a detailed investigation of diagonal and off-diagonal terms in the dynamical screening of a narrow band system. The tight-binding approach is economical and very much simpler than a calculation based on the full energy bands and wavefunctions of the system. A matrix is necessary to describe the screening when local field effects are important.^{1,8} The difficulty in calculating the inverse dielectric matrix for a range of momentum transfers and frequencies has been the main obstacle to understanding the effect of local field terms.

The tight-binding formulation is based on a model developed by Prakash and Joshi⁹ and extended by Hanke to the lattice dynamics of Pd and Ni.¹⁰ One assumes that the band structure of the system is adequately described by a non-interacting band model. Then one connects the high-symmetry points in the band structure according to compatibility and which atomic level they represent by symmetry (for example Γ_{12} connects with L_3 in FCC structures because both states represent $d_{m=2}$). The bands are then described as parabolas with an effective mass assigned to give them the optimal shape. The Bloch states in the tight-binding formulation are just

$$\psi_{\mathbf{v}}^{\mathbf{k}}(\mathbf{r}) = \sum_{\ell} e^{i\mathbf{k} \cdot \mathbf{R}_{\ell}} u_{\mathbf{v}}(\mathbf{r} - \mathbf{R}_{\ell}), \quad (1)$$

where $u_{\mathbf{v}}$ is the appropriate atomic wave function. Although these approximations are fairly extreme, the model dielectric screening, when used in calculations of the phonon dispersion for Pd and Ni, gives good results.¹⁰

The calculations of dielectric screening with this tight-binding approach can be quite compact. For example, we may consider a two-band model where the d subbands are tightly bound and the s subbands are free electron-like. In most cases, the largest contribution to the dynamical inverse dielectric matrix comes from the s-s and d-d intraband transitions. For these terms the dynamical matrix is

$$\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) = \frac{1}{\epsilon_0(\vec{q}+\vec{G}, \omega)} [\delta_{\vec{G}, \vec{G}'} + \frac{v(\vec{q}+\vec{G})}{\epsilon_0(\vec{q}+\vec{G}; \omega) N^{-1}(\vec{q}, \omega) - \sum_{\vec{H}} A(\vec{q}+\vec{H})^2 v(\vec{q}+\vec{H}) / \epsilon_0(\vec{q}+\vec{H}; \omega)} A(\vec{q}+\vec{G}) A^*(\vec{q}+\vec{G}')] \quad (2)$$

where $\vec{G}, \vec{G}'$ and $\vec{H}$ are reciprocal lattice vectors. The function ϵ_0 is just the RPA dielectric function for the electron gas and gives the s-s contribution.

The coulomb interaction is

$$v(\vec{q}) = \frac{4\pi e^2}{N\Omega_0 q^2} \quad (3)$$

where Ω_0 is the unit cell volume and N is the number of unit cells. The term

$N(\vec{q}, \omega)$ is the d polarization and is written

$$N(\vec{q}, \omega) = \sum_{\vec{k}} \left[\frac{f(d_m, \vec{k})(1-f(d_m, \vec{k}+\vec{q}))}{\omega + E(d_m, \vec{k}) - E(d_m, \vec{k}+\vec{q}) + i0^+} - \frac{f(d_m, \vec{k}+\vec{q})(1-f(d_m, \vec{k}))}{\omega + E(d_m, \vec{k}) - E(d_m, \vec{k}+\vec{q}) - i0^+} \right] \quad (4)$$

If $E(d_m, \vec{k}) = E_0 + \hbar^2 k^2 / 2m_d$, Eq.(4) is just the Lindhard formula and can be solved analytically. Note, however, that one could use a more accurate band structure in Eq. (4) and find $N(\vec{q}, \omega)$ numerically. The overlap matrix element is

$$A(\vec{q}) = \int_{N\Omega_0} u_{dm}(\vec{r}) e^{-i\vec{q} \cdot \vec{r}} u_{dm}(\vec{r}) d\vec{r} \quad (5)$$

where in the tight-binding approximation we neglect overlaps between sites.

The terms $N(\vec{q}, \omega)$ and $A(\vec{q})$ are in general matrices, but become single elements in the case where we only consider $m=m'$ and $\vec{R}_\ell = \vec{R}_\ell'$. Note, however, that in

the case of d-bands the matrices are in the tight-binding basis and are small for narrow bands. The quantity $\dots$ in (9) can be calculated in a straight-

forward fashion as shown by Hanke.¹⁰

The frequency-dependent inverse dielectric matrix in Eq.(2) is a direct generalization of Hanke's static result in Ref. 10. The complete ϵ^{-1} contains bubble diagrams to all orders in the RPA and can be generalized to include exchange effects via ladder diagrams. Thus one can treat the effects of plasmons and exciton-like states in the bands with the same formalism. One can even treat intrinsic excitons in the band gap as we will discuss below. With the same model, we will be able to treat on an equal footing the most important electronic effects contributing to the dielectric screening and to possible superconducting effects.

When one adds interband terms, one replaces Eq. (2) by a matrix equation. If only d-d interband terms are important, the matrix equation is a direct generalization of Eq. (2) but with a different polarization $N(\vec{q}, \omega)$ than the intraband polarization. However, if d-s intraband terms are present, the situation is more complicated. The dielectric d-s matrix is now given by

$$\epsilon_{ds}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) = \frac{1}{\Omega_0} v(\vec{r}+\vec{G}) \sum_{\vec{m}} \sum_{\vec{k}} \sum_{\vec{H}} N_m^{ds}(\vec{q}+\vec{H}, \vec{k}; \omega) A_m^{ds}(\vec{k}+\vec{H}-\vec{G}) A_m^{ds}(\vec{k}+\vec{H}-\vec{G}')^* \quad (6)$$

Here the overlap matrix element is

$$A_m^{ds}(\vec{k}+\vec{H}-\vec{G}) = \left(\frac{1}{\Omega_0}\right)^{1/2} \int_{N\Omega_0} u_{dm}^*(\vec{r}) e^{i(\vec{k}+\vec{H}-\vec{G}) \cdot \vec{r}} d\vec{r} \quad (7)$$

where we assume that the s state is a plane wave. Since the summation over $\vec{k}$ is not contained in N_m as it is in the intraband case, we cannot evaluate ϵ^{-1} by taking the inverse of matrices in the tight-binding basis. We must invert ϵ directly in the $\vec{G}, \vec{G}'$ basis. When all terms are included, this means we must solve the equation

$$\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) = [\delta_{\vec{G}, \vec{G}'} - \epsilon_{ss}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) - \epsilon_{dd}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) - \epsilon_{ds}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) - \epsilon_{sd}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega)]^{-1} \quad (8)$$

Moreover, since the summation over k in Eq.(6) includes the terms $N_m^{ds} A_m^{ds} A_m^{ds*}$, we cannot convert to a $\vec{k}$ integral which can be solved analytically even in the effective mass approximation. We must do the summation over $\vec{k}$ in Eq.(6) numerically. We shall discuss these issues further for the calculations on CuCl in Sec. III. C.

B. Exchange Effects

We can extend Eq.(2) or Eq.(8) to include exchange effects. These effects must be included if we are to study excitons and exciton-like states. The simplest way to add exchange is to assume a local form for the exchange interaction

$$v(\vec{q}) [1-f(\vec{q})]$$

The function $f(\vec{q})$ accounts approximately for exchange processes between electrons of parallel spins. In the Hubbard approximation¹¹ it is

$$f(\vec{q}) = \frac{q^2}{2(q^2 + k_{F_d}^2)} \quad (9)$$

where k_{F_s} and k_{F_d} are the Fermi momenta of the s and d bands respectively. Now the terms ϵ_0 and N^{-1} in Eq.(2) become

$$\epsilon_0(\vec{q}, \omega) = \frac{1 - v(\vec{q}) N_0(\vec{q}, \omega)}{1 + f(\vec{q}) v(\vec{q}) N(\vec{q}, \omega)} \quad (10)$$

$$N^{-1}(\vec{q}, \omega) = N_0^{-1}(\vec{q}, \omega) + f(\vec{q}) v(\vec{q}) \quad (11)$$

where $N_0(\vec{q}, \omega)$ is just the quantity in Eq.(4). On the other hand when d - s transitions are important, it is convenient to write

$$\epsilon_{ds}^x(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) = [1-f(\vec{q})] \epsilon_{ds}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega)$$

where ϵ_{ds} is given by Eq.(6) and

$$\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) = \{[\epsilon^x(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega)]^{-1} - \delta_{\vec{G}, \vec{G}'}\} \frac{1}{1-f(\vec{q})} + \delta_{\vec{G}, \vec{G}'} \quad (12)$$

Calculations have shown that in some cases Eq.(9) gives reasonable results for the exchange contribution¹⁰, but in other cases it gives a significant underestimate.¹ In the work in Sec.III.C we have chosen to replace $f(\vec{q})$ by $Cf(\vec{q})$ where C is an adjustable constant. We have chosen C such that we get the correct fundamental exciton binding energy.

One can make a detailed investigation of the exchange effect. This will be the purpose of our next calculation. In a generalization of Eq.(8), the polarizability matrix including exchange is¹

$$\underline{\underline{N}}^{-1}(\vec{q}, \omega) = \underline{\underline{N}}_0^{-1}(\vec{q}, \omega) + 1/2 \underline{\underline{v}}^x(\vec{q}). \quad (13)$$

Now the neglect of overlaps between sites in $A(\vec{q})$ makes the coulomb matrix element

$$\sum_{\vec{G}} |A(\vec{q}+\vec{G})|^2 v(\vec{q}+\vec{G}) = \sum_{\ell} \cos \vec{q} \cdot \vec{R}_{\ell} \int d\vec{r} d\vec{r}' |u_{dm}(\vec{r})|^2 v(\vec{r}-\vec{r}') |u_{dm}(\vec{r}'-\vec{R}_{\ell})|^2. \quad (14)$$

Thus to the same degree of approximation, the exchange would be

$$v_{\ell\ell}^x(\vec{q}) = \int d\vec{r} d\vec{r}' |u_{dm}(\vec{r}-\vec{R}_{\ell})|^2 v(\vec{r}-\vec{r}') |u_{dm}(\vec{r}')|^2 \quad (15)$$

where we have a diagonal matrix which is independent of $\vec{q}$. Eqs. (13) and (15) provide a more appropriate approximation for exchange when the system has narrow bands and thus has certain large exchange matrix elements.

C. Calculations for CuCl

We have applied our tight-binding formulation to calculations of the dielectric screening for CuCl. Recent experimental measurements of anomalously large diamagnetism¹²⁻¹⁴ for samples under pressures from 5 to 25 kb and at temperatures up to 240°K have stirred considerable interest in the possibility of high temperature superconductivity in this material. Calculations of the valence and conduction bands¹⁵⁻¹⁷ all indicate that CuCl is a direct gap semiconductor with a zincblende structure and that it remains so under the pressures used in the experiments.

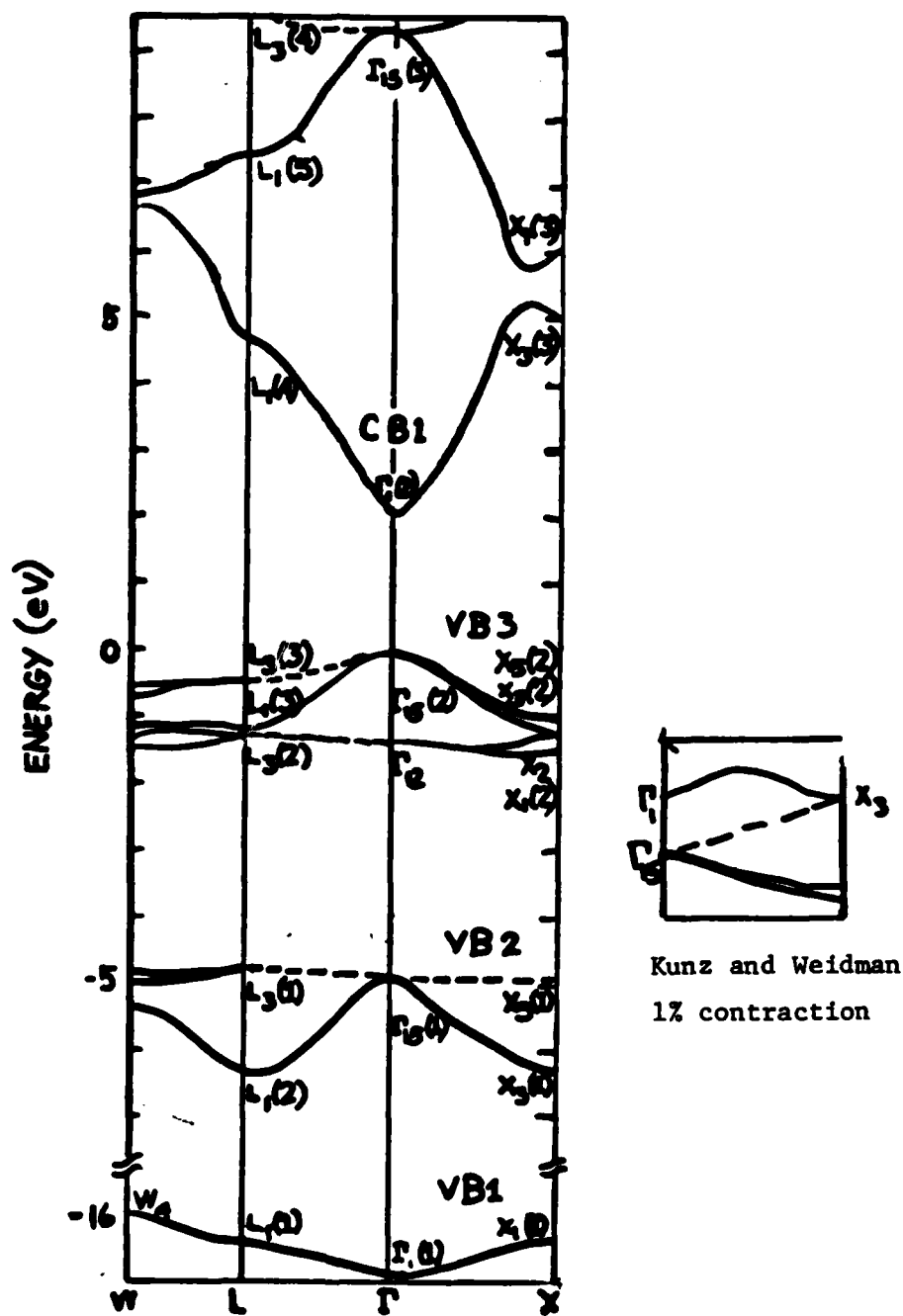


Figure 1. Equilibrium energy bands of CuCl.

Thus, there is no evidence to support the "exciton dielectric" model of superconductivity in CuCl proposed by Abrikosov¹⁸ which is based on the existence under pressure of an indirect gap less than the exciton binding energy. However, Collins et al.⁵ have recently proposed another mechanism based on the presence of impurity levels such as O^{--} just below the conduction band edge. They suggest that under pressure the X point moves down and that the O^{--} levels pressure-ionize to produce free carriers around the X point. The lowering of the X point under pressure to a position degenerate with the Γ point is supported by the calculations of Kunz and Weidman.¹⁵ Collins et al.⁵ then show that an exciton-mediated high temperature super-conducting state can exist assuming an appropriate exciton-electron interaction and density of free carriers. Nobody, however, has addressed the fundamental question of whether the exciton-mediated electron-electron interaction is attractive. This is the purpose of the present calculations.

We have chosen the band structure of Zunger and Cohen¹⁶ as the starting point for this calculation. The equilibrium valence band structure is divided into three non-overlapping regions. The lowest VB1 band is 90% Cl 3s character and is between 10 and 12eV from the predominantly (75%) Cl 3p VB2 band. In this calculation we are only interested in the mostly Cu 3d VB3 band which is 3.5 eV above VB2. The VB3 band has a lower nearly dispersionless subband and a higher subband 1.5 eV wide which contains 24% Cl 3p and 76% Cu 3d character at the zone center. The magnitude of these orbital hybridizations agrees well with experimentally-deduced values based on exciton spin-orbit splitting (25% Cl 3p)¹⁹ and other measurements. The lowest conduction band CB1 is mostly Cu 4s at the zone center but has d-p character at $X_3(3)$. The insert in Fig.1 shows the bands VB3 and CB1 in the calculation of Kunz and Weidman.¹⁵ Here a 1% lattice contraction has rendered the points Γ_1 and X_3 nearly degenerate.

We have rendered the bands in Fig. 1 in the effective mass approximation

Table I. Band structure parameters

lattice parameter	10.215 a.u.
crystal structure	zincblende
effective masses (in units of m_e):	
$m\{\Gamma_{12} - (X_1, X_2)\}$	20
$m\{\Gamma_{15}(2) - (X_3, X_5)\}$	5.1
$m\{\Gamma_1(2) - X_1(3)\}$	1.28
$m\{\Gamma_{15}(3) - X_3(3)\}$	1.2
energy levels at high symmetry points (a.u):	
Γ_{12}	-.051
$\Gamma_{15}(2)$	0.0
$\Gamma_1(2)$	.074
$\Gamma_{15}(3)$	.342
$X_1(2), X_2$	-.041
$X_5(2), X_3(2)$	-.037
$X_3(3)$	.185
$X_1(3)$	.222

as discussed in Sec. III.A. For the VB3 bands we have used the Γ and X points to determine the effective masses (see Prakash and Joshi for details³) and have ignored the non-degeneracy at X in the two subbands. For the conduction bands we have connected $\Gamma_{15}(3)$ to $X_3(3)$ because these pairs are s-like and d-p-like respectively,²⁰ and we must connect points allowing the same symmetry when we assume non-hybridized bands.³ The curvatures of the bands near $X_3(3)$ and $X_1(3)$ suggest an avoided crossing of this type. The zone boundary at X is at .615 a.u. for CuCl; but because we are using a spherical approximation for the energy bands, it is appropriate to use the Wigner-Seitz sphere radius to define the Fermi momentum. This value is .605 a.u. All the band structure parameters are given in Table I.

In Sec. III.A. we expressed the valence bands in terms of d atomic wavefunctions and the s-like conduction bands in terms of plane waves. Here we wish to take into account also the p character of the valence band. We can do this by allowing the valence bands to be Cu 3d- Cl 3p bonding states and the $\Gamma_{15}(3)$ - $X_3(3)$ conduction band to be a Cu 3d-Cl 3p anti-bonding state. This hybridization is allowed because both Γ_{15} and X_3 can have d-p character. We use a mixing of 75% Cu and 25% Cl for the bonding state and 25% Cu and 75% Cl for the anti-bonding state. Besides being consistent with the experiment, this result is in agreement with calculations at Γ_{15} .¹⁷ For the atomic Cu 3d levels we choose the wavefunction obtained by Wachters,²¹ and for the Cl 3p levels we use the wavefunctions of Veillard.²²

The wavefunctions representing the different bands should all be mutually orthogonal. This is an important property related to the finite value of $\epsilon(q,q,\omega)$ as $q \rightarrow 0$ for a semiconductor. We can see from Eq.(6) that $\epsilon(0,0,\omega)$ has an infinite factor $v(0)$. However, the overlap $A(\vec{q})$ in Eq.(5) between orthogonal states m and m' is zero at $q=0$. The result is that the term in Eq.(6) vanishes. On the other hand, a metal has intraband transitions so that $A(0)$ does not vanish in those cases, and $\epsilon(0,0;0)$ takes on an infinite value which expresses perfect static screening. Our bonding and antibonding d-p states are automatically

Table II. Comparison between $\epsilon(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; 0)$ with and without d-s orthogonality correction at $q=.06$ a.u.

$\vec{G}$	ϵ with orthog.	ϵ without orthog.
000	1.0003	206.7976
111	1.3053	1.7212
200	1.2251	1.5528
220	1.0926	1.2007
311	1.0755	1.1422
222	1.0643	1.1134
400	1.0441	1.0745
331	1.0369	1.0551
420	1.0281	1.0410
422	1.0221	1.0310
333	1.0201	1.0256
511	1.0216	1.0287
440	1.0135	1.0170
531	1.0128	1.0155
442	1.0106	1.0125
600	1.0111	1.0133

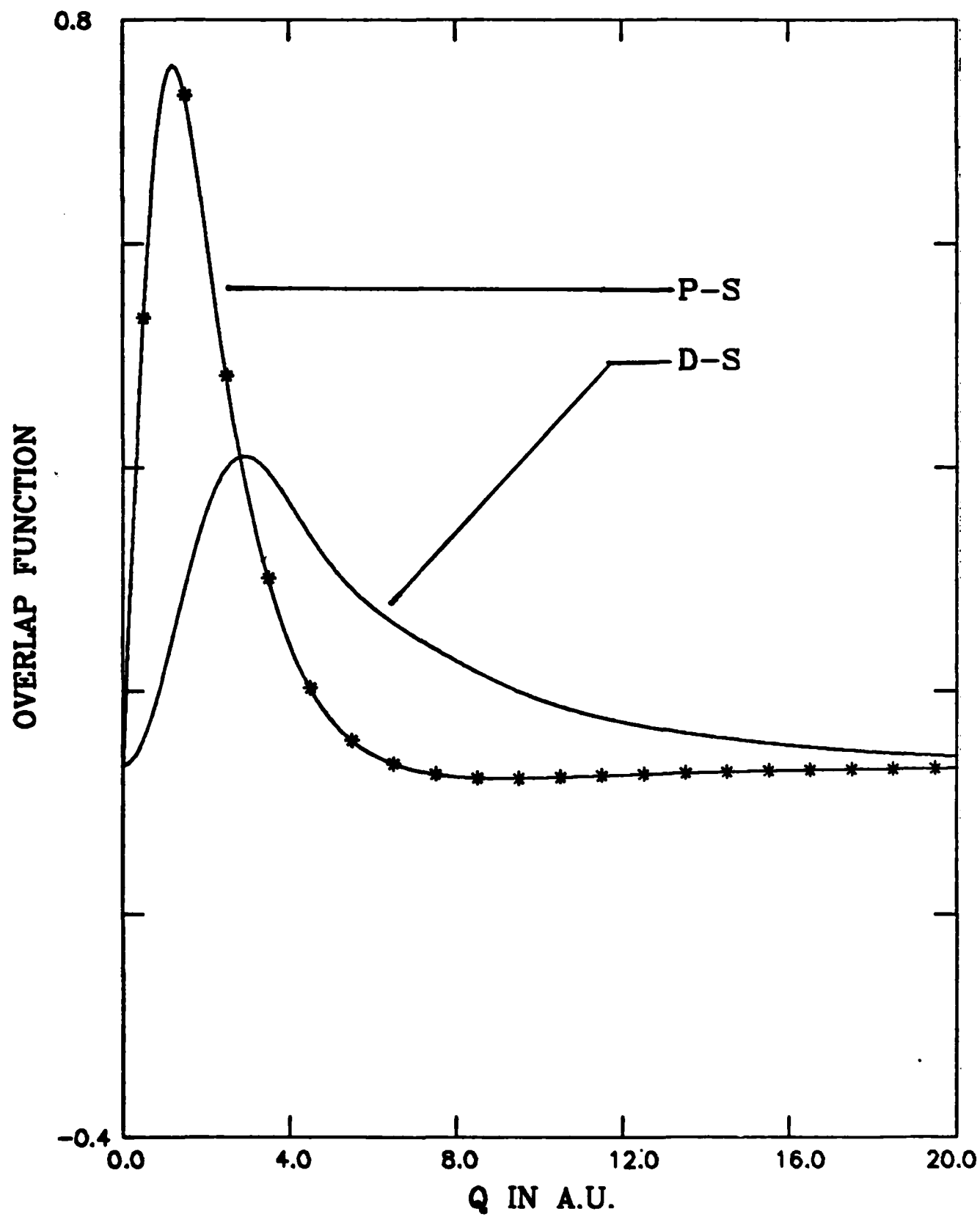


Figure 2. The overlap function $A_{ds}(\vec{q})$ and $A_{ps}(\vec{q})$. The orthogonality correction is not included.

orthogonal. However, we must orthogonalize the plane wave states to the atomic d and p states. Prakash and Joshi⁹ did not do this and thus grossly overestimated the contribution of d-s transitions to $\underline{\epsilon}$ at small q. For a comparison of calculations of $\underline{\epsilon}$ with and without d-s orthogonality, we tabulate in Table II some diagonal results for $q=.06$ a.u., $\omega=0$ and various G values.

The size of the overlap terms $A(\vec{q})$ determine the strength of the d-s, p-s and so on contributions to $\underline{\epsilon}$. In Fig. 2 we compare the d-s and p-s overlap results as a function of q. We see that the d-s overlap falls off gradually due to the localization of the d state. The p-s overlap peaks earlier and falls off much more rapidly since the p state is less localized. The p-s result is also a good deal larger in magnitude at the peak than the d-s result. Even though the p mixing coefficient is less than the d coefficient in the d-p bonding state, the p-s term contributes significantly to $\underline{\epsilon}$. When totalled, the resulting contribution to ϵ from the valence to s band transition is greater than from the bonding to antibonding transition. This is a bit surprising since one might at first glance expect d-d interband transitions to dominate. As a consequence of this result, we cannot use the matrix equivalent of Eq.(2) to find $\underline{\epsilon}^{-1}$, but must rather use Eq. (8) with the d-p replacing d in all transitions. Fortunately, we do not have to consider a very large matrix in $\vec{G}, \vec{G}'$ due to the rapid falloff of the ds-p overlap and also $v(\vec{q}+\vec{G})$.

We adjust the exchange parameter C to fit the empirical exciton binding energy as discussed in Sec. III.B. The binding energy is .38 eV so that the pole in ϵ^{-1} must occur at .38 eV below the conduction band edge. The pole corresponds to the zero of $\det [\underline{\epsilon}]$ as discussed in Sec.IV.A. A value of $C=3.6561$ gives a pole at the appropriate binding energy. This is a good deal greater than the value of $C=1$ appropriate to the interacting electron gas. It is, however, consistent with the result of Hanke¹⁰, who found that the unadjusted Hubbard exchange factor did not give an optical absorption spectrum with the continuum exciton peak shifted toward the threshold as was seen experimentally. A value of C greater than

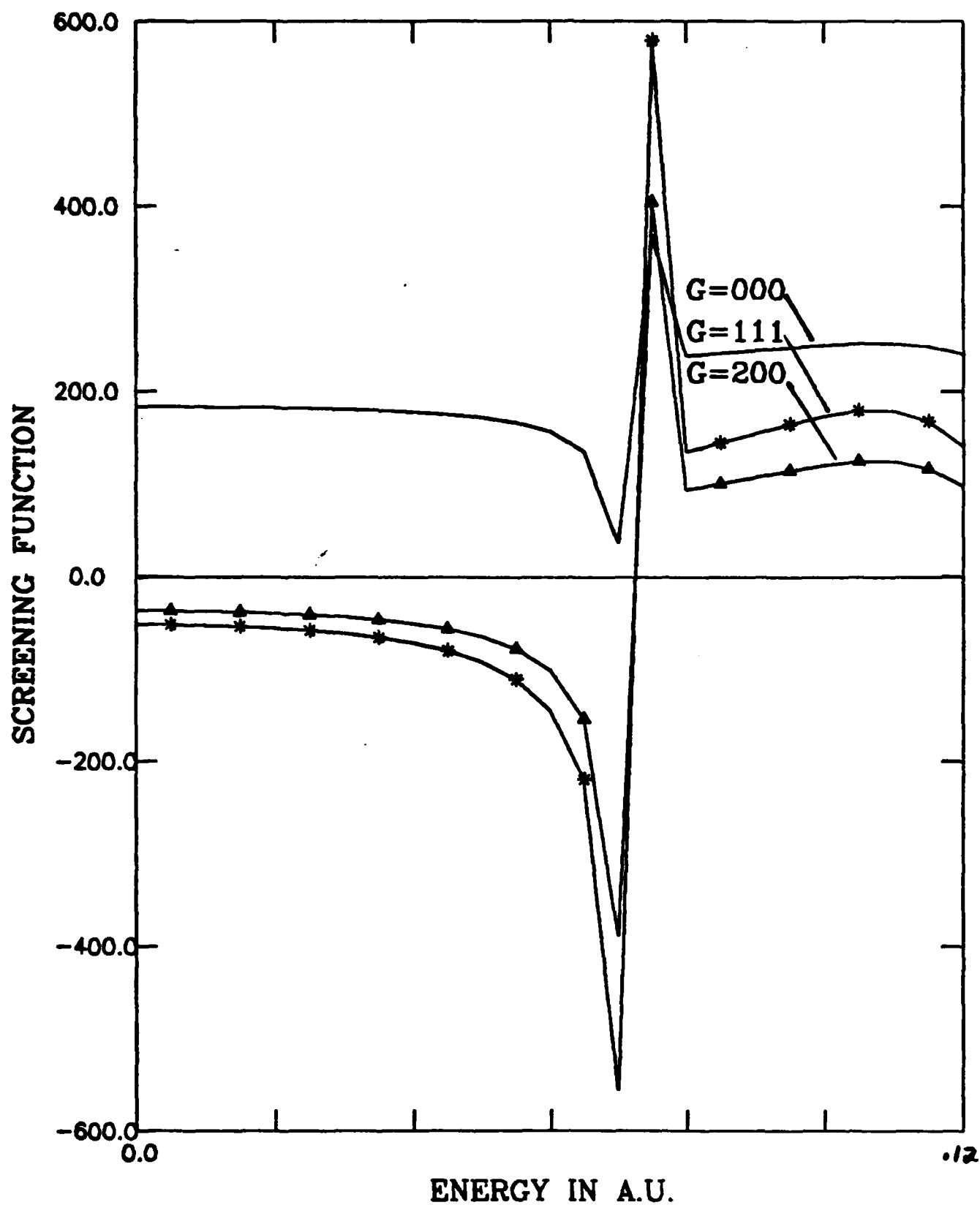


Figure 3. $\text{Re}\{V_{\text{sc}}(\vec{q}+\vec{G}, \omega)\}$ at $q=.25$ a.u. for $\vec{G}=000, 111$ and 200 . The vector q is in the 100 direction.

one would have shifted the exciton peak to lower energies.

Some of our results for the dynamical screening are shown in Fig. 3-5. The exciton pole occurs at $\omega=.06$ a.u. above the top of the valence band and thus we explore excitation energies in this region. It is most informative to look at the screened interaction since this is the quantity that enters into the superconducting equations. The screened interaction is given by

$$V_{sc}(\vec{q}+\vec{G},\omega) = \sum_{\vec{G}'} \epsilon^{-1}(\vec{q}+\vec{G},\vec{q}+\vec{G}';\omega) v(\vec{q}+\vec{G}') \quad (16)$$

In Fig. 3 we give the real part of the screened interaction at $q=.25$ a.u. for $\vec{G}=000,111$ and 200 . The results for $\vec{G}=000$ are repulsive at all frequencies, but the other results are attractive below the exciton pole and repulsive above it. Since the exciton pole is in the band gap, the attractive region of the V_{sc} is real. These results show the importance of the exciton pole in determining the region of attractive interaction. To explore further the q -dependence of V_{sc} , we present in Fig.4 a calculation at $\omega=.04$ a.u. We see that at $q \rightarrow 0$, V_{sc} has a positive pole. This effect is due to the lack of perfect screening in semiconductors and insulators discussed above. The effect of this pole on any superconducting state would be disastrous, and screening the pole is one reason why free carriers in the conduction band are necessary. However, Inkson and Anderson²³ show that the screening is not enough to enhance superconductivity in the case of a Si layer on a metal. The issue of whether free carrier screening will remove the repulsive pole in V_{sc} for a system like CuCl, which has stronger exciton effects than Si, is critical and one that we shall address in our next calculations. As a final calculation, we show in Fig. 5 the frequency dependence of the real part of V_{sc} at $q=.25$ a.u. and $\vec{G}=111$ with and without local field effects. The local field effects are the differences between V_{sc} calculated by inverting the matrix $\underline{\epsilon}$ and calculated by

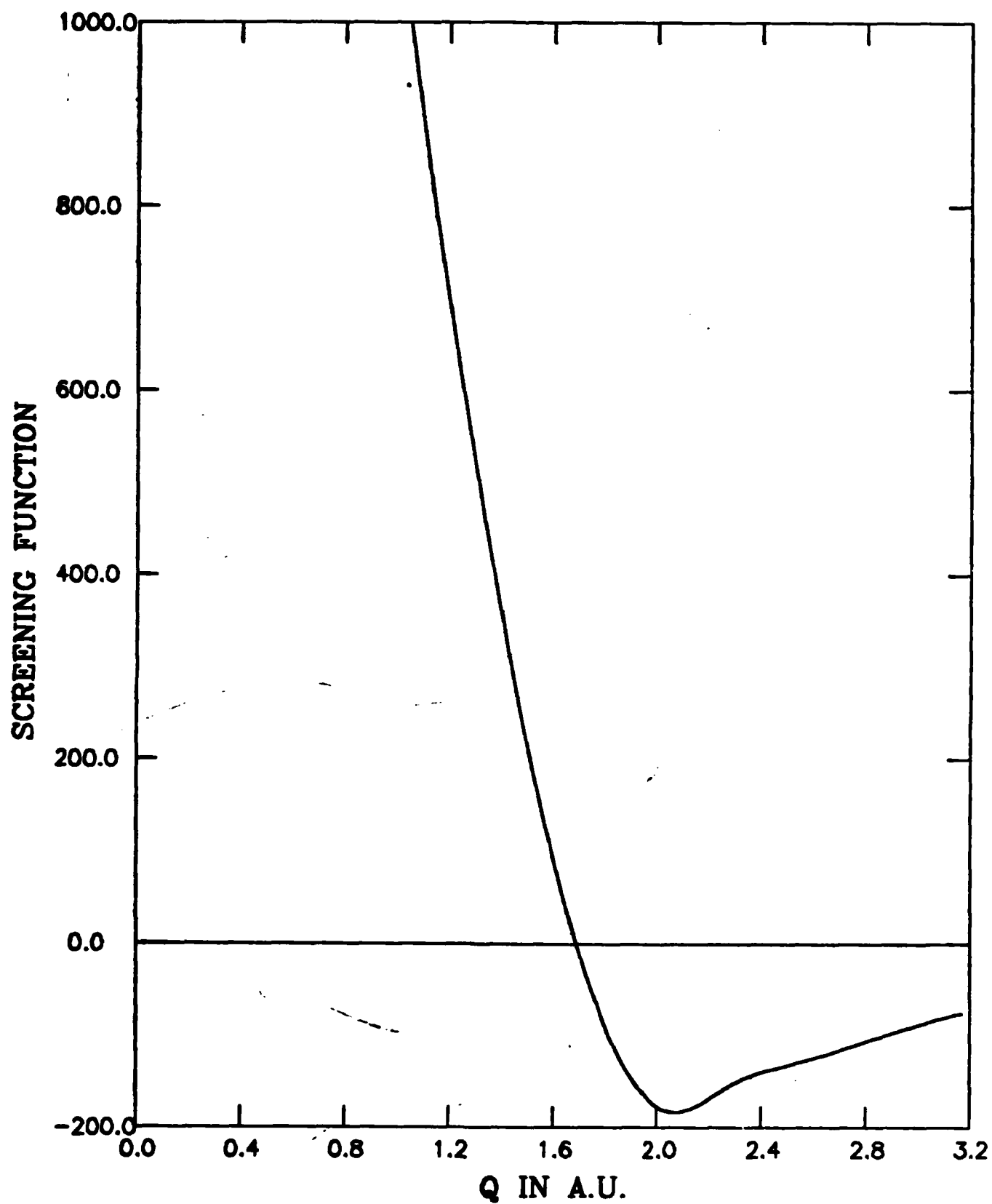
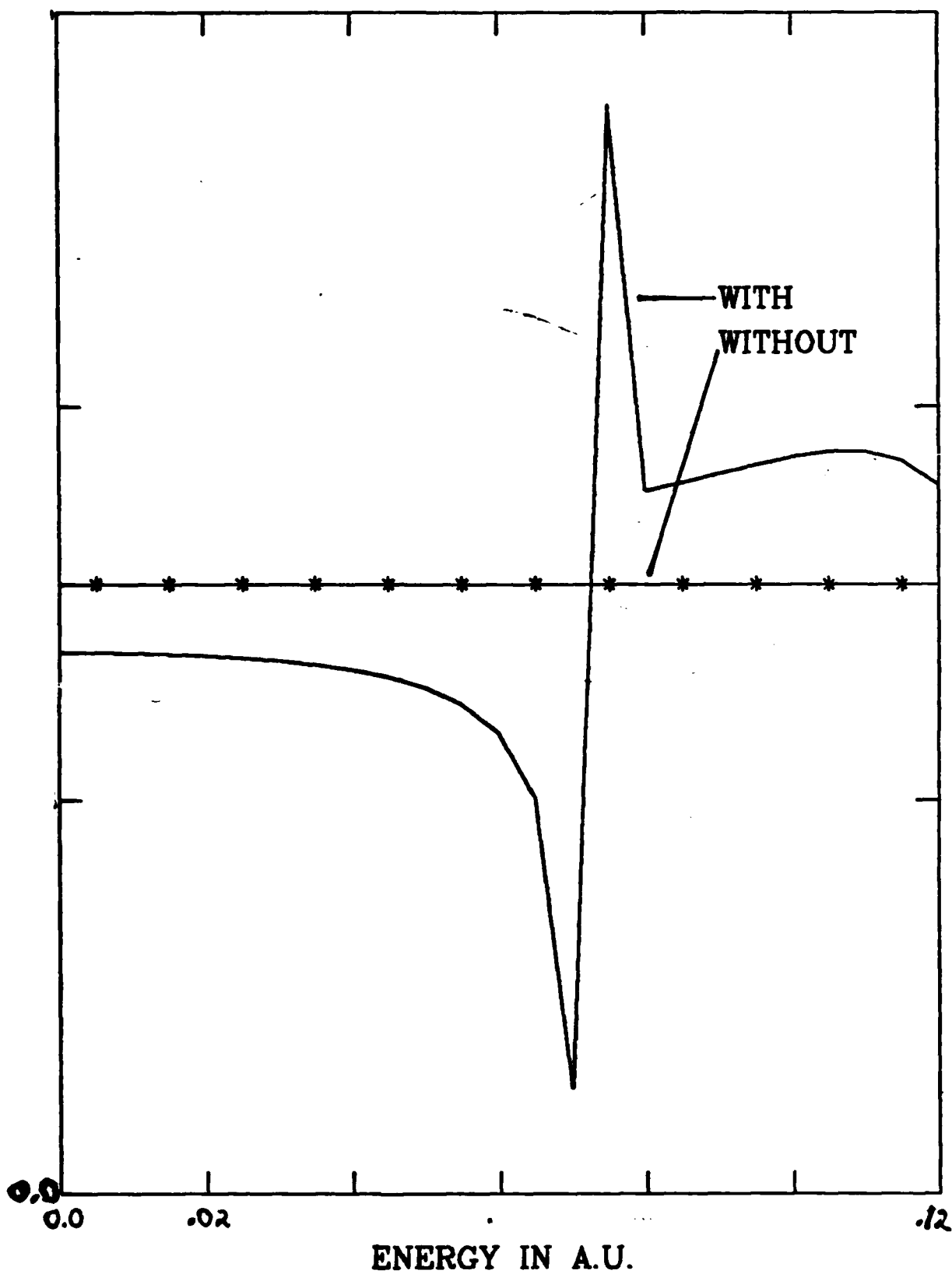


Figure 4. The screened interaction $V_{sc}(\vec{q}, \omega)$ at $\omega = .04$ a.u.. There is a positive pole at $q=0$.

400.

SCREENING FUNCTION



ENERGY IN A.U.

Figure 5. $\text{Re}\{V_{\text{sc}}(\vec{q}+\vec{G}, \omega)\}$ with and without local field effects. The interaction is evaluated at $q=.25$ a.u. and $\vec{G}=111$.

using just the reciprocals of the diagonal elements of $\underline{\epsilon}$. We see that the effects are quite significant.

In summary, we have presented a calculation of CuCl which shows that the d-like valence band to s-like conduction band transitions are important, that p admixtures in the valence bands affect these transitions significantly, and that orthogonalization of the conduction bands with respect to the valence states is necessary. We find that the correct location of the exciton pole is essential to describing the frequency dependence of V_{sc} . Our next step is to include free carriers, as from the model of Collins *et al.*,⁵ and to assess the screening of the repulsive pole at $V_{sc}(\vec{q}=0)$. It would also be interesting to look at the dispersion and strength of the exciton pole as we vary $\vec{q}$. We also must test our exchange approximation with calculations of other properties, such as optical constants, and by comparing with more exact expressions such as in Eq.(15).

IV. References

1. W. Hanke and L. J. Sham, Phys. Rev. B 12, 4501 (1975).
2. See, for example, P. W. Baumeister, Phys. Rev. 121, 359 (1961).
3. D. Hulin, A. Mysyrowicz and C. Benoit a la Guillaume, Phys. Rev. Lett. 45, 190 (1980).
4. D. C. Reynolds and T. C. Collins, Excitons: Their Properties and Uses, p. 252 and references therein (Academic, New York, 1981).
5. T. C. Collins, M. Seel, J. J. Ladik, M. Chandrasekhar and H. R. Chandrasekhar, Phys. Rev. B 27, 140 (1983).
6. J. M. Lockhart, F. C. Witteborn and W. M. Fairbank, Phys. Rev. Lett. 38, 1220 (1977).
7. R. S. Hanni and J. M. Madey, Phys. Rev. B 17, 1976 (1978).
8. W. Hanke and L. J. Sham, Phys. Rev. B 21, 4656 (1980).
9. S. Prakash and S. K. Joshi, Phys. Rev. B 2, 915 (1970).
10. W. Hanke, Phys. Rev. B 8, 4591 (1973).
11. J. Hubbard, Proc. R. Soc. A 243, 336 (1958).
12. N. B. Brandt, S. V. Kuvshinnikov, A. P. Rusakov and V. M. Smernov, JETP Lett. 27, 33 (1978).
13. C. W. Chu, A. P. Rusakov, S. Huang, S. Early, T. H. Geballe and C. Y. Huang, Phys. Rev. B 18, 2116 (1978).
14. I. Lefkowitz, J. S. Manning and P. E. Bloomfield, Phys. Rev. B 20, 4506 (1979).
15. A. B. Kunz and R. S. Weidman, J. Phys. C 12, L 371 (1979).
16. A. Zunger and M. L. Cohen, Phys. Rev. B 20, 1189 (1979).
17. L. Kleinman and K. Mednick, Phys. Rev. B 20, 2487 (1979).
18. A. A. Abrikosov, JETP Lett. 27, 219 (1978).

19. M. Cardona, Phys. Rev. 129, 69 (1963).
20. J. C. Slater, Symmetry and Energy Bands in Crystals (Dover, New York, 1972), pp. 347.
21. A. J. H. Wachters, J. Chem. Phys. 52, 1033 (1970).
22. A. Veillard, Theoret. Chim. Acta 12, 405 (1968).
23. J. C. Inkson and P. W. Anderson, Phys. Rev. B 8, 4429 (1973).

V. Publications and Presentations

The following papers have been published or presented:

1. "Optical Constants of TiO_2 ," Handbook of Optical Constants (Pergammon, New York, 1982).
2. "Exciton Coupling and the Effective Electron Interaction in Narrow Band Materials," APS March Meeting, Los Angeles (1983).

The following paper has been submitted:

1. "Local Field Effects on Exciton Coupling in CuCl and CdS Under Pressure," High Pressure in Science and Technology Conference, 1983.

The following paper is to be submitted:

1. "Dynamic Dielectric Response Model of the Effective Electron Interaction in Narrow Band Materials."

The following paper is in preparation:

1. "The Exciton Mediated Effective Electron Interaction and the Possibility of Superconductivity in CuCl and CdS Under Pressure."

END

FILMED

9-83

DTIC