Theoretical studies of possible excitonic superconducting state in CuCl and CdS

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(Received 19 April 1982)

To explain the observed diamagnetic anomalies which are coupled with high conductivity in CuCl and CdS samples, an excitonic mechanism of superconductivity based on the presence of impurities is outlined. To formulate the theoretical model on a more fundamental level, four-component field operators have been introduced in analogy to the Nambu formalism. Generalized Eliashberg equations for the self-energy are derived for both singlet and triplet pairs. Numerical model calculations for the effective interaction are presented for different impurity concentrations and different gaps (exciton frequencies). Conjectures for the further development of the theory, together with proposed experiments, conclude this study.

I. INTRODUCTION

High-temperature superconductivity has long been a cherished goal, which if achieved would have great technological importance. Currently, the highest temperature at which superconductivity has been observed is approximately 25 K (in the $A15$ compounds). Thus the recent reports of anomalously large diamagnetism, and its possible relation to the Meissner effect,[1–6] in CuCl and CdS at temperatures above that of liquid nitrogen has stimulated much interest in these materials as possible high-temperature superconductors.

In CuCl the diamagnetic susceptibility has been reported[1–3] to be anywhere between 7% and 80% of the ideal Meissner value ($\chi_v = -1/4\pi$ cgs units) for superconducting metals. The diamagnetic anomaly[2] was accompanied by a sharp drop in the resistivity, as well as by two peaks in a simultaneous differential thermal analysis (DTA) measurement at the onset and completion of the anomaly. These effects were observed over a temperature range of 10 to 20 K around a mean temperature of 240 K, and at hydrostatic pressures of 5 to 25 kbar. In a different experiment Lefkowitz *et al.*[3] reported anomalous diamagnetism in disordered, glasslike CuCl. All the anomalies were observed only when the samples were rapidly cooled or warmed.

In pressure-quenched CdS large diamagnetism approaching 100% flux exclusion was reported at 77 K by Brown *et al.*[4] The samples were pressurized to 40 kbar or more and explosively released. At 30 kbar CdS undergoes a wurtzite-to-NaCl phase transition,[7] and the pressure-quenched samples transform from the wurtzite structure to a mixture of zinc-blende and NaCl structures. They had a black sheen and consisted of a compact powder matrix with embedded lenticular platelets. The diamagnetic anomaly disappeared after a day or two of temperature cycling. In a later experiment Cote *et al.*[8] showed that the structural behavior of the samples that exhibited the diamagnetic anomaly was similar to those that contained large concentrations of Cl as an impurity. In an independent study Nam *et al.*[6] also found diamagnetism (10—20%) of the ideal value.

While several different groups[1–6] have repeated these measurements and observed the large diamagnetism, the lack of consistency of results from sample to sample plagues their interpretation. This is likely due to important differences in the sample properties. Furthermore, in most cases, impurities are believed to be present, but their nature and concentration is not always well known (especially in the CuCl samples).

Several theories have attempted to explain the observed effects. A number of them were based on excitonic mechanisms suggested by Little,[9] Halperin and Rice,[10] Ladik *et al.*,[11] Ginzburg,[12] and Allender, Bray, and Bardeen.[13] The first model, suggested by Abrikosov[14] and Rusakov,[15] involves an excitonic mechanism of superconductivity, which requires an indirect band gap equal to or less than the exciton binding energy 0.3 eV. This aspect of

the theory is not supported by band-structure calculations[16–19] for pure CuCl, nor by optical measurements,[20–22] which conclusively indicate a direct fundamental gap at the center of the Brillouin zone with a gap value of 3.4 eV. Other mechanisms, such as disproportionation of Cu,[2,23] piezoelectric polarization,[24] or coupling between electrons via optical phonons[25] have been suggested, but none proves or disproves the existence of a diamagnetic anomaly with any certainty.

The CuCl samples in some cases have O^{2-} impurities in them,[26] and the experiments in CdS have clearly shown that the diamagnetic anomaly is not observed in pure samples but in samples containing a large number of impurities. Nam *et al.*[6] observe the anomaly in samples doped with Li, while Brown *et al.*[4] and Homan *et al.*[5,8] find a high concentration of Cl in their samples. Therefore the presence of impurities and defects has to be included in electronic band-structure calculations in order to compute the densities of electronic states under pressure that may contribute to the diamagnetism and high conductivity.

In the next section of this paper another model for an excitonic mechanism taking advantage of the presence of impurities will be briefly outlined. After that the generalized Eliashberg equations[27] are derived for both singlet and triplet electron pairs. Next, numerical model calculations based on the aforementioned formalism are presented for CuCl and CdS. The final section of this paper includes the conclusions along with conjectures for the further development of the theory together with proposed experiments.

II. PROPOSED MODEL

The proposed model is based on self-consistent-field Hartree-Fock calculations of the band structures of CuCl (Ref. 19) and CdS (Ref. 28). In CuCl this includes the effect of impurities, defects, and pressure.[19] According to the calculated band structure of CuCl at atmospheric pressure, the fundamental gap is direct at $\vec{k}=0$ and has an energy of 4 eV, in reasonable agreement with Cardona's[20] measurement of 3.4 eV. The valence band consists mainly of the d bands of Cu and is relatively narrow. The line of most physical interest is the Γ-X line. The X point in the lowest conduction band (CB) is about 1 eV higher than the bottom of the CB at Γ. The direct gap at X is about 7.5 eV, in reasonable agreement with Goldman's analysis.[29] As pressure is applied the CB at X begins to move down in energy relative to the CB at Γ. This is calculated by decreasing the lattice constant by 1% and 5% of its normal value. A linear interpolation of band energies versus lattice constant indicates that Γ and X become degenerate at a lattice-constant reduction of 0.2%, which may be consistent with the pressure of 6 kbar that Chu *et al.*[2] used. Thus, though an indirect gap is present, its value is not near 0.35 eV as suggested by Abrikosov.[14] As the pressure is increased the band at X continues to decrease in energy.

The O^{2-} impurity level is calculated to be very shallow.[19] The calculations show that, as a function of hydrostatic pressure with or without uniaxial stress, the O^{2-} impurity level rapidly approaches the conduction band. A 1% reduction in the lattice constant brings the O^{2-} level with an exciton's binding energy from the conduction band. Electrons could then pressure ionize from O^{2-} and can become superconducting via an excitonic mechanism. The pressure-ionization process is possible for an impurity-defect combination as well. Namely, these carriers can couple to the exciton field which forms an electronic polaron, as formulated by Devreese *et al.*[30] The electron is clothed in about one virtual longitudinal exciton. The exciton coupling reduces the average e^--e^- repulsion in the CB by 0.54 Ry (in the static limit).[19] The critical temperature T_c at which superconductivity might occur is

$$T_c = 1.14\frac{\hbar\omega_{\mathrm{ex}}}{k_B}\exp\left[-\frac{1}{UD(E_F)}\right],$$

where $\hbar\omega_{\mathrm{ex}}$ is the binding energy of the free exciton, k_B is Boltzmann's constant, U is the coupling between the exciton and the electron, and $D(E_F)$ is the density of states at the Fermi surface. T_c was then calculated for several values of conduction-electron density $N(E)$ assuming (a) that the conduction band at Γ alone contributed to $D(E_F)$ and (b) that both electronic states at Γ and X contribute to $D(E_F)$ [when the Γ and X points are degenerate, this produces the largest $D(E_F)$]. It was found that for carrier densities of 10^{-1} e^-/unit cell, T_c for a nondegenerate CB was 38 K while it was 1745 K for the degenerate case. For $N(E)=10^{-2}$ the corresponding numbers are 10^{-2} and 55 K, respectively. Therefore it is possible that with 10^{-2} e^-/unit cell superconductivity close to or above liquid-nitrogen temperatures can be achieved.

A crucial point of this model is that there is an optimum range of electron densities for which superconductivity is possible at moderately high temperature. Too small an electron density causes a low density of states at the Fermi surface, and consequently a low T_c. On the other hand, the number of carriers should not be so large that it quenches out the exciton field. In other words, the density of free carriers in the CB should be such that the screening

length is greater than the radius of the electronic polaron. The free-carrier density that would quench the exciton field is given by the Thomas-Fermi approximation

$$k_{\mathrm{TF}}=\left[\frac{6\pi eN}{E_F}\right]^{1/2},$$

where N is the free-carrier density and E_F is the Fermi energy. With the use of the band parameters, a cutoff density $N\simeq 10^{-2}$ was obtained.

The model based on the above calculations predicts the following features: Owing to the heavy mass (narrow widths) of the valence band, the exciton cannot follow the motion of the conduction electrons. As long as there are not too many conduction electrons, the repulsion between them will be screened by the virtual excitations of the d-band electrons causing a local polarization field. This polarization field will have a positive local field and a negative part which is less localized (the hole arising from the d band and the electron from the s band). A pressure-ionized electron from O^{2-} which is now in the conduction band will scatter more strongly on polarized d-band electrons of like spin. This acts as a hole that will attract a second electron in the conduction band that will be of the same spin as the first electron. Thus the polarization field is generated by the same kind of particles as the scattered conduction electrons. Therefore, the physical situation is similar to that of ^{3}He, which has the lowest-energy state by coupling particles of parallel spins.

This model clearly shows that high-temperature superconductivity is possible through an impurity-based mechanism. It does not arise merely from the intrinsic band structure of CuCl but by a combination of the band structure under stress [which shows a degeneracy of the conduction band at the X and Γ points at moderate pressures (0.2% lattice contraction)] with an impurity such as O^{2-}, whose levels lie within an exciton's binding energy of the CB. The impurities donate electrons both to the Γ and X points in the conduction band and therefore create a sufficiently large density of states at the Fermi surface in the CB which is necessary for a superconducting mechanism.

So far there have been no published theories that explain the diamagnetic anomaly in CdS. Kunz, Weidman, and Collins,[28] however, propose that an impurity mechanism similar to that in CuCl may be responsible for effects in CdS. Nam *et al.*[6] have observed the anomaly in a sample of CdS doped with Li but not in pure CdS. Cote, Capsimalis, and Homan[8] analyzed samples in which they observed the anomaly and found that these samples had a metastable rocksalt phase after pressure quenching, a phase that was pronounced in samples rich in Cl. Kunz *et al.*[28] have calculated that the rocksalt structure has an indirect band gap at X, which contributes to a high enough density of electronic states. Therefore, with a large number of impurities, the NaCl phase of CdS could be host to the diamagnetic anomaly in a manner similar to CuCl.

III. THEORETICAL FORMULATION

To derive a generalized Eliashberg equation[27] that can be used to investigate the model outlined in the preceding section on a more fundamental level, an effective Hamiltonian can be constructed which preserves the simplicity of the Feynman-Dyson series. First consider the following system of electrons interacting via a two-body potential V:

$$\mathscr{H}=\sum_{\vec{k},\sigma}\epsilon_{\vec{k}}\hat{n}_{\vec{k}\sigma}+\frac{1}{2}\sum_{\substack{\vec{k},\vec{k}',\vec{q},\\ \sigma,\sigma'}}\langle\vec{k}+\vec{q},\vec{k}'-\vec{q}\,|\,V\,|\,\vec{k},\vec{k}'\rangle\hat{C}^{\dagger}_{\vec{k}+\vec{q},\sigma}\hat{C}^{\dagger}_{\vec{k}'-\vec{q},\sigma'}\hat{C}_{\vec{k}',\sigma'}\hat{C}_{\vec{k},\sigma}\equiv\mathscr{H}_0+\mathscr{H}_{\mathrm{int}}\,, \tag{1}$$

where $\vec{q}$ is the change in momentum of the electrons after the interaction, $\epsilon_{\vec{k}}$ is the energy of the electrons described by a plane wave $\vec{k}$, the $\hat{C}_{\vec{k}}$'s are destruction operators of the electronic state with wave vector $\vec{k}$, $\hat{n}$ is the number operator, and σ represents the spin of the electron. In the Hartree-Fock approximation one linearizes the interaction term with respect to a given state $|0\rangle$, i.e., one approximates

$$\hat{C}^{\dagger}_1\hat{C}^{\dagger}_2\hat{C}_3\hat{C}_4\simeq\langle 0|\hat{C}^{\dagger}_1\hat{C}_4|0\rangle\hat{C}^{\dagger}_2\hat{C}_3-\langle 0|\hat{C}^{\dagger}_1\hat{C}_3|0\rangle\hat{C}^{\dagger}_2\hat{C}_4+\langle 0|\hat{C}^{\dagger}_2\hat{C}_3|0\rangle\hat{C}^{\dagger}_1\hat{C}_4-\langle 0|\hat{C}^{\dagger}_2\hat{C}_4|0\rangle\hat{C}^{\dagger}_1\hat{C}_3\,. \tag{2}$$

The state $|0\rangle$ is then determined self-consistently in terms of the eigenstates of the linearized Hamiltonian.

The next step is to introduce a modified zeroth-order Hamiltonian

$$\mathscr{H}'_0=\mathscr{H}_0+\mathscr{H}_\chi-\mu N\,, \tag{3}$$

where

$$\mathscr{H}_\chi=\sum_{\vec{k},\sigma}\chi_{\vec{k}}\hat{n}_{\vec{k}\sigma} \tag{4}$$

is the Hartree-Fock potential, and the term

$$\mu N=\mu\sum_{\vec{k},\sigma}\hat{n}_{\vec{k}\sigma}\ , \tag{5}$$

where μ is the chemical potential, just shifts the energy. $\mathscr{H}'_{\rm int}$ then becomes

$$\mathscr{H}'_{\rm int}=\mathscr{H}_{\rm int}-\mathscr{H}_{\chi} \tag{6}$$

This gives $\mathscr{H}'=\mathscr{H}'_0+\mathscr{H}'_{\rm int}=\mathscr{H}-\mu N$. Thus the Hartree-Fock approximation is equivalent to requiring that the elementary excitation spectrum of $\mathscr{H}'_0$ is to first order unaffected by the residual interaction $\mathscr{H}'_{\rm int}$.

In order to build an effective Hamiltonian that can explain superconductivity one mixes the N and $N\pm2$ states together; so one breaks the conservation of the number of particles and adds operators of the form $\hat{C}^{\dagger}_{\vec{k}\sigma}\hat{C}^{\dagger}_{-\vec{k}\sigma'}$ to $\mathscr{H}'_0$ and subtracts the same from $\mathscr{H}'_{\rm int}$. At this point it is convenient to introduce new field operators, which are extensions of the Nambu[31] formalism, so that antiparallel spins may be included as well as parallel ones.

Considering the following field operators,

$$\underline{\hat{\psi}}_{\vec{k}}=\begin{bmatrix}\hat{C}_{\vec{k}\uparrow}\\ \hat{C}^{\dagger}_{-\vec{k}\downarrow}\\ \hat{C}_{\vec{k}\downarrow}\\ \hat{C}^{\dagger}_{-\vec{k}\uparrow}\end{bmatrix},\quad \underline{\hat{\psi}}^{\dagger}_{\vec{k}}=(\hat{C}^{\dagger}_{\vec{k}\uparrow},\hat{C}_{-\vec{k}\downarrow},\hat{C}^{\dagger}_{\vec{k}\downarrow},\hat{C}_{-\vec{k}\uparrow})\ , \tag{7}$$

one has

$$\underline{\hat{\psi}}^{\dagger}_{\vec{k}}\tfrac{1}{2}(\underline{1}\otimes\vec{\underline{\sigma}}_3)\underline{\hat{\psi}}_{\vec{k}}=\tfrac{1}{2}(\hat{C}^{\dagger}_{\vec{k}\uparrow}\hat{C}_{\vec{k}\uparrow}-\hat{C}_{-\vec{k}\downarrow}\hat{C}^{\dagger}_{-\vec{k}\downarrow}+\hat{C}^{\dagger}_{-\vec{k}\uparrow}\hat{C}_{-\vec{k}\uparrow}-\hat{C}_{\vec{k}\downarrow}\hat{C}^{\dagger}_{\vec{k}\downarrow})=\tfrac{1}{2}(\hat{n}_{\vec{k}\uparrow}+\hat{n}_{-\vec{k}\downarrow}+\hat{n}_{-\vec{k}\uparrow}+\hat{n}_{\vec{k}\downarrow}-2) \tag{8}$$

The convention for the outer product of the Pauli spin matrices and the 2×2 unit matrix is

$$\underline{1}\otimes\vec{\underline{\sigma}}_3=\begin{bmatrix}1&0&0&0\\0&-1&0&0\\0&0&1&0\\0&0&0&-1\end{bmatrix},\quad \vec{\underline{\sigma}}_3\otimes\underline{1}=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix}. \tag{9}$$

The operator $\frac{1}{2}\underline{1}\otimes\vec{\underline{\sigma}}_3$ is defined as $\underline{\tau}_3$.

The 4×4 operators which give the singlet and the three triplet states are the following:

$$\tfrac{1}{2}\vec{\underline{\sigma}}_3\otimes\vec{\underline{\sigma}}_1=\underline{S}_0\ \text{ for } S_z=0,\ S=0\ , \tag{10}$$

$$\tfrac{1}{2}i\vec{\underline{\sigma}}_3\otimes\vec{\underline{\sigma}}_2=S_1\ \text{ for } S_z=0,\ S=1\ , \tag{11a}$$

$$\frac{1}{2\sqrt{2}}i(\vec{\underline{\sigma}}_1\otimes\vec{\underline{\sigma}}_2+\vec{\underline{\sigma}}_2\otimes\vec{\underline{\sigma}}_1)=\underline{S}_2\ \text{ for } S_z=1,\ S=1\ , \tag{11b}$$

$$\frac{1}{2\sqrt{2}}i(\vec{\underline{\sigma}}_1\otimes\vec{\underline{\sigma}}_2-\vec{\underline{\sigma}}_2\otimes\vec{\underline{\sigma}}_1)=\underline{S}_3\ \text{ for } S_z=-1,\ S=1\ . \tag{11c}$$

The above operators have been normalized (their inner product with themselves is unity). Another relation is

$$\underline{\tau}_3\underline{S}_i\underline{\tau}_3=-\tfrac{1}{4}\underline{S}_i\ , \tag{12}$$

which will be used below.

With the above definitions one can write $\mathscr{H}'_0$ as

$$\mathscr{H}'_0=\sum_{\vec{k}}\underline{\hat{\psi}}^{\dagger}_{\vec{k}}\left[\tilde{\epsilon}_{\vec{k}}\underline{\tau}_3+\sum_{i=0}^{3}\phi_{i\vec{k}}\underline{S}_i\right]\underline{\psi}_{\vec{k}}+\sum_{\vec{k}}\tilde{\epsilon}_{\vec{k}}\ , \tag{13}$$

where

$$\tilde{\epsilon}_{\vec{k}}=\epsilon_{\vec{k}}+\chi_{\vec{k}}-\mu \tag{14}$$

and the $\phi_{i\vec{k}}$ are the "gaps" belonging to the above four cases. $\mathscr{H}'_{\rm int}$ becomes

$$\mathscr{H}'_{\rm int}=\frac{1}{2}\sum_{\vec{k},\vec{k}',\vec{q}}\langle\vec{k}+\vec{q},\vec{k}'-\vec{q}\,|\,V\,|\,\vec{k},\vec{k}'\rangle(\hat{\underline{\psi}}^{\dagger}_{\vec{k}+\vec{q}}\underline{\tau}_3\hat{\underline{\psi}}_{\vec{k}})(\hat{\underline{\psi}}^{\dagger}_{\vec{k}'-\vec{q}}\underline{\tau}_3\hat{\underline{\psi}}_{\vec{k}'})-\sum_{\vec{k}}\hat{\underline{\psi}}^{\dagger}\left[\chi_{\vec{k}}\underline{\tau}_3+\sum_{i=0}^{3}\phi_{i\vec{k}}\underline{S}_i\right]\hat{\underline{\psi}}_{\vec{k}}\ . \tag{15}$$

The Green's matrix elements in terms of the Nambu operators can be written as

$$G_{0\alpha\beta}(\vec{p},t)=-i\langle 0\,|\,\hat{T}[\hat{\psi}_{\vec{p}\alpha}(t)\hat{\psi}^{\dagger}_{\vec{p}\beta}(0)]\,|\,0\rangle\ , \tag{16}$$

where $\hat{T}$ is the time-ordering operator and

$$\hat{\psi}_{\vec{p}}(t)=e^{i\mathscr{H}'_0t}\hat{\psi}_{\vec{p}}(0)e^{-i\mathscr{H}'_0t}\ . \tag{17}$$

For example,

$$G_{011}(\vec{p},t)=-i\langle 0\,|\,\hat{T}[\hat{C}_{\vec{p}\uparrow}(t)\hat{C}^{\dagger}_{\vec{p}\uparrow}(0)]\,|\,0\rangle\ . \tag{18}$$

In order to remove the infinite c-number term for $\mathscr{H}'_0$, it is convenient to define $\underline{G}_0(\vec{p},t=0)$ as

$$G_{011}(\vec{p},t=0)=\lim_{t\to 0-}G_{011}(\vec{p},t)\ , \tag{19a}$$

$$G_{022}(\vec{p},t=0)=\lim_{t\to 0+}G_{022}(\vec{p},t)\ , \tag{19b}$$

$$G_{033}(\vec{p},t=0)=\lim_{t\to 0-}G_{033}(\vec{p},t)\ , \tag{19c}$$

$$G_{044}(\vec{p},t=0)=\lim_{t\to 0+}G_{044}(\vec{p},t)\ . \tag{19d}$$

Using the above definitions, one obtains

$$\underline{G}_0(\vec{p},p_0)=\frac{\left[p_0\underline{\mathbb{1}}+\tilde{\epsilon}_{\vec{p}}\underline{\tau}_3+\sum_{i=0}^{3}\phi_{i\vec{p}}\underline{S}_i\right]e^{i\delta p_0\underline{\tau}_3}}{p_0^2-\tilde{\epsilon}^2_{\vec{p}}-\sum_{i=0}^{3}\phi^2_{i\vec{p}}+i\delta}\ , \tag{20}$$

which gives the BCS-type definitions for the energy $E_{\vec{p}}$,

$$E^2_{\vec{p}}=\tilde{\epsilon}^2_{\vec{p}}+\sum_{i=0}^{3}\phi^2_{i\vec{p}}\ . \tag{21}$$

The restriction determining the chemical potential μ is given by the following equation for the total number of electrons per unit volume N_0:

$$\left\langle 0\left|\sum_{\vec{p},\sigma}\hat{n}_{\vec{p}\sigma}\right|0\right\rangle=\sum_{\vec{p}}(-i)[G_{011}(\vec{p},t=0)-G_{022}(\vec{p},t=0)+G_{033}(\vec{p},t=0)-G_{044}(\vec{p},t=0)]$$

$$=2\sum_{\vec{p}}(-i)\mathrm{Tr}[\underline{\tau}_3\underline{G}_0(\vec{p},t=0)]\equiv N_0\ . \tag{22}$$

We can further write

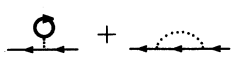
$$-i\underline{G}_0(\vec{p},t=0)=-i\int\underline{G}_0(\vec{p},p_0)\frac{dp_0}{2\pi}=\frac{(E_{\vec{p}}-\tilde{\epsilon}_{\vec{p}})\underline{\tau}_3-\sum_{i=0}^{3}\phi_{i\vec{p}}\underline{S}_i}{2E_{\vec{p}}}\ . \tag{23}$$

Substituting this into the previous equation and changing the sum $\sum_{\vec{p}}$ to an integral, one has

$$\int_{\epsilon_{\vec{p}}+\chi_{\vec{p}}<\mu}\left[1-\frac{\tilde{\epsilon}_{\vec{p}}}{E_{\vec{p}}}\right]\frac{d^3p}{(2\pi)^3}=2\int v^2_{\vec{p}}\frac{d^3p}{(2\pi)^3}=N_0\ . \tag{24}$$

μ must be set so that the above equation is valid.

Consider the lowest-order diagrams of the self-energy corrections, i.e.,



One finds for the self-energy Σ,

$$\underline{\Sigma}(p)=-i\underline{\tau}_3\int\langle\vec{p},\vec{p}\,'\,|\,V\,|\,\vec{p},\vec{p}\,'\rangle\mathrm{Tr}[\underline{\tau}_3\underline{G}_0(p')]\frac{d^4p}{(2\pi)^4}+i\int\langle\vec{p}\,',\vec{p}\,|\,V\,|\,\vec{p},\vec{p}\,'\rangle\underline{\tau}_3\underline{G}_0(p')\underline{\tau}_3\frac{d^4p}{(2\pi)^4}$$
$$-\left[\chi_{\vec{p}}\underline{\tau}_3+\sum_{i=0}^{3}\phi_{i\vec{p}}\underline{S}_i\right]. \tag{25}$$

Since $\underline{\Sigma}(p)=\underline{0}$ in the generalized Hartree-Fock (HF) model by construction, a BCS-type gap equation is obtained by noting that $\underline{\tau}_3$ and the $\underline{S}_i$'s are linearly independent,

$$\phi_{i\vec{p}}=-\frac{i}{4}\int\frac{d^4p'}{(2\pi)^4}\langle\vec{p}\,',\vec{p}\,|\,V\,|\,\vec{p},\vec{p}\,'\rangle\frac{\phi_{i\vec{p}\,'}}{p_0'^2-E^2_{\vec{p}\,'}}$$
$$=-\tfrac{1}{4}\int\frac{d^3p'}{(2\pi)^3}\langle\vec{p}\,',\vec{p}\,|\,V\,|\,\vec{p},\vec{p}\,'\rangle\frac{\phi_{i\vec{p}\,'}}{2E_{\vec{p}\,'}}. \tag{26}$$

An alternative way to the generalized HF scheme is that of self-consistent perturbation theory. Following Nambu, the general form of $\underline{\Sigma}(p)$ is

$$\underline{\Sigma}(p)=[1-Z(p)]p_0\underline{1}+\chi(p)\underline{\tau}_3+\sum_{i=0}^{3}\phi_{ip}\underline{S}_i\,. \tag{27}$$

In the approximation of first-order self-consistent perturbation theory $Z(p)=1$ and $\underline{\Sigma}(p)$ is given by the equation obtained above but without the subtracted HF potential and gap parameters. Furthermore, the quantities χ and ϕ in (27) are functions of the four-momentum $p=(\vec{p},p_0)$ rather than the three-momentum $\vec{p}$. This generality is required to treat retardation effects. In the following we use this definition of $\underline{\Sigma}(p)$.

We replace the Coulomb and exchange contributions by the matrix elements of an effective screened Coulomb interaction $V_c(p-p')=V(q)/\kappa(q)$, $\kappa(q)$ being the wave-vector- and frequency-dependent dielectric function. To simplify the algebra further the Bloch states are approximated by plane-wave states so that the matrix elements of the screened Coulomb interaction are given by $4\pi e^2/[\,|\,\vec{q}\,|\,^2\kappa(q)]$. The screened Coulomb part of the self-energy $\underline{\Sigma}(p)$ is then

$$\underline{\Sigma}^C(p)=i\int\frac{d^4p'}{(2\pi)^4}\underline{\tau}_3\underline{G}_0(p')\underline{\tau}_3\frac{4\pi e^2}{|\,\vec{q}\,|\,^2\kappa(q)} \tag{28}$$
$$(q=p-p')\,.$$

As a small number of electrons are added to the conduction band of CuCl- or CdS-like materials, polarization of the valence band will occur. Since only a comparatively small number of electrons is in the conduction band, a rigid-band approximation can be made. This implies that $\tilde{\epsilon}_p$ remains the same. Assuming for the moment that the interaction is spin independent (which in reality is not the case), the lowest-order dressed exciton contribution to the self-energy becomes

$$\underline{\Sigma}^{\mathrm{ex}}(p)=i\int\frac{d^4p'}{(2\pi)^4}\underline{\tau}_3\underline{G}_0(p')\underline{\tau}_3$$
$$\times\sum_{\lambda}(\bar{g}_{pp'\lambda})^2D_\lambda(p-p')\,, \tag{29}$$

where the screened exciton Green's function $D_\lambda(q)$ is given by

$$D_\lambda(q)=\frac{2\Omega_{q\lambda}}{q_0^2-\Omega_{q\lambda}^2/\kappa(q)+i\delta}\,. \tag{30}$$

Here λ is a polarization index and $\bar{g}_{pp',\lambda}$ is the screened coupling constant $g_{pp'\lambda}/\kappa(q)$. In the following calculations the polarization index will be dropped and $\Omega_{q\lambda}$ will be approximated by a single dispersionless exciton frequency ω_{ex}.

A theoretical treatment of the coupling of carriers in the conduction band to the exciton field has been given by Devreese, Kunz, and Collins.[30] According to this treatment the matrix element of the exciton-electron interaction g_q is defined as (in a way consistent with the Frölich Hamiltonian)

$$g_q=-i\frac{\hbar\omega_{\mathrm{ex}}}{|\,\vec{q}\,|}\left[\frac{\hbar}{2m\omega_{\mathrm{ex}}}\right]^{1/4}(4\pi\alpha)^{1/2}\,, \tag{31}$$

with the dimensionless coupling constant α given by

$$\alpha=\frac{e^2}{2\sqrt{\hbar/2m\omega_{\mathrm{ex}}}}\left[\frac{1}{\hbar\omega_{\mathrm{ex}}}\right](1-1/\epsilon_\infty)\,. \tag{32}$$

ϵ_∞ is the optical dielectric constant. The restriction on this treatment is that it is assumed that the densi-

ty of free carriers in the conduction band is small enough so that the screening length $l_{\rm scr}$ is greater than the radius of the electronic polaron r_p. Otherwise the electron-exciton coupling will be broken. Under this restriction we obtain for $(\bar{g}_q)^2$,

$$|\bar{g}_q|^2=\frac{4\pi e^2}{|\vec{q}|^2\kappa(q)^2}\hbar\omega_{\rm ex}\tfrac{1}{2}(1-1/\epsilon_\infty)\,. \tag{33}$$

To get a reasonable but still simple description of the screening we have to find a simple form for the dielectric function $\kappa(q)$ which describes the physical effect in our model. Since the density of carriers in the conduction band is presumed to be small, we use the Thomas-Fermi dielectric function of the free-electron gas

$$\kappa(\vec{q},0)=1+\frac{k_{\rm TF}^2}{|\vec{q}|^2} \tag{34}$$

with

$$k_{\rm TF}^2=6\pi N_0 e^2/E_F=4\pi e^2 D(E_F)\,, \tag{35}$$

N_0 being the number of particles per unit volume and $D(E_F)$ the density of states at the Fermi energy. The Thomas-Fermi approximation is good for $|\vec{q}|\to 0$. The use of the limiting region $|\vec{q}|\to 0$ is justified since the basic assumption is that only states with $|\vec{k}|$ and $|\vec{k}'|$ near $|\vec{k}_F|$ (states near the Fermi surface) contribute strongly to the formation of a superconducting state.

Adding the exciton contribution to the Coulomb term the total self-energy finally becomes

$$\underline{\Sigma}(p)=\underline{\Sigma}^C(p)+\underline{\Sigma}^{\rm ex}(p)=i\int\frac{d^4p'}{(2\pi)^4}\underline{\tau}_3\underline{G}_0(p')\underline{\tau}_3 V_{\rm eff}(p-p')$$

$$=i\int\frac{d^4p'}{(2\pi)^4}\underline{\tau}_3\left[\frac{p_0'\underline{\mathbb{1}}+\tilde{\epsilon}_{p'}\underline{\tau}_3+\sum_{i=0}^{3}\phi_{ip'}\underline{S}_i}{p_0'^2-E_{p'}^2+i\delta}\right]\underline{\tau}_3\frac{4\pi e^2}{|\vec{q}|^2\kappa(q)}\left[\frac{[\hbar\omega_{\rm ex}^2/\kappa(q)](1-1/\epsilon_\infty)}{q_0^2-\omega_{\rm ex}^2/\kappa(q)+i\delta}+1\right], \tag{36}$$

where the effective potential is defined as

$$V_{\rm eff}(q)=\frac{4\pi e^2}{|\vec{q}|^2\kappa(q)}\left[\frac{[\hbar\omega_{\rm ex}^2/\kappa(q)](1-1/\epsilon_\infty)}{q_0^2-\omega_{\rm ex}^2/\kappa(q)+i\delta}+1\right]. \tag{37}$$

From (37) we see that for certain concentrations and $q_0^2<\omega_{\rm ex}^2/\kappa(q)$ this effective interaction between electrons due to the screened Coulomb interaction and the exchange of virtual dressed excitons can become attractive corresponding to an overscreening of the Coulomb repulsion between the electrons. For $q_0^2>\omega_{\rm ex}^2/\kappa(q)$ the effective repulsion is stronger. For $q_0^2\gg\omega_{\rm ex}^2/\kappa(q)$ the excitonic polarizability becomes negligible and only the screened Coulomb repulsion between the carriers in the conduction band remains. The attractive region is responsible for the superconductivity.

IV. NUMERICAL MODEL CALCULATIONS OF $V_{\rm eff}$

In order to assess a numerical solution of the equation for $\underline{\Sigma}$ we need a simple model band structure for $\tilde{\epsilon}_p\simeq\tilde{\epsilon}_{\vec{p}}$, the conduction band. To fit the CuCl self-consistent-field conduction band of Collins, Kunz, and Weidmann,[19] we have parametrized it in the following effective-mass approximation:

$$\epsilon'_{\vec{p}}\equiv\epsilon_{\vec{p}}+\chi_{\vec{p}}=\begin{cases}2\dfrac{|\vec{p}|^2}{2M_\Gamma}, & 0\le|\vec{p}|\le\frac{1}{10}p_X\\[2ex] \dfrac{(0.2p_X)^2}{2M_\Gamma}-2\dfrac{(|\vec{p}|-0.2p_X)^2}{2M_\Gamma}, & \frac{1}{10}p_X\le|\vec{p}|\le\frac{2}{10}p_X\\[2ex] \dfrac{(0.2p_X)^2}{2M_\Gamma}-\dfrac{1}{2}\dfrac{(|\vec{p}|-0.2p_X)^2}{2M_\Gamma}, & \frac{2}{10}p_X\le|\vec{p}|\le\frac{3}{10}p_X\\[2ex] \dfrac{9}{14}\dfrac{(|\vec{p}|-p_X)^2}{2M_X}, & \frac{3}{10}p_X\le|\vec{p}|\le p_X=\dfrac{2\pi}{a}\,.\end{cases} \tag{38}$$

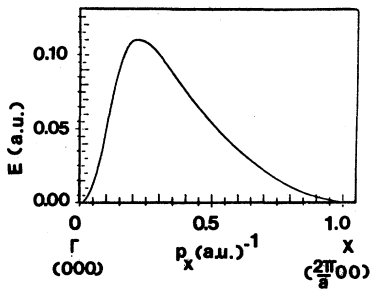


FIG. 1. Model band structure for the conduction band.

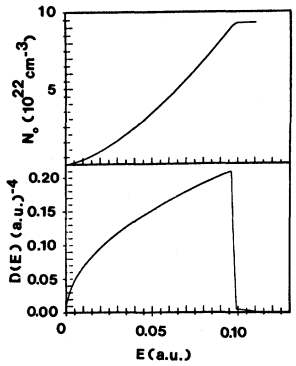


FIG. 2. Density of states $D(E)$ (a.u. unit volume)$^{-1}$ and integrated density of states $N_0(E)$ (cm^{-3}) which gives the number of particles per cm^3.

The numerical constants were fixed by requiring continuous $|\nabla\epsilon'_{\vec{p}}|$, $M_X=9M_\Gamma$, $\epsilon'(p_X)=\epsilon'(p_\Gamma)$ (X point degenerate with Γ point), and maximum at $0.2p_X$. The effective mass at the Γ point was assumed to be $0.2m_e$ and the bandwidth to be ~ 3 eV. Assuming spherical symmetry (the surface of constant energy is then the surface of a sphere in $\vec{p}$ space) the density of states is easily calculated,

$$D(E)=\frac{m^{3/2}}{2\pi^2}\begin{cases}\sqrt{E}+(28)^{3/2}\sqrt{E}, & 0\le E\le 0.02\dfrac{p_X^2}{2m}\\ \left[\dfrac{(0.2p_X)^2}{2m}-E\right]^{1/2}+(28)^{3/2}\sqrt{E}, & 0.02\dfrac{p_X^2}{2m}\le E\le 0.035\dfrac{p_X^2}{2m}\\ \left[\dfrac{(0.2p_X)^2}{2m}-E\right]^{1/2}+4^{3/2}\left[\dfrac{(0.2p_X)^2}{2m}-E\right]^{1/2}, & 0.035\dfrac{p_X^2}{2m}\le E\le 0.04\dfrac{p_X^2}{2m}\end{cases} \tag{39}$$

where $m=M_\Gamma=0.2m_e$. The model band structure for the conduction band is given in Fig. 1; the density of states and the integrated density of states (in inverse cubic centimeters) which gives the number of particles per cm^3 are shown in Fig. 2.

We now solve the integral in Eq. (24) which determines the chemical potential for different values of N_0 and $\sum_i \phi_{ip}^2$. The results given in Table I show that μ is not a very sensitive function of the gap parameter $\Delta^2=\sum_i \phi_{ip}^2$. By varying Δ^2 over 3 orders of magnitude μ does not change much. In a very good approximation we can therefore neglect the shift of the chemical potential between the normal and superconducting states.

From Table II, where the total number of carriers in the conduction band is broken up into contributions from electrons around the Γ and X points [as obtained from solving the integral Eq. (24)], it can be seen that most of the carriers are concentrated around the X point. We therefore use in the follow-

TABLE I. Chemical potential μ for different particle concentrations and gap parameters $\Delta^2=\sum_i \phi_{ip}^2$. Energies are given in atomic units.

N_0 (cm^{-3})	$\mu(\Delta^2=0)=E_F$	$\mu(\Delta^2=10^{-5})$	$\mu(\Delta^2=10^{-4})$	$\mu(\Delta^2=10^{-3})$	$\mu(\Delta^2=10^{-2})$
10^{17}	0.000 01(0)	0.000 01(6)	0.000 01(6)	0.000 01(6)	0.000 01(6)
10^{18}	0.000 05	0.000 07(5)	0.000 07(5)	0.000 07(6)	0.000 07(6)
10^{19}	0.000 22	0.000 34	0.000 35	0.000 35	0.000 35
10^{20}	0.001 02	0.001 46	0.001 56	0.001 61	0.001 62
10^{21}	0.004 76	0.005 73	0.006 54	0.007 13	0.007 41
5×10^{21}	0.013 90	0.015 21	0.016 95	0.019 27	0.020 97
10^{22}	0.022 09	0.023 47	0.025 57	0.028 99	0.032 39

TABLE II. Contributions to the concentration of electrons N_0, from carriers around the Γ point N_Γ, and around the X point N_X.

E_F (a.u.)	N_0 (cm^{-3})	N_Γ (cm^{-3})	N_X (cm^{-3})
0.000 01	10^{17}	6×10^{14}	10^{17}
0.000 05	10^{18}	7×10^{15}	10^{18}
0.000 22	10^{19}	7×10^{16}	10^{19}
0.001 02	10^{20}	7×10^{17}	10^{20}
0.004 76	10^{21}	7×10^{18}	10^{21}
0.013 90	5×10^{21}	3×10^{19}	5×10^{21}
0.022 09	10^{22}	6×10^{19}	10^{22}

ing calculations for k_{TF} and the screening length l_{scr} the effective mass $M_x=9M_\Gamma=1.8m_e$. These values are given in Table III.

Using the same effective mass for the calculation of the polaron radius $r_p=\sqrt{1/2m\omega_{ex}}$,[30] one finds $r_p=2.75$, 1.59, and 1.23 a.u. for $\omega_{ex}=1$, 3, and 5 eV, respectively, modelling three different gaps [the experimental value for the gap in CuCl is 3.4 eV, the energy to create the exciton is about 3.1 eV (Ref. 19)]. If one compares these values with the screening lengths in Table III a cutoff concentration of about 10^{19}, 5×10^{20}, and 10^{21} particles per cm^3 is found ($l_{scr}>r_p$).

Finally, in Fig. 3 the effective interaction $V_{eff}(q)$ between electrons due to the screened Coulomb interaction and the exchange of dressed virtual excitons, as given by Eq. (37), is plotted for three different gaps ($\simeq$exciton frequencies) and for different carrier concentrations in the conduction band. With the approximation $\kappa(q)\sim k_{TF}^2/|\vec{q}|^2$ the effective potential can be rewritten as

$$V_{eff}(q)=\frac{4\pi e^2}{k_{TF}^2}\left[\frac{\hbar\omega_{ex}^2}{\dfrac{k_{TF}^2(1-1/\epsilon_\infty)}{\dfrac{q_0^2}{|\vec{q}|^2}-\dfrac{\omega_{ex}^2}{k_{TF}^2}+i\delta}+1}\right].$$

In Fig. 3, $V_{eff}(q)$ is shown as a function of $q_0/|\vec{q}|$.

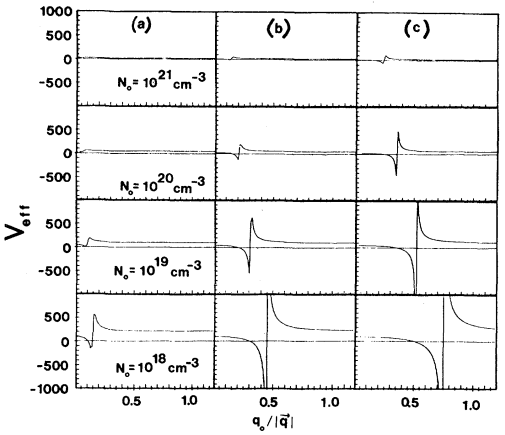


FIG. 3. Effective interaction $V_{eff}(q)$ between electrons due to the screened Coulomb interaction and the exchange of dressed virtual excitons, for different carrier concentrations N_0 and for an exciton frequency ω_{ex} of (a) 1 eV, (b) 3 eV, and (c) 5 eV.

The resonance occurs at ω_{ex}^2/k_{TF}^2, corresponding to the resonance at the dressed exciton frequency $q_0^2=\omega_{ex}^2/\kappa(q)$. The attractive region to the left of this resonance allows for superconductivity. For the optical dielectric constant ϵ_∞ a value of 2.174 for CuCl (Ref. 19) was used. The cutoff concentrations (vanishing attractive region) are about the same as those obtained with the preceding argument that the electrons can interact with the exciton field for screening lengths $l_{scr}>r_p$.

These results described above model CdS as well because the band structure of its NaCl phase is similar to that of CuCl. The main difference between CdS and CuCl for this model is reflected in the exciton coupling constant. The larger ϵ_∞ value for CdS (~8 instead of ~2) causes a larger magnitude of its V_{eff}.

V. CONCLUDING REMARKS

A theoretical model has been proposed for the excitonic mechanism of superconductivity in CuCl

TABLE III. Density of states $D(E_F)$ at the Fermi energy, Thomas-Fermi parameter k_{TF}, and screening length $l_{scr}=1/k_{TF}$ for different carrier concentrations N_0.

N_0 (cm^{-3})	$D(E_F)$ (a.u. unit volume)$^{-1}$	k_{TF} (a.u.$^{-1}$)	l_{scr} (a.u.)
10^{17}	0.0021	0.1639	6.1011
10^{18}	0.0048	0.2451	4.0801
10^{19}	0.0100	0.3550	2.8171
10^{20}	0.0216	0.5209	1.9198
10^{21}	0.0466	0.7656	1.3062
5×10^{21}	0.0797	1.0007	0.9992
10^{22}	0.1005	1.1236	0.8899

and CdS and numerical calculations for the effective interaction potential in CuCl have been presented. When the X and Γ points of the conduction bands are nearly degenerate, (5—10 kbar hydrostatic pressure[19]) most of the carriers are present near the X point. There then exists a region of attractive electron-electron interaction coupled by an exciton field that may cause superconductivity. Cutoff electron densities are found for the attractive interaction for three different energy gaps, which are in essential agreement with the simpler requirement that the screening length be larger than the radius of the polaron.

The present calculations were made, for simplicity, independent of spin. The next step in the calculations is to use spin-dependent coupling constants. Magnetic field effects will then be studied. Since the polarizing medium (valence electrons) is the same as the particles being coupled (conduction electrons), one has the strong possibility that p-wave pairing states are the lowest-energy states. This is analogous to the ^{3}He case.

Experimentally it will be possible to verify the predictions of the band-structure calculations by performing luminescence measurements under pressure. An intrinsic exciton or one bound to a donor impurity will be associated with the Γ point at zero pressure. As pressure is applied and the Γ and X points become degenerate, phonon replicas will appear. The bound exciton will also pressure ionize as predicted by Collins *et al.*[19] and contribute to the large number of carriers at the X point.

ACKNOWLEDGMENT

One of us (J.L.) would like to express his sincere thanks to the Fond der Chemischen Industrie for financial support.

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