[9] One normally assumes that HOPG is rotationally disordered about the c axis on a length scale of $\sim 1\ \mu$m. A large, nearly single-crystal region was found in RHEED essentially by chance.

[10] P. M. Williams, Nuovo Cimento 38B, 216 (1977).

[11] G. S. Painter and D. E. Ellis, Phys. Rev. B 1, 4747 (1970).

[12] Table I and Fig. 1 show that the π band at Γ is split by 1 eV due to interplanar interaction.

[13] R. F. Willis, B. Fitton, and G. S. Painter, Phys. Rev. B 9, 1926 (1974).

[14] Because of the existence of three inequivalent sites per Li in the $\sqrt{3}\times\sqrt{3}$ superlattice, long-range rotational disorder of Li is likely to occur, even when single-crystal graphite is used. This is well documented for other compounds: P. Lagrange, D. Guérard, and A. Hérold, Ann. Chim. (Paris) 3, 143 (1978).

[15] T. Inoshita, K. Nakao, and H. Kamimura, J. Phys. Soc. Jpn. 43, 1247 (1977).

[16] M. Zanini and J. E. Fischer, Phys. Rev. B 18, 2020 (1978).

[17] J. E. Fischer, in "Physics and Chemistry of Materials with Layered Structures," edited by F. Lévy (D. Riedel, Dordrecht, to be published), Vol. 6.

[18] C. Kunz, H. Petersen, and D. W. Lynch, Phys. Rev. Lett. 33, 1556 (1974).

[19] S. P. Kowalczyk, F. R. McFeeley, L. Ley, R. A. Pollack, and D. A. Shirley, Phys. Rev. B 9, 3573 (1974).

[20] The energy scale for the photoyield was obtained by subtracting the Li 1s binding energy (with respect to the Fermi energy) from the measured photon energy.

Donor-Acceptor Recombination Spectra in CuCl

D. C. Reynolds, R. J. Almassy, and C. W. Litton
Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio 45433

and

G. L. Koos and A. B. Kunz
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61820

and

T. C. Collins
Air Force Office of Scientific Research, Bolling Air Force Base, Washington D. C. 20338

(Received 5 September 1979)

This Letter reports donor-acceptor pair spectra in CuCl crystals. A simple neutral-donor, neutral-acceptor complex does not explain the data. Recent calculations have predicted an O^{--} level near the conduction-band minimum. It is this level which is speculated to be the source of electrons for the highly conducting state of this potentially excitonic superconducting material. The photoluminescence results reported in this paper do not confirm the O^{--} level but would be consistent with its existence.

The optical properties of CuCl have been studied by a number of investigators over a period of nearly twenty years,[1-5] investigations which have established the free-exciton structure as well as the energy band structure at the center of the Brillouin zone. In the earlier work, some extrinsic spectral structure was also observed including transitions associated with neutral acceptor bound excitons.[5] Recently, a series of very interesting experiments on CuCl have revealed that the magnitude of its magnetic susceptibility varies over a wide range, from $\sim -10^{-6}$ to -1, under controlled experimental conditions. For example, Brandt *et al.*[6] have shown that CuCl samples, when cooled at a rate of 20 °K/min under a hydrostatic pressure of 5 kbar, undergo a series of transitions from a state of weak diamagnetism to one of strong diamagnetism ($\kappa \sim -1$) at a temperature of approximately 170 °K. The transition to a strongly diamagnetic state was accompanied by a sharp increase in electrical conductivity. Similar experiments were also performed by Chu *et al.*,[7] in which a strong diamagnetism ($\kappa \sim -0.1$) was also observed. Although still a conjecture, there is a nevertheless a strong possibility that CuCl, and perhaps related materials, may be capable of supporting a supercurrent at elevated temperatures and pressures. These experiments have stimulated a renewed interest in CuCl, its electrical and optical properties, and its energy band structure. The energy band structure of CuCl has been recently calculated by Kunz, Weidman, and Collins,[8] which included a theoretical study of possible defect and or impurity levels. These calculations have predicted an O^{--} bound-electron level lying near to the conduction band minimum. It is this level which is speculated to be the source of electrons for the highly conducting state. The present investigation describes the first observation of donor-acceptor pair spectra in CuCl. It will be shown that one component of the donor-acceptor pairs must be doubly charged, a characteristic which would be compatible with the O^{--} center.

The samples employed were water-clear single crystals grown from the vapor phase, by a technique similar to that of Chu *et al.* Photoluminescence was excited with a high-pressure Hg-lamp at sample temperatures $<2\,^{\circ}$K. Spectral analysis of the luminescence was provided by a high-resolution, high-dispersion spectrograph (~1 Å/mm) which employed photographic recording of the spectral data. Zeeman splittings of the spectral lines were produced by magnetic fields up to 40 kG, with the samples oriented in the Voigt configuration ($\vec{q}\perp\vec{H}$).

Photoluminescence spectra were analyzed from three samples as well as from different parts of the same sample. Some of the emission lines were common to all samples while others were uniquely observed in a particular sample. More than 60 lines have been observed in the energy region 3.111 16–3.203 47 eV. Shown in Fig. 1 is a typical spectrum, a section of which has been expanded (between 3.158 71 and 3.203 47 eV) to more clearly illustrate some of the details. The line at 3.180 10 eV is a bound-exciton line previously reported by Certier, Wecker, and Nikitine.[5] All of the pair lines were characterized by a four-component magnetic field splitting, and polarization data showed that the low- and high-energy components were π lines. A geometrical construction of the magnetically split components of the line at 3.162 34 eV is illustrated in Fig. 2. The splitting is typical of the magnetic field behavior of all of the pair lines although the magnitude of this splitting does vary somewhat from line to line.

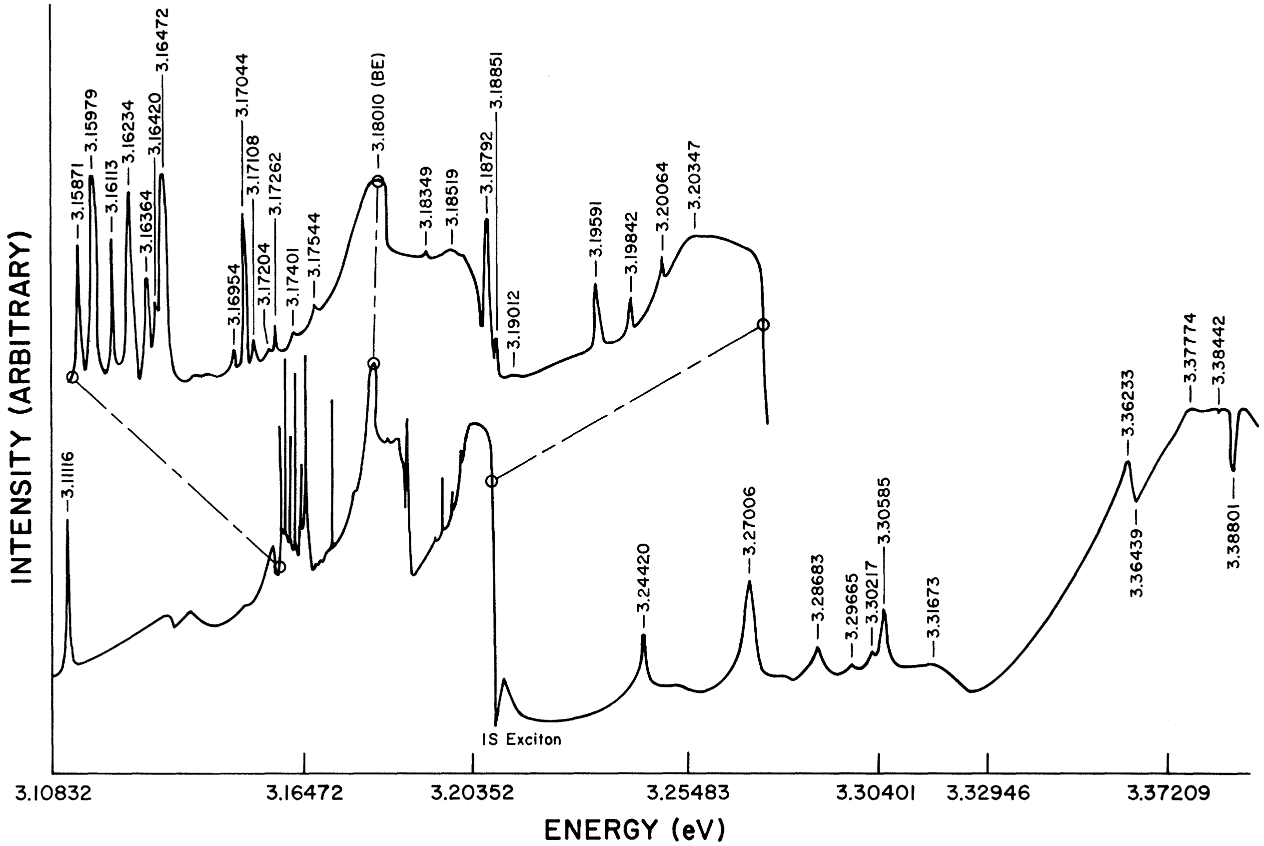

FIG. 1. Photoluminescence spectra showing donor-acceptor pair recombination in CuCl. Expanded scale shows spectra in greater detail.

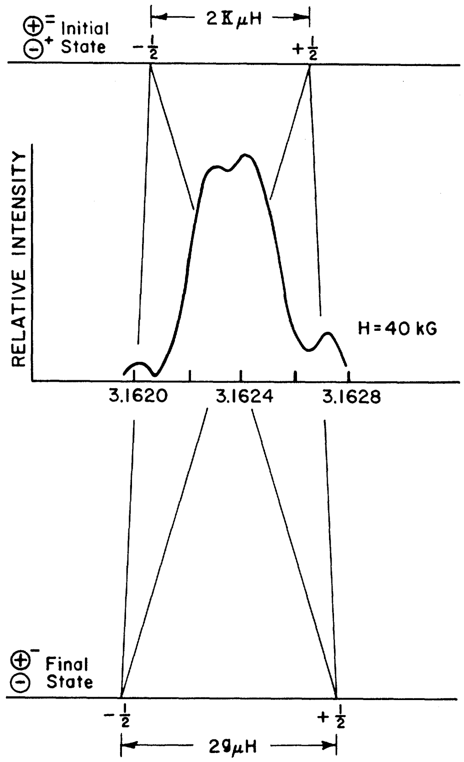

FIG. 2. Transition nomogram showing behavior of 3.162 34-eV line in applied 40-kG magnetic field. The field-split lines are shown for the polarization $E \perp H$ in which the σ lines are allowed. $g_e = 1.73$; $K = -1.32$.

From the magnetic-field data a number of conclusions can be drawn. CuCl crystallizes in the zinc-blende structure which is common to many II–IV and III–V compounds. In virtually all such materials, the top valance band is of Γ_8 symmetry while the lower valence band is of Γ_7 symmetry. CuCl, on the other hand, is characterized by a negative spin-orbit splitting, as a result of a mixing of Cu *d* electrons overlapping with the Cl *p* potential sites. This interaction reverses the valence band ordering, putting the Γ_7 band highest, which is reflected in the four-component splitting, and also in the four-component splitting of the bound exciton reported by Certier, Wecker, and Nikitine.[5]

From the Γ_6 conduction band and the Γ_7 valance band a triply degenerate Γ_5 transition and a singly degenerate Γ_2 transition are possible. Assume that the pairs are made up of simple donors and acceptors, in which case the upper state will consist of a $J = 1$ and a $J = 0$ state, depending on the orientation of the spins, and the lower state will always be a singlet, as shown in Fig. 3. For this simple donor-acceptor complex, one would expect to observe a zero-field splitting due to the exchange interaction between the electron and hole spins; this is not observed experimentally. In the presence of an external magnetic field, the $J = 1$ state will split into three components while the $J = 0$ state will not split. The optical transitions from this magnetic-field–split configuration result in a low-energy σ line and a high-energy σ line, with the intermediate-energy lines being π lines. Just the opposite is observed experimentally. Thus, the simple donor-acceptor model can be ruled out because of the absence of an exchange splitting and the observed polarization which is not compatible with the simple model.

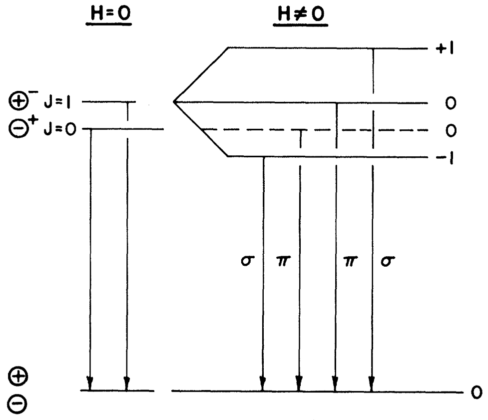

FIG. 3. Transitions expected from a simple donor-acceptor complex in zero and nonzero applied magnetic field. These transitions are based on a Γ_6 conduction-band minimum and a Γ_7 valence-band maximum.

Consider now another type of donor-acceptor complex, one in which the donor is doubly charged, as diagrammed in Fig. 2. With such a model it is possible to account for all of the experimental data. In the upper state the two electron spins will pair leaving an unpaired $J = \frac{1}{2}$ hole state, while the lower state will contain a $J = \frac{1}{2}$ unpaired electron state. Moreover, in the presence of an applied magnetic field, both the upper and lower states will split as doublets, accounting for the observed four-component splitting of the spectral lines. In order that the low-energy component and the high-energy component be π lines it is necessary that either the electron *g* value or the effective hole *g* value (K) be negative. It has already been shown by Certier, Wecker and Nikitine[5] that the hole *g* value in CuCl is negative. Thus, the data are consistent with previous observations. For the line shown in Fig. 2, an electron *g* value $g_e = 1.73$ and a hole *g* value $K = -1.32$ were calculated. Donor-acceptor pair spectra are frequently characterized by a convergence limit which implies that the pairs are randomly distributed throughout the lattice. The absence of such a limit indicates a nonrandom distribution of the pairs, which is not uncommon. For example, Henry, Nassau, and Shiever[9] observed a nonrandom double donor-acceptor pair distribution in CdS and Reynolds, Litton, and Collins[10] observed a nonrandom double acceptor-donor pair distribution in the same material.

An analysis for oxygen was performed on one of the CuCl samples by means of Auger-electron spectroscopy (AES) according to the following procedures. Variation of the O content from the surface to the interior of the sample was determined by sputtering away the CuCl over a 1-mm-diam spot to a depth of 15 μm and periodically monitoring the first-derivative Auger spectra of the sputtered area. The sputtering was carried out at relatively high energy and rates over a period of several hours in an ultrahigh-vacuum system (1×10^{-10} Torr base pressure) backfilled with high-purity argon to total pressure of 4×10^{-5} Torr. In addition to Cl and Cu in approximately stoichiometric proportions, presputter AES surface scans showed relatively weak *KLL* transitions of approximately equal strengths at 272, 379 and 503 eV, indicating the presence of surface-adsorbed C, N, and O, respectively. The surface layer was removed by low-energy sputter cleaning procedures. However, after sputtering away only a few nanometers, AES scans over the range 0–2000 eV (5-keV beam energy) showed extremely weak O(503) and C(272) peaks, an observation which persisted to a depth of approximately 10 μm. Typical of these scans is the high-gain spectrum shown in Fig. 4 accentuating the energy range of O and C. By the time 15 μm of sample was sputtered away, O was below the detection limit of the spectrometer, $\sim1\times10^{19}/\text{cm}^3$. Crude calculations indicate that the O concentration within the first 10 μm of sample depth was very high, between 8×10^{18} and $2\times10^{19}/\text{cm}^3$. Thus, the Auger results clearly confirm that O was present at high concentrations within the sample volume excited for photoluminescence.

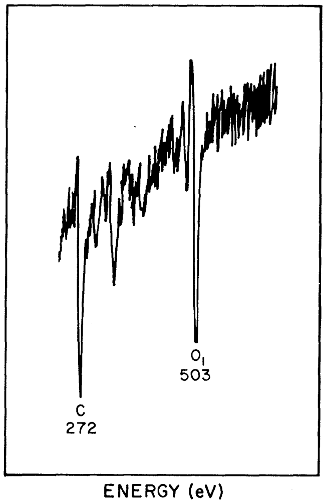

FIG. 4. First-derivative Auger spectrum of a CuCl photoluminescence sample taken under high-gain conditions at a depth of 10 μm from the surface.

The available data are not sufficient to confirm the presence of doubly charged O, nor to confirm that the O^{--} level predicted by Kunz, Weidman, and Collins[8] is one component of the observed donor-acceptor complex, but the photoluminescence data are consistent with the O^{--} center being one component of the complex. It is recognized that other chemical species or host defects may give rise to the observed pair spectra and thus cannot be ruled out at this time. It is clear, nevertheless, that one component of the complex must be doubly charged in order to explain the data. It is further clear from these data that electron donors play a nonnegligible role in the properties of CuCl and may well be in part responsible for the observed diamagnetic anomaly.

---

[1] R. Reiss and S. Nikitine, C. R. Acad. Sci. 250, 2862 (1960).

[2] S. Nikitine, J. Ringeissen, and J. L. Deiss, J. Phys. 23, 890 (1962); S. Nikitine, Prog. Semicond. 6, 233 (1962).

[3] M. Cardona, Phys. Rev. 129, 69 (1963).

[4] M. Veta and T. Goto, J. Phys. Soc. Jpn. 20, 401, 1024 (1965).

[5] M. Certier, C. Wecker, and S. Nikitine, J. Phys. Chem. Solids 30, 2135 (1969).

[6] N. B. Brandt, S. V. Kurshinnikov, A. P. Rusakov and M. V. S. Emygonov, Pis'ma Zh. Eksp. Teor. Fiz. 27, 33 (1978). [JETP Lett. 27, 37 (1978)].

[7] C. W. Chu, A. P. Rusakov, S. Huang, S. Early, T. H. Geballe, and C. Y. Huang, Phys. Rev. B 18, 2116 (1978).

[8] A. B. Kunz, R. S. Weidman, and T. C. Collins, to be published.

[9] C. H. Henry, K. Nassau, and J. W. Shiever, Phys. Rev. Lett. 24, 820 (1970).

[10] D. C. Reynolds, C. W. Litton, and T. C. Collins, Solid State Commun. 17, 15 (1975).