density. The development of a theoretical understanding of the semiconductor-metal transition beginning from the soliton concept remains as a fascinating and important problem.

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Definite Experimental Evidence against Intrinsic Electron-Hole Superconductivity in Pure CuCl

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Optical absorption measurements on very pure CuCl single crystals, prepared by a novel process, show the exponential drop of the *direct* optical absorption edge to continue below an absorption coefficient $K \sim 10^{-2}$ cm^{-1}. This rules out unambiguously the existence of an *indirect*-gap absorption below 3 eV, which is not only consistent with band-structure calculations but also excludes pure CuCl from being a suitable candidate for intrinsic high-T_c superconductivity (on the grounds of existing theories).

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Studies of excitons, phonons, piezoelectricity, and ionic conductivity have maintained a steady interest in CuCl for more than two decades. But CuCl suddenly stepped into the limelight when diamagnetic anomalies at as high a temperature as ~200 K were reported for a few samples and speculatively assigned to a Meissner-Ochsenfeld effect.[1-4] So far the theories invoked to explain such an observation of superconductivity in CuCl rely on the existence of a narrow energy gap and the associated excitons.

In a first class of theories (the "extrinsic" way), the electrons in *metallic Cu precipitates* form pairs via exchange of virtual excitons in the adjacent insulating CuCl.[5-7] In contrast to this extrinsic mechanism, a second ("intrinsic") possibility for superconductivity in bulk CuCl has also been discussed.[8-10] If one assumes that the conduction and valence bands cross at different points in reciprocal-lattice space (in CuCl after application of pressure) and the resulting holes are very much heavier than the electrons, then the excitations of the hole Wigner lattice would mediate, like phonons, superconductivity of the mobile conduction band electrons. We see that the nature of the band gap in CuCl and its width are of crucial importance if these theoretical models for superconductivity are to be applied to CuCl.

Zinc-blende–structured CuCl was assumed to have a direct gap of 3.4 eV at the center Γ of the Brillouin zone[11] until Rusakov suggested the existence of a lower conduction-band minimum at the X point separated by only ~ 0.3 eV from the top of the valence band at Γ.[9] Shortly after, optical absorption data were interpreted in support of the narrow–indirect-gap model,[12] and Abrikosov presented a detailed application to CuCl of the intrinsic "excitonic" superconductivity theory.[8] Subsequently, the band structure was recalculated by use of a variety of different techniques, and despite many controversial details, the majority of the results agreed on a direct band gap at Γ.[13-17] An extensive discussion on high-temperature superconductivity in CuCl is given by Wilson.[18] Faced with the experimental and theoretical situation and considering the all-important role played by the proposed narrow indirect gap in explaining the anomalies in CuCl, we carefully investigated the optical absorption of highly pure CuCl crystals. The results we present in this Letter are unambiguous and of consequence to the theory of excitonic superconductivity in CuCl. No indirect band gap exists below the well-known 3.4-eV direct gap.

In order to prepare CuCl which gave unambiguous and reproducible experimental results we avoided the use of HCl and H_2O. The novel method we applied is the direct reaction of ultrapure copper metal with carbon tetrachloride in a sealed and evacuated silica tube. After two steps (the details of which are described elsewhere[19]), we obtain CuCl single crystals and carbon as physically separated end products. The CuCl crystals are clear, colorless, and not at all photosensitive, in contrast to reports found in the literature. Further, the hygroscopic nature of CuCl prepared by traditional techniques is dramatically reduced in our material. We did not find it necessary to take any precautions against moisture during the measurements. Finally, we find the stoichiometry of our pure CuCl, after a total Cu analysis of two samples, to be an average $Cu_{1+x}Cl_{1-x}$, x being $(7 \pm 2) \times 10^{-4}$. This extremely small deviation from exact stoichiometry goes in the desired direction, since Cu deficiency is a notorious problem encountered in the crystals grown by traditional techniques, and Cu deficiency can lead to cupric ions. For the optical measurements, the crystals were cut in platelets of different thickness (d, up to 5 mm) and polished mechanically until the parallel surfaces were optically smooth. The optical transmission was measured at ambient conditions with a Cary Model-17 spectrometer for wavelengths $\lambda < 2.5$ μm and a Perkin-Elmer Model-283 spectrometer for $2.5 < \lambda < 50$ μm. Already at first glance the absorption coefficient K is obviously smaller than say ~ 1 cm^{-1} in the visible spectral range, because the crystals are clear and colorless. Therefore we determined K in a *differential* absorption arrangement: The transmissivities of two samples, identical except in thickness, were compared with each other. In contrast to the single-sample technique applied so far for CuCl, in this configuration the surface reflectivity losses cancel out, eliminating the difficult task of a very accurate measurement of the absolute value of the reflectivity.

In Fig. 1, the energy dependence of the absorption coefficient K is shown on a logarithmic scale. Below ~ 0.1 eV, K rises above the instrumental background of ~ 0.2 cm^{-1} and increases rapidly due to lattice absorption. In recent detailed studies the local maxima, the arrows indicate two examples, were identified as multiphonon processes.[20] In the range of overlap, our data are in agreement with Hadni *et al.*[21] and we invoke also

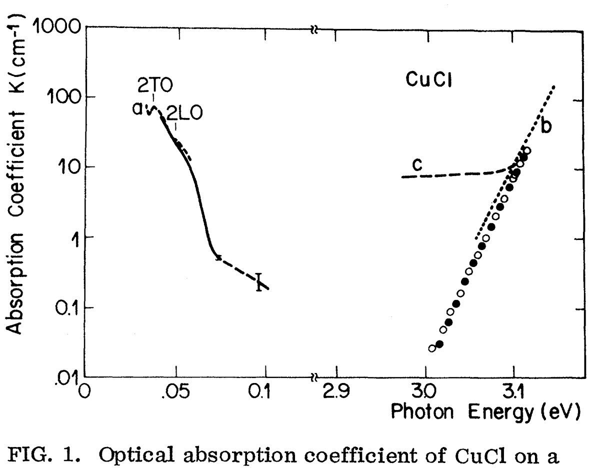

FIG. 1. Optical absorption coefficient of CuCl on a semilogarithmic scale. Open and closed symbols represent two data sets obtained on pure CuCl prepared by the new method. Curves *a*, *b*, and *c* are for comparison from Refs. 20, 21, and 12, respectively. Multiphonon absorption is indicated by 2TO and 2LO (Ref. 20).

phonon overtones to explain the wide shoulder between 70 and 100 meV. In the remaining energy window between 0.1 and 3 eV, the spectral dependence of K is flat, and K does not exceed 0.2 and 0.02 cm^{-1} below and above 0.5 eV, respectively. As further evidence for the high quality of the crystals, no impurity bands are detected and what is more important, no double line shows up near 0.35 eV.

Above 3 eV the fundamental absorption sets in. Phonon-broadened exciton absorption leads to the typical spectral and temperature dependence of K, known as the Urbach behavior and studied in detail earlier.[22] Only very recently has the microscopic mechanism underlying the Urbach behavior been clarified in favor of the electric-field–ionized exciton model.[23] According to this model, the electron can tunnel away from the hole under the action of electric microfields associated with phonons, resulting in an exponentially decaying density of states below the absorption threshold. The central result of our measurements (open and closed symbols in Fig. 1) shows that the absorption coefficient in pure CuCl depends *exponentially* on energy not only for $K \gtrsim 1$ cm^{-1}, but also at least down to $K \sim 10^{-2}$ cm^{-1}. Such a uniform behavior of K over more than 4 decades clearly originates in the same absorption mechanism, namely the above-mentioned exciton-phonon interaction. It particularly rules out any interband absorption across an indirect band gap of less than 3 eV.

Our results compare well with Ref. 22 in the range of overlap, considering the slightly different temperatures of measurement (dash-dotted line in Fig. 1). However, the disagreement with the data of Rusakov *et al.*[12] is striking (see also Fig. 2): At 3 eV, our samples are more transparent by more than two orders of magnitude. Such a dramatic discrepancy can only be accounted for by high impurity levels and/or nonstoichiometry in their crystals, in addition to the limited accuracy inherent to a single-sample absorption measurement.

To verify this and to investigate the origin of the reported ~0.3-eV absorption lines in their data, we have grown crystals from CuCl prepared in the traditional manner from HCl solution. As shown in Fig. 2, the optical absorption coefficient of such a sample has the same order of magnitude and a similar spectral dependence as the material used in Ref. 12. Furthermore, among a variety of impurity lines observed in the infrared region, most of them being typical of O-H and O-Cl vibrations, we also find the two lines between 0.35 and 0.36 eV with the same intensity ratio as reported by Rusakov *et al.*[12] But instead of ascribing them to s and p excitons preceding excitations across the indirect gap of ~0.3 eV, the existence of which we have just disproven, we ascribe them to H-Cl vibrations. Such an interpretation is not only based on comparison with known HCl vibration energies, but HCl is also to be expected as a major impurity left from the crystal preparation process. The concentration of HCl in our intentionally doped samples can be estimated to be about 100 ppm, starting from known absorption coefficients.

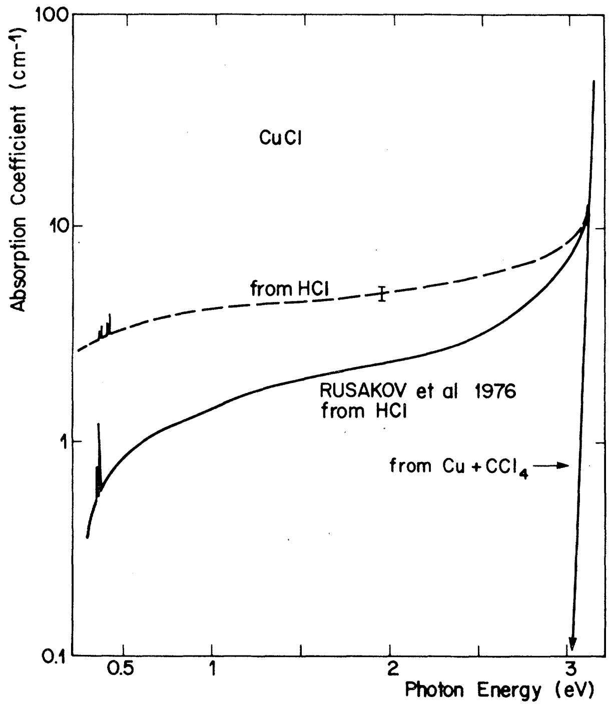

FIG. 2. Comparison of the optical absorption coefficient of CuCl prepared by different methods. If precipitated from HCl solution, CuCl exhibits a broad background absorption in addition to sharp impurity lines.

In addition, we have also investigated the optical and the electrical properties of our pure samples at high pressures and ambient temperature. Here, we mention only the results of interest in this context. The band gap *opens* under application of pressure by 1.8 ± 0.1 meV/kbar in the zinc-blende phase up to 51 ± 1 kbar, where the crystal transforms into the tetragonal phase. After a reduction of the gap by ~0.25 eV at this structural transition, it continues to open as the pressure is increased. The electrical resistivity of our pure CuCl is $>10^7$ Ω cm, varies a little (<1 decade) up to 50 kbar, *increases* in the tetragonal phase (by more than 1 decade), and finally *drops* in the rock-salt phase by more than three orders of magnitude. This is in pronounced contrast to the samples which showed the diamagnetic anomalies and were grown in the traditional way. There, the resistivity *decreased* by up to 6 decades in the tetragonal phase, possibly as a result of pressure ionization of impurities. We are left with the fact that CuCl has an energy gap of more than 3 eV, which does not close under pressure and changing the temperature has little influence on it either. Therefore, it is hard to see how the theoretical concepts developed in the past for high-T_c superconductivity, either of intrinsic or "interfacial" type, can give rise to superconductivity in pure CuCl. However, a recent model including piezoelectric polarization due to the elastic strain of grain boundary dislocations may be seen as an interesting attempt to overcome the wide-band-gap problem in CuCl.[24]

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