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Anomalies in cuprous chloride

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Systematic investigation has been made on CuCl crystals prepared by different methods. The occurrence of different high-pressure phases and various anomalies are found to depend sensitively on the sample conditions. Four-lead electrical measurements showed that all the pressure-induced phases of the thermally equilibrated CuCl crystals studies had positive although small activation energies. A diamagnetic anomaly above 90 K over a temperature range of 10–20 K was observed in the ac magnetic susceptibility of rapidly warmed samples. A sharp increase of electrical conductivity and two extrema of the differential-thermal-analysis signal accompanied the diamagnetic anomaly.

I. INTRODUCTION

Cuprous halides crystalize in the zinc-blende structure in a tetrahedral coordination and therefore in some sense are related to the isoelectronic sequency of group-IV elements, and III-V and II-VI compound semiconductors. However in many ways the cuprous halides are anomalous when compared to other members of the isoelectronic sequence. Of particular interest are their peculiar high-pressure-phase diagrams,[1–5] which do not exhibit the general features[6] expected of the sequence.

Recently, two-lead electrical-resistivity measurements[7–9] at room temperature on CuCl, the most unstable cuprous halide, showed a sharp resistivity drop by a factor of $\sim 10^6$ at ~ 40 kbar, and then a sharp rise by ~ 10 at ~ 60 kbar followed by another rapid increase by $\sim 10^5$ above ~ 90 kbar. The transition back to a highly insulating phase above ~ 90 kbar has been taken as the supporting evidence for the proposition[9] that the high conductivity of CuCl at pressures between ~ 40 and ~ 90 kbar is not due to an irreversible pressure-induced sample decomposition but should be the characteristic of the CuCl samples. The appearance of this high conductivity in CuCl at such a relatively low pressure of ~ 40 kbar is thus indeed unusual, in view of the large direct band gap[10] of 3.4 eV observed optically at the center of its Brillouin zone. A metallic character has been suspected[7–9] in these highly conducting phases. Furthermore, a highly ionic zinc-blende structure, such as CuCl, would have been expected to collapse directly to a good insulator with the NaCl structure.[6] A high-pressure x-ray study[8] demonstrated that within the experimental resolution, the transition at ~ 40 kbar was isostructural, while those at ~ 60 and ~ 90 kbar were not; and corresponded, respectively, to a cubic (zinc-blende) to tetragonal, and a tetragonal to cubic (NaCl) transition. The phase diagram of CuCl was further complicated by the recent report[11] of anomalies observed in

compressibility and differential-thermal-analysis measurements indicative of more phase transitions at pressures below 40 kbar. Preliminary results indicated a diamagnetic ac susceptibility anomaly at 85 K in an isobaric run at ~22 kbar,[7] and at ~20 kbar in an isothermal run at 4.2 K.[9] A modified-energy-band model[12] including an indirect band gap comparable to the binding energy of the direct excitons was proposed for CuCl to explain the different anomalies. The model led to interesting speculations concerning the very nature of CuCl both at atmospheric and high pressure. The main motivation behind the present investigation is to elucidate this aspect of CuCl.

We have carried out a systematic investigation on CuCl prepared by different techniques. The occurrence of the highly conducting phases under various pressures was found to depend sensitively on the sample conditions. However, the activation energy at atmosphere pressure was not. A four-lead technique was successfully employed to determine the temperature dependence of the resistivity of CuCl under different pressures. Small and positive activation energies were found for all high-pressure phases; 0.014 eV for the most conducting phase between ~40 and ~60 kbar and ~0.07 eV between ~60 and ~90 kbar in contrast to the value of 0.39 eV at atmospheric pressure. Additional anomalies were detected, although only some of the previous observations were reproduced. Upon rapid warming, an ac magnetic-susceptibility anomly with a width of ~10–20 K was observed above 90 K, corresponding to a paramagnetic-diamagnetic-paramagnetic transition with increasing temperature. The signs and magnitudes were determined by comparison with the known paramagnetic-ferromagnetic and paramagnetic-diamagnetic transitions run concurrently. The size of the anomaly grew both with increasing pressure and rate of heating of the sample. A diamagnetic signal as large as ~7% of that for a perfect superconductor (i.e., for complete shielding) was obtained. Accompanying the susceptibility anomaly was a sharp drop in resistivity in the "diamagnetic" region subtended by two narrow kinks in the differential-thermal-analysis data. A similar and much larger susceptibility anomaly was subsequently reproduced by Brandt *et al.*[13] The results and different possible explanations of the anomalies will be discussed.

II. EXPERIMENTAL RESULTS

CuCl is a photosensitive material which disproportionates to a more stable compound $CuCl_2 + Cu$ in the presence of light and air, especially when the humidity is high or moisture is present. All samples were therefore prepared and assembled under dim red light with minimum exposure to air in order to avoid sample deterioration.

A. Sample preparations

It has been demonstrated that the reproducibility of the highly conducting phases in CuCl under pressure is poor.[7,8] We decided to investigate CuCl samples prepared under different conditions. Three methods of preparation were used, and in addition two sets of flux-grown single crystals which were kindly supplied by Hanson of Arizona State University and Kaminov of Bell Labs. Freshly prepared samples, which also seemed to be the least contaminated, were grown from the vapor, the melt, and the gel.

Several steps[14] were taken to obtain pure CuCl samples. First, clear CuCl crystals were precipitated from a 15-vol.% HCl solution of analytical reagent grade $CuCl_2 \cdot 2H_2O$ at 90 °C. High-purity Cu-metal granules were kept in the solution and in intimate contact with the CuCl crystals. The CuCl was purified and obtained as a white powder by recrystallization from dilute HCl solution. The powder was washed in ethyl alcohol for immediate use in crystal preparations.

A quartz chamber with a long narrow neck shown in Fig. 1 was used for growing polycrystalline samples. The purified CuCl powder was fed to the chamber until half filled. It was fused in vacuum, or in He or H_2. The polycrystalline fused CuCl samples were stored in the dark in vacuum or in a 1-vol % HCl water solution in the presence of Cu granules and either used directly, or further purified as follows.

A second method employing further distillation was used to remove any possible CuO and excess Cu formed during the fusing process. The quartz chamber was evacuated during heating. The vapor of the melt at 650 °C began to condense at the narrow constriction at room temperature in the long narrow neck away from the chamber (Fig. 1). After about 20 min, the solid condensate was greenish, indicating the slight transformation of CuCl to $CuCl_2$ during the low-pressure evaporation, which blocked off the tube. The molten CuCl was thus forced to evaporate at a higher vapor pressure. The solid condensate of this high-pressure vapor formed a transparent and colorless ingot of pure CuCl. A small quantity of black powder residual believed to be CuO and Cu was found inside the chamber after evaporation. The polycrystalline pure CuCl grown from the vapor was then heated up to 450 °C in vacuum and quenched quickly to room

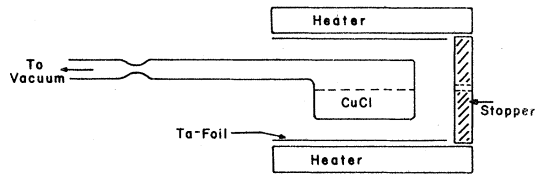

FIG. 1. Quartz-chamber arrangement for preparation of CuCl polycrystals.

temperature to retain the zinc-blende structure.

Fresh single crystals of CuCl were prepared by a third method using the gel-growth process which has been shown to be capable of yielding large high-purity samples.[15] The pyramidlike crystals of 1–4 mm on one edge were grown over a three-week period in solutions containing purified CuCl, HCl, H_2SO_4, and Na_2SiO_3. The grown temperature of 15 °C was found to improve the purity and optical perfection of the crystals obtained over gels kept at 25 °C. This was presumably due to the slower growth at the lower temperature. All operations were carried out using dark-room procedures.

B. Sample characterization

Powder-pattern x-ray analysis indicated that samples prepared as described above were single phase in the zinc-blende structure, although when examined under a polarization microscope some showed wurtzite-structure inclusions. The $g \sim 2$ resonance line at 77 K in the ESR spectra observed[16] in $CuCl_2 \cdot 2H_2O$ was not detected in the freshly prepared CuCl samples. However, the line did appear in the samples after exposure to air and/or light, e.g., in the greenish or bluish CuCl samples. The strength of the $g \sim 2$ line increased with the age of the sample. Only transparent and colorless CuCl samples with no or only slight wurtzite structure were used for the present study.

Qualitative emission spectral analysis was carried out on the polycrystalline samples grown from melt and on the single crystals grown from gel. Minimum impurities were found in the center portion of the ingot. They were, in ppm: Li, <12; Be, =1.2; B, <1.2; Na, <40; Mg =2.5; Al, =4; Si, =6; P, <120; K, <120; Ca, =10; Ti, <12; V, <4; Cr, <4; Mn, <4; Fe, <12; Co, <12; Ni, <12; Zn, <40; Ga, <4; Ge, <4; Sr, <1.2; Nb, <40; Mo, <4; Ag, =2; Cd, <4; In, <12; Sn, <12; Sb, <40; Ba, <4; Ta, <400; W, <120; Tl, <40; Pb, <12; and Bi, <4, where "<" stands for the detection limit of the analysis. Additional impurities of S (~100) and Na (~100) were found in the gel-grown single crystals. No analysis was made on the flux-grown single crystals. However, they are believed to be contaminated by the fluxing agent,[15] e.g., KCl.

C. Measurement of resistivity (ρ), differential thermal analysis (DTA), compressibility (κ), and ac magnetic susceptibility (χ) under pressure

Two basic types of pressure rigs were used to generate the high pressure needed for the present study. The 3.6–12-mm-diam Bridgman anvil sets[17] with silver-chloride single crystal, Teflon, or steatite as the pressure medium provided a quasihydrostatic pressure up to ~100 kbar for measurements on 0.1–0.2-mm-thick plates cut from the samples described above. Recessed anvils were also tested to introduce better hydrostatic conditions. However, the results were similar. The pressure was determined at room temperature by a calibrated pressure gauge. The second apparatus, a piston-cylinder arrangement with a Teflon cell[18] containing the 1 : 1 mixture of *n*-pentane and isomayl-alcohol pressure medium, gave hydrostatic pressures up to 32 kbar for the simultaneous measurements of ρ, DTA, κ, and χ on ~1.5-mm-diam × 3.5-mm-long cylindrical samples. At low temperature the pressure for this rig was determined by a superconducting Pb manometer. The isobaric runs were carried out by locking the pressure at room temperature using a Be-Cu clamp before varying the temperature of the samples together with the clamp. The temperature was measured with a chromel-alumel thermocouple above 20 K and a Ge thermometer below.

Both two- and four-lead measurements were carried out. Guard rings were used to remove spurious readings due to current leakage, which could be large for highly resistive samples like CuCl at atmospheric pressure. Pressure contacts were easily established for ρ measurements for the Bridgman anvil rig. However, for the piston-cylinder arrangement, Cu leads had to be impregnated in the samples compacted at ~7 kbar. This was accomplished by forcing the leads into the sample in a press before reannealing at ~150 °C. The dc current used was 1 μA. The resistivity of the 1 : 1 *n*-pentane and isoamyl-alcohol pressure medium was monitored to be more than ten times that of the sample at 300 K and 1 bar, and to increase rapidly with decreasing temperature and increasing pressure.

The DTA measurments under pressure were made by embedding a thermocouple temperature sensor in the compacted sample while connecting the reference junction to the high-pressure cell. The temperature of the sample was changed by lowering or raising the high-pressure clamp inside a liquid-helium or nitrogen cryostate and also by directing a heat lamp onto the clamp.

The room-temperature κ was determined as a function of pressure using a microstrain gauge technique[19] by gluing a "micromeasurement"-modified karma gauge on a slab of an annealed CuCl sample compacted under ~7 kbar. A similar gauge mounted on an aluminum slab sitting right next to the CuCl sample was used as a reference. In this case, the pressure was monitored by a constantan strain gauge.

An ac inductance bridge method was employed to determine χ between 1 and 300 K under pressures up to 32 kbar. To remove the large background temperature drift, the two secondary bucking coils directly wound on the sample and the manometer (and/or reference) were put inside the high-pressure cell. The total drift including the skin effect of the manometer,

i.e., Pb, between 1 and 300 K can be made less than 15% of the signal of a perfect diamagnet with the same size as the sample. The relative drift can be further reduced by using a larger sample. The improvement in filling factor of ~900, compared with the previous technique[7] where the secondary coils were wound on a 29-mm-diam coil form surrounding the high-pressure cell, enhanced the sensitivity of the technique in spite of the smaller number of turns of the coils used. The operating frequency was 400 Hz, but the general temperature dependence of χ remained the same when check at 10 Hz. The sign and scale factor for converting the bridge throw into susceptibility units was obtained from the sign and magnitude of the signal of the Pb transition. The correction due to the skin effect of the Pb in the normal state is insignificantly small in the present work. The details of the technique will be published elsewhere.

III. RESULTS AND DISCUSSION

Some typical characteristics of the CuCl crystals prepared by different methods are summarized in Table I. All but CuCl-*E* crystals, which were flux grown several years ago, were transparent and colorless at 300 K, and did not show the $g \sim 2$ ESR line at 77 K possibly indicating the absence of the Cu^{2+} ions (or less than a few ppm). No ESR study was made on CuCl-*F* crystals. All but CuCl-*F* were found to transform under pressure to a more conducting phase. In spite of similarities at atmospheric pressure, subtle differences existed in the high-pressure phases. The critical pressure (P_{Cl}) for the first pressure-induced phase transition and the resistance ratio (ρ/ρ_p) of the phase below P_{Cl} to that above P_{Cl} depend sensitively on the preparation method and the age of the sample. For instance, P_{Cl} and ρ/ρ_p were 40 kbar and $\sim 10^7$, respectively, for CuCl-*A* but >90 and 10^3 for the CuCl-*D* grown in H atmosphere. Both P_{Cl} and the width of the transition at P_{Cl} increase with the age of the sample possibly due to the increase in Cu^{2+} concentration. The variations of P_{Cl} and ρ/ρ_p might have resulted from the different gas impurities (H_2 in the case of sample *D*) or the included flux in the flux-grown crystals (samples *E*). Without further microstructural and chemical analyses, no specific causes can be identified at this time. No correlation between P_{Cl} and ρ/ρ_p, and the resistivity at 300 K and 1 bar was observed, although higher resistivity in general represented a purer sample, and a low P_{Cl} seemed to be accompanied with a higher ρ/ρ_p. However, in spite of the gross resemblance of most of the CuCl crystals at 300 K and 1 bar, they appeared in different colors at high temperatures, as shown in Table I. This may provide a simple criterion for the preparation of desirable crystals.

A typical pressure dependence of ρ at 300 K up to 110 kbar for the polycrystalline CuCl-*A* is shown in Fig. 2. Three different phase transitions were observed, signaled by a drop in ρ of $\sim 10^7$ at 40 kbar, an increase in ρ of ~10 at 60 kbar, and another increase of $>10^5$ above 90 kbar, respectively. It should be noted that the ρ of other CuCl crystals shared the general features of CuCl-*A* depicted in Fig. 2, except for the anomaly at 60 kbar. In view of the larger ρ/ρ_p of CuCl-*A*, the absence of the ρ anomaly at 60 kbar in CuCl-*B*, -*C*, -*D*, and -*E* might represent the absence, in these latter crystals, of the most conducting phase between 40 and 60 kbar existing in CuCl-*A*. To obtain the most conducting phase between 40 and 60 kbar in CuCl-*A*, cycling the pressure was found necessary, presumably to provide a most hydrostatic condition across the sample inside the anvils. The results are given in Fig. 3.

TABLE I. Typical characteristics of CuCl crystals prepared from vapor (*A*), gel (*B*), melt in vacuum or He atmosphere (*C*), melt in H atmosphere (*D*), flux from Hanson (*E*), and flux from Bell (*F*).[a]

	A	*B*	*C*	*D*	*E*	*F*
Color (300 K)	Colorless and transparent	Colorless and transparent	Colorless and transparent	Colorless and transparent	Blush ···	Colorless and transparent
Color (>420 °C)	Reddish		Blush	Reddish	···	···
Color (>600 °C)	Dark red	···	Dark green	Reddish	···	···
$g=2$ line (77 K)	No	No	No	No	Yes (weak)	···
ρ (300 K) (Ω cm)	$\sim 5\times 10^6$	$\sim 10^6$	$\sim 10^6$	$\sim 10^8$	$\sim 10^6$	$\sim 10^7$
P_{Cl} (kbar)	40	40–45	45–50	90	60	>100
$\rho(P<P_{Cl})/\rho(P>P_{Cl})$	10^7	10^6	10^4–10^6	10^3	10^3	
Phase II*a*	Yes	No	No	No	No	No
χ anomaly	Yes	···	···	···	···	···

[a] ···, data were not taken.

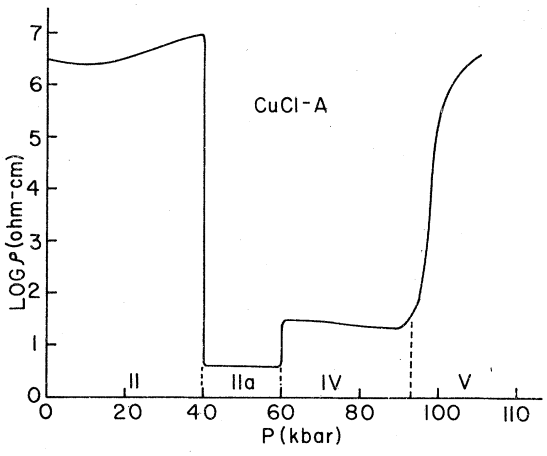

FIG. 2. Schematic pressure dependence of ρ of CuCl-*A* at 300 K.

No attempt was made to determine the crystal structures of these different high-pressure phases by simultaneous x-ray measurements. However, by comparing the resistivity versus pressure curves of the present study with those previously obtained,[8,9] it is tempting to associate the phase transition at 40, 60, and 90 kbar detected here with the isostructural (zinc-blende)$_x$ the cubic (zinc-blende) to a tetragonal, and the tetragonal to a cubic (NaCl) transformations determined by x-ray diffraction.[8] The phases are labeled as II, IIa, IV, and V in Fig. 2. Such an association is not without question. According to the previous high-pressure x-ray measurements[8] a ~11.5% volume reduction was detected at 60 kbar but not more than 1% at 40 kbar. It thus became very puzzling to observe that our sample leads were more susceptible to breaking off on cycling the pressure around 40 kbar rather than at 60 kbar.

The temperature dependence of ρ and thus the activation energies (E_a), for the different phases of CuCl-*A* were determined under pressure with both the two- and four-lead techniques. For phases II and IV, the resistivity of which was high compared with the lead and contact resistance, both measuring techniques gave the same E_a. However, only four-lead technique was used for determining the E_a of phase IIa. The results are given in Fig. 4.

From a high-pressure study it has been concluded[4] that while the electrical conductivity ($\sigma = 1/\rho$) of CuCl consisted of both electronic and ionic parts, the electronic contribution predominates below ~500 K. At atmospheric pressure, $E_a = 0.39 \pm 0.01$ eV is in fairly good agreement with previous ρ measurements[20] but in strong contrast to the optical data[10] which would predict an E_a of 1.75 eV. This value of E_a did not seem to depend on samples which had different room-temperature resistivities and thus different impurity concentrations. If the conductivity is to be attributed to a low-lying conduction-band minimum at the X point[12] of the Brillouin zone then the sample-independent activation energy is of course understandable. Unfortunately, the clear and colorless appearance of the CuCl crystals at 1 bar seems difficult to reconcile with the existence of such a conduction minimum. Otherwise, one must postulate that all the dominant electrically active impurity or defect levels have the same activation energy. This latter suggestion is consistent with the results of previous studies on $CuCl_x$.[21]

Two activation energies were observed for each of the two phases, IIa and IV. The quantity E_a of phase IIa was found to be 0.07 ± 0.01 eV above 170 K and 0.014 ± 0.005 eV below 170 K at 55 kbar, whereas E_a

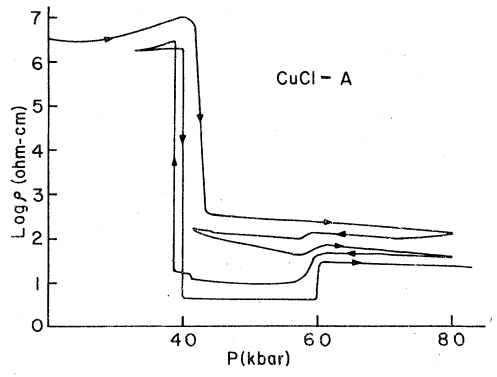

FIG. 3. Pressure-cycling effect on ρ of CuCl-*A* at 300 K.

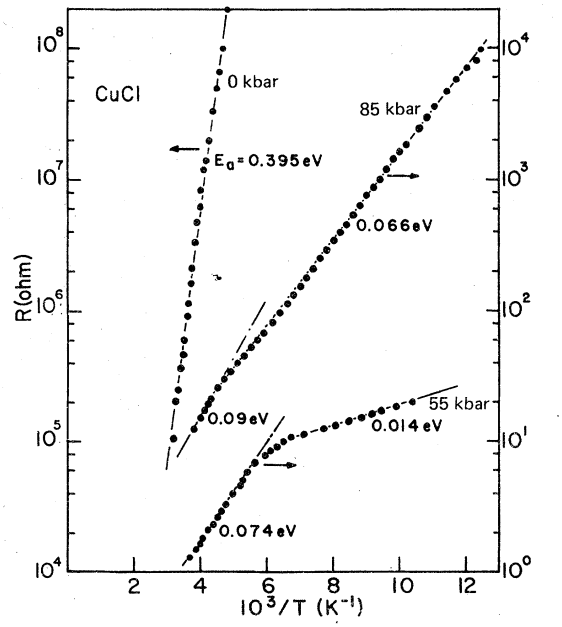

FIG. 4. Temperature dependence of ρ of different phases of CuCl-*A*.

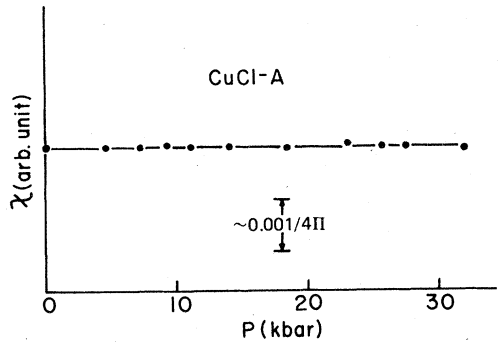

FIG. 5. Pressure effect on χ of CuCl at 300 K.

of phase IV was found to be 0.09 eV above 210 K and 0.07 eV below 210 K at 85 kbar. For CuCl-*B* and -*C*, E_a remains in the range between 0.10 and 0.06 eV. The similarity between the E_a's for phase II*a* above 170 K and phase IV below 210 K suggest that the appearance of two E_a's in each of two phases, II*a* and IV, is due to the incomplete phase transition of the samples under pressure. This is consistent with the observation mentioned earlier that CuCl usually transforms directly first into phase IV under pressure and phase II*a* appears only on cycling the pressure. The positive activation energies observed by us using the four-lead technique rules out the possibility of metallic behavior in these highly conducting phases of thermally equilibrated CuCl under pressure, in contradiction to the previous suggestions.[7–9]

Compressibility measurements on CuCl-*A* at 300 K under hydrostatic pressure up to 24 kbar did not exhibit any reproducible anomaly in CuCl suggesting the phase transition previously observed.[11] The strain gauge technique employed by us had a resolution

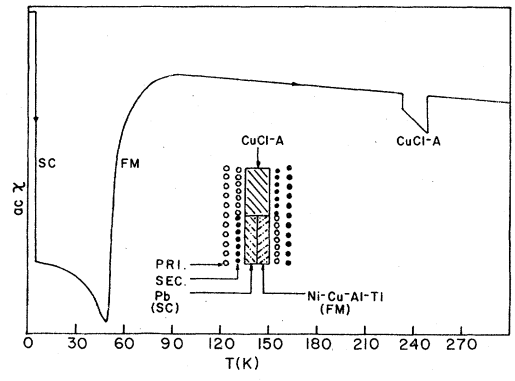

FIG. 6. Schematic temperature dependence of χ of a rapidly warming CuCl sample, a superconducting Pb, and a ferromagnet $Ni_{66}Cu_{29}Al_3Ti_2$. It should be noted that the sample coil and the coil around the superconductor and the ferromagnet were oppositely connected to each other. The strong temperature dependence of χ between 7 and 50 K is attributed to the skin effect of Pb and the magnetic signal of the ferromagnet.

about two to three orders of magnitude larger than the size of the anomalies appearing in the dilatometric results.[11] The reason for the disagreement is yet to be determined.

The ac magnetic susceptibility of CuCl-*A* was determined at 300 K as a function of hydrostatic presure up to 32 kbar. As shown in Fig. 5, no anomaly was observed consistent with the absence of κ anomaly. The temperature dependence of χ of the CuCl-*A* crystals was also determined at different pressures up to 32 kbar. During slow cooling and warming at a rate <1 K/min, there appeared no anomaly in all of our samples except one where a small step, corresponding to a signal about 0.2% of a perfect diamagnet was detected at $\sim$100 K and above 20 kbar. However, on rapid warming, a reproducible anomaly in all samples investigated was observed. The temperature at which the anomaly occurred varied between 90 and 250 K, depending on samples, but did not depend sensitively on the pressure. The size of the anomaly depends on the warming rate and the pressure, the width of the anomaly being approximately 10–20 K. However, the detailed effects have yet to be determined. The schematic temperature dependence of χ (including the background drift) of a fast-warmed sample is depicted in Fig. 6 together with the sample arrangement within the high-pressure cell. In one of the secondaries was a cylinder of the CuCl crystal and in the other oppositely wound but otherwise identical secondary were

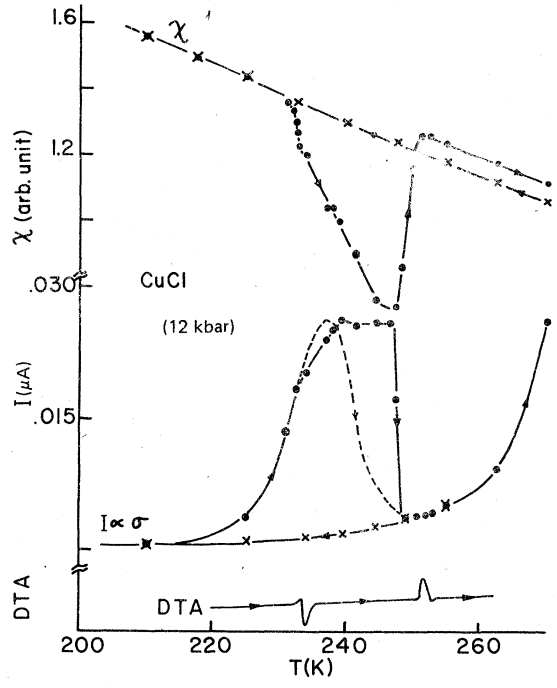

FIG. 7. χ, I, and anomalies of CuCl. I was the current flowing through the sample and therefore a measure of σ of the sample. The dashed curve represented the expected results due to the detrapping of charges by thermal excitation.

two half cylinders of Pb and $Ni_{66}Cu_{29}Al_3Ti_2$. The Pb, a superconductor, and the $Ni_{66}Cu_{29}Al_3Ti_2$, a ferromagnet, were used as signal calibrators with signals shown in Fig. 6. By comparing the signs and the magnitudes, it was concluded that the anomalous signal due to CuCl was diamagnetic in nature over a temperature range of 10–20 K around 240 K and about 7% of the signal due to a perfect diamagnet. This represent the maximum χ anomaly observed by us so far. The σ of the sample and the DTA signal were also simultaneously monitored. Because of experimental difficulties in imbedding too many leads into the sample, only the two-lead method was used to determine the conductivity by measuring the current (I) flowing through the sample. The results at 12 kbar and with a warming rate of 5 K/min are shown in Fig. 7. σ shows a sharp increase by a factor of 40 as χ becomes diamagnetic and returns rapidly to normal as χ does the same at a higher temperature. The DTA signal shows two extrema indicative of two phase transitions at the onset and the completion of the χ anomaly. Several possibilities leading to the observed unusual behavior of χ are discussed.

(a) Equipment interference—A sudden change of voltage across the sample due to the change of sample σ can lead to a simultaneous change in χ. To remove any such possible interference, χ, σ, and DTA were measured separately. All anomalies were reproduced.

(b) Volume effect—A sudden volume change associated with a phase transition can generate some relative movement in the windings of the secondary, which can in turn result in a step in χ. The strain of the CuCl crystal was measured during fast warming at 1 bar and no anomaly $>10^{-5}$ was deteced from 4.2 to 300 K. The χ experiment was repeated but with plastic (with thermal-expansion coefficient larger than CuCl) and carbon (with thermal expansion smaller than CuCl) cylinders in place of the CuCl sample. No χ anomaly was detected. This is consistent with the negligibly small pressure effect on the temperature of the anomaly observed. Therefore the volume effect, if any, should be small.

(c) Eddy-current effect—High σ within a narrow temperature range can generate an apparent diamagnetic χ anomaly, due to the eddy current, of the type observed. For a long cylindrical sample, a penetration depth of 0.5 mm, or 0.6 times the radius of the sample would be needed to reproduce a 7% diamagnetic χ anomaly. A homogeneous sample would require a σ $\sim$10 times that of Cu at 200 K for our operating frequency of 400 Hz. However the observed σ of CuCl at the anomaly is $\sim 10^{-5}$ $(\Omega\ \text{cm})^{-1}$, less than 10^{-11} times that of Cu at 200 K. Hence the eddy-current shielding effect if present, must be associated with highly conducting metallic domains in the sample separated by insulating sections or layers which perhaps are present due to the incomplete transformation of the sample.

(d) Thermal excitation of trapped charges—Detrapping charge carriers by thermal excitation in a semiconductor can result in an increase in the electrical current in the sample.[22] Assuming that there are no recombination and no retrapping, and that only single trapping occurs, the current induced is proportional to the product of two factors; the thermal-excitation probability and the population of the trapped charges. The former increases with increasing temperature while the latter decreases. A peak is thus expected in the I vs T curve. However, a current of detrapped charges of $\sim 10^{-8}$ A (of the order of the maximum I shown in Fig. 7) would only give rise to a χ anomaly about 3 orders of magnitude too small to account for the observed anomaly, even with the current flowing in an optimal way to produce a maximum magnetic field. Furthermore, the sign of the χ anomaly so generated should critically depend on the polarities of the applied electric field during cooling and warming, and the I vs T curve should be a smooth function of temperature; both are in contradiction to our observations. In addition, the appearance of the χ anomaly in the absence of an externally applied bias field across the sample [as described in (a)] makes this possibility extremely unlikely.

(e) Cooperative effects—The DTA signals in Fig. 7 indicate that the χ and σ anomalies are associated with the first-order phase transitions. A low-frequency acoustical resonance accompanying a ferroelectric phase transition can enhance charge movements and thus result in a χ anomaly at a well-defined frequency at a fixed temperature. However, the observations of the χ anomaly at the same temperature and at 10 and 400 Hz make this proposition very unlikely. Further, the χ anomaly of this nature is about three orders of magnitude too small. If CuCl undergoes a nonmagnetic to weak-ferromagnetic (Dzialoshinsky-Moriya type) phase transition[23] under hydrostatic pressure and the strain due to rapid warming (or cooling) subsequently induces a sudden weak-ferromagnetic to antiferromagnetic transition, a sudden shift in ac χ in the diamagnetic sense can occur. However, we found no magnetic phase transition induced in CuCl by hydrostatic pressures up to 32 kbar at room temperature as shown in Fig. 5, or by rapid cooling and warming between 77 and 500 K at 1 bar from ESR and χ studies. In addition, the near return of χ to its normal value at higher temperature (e.g., $>$250 K, Fig. 7) does not seem to be compatible with this suggestion. On the other hand, if the phase transition as evidenced by the DTA anomalies involve a small amount of a superconducting second phase, all measurements would easily be accounted for.

IV. CONCLUSION

A systematic study on CuCl crystals prepared by four independent methods has been made. We found

that the critical pressures for inducing different phase transitions are sensitive to the sample preparation techniques and ages. Impurities in flux-grown crystals are believed to be important in suppressing transitions. Subtle differences were observed in samples seemingly identical at room temperature. For instance, the most conducting phase IIa was generated only in crystals grown from the CuCl vapor. Four-lead electrical measurements demonstrated that there exist no metallic behavior in any of the high-pressure phases of our thermal-equilibrium CuCl crystals although the resistivity of the IIa phase is about the same as previously observed. Previously reported phase transitions[11] and the diamagnetic χ anomaly[7,8] below 25 kbar[7,9,11] were not reproduced. However, a χ anomaly was detected between 90 and 250 K but only in the rapidly warming CuCl crystals and over a narrow temperature range. Accompanying the anomaly were a flat σ maximum and two DTA extrema subtending the χ anomaly in the DTA signal.

The evidence in favor of any of the possible models (a)–(d) discussed above accounting for all observations is not at all convincing. The easiest explanation for the χ anomly using the eddy-current shielding effect would require a transition to some new phase with a conductivity greater than ten times that for Cu at 200 K.

A speculative model which can account for all the results would involve superconductivity at the Cu-CuCl interface. The Cu-CuCl interface is assumed to form and disappear reversibly at the first-order phase transitions due to the disproportionation of $2CuCl \rightarrow 2Cu + CuCl_2$. The superconductivity would presumably be of the type proposed by Allender, Bray, and Bardeen[24] in the metal-semiconductor interface. The intimate contact between the metal electrons and the semiconductor in their model and the disproportionation reaction would perhaps be affected by some combination of hydrostatic pressure and strain, the latter being caused by rapid temperature excursion. Another speculative model invoking superconductivity due to the intrinsic properties of CuCl under pressure has been proposed by Abrikosov.[25] In this later model, superconductivity in the "excitonic metallic" IIa phase, which occurred only between ~40 and 60 kbar, was emphasized. However, our results show that the χ anomaly appears below 30 kbar and that the IIa phase is not metallic.

It should be noted that most of the previous experiments were done isothermally under pressures in contrast to ours done isobarically. In view of the delicate dependence of the transitions on the sample conditions and thermal cyclings, more studies seem needed for the clarification of the disagreements between the present and previous studies.

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