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Investigations of the pressure dependence of structural, chemical, electrical, and magnetic properties of cuprous chloride (CuCl)

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Extensive x-ray, bulk-compressibility, electrical-resistivity, magnetic-susceptibility, microwave-absorption, and ESR measurements have been carried out under conditions of varying pressure and temperature on freshly prepared samples of CuCl. Based on both magnetic-susceptibility and microwave-absorption data, no evidence is found to support the existence of a superconducting transition in the interval between 300 and ~10 K and at pressures up to about 10 GPa. Structural phase transitions have been identified at 5–6 GPa and 10–11 GPa with about 12% and 1% volume reductions, respectively. Evidence is also reported of a sluggish pressure-induced, metal-like transition which may be associated with the disproportionation reaction: $2CuCl \rightarrow CuCl_2 + Cu$. These results are discussed in the light of recent magnetic anomalies reported for CuCl, and explanations are proposed to explain them.

I. INTRODUCTION

Under ambient thermodynamical conditions, there are thirty-five materials of the A^nB^{VIII-n} type which crystallize in the tetrahedrally coordinated zinc-blende structure, in addition to the four Group-IV elements: C, Si, Ge, and α-Sn in the equivalent monatomic diamond structure. By application of pressure, most of these materials can be transformed from this covalent, semiconducting form into either an ionic or metallic phase. However, high-pressure conductivity measurements of Serebryanaya *et al.*[1] and Chu *et al.*[2] indicate that, at room temperature, freshly prepared CuCl transforms first into a highly conducting phase at 4 GPa followed by a transformation near 10 GPa back to a poorly conducting form. Of even greater interest, perhaps, are the observations of Brandt *et al.*: They claim that, at a pressure of about 500 MPa and on rapid cooling (>20 K/min), selected samples of CuCl undergo very strong diamagnetic transitions beginning at about 170 K and stabilizing just below 100 K.[3] They have speculated that this may be evidence of a Meissner effect, thereby implying the existence of a superconducting state. Additional supporting evidence for the existence of a diamagnetic anomaly was provided by Chu *et al.*,[4] who reported that certain samples of CuCl, on rapid *warming* at elevated pressures (~1.2 GPa), exhibit a diamagnetic transition "... over a temperature range of 10–20 K around 240 K and about 7% of the signal due to a perfect diamagnetic."[4]

Under normal conditions, CuCl is an inherently unstable compound. In perhaps the earliest pressure related study, Bridgman reported considerable difficulty in obtaining a satisfactory specimen for bulk compressibility measurements.[5] Since that time, numerous pressure-related experiments have been carried out on CuCl; these data are summarized in the composite phase diagram shown in Fig. 1. The earliest measurements used in this phase diagram are those on optical absorption by Edwards and Drickamer.[6] These results have not been corrected for changes in the pressure scale which have been made since 1961; such corrections would have the effect of reducing the flatness in these curves at elevated pressures. The higher-temperature phase boundaries in Fig. 1 (solid lines) were determined from the differential-thermal-analysis (DTA) measurements of Rapoport and Pistorius.[7] The structures of phases I, II, and III are believed to be wurtzite, sphalerite (or zinc blende), and one similar to that of β-AgI, respectively. The pressure dependence of the electrical resistivity of CuCl was first measured between 370 and 670 K by Bradley, Munro, and Spencer,[8] who identified cusps at about 4 and 6 GPa although they, and subsequently others,[1] found no evidence of a structural phase transition in the 4-GPa region. Meisalo and Kalliomäki[9] interpreted their x-ray-diffraction (XRD) and polarizing-microscopy data as indicative of a tetragonal phase for region IV and the rock-salt (or NaCl) structure for region V. Subsequent work, including that reported here, indicates that their pressure determination for the room-temperature IV–V boundary (which they based on a single data point) is low by about 4 GPa. Apparently NaCl was not used as an internal pressure calibrant

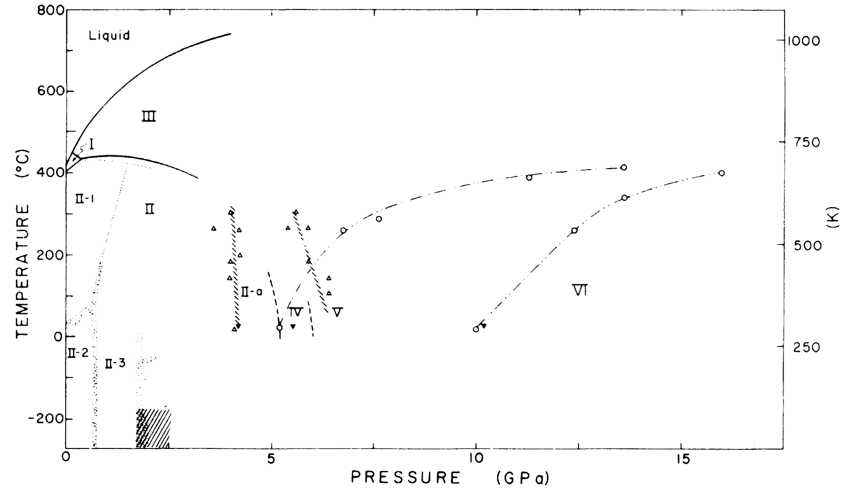

FIG. 1. Phase diagram of CuCl based on published data from a variety of different experiments (see text for references): solid line - differential thermal analysis (DTA); dashed line - XRD and microscopy; ○ and broken curve - optical absorption; Δ, ▼, and \\\\\ - electrical conductivity; dotted region - DTA and dilatometry; ///// - magnetic permeability.

for all runs in their work. The aforementioned resistivity studies of Serebryanaya *et al.*[1] are the basis for the II–IIa, IIa–IV, and IV–V room-temperature boundaries. Moreover, Rusakov *et al.*[10] also reported DTA and dilatometry data below 2.5 GPa in the temperature range from 4.2 to 800 K; these are the bases for the three isostructural regions designated II-1, II-2, and II-3 in Fig. 1. Finally they also reported a magnetic permeability minimum from 0.7 to 2.6 GPa with strongest effects in the pressure range from 1.8 to 2.6 GPa at 4.2 K.

Given the complex phase diagram of CuCl, the most spectacular properties of this material are still the reported strong diamagnetic anomalies which have been reported and inference to high T_c superconductivity,[11] which may be[4] an example of the modified excitonic superconductivity proposed by Allender, Bray, and Bardeen.[12] Alternately, Blount and Phillips[13] have suggested that many of the seemingly anomalous properties of CuCl may be attributable to a pressure induced Guinier-Preston transitional precipitate disproportionation reaction: $2\mathrm{CuCl} \rightarrow \mathrm{Cu} + \mathrm{CuCl_2}$. While Chu *et al.*[4] and Wilson[14] have speculated that the disproportionation reaction may, in fact, enhance the conditions necessary to activate excitonic superconductivity of the Allender *et al.*[12] model.

The work reported here was carried out to provide additional experimental data on the high-pressure properties of CuCl. Specifically it was intended to remove some of the unanswered questions raised recently.[1–4] A wide range of high-pressure experiments have been carried out: viz., electrical resistance, x-ray diffraction, bulk compressibility, optical observations, magnetic susceptibility, microwave resonance, and ESR.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. Sample preparation

Two types of CuCl samples were used in this study. Most of the measurements were performed on freshly (usually no more than several days old) purified CuCl powders prepared as follows: high purity, commercial CuCl was dissolved in 5*N* HCl to saturation, then to excess. This was treated with additional Cu powder to reduce the cupric ion concentration, filtered into distilled water for a final dilution of 10:1. The white CuCl precipitate was filtered, washed with aliquots of glacial acetic acid, absolute ethanol, and absolute diethyl ether, following by drying at 100 °C for 30 min. The product was stored in a vacuum dessicator.

Some of the x-ray studies and one of the electrical resistance runs were performed on single-crystal samples grown from the same starting material via a gel technique developed by Armington and O'Conner.[15]

B. Electrical-resistance measurements

The pressure dependence of the room-temperature dc electrical resistivity as measured to 6.5 GPa is shown in Fig. 2. These data were recorded using three different electrode materials (Pt, Cu, and graphite) in a tetrahedral press, following a procedure similar to that discussed elsewhere.[16] Definite effects of the electrode material were found; i.e., it appears that reactions at the electrode-CuCl interface tend to alter the apparent CuCl resistivity. In particular, when Cu electrodes were used, the resistivity tended to decrease in the pressure region between 3–5 GPa

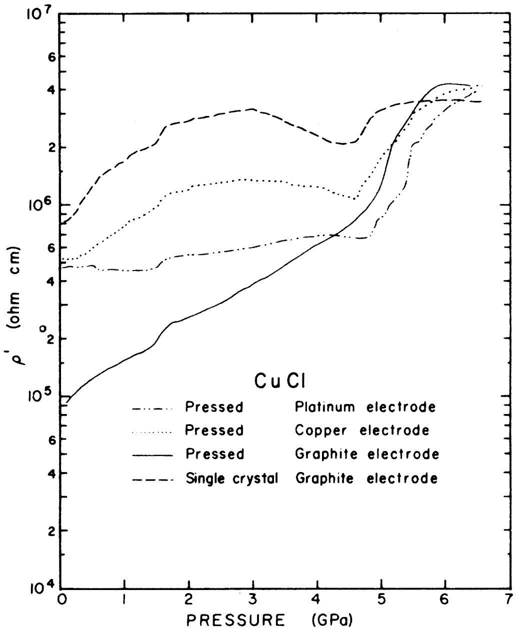

FIG. 2. Pressure dependence of the electrical resistivity to 6.5 GPa measured with Pt, Cu, and graphite electrodes.

and tended to mask the step increase seen around 1.5 GPa. A much larger resistivity increase up to the discontinuity near 5 GPa was observed with graphite electrodes, which amounted to about 230%. This is above the II–IIa transition at 4.2 GPa, but below the II–IV transition reported by Bradley *et al.*,[8] who used nonreactive Pt electrodes. The single-crystal data were recorded with graphite electrodes; the results bear a striking similarity to those recorded with the Cu electrodes in that the transition at 1.5 GPa tends to be accentuated, whereas the higher-pressure transition is partially suppressed.

Chu *et al.* reported resistance measurements using Cu-coated leads in their earlier work[2] and Cu leads in their Bridgman-anvil apparatus.[4] However, until the CuCl-electrode interface effects are fully understood, caution should be exercised when other than inert electrodes such as Pt are used. Recognizing that CuCl is at least in part an ionic conductor, filamentary growth of Cu would not be unexpected. This again would suggest the use of an electrode material other than Cu, even though this would limit observations to effects on the electronic conductivity. It should also be noted that a nonohmic behavior was observed in several samples when the measuring current was altered; although the reason for this variance has not been determined.

Resistance data recorded on decreasing load are shown in Fig. 3. Measurements with the graphite electrodes were taken at both room temperature and at about 95 K; those recorded with Cu electrodes were obtained only at room temperature. The details of the resistance variations in the lower-pressure region appear to be suppressed in the low-temperature data and the increase in resistance upon cooling at approximately 6.5 GPa is suggestive of semiconducting behavior. The room-temperature data tend to show considerable low-pressure structure as evidenced by several local minima and maxima. This could be indicative of more phases at 300 K, as compared to 95 K, or possibly, of unfavorable kinetics in the transformation process at the lower temperature. It is not possible to determine the pressures of these extrema since the tetrahedral press used in these measurements is only calibrated for data recorded under increasing load.

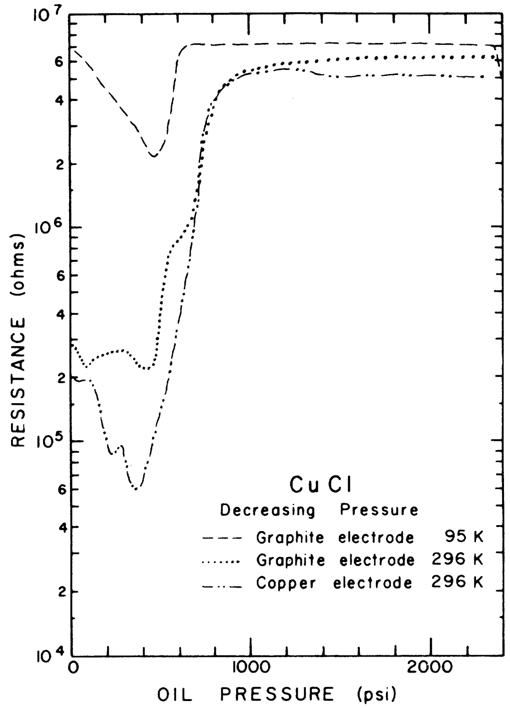

FIG. 3. Resistance data recorded on decreasing load with graphite and Cu electrodes. (The oil pressure corresponds to the driving pressure on the tetrahedral rams.)

C. X-ray-diffraction measurements

The x-ray-diffraction data were recorded from CuCl powder sealed in a gasketed diamond-anvil pressure cell in the standard manner.[17] In most runs, the sample was premixed with the NaCl pressure calibrant and immersed in a 4:1::methanol:ethanol hydraulic fluid. The alcohol solution was freshly prepared and stored over lime to reduce the possibility of hydroscopic reactions with the CuCl. In one run, the NaCl calibrant was replaced by a ruby chip and the pressure determined from the shift of ruby fluorescence peaks in the usual manner.[18]

The results of the x-ray measurements are plotted in Fig. 4. The ambient-pressure sphalerite structure persists up to 5–6 GPa, where a first-order phase transition to a tetragonal structure is observed. A second structural transition is detected at about 10–11 GPa from the tetragonal to a rock-salt structure. These are presumed to be the II–IV and IV–V transitions respectively; thus, phase V is seen to persist up to our highest pressure measurement, 22.5 ±0.6 GPa. The volume discontinuities associated with these transitions are estimated to be about 12% and 1%, respectively. Most recently, we have tracked the II–IV phase boundary to cryogenic temperatures. Based on extrapolated data, we estimate that phase II can be retained up to about 4 GPa at absolute zero. The details of these measurements are given in Ref. 19.

Comparison is made in Fig. 4 with other published structural data on CuCl. The agreement with the Serebryanaya *et al.*[1] data is probably within the combined experimental error. However, Meisalo, and Kalliomäki[9] report the IV–V transition at 6 GPa, substantially below our 10–11 GPa estimate. It is possible that this variance is due to sample differences. These volume changes are in accordance with those obtained previously.

Finally, it should be noted that, optical monitoring of the pressure cavity showed that both phases II and IV were transparent in white light. However after the x-ray measurements were made to 22.5 GPa, the sample which was initially transparent (phase V), appeared to be opaque.

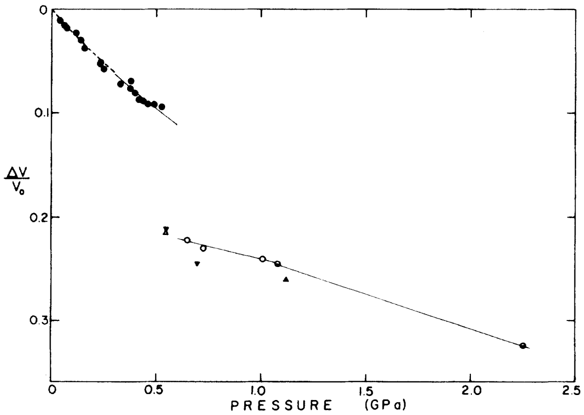

FIG. 4. Phase identification and pressure dependence of the fractional volume change of CuCl based on x-ray diffraction data to 2.6 GPa. Dashed line - Ref. 5; ∇ - tetragonal phase, Ref. 9; ▼ - NaCl phase, Ref. 9; Δ - tetragonal phase, Ref. 1; ▲ - NaCl phase, Ref. 1; ● - sphalerite phase, this work; ○ - tetragonal phase, this work; ◓ - NaCl phase, this work.

D. Bulk-compressibility measurements

To supplement our microscopic (x-ray) compressibility data, measurements were also carried out on bulk samples using standard piston-displacement techniques described previously.[20] The results are plotted in Fig. 5 for both CuCl and $CuCl_2$. Excellent agreement is seen with both our x-ray data and the original work of Bridgman.[5] However, the dilatometry measurements of Rusakov *et al.*[10] show roughly a threefold increase in the compressibility in addition to a discontinuity at about 0.6 GPa. We see no evidence of such a discontinuity in this range, nor do we have any explanation for the significant variance between the data of Rusakov and the other workers.

Also plotted in Fig. 5 are our bulk-compression measurements on anhydrous $CuCl_2$. These measurements were undertaken in order to assess the effects of pressure on the disproportionation reaction. The $CuCl_2$ was prepared by heating cupric chloride dihydrate at 120 °C for about 3 days; the final material was a dark brown powder. Our compressibility measurements on CuCl and $CuCl_2$ are combined with similar measurements of Vaidya and Kennedy[21] on metallic Cu to permit evaluation of the pressure dependence of the molar volume change realized from the disproportionation reaction. The volume derived free-energy term is plotted in Fig. 6: at am-

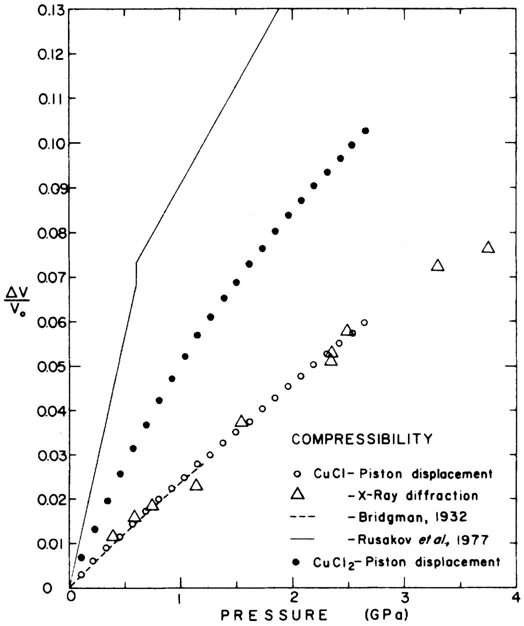

FIG. 5. Pressure dependence of the fractional volume change of CuCl and $CuCl_2$ based on piston-displacement data to 2.6 GPa.

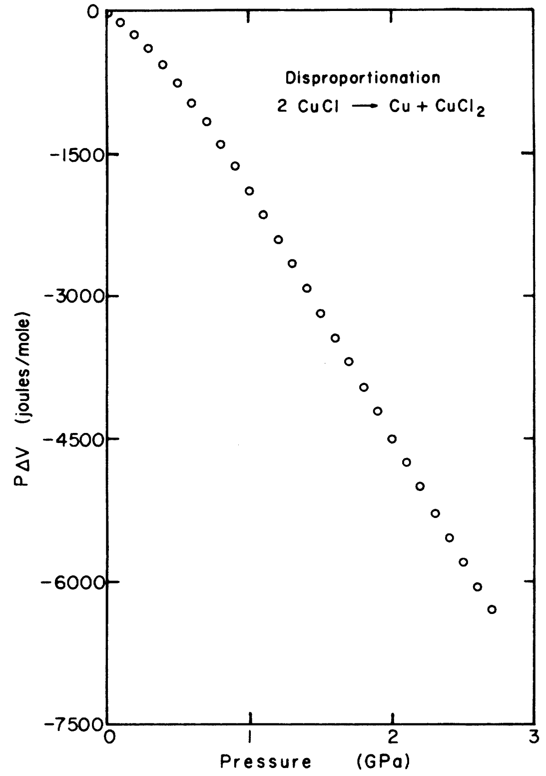

FIG. 6. Pressure dependence of the molar volume related free-energy change associated with the disproportionation reaction: $2CuCl \rightarrow CuCl_2 + Cu$ as computed from compressibility data.

bient pressure, conversion of 2 moles of CuCl into 1 mole each of Cu and $CuCl_2$ results in a volume reduction of about 2.1% or 1 cm^3. This corresponds to a $P\Delta V$ term of −0.1 J/mole. At 2.6 GPa, the volume reduction is −2.33 cm^3/mole or 5.2%, corresponding to −6.291 kJ/mole. We note that the $P\Delta V$ term is essentially linear with increasing pressure above 0.7 GPa. Information concerning the compressibility of anhydrous $CuCl_2$ is needed before $P\Delta V$ can be predicted above 2.7 GPa. Recalling that at about 5 GPa there is a 12% volume reduction due to the CuCl II–IV phase transition, it appears that the disproportionation reaction would be more favorable in the lower-pressure regime. It should be noted however that: (i) we have no information about the effect of pressure on $CuCl_2$ above 2.6 GPa, e.g., it too may also undergo a first-order phase transition, (ii) there are other disproportionation reactions which may be possible, e.g., $3CuCl \rightarrow Cu_2Cl_3 + Cu$ or $4CuCl \rightarrow Cu_3Cl_4 + Cu$, and (iii) there are other terms in the Gibbs-free-energy expression which are not known. The present measurements show, however, that the volume change for the reaction, $2CuCl \rightarrow CuCl_2 + Cu$ is negative up to 2.6 GPa, so that it is not ruled out by the principle of Le Châtelier.

E. Optical observations

Some of the most striking features of the high-pressure properties of CuCl are those observed in transmitted white light. In this regard, we have repeated some of the earlier experiments of Van Valkenburg.[22] The pressure dependence of the optical transmissivity has been monitored with white light through the anvils of a nongasketed diamond-anvil cell. The series of microphotographs (Fig. 7) shows changes in a sample of CuCl as a function of time after initial pressurization. The sample was subjected to pressures ranging from ambient at the periphery to a maximum of about 10 GPa near the center. A dark central ring appeared immediately after pressurization, and it was observed that the opacity of the central region grew with time. Approximately 12 to 20 h were required to achieve the maximum opacity as seen in Fig. 7(d), although the apparent growth of this region always stopped short of the initially formed annular ring. Upon release of the pressure, the specimen returned to its original state, usually within hours; the rate of reversal, however, could be significantly retarded by cryogenic cycling under pressure. It is also noted that during this reversal, the sample passed through an intermediate brownish phase, as was also noted by Van Valkenburg.[22]

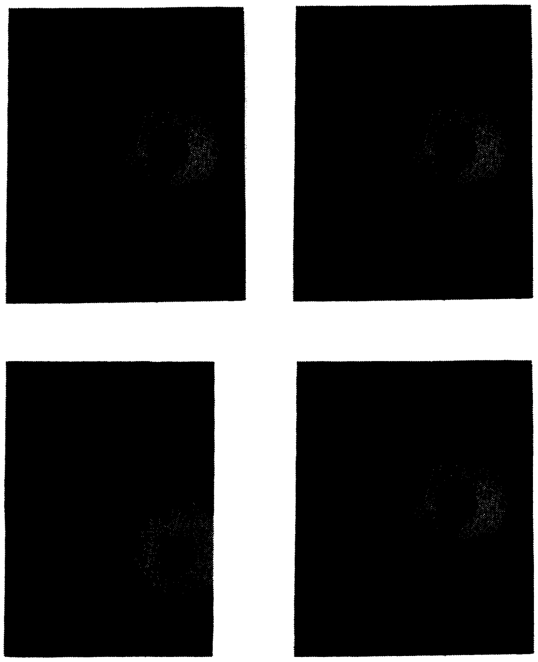

FIG. 7. Microphotographs of CuCl pressed between the anvils of an ungasketed diamond-anvil pressure cell. The pressure is estimated to be about 10 GPa near the center and drops off to ambient at the periphery; (a) immediately after pressurization, (b) after 1 h, (c) after 3 h, and (d) after 24 h.

F. Magnetic-susceptibility and microwave-resonance measurements

In separate experiments, carried out in the same manner as the optical observations discussed above, i.e., in a nongasketed, diamond-anvil cell, the pressure dependence of both the magnetic-susceptibility and the microwave-absorption properties of CuCl were examined. The susceptibility of the pressure chamber was monitored with an ac mutual-inductance bridge operated at a frequency of 3 kHz and identical to that described in Ref. 23. In the case of the microwave measurements, the CuCl filled pressure cavity was contained in a helical microwave resonator. We believe this represents the first example of a microwave-resonance measurement in a diamond-anvil cell; the details will be discussed elsewhere.[24]

In each of the two measurements, we observed an apparent effect associated with the growing opacity discussed above. In the case of the susceptibility measurements, we noted that a continuing drift in the balance point of the bridge was noted as the opacity of the sample grew. Optical stability was accompanied by susceptibility stabilization, as evidenced by a relatively small variation of the signal 24 h after pressurization. Similar results were obtained with the microwave measurements: immediately after pressurization, there was a significant and continued decrease in the Q of the resonance cavity accompanied by a shift of the resonance frequency ω_0. As the growth of the opaque phase waned, both Q and ω_0 stabilized. This is consistent with the supposition that CuCl undergoes a change to a more metal-like or conductive form during this process.

The mutual inductance coils used here are wound on a form specifically designed to replicate the truncated conical tips of the diamond anvils used in the pressure cells. Moreover, it is difficult to estimate both the percentage of transformed CuCl and its relative position in the pressure cavity. It is therefore not possible to determine the absolute magnitude of the susceptibility change reported here. It should also be noted that the rate of transition, and even the existence of this modification, appears to be dependent on the age of the samples. In some cases, with samples purified in the manner discussed in Sec. II A, many months prior to the measurement, the effect was not seen.

G. ESR measurements

As noted above and in Refs. 4, 13, and 14, the anomalous behavior of CuCl may be associated with pressure induced disproportionation. Accordingly, we sought to determine whether or not evidence of Cu^{2+} ions in the samples and any change in the Cu^{2+} concentration could be established as a result of pressurization.

In the first series of experiments, comparisons were carried out between samples at ambient pressure and those quenched from various pressures in the tetrahedral press. The procedure was to pressurize the material to the desired limit (not exceeding 6.5 GPa) and to hold that pressure for about 24 h. Before releasing the load, the pressure chamber was cooled with liquid N_2 to about 95 K. The pressure was then dropped and the sample encapsulated in a quartz tube and immersed in a liquid-N_2 bath for storage. Ambient pressure ESR scans were then performed on the samples at room temperature, liquid-N_2, and liquid-He temperatures.

The results of these experiments indicated no evidence of any pressure effect on the amount of Cu^{2+} present. The ESR spectra from both the virgin and prepressed samples are shown in Figs. 8(a) and 8(b), respectively. We attribute both spectra to the presence of Cu^{2+} at a level of about 0.03%. This concentration level was essentially independent of pressure. The g values and ESR line shapes of these powdered samples indicate that the Cu^{2+} is probably in an octahedral environment.[25] The only effect which was observed to depend on pressure was an increased distortion of the octahedral site symmetry of the Cu^{2+} ion with samples pressed to the higher loads [cf. Figs. 8(a) and 8(b)]. Moreover, the single-crystal samples showed no orientation dependence of the Cu^{2+} line, thereby suggesting that locations of the Cu^{2+} ions were not symmetrically related to the CuCl lattice.

Somewhat contradictory results were obtained in a preliminary electron spectroscopy for chemical analysis (ESCA) which did suggest the presence of a $2p^{3/2}$ electron peak at about 935 eV, in addition to the very strong Cu^+ peak at 932 eV. However, the

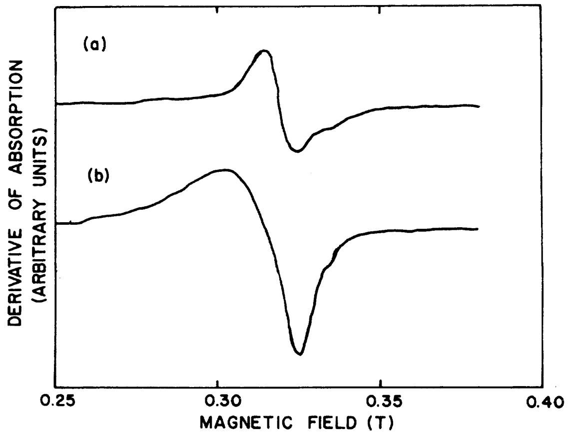

FIG. 8. ESR spectra at 4.2 K and 9.17 GHz in CuCl. (a) Sample at ambient pressure, (b) sample pressed to 7 GPa and maintained at or below 77 K. Samples pressed to as low as ~0.15 GPa exhibit spectra very similar to that shown in (b). Signal amplitudes in (a) and (b) are not drawn to scale.

signal-to-noise ratio encountered in these runs was not sufficiently high to allow a definite conclusion.

Following this, an attempt was also made to carry out *in situ* ESR measurements. Like the microwave-absorption work, we believe this to be the first example of such measurements in a diamond-anvil pressure cell and the experimental details are reported elsewhere.[24] Unfortunately these measurements are complicated by the presence of a strong $g = 2$ line which originates from impurities in the diamond anvils; i.e., the strong signal at about 0.32 T in Fig. 9 is also present in the absence of the sample. Despite this impediment, the data do suggest the growth of an additional signal in the same region. More specifically, the microwave-absorption curves of CuCl under fixed load conditions similar to those established for Fig. 7 are shown in Fig. 9. The traces were taken at increasing time following the application of load. The shoulder identified by the arrow at a field of about 0.325 T is observed to grow with time, concurrently with the increase in opacity discussed in Sec. II E. This shoulder could be interpreted as due to the presence of Cu^{2+}.

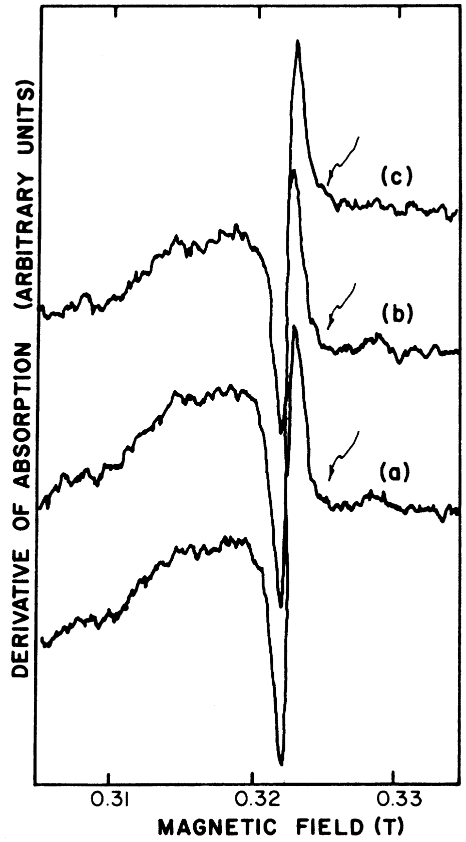

FIG. 9. ESR traces of CuCl recorded as a function of time following the application of load. The shoulder at about 0.325 T, indicated by the arrow on curve (c), could be associated with the presence of Cu^{2+}.

H. Low-temperature measurements

Lastly, several CuCl samples held at ~10 GPa were cooled to liquid-He temperatures as rapidly as possible (~0.15 K/s), in a Heli-tran refrigerator,[26] from room temperature down to about 10 K in some cases while monitoring the ac susceptibility and in others while monitoring the microwave-absorption properties. However, in neither instance was any evidence of a superconducting transition observed. Data were also collected during slower cooling and warming scans with the same negative results. It is evidenced that all phases occurring between ~10 GPa and ambient pressure were present in these runs.

III. DISCUSSION

The main conclusion to be drawn from these experiments is that much more experimentation is needed before the high pressure electric, magnetic, and optical properties of CuCl can be fully understood. Indeed there are an abundance of contradictions and it is highly probable that many of these are traceable, at least in part, to sample differences. However, it is difficult to imagine small variations in sample properties as being responsible for the large differences in compressibility reported in Sec. II D. There are also discrepancies, as noted in the text, in the high-pressure-resistivity data, and low-temperature-susceptibility measurements.

We do, however, confirm the existence of two pressure-induced structural phase transitions, and we observe that, in freshly purified samples, portions of phase V grow opaque under nonhydrostatic pressures. The opacity was also observed in the gasketed runs, but after the pressure had been advanced well above the ~10-GPa hydrostatic limit. This opacity appears to have an electrical signature since it parallels changes in both the ac-magnetic-susceptibility and the microwave-absorption properties of the sample that occur during its growth.

In situ ESR data are presented which could be associated with the growth of Cu^{2+} ions. The prospective disproportionation reaction, $2CuCl \rightarrow Cu + CuCl$, does appear to be favored at increased pressures based on the expected volume changes.

Finally, neither ac-susceptibility nor microwave-absorption measurements show evidence of a superconducting transition in the range from 300 to ~10 K and up to about 10 GPa, for samples cooled at rates up to ~0.15 K/s.

It is suggested that much more work is required not only to fully characterize those samples of CuCl believed to be responsible for the anomalous results, but also the measurements themselves.

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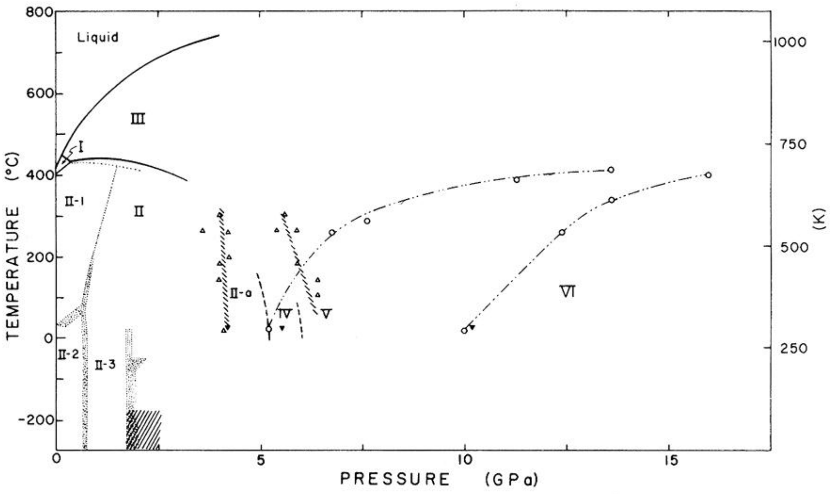

FIG. 1. Phase diagram of CuCl based on published data from a variety of different experiments (see text for references): solid line - differential thermal analysis (DTA); dashed line - XRD and microscopy; ○ and broken curve - optical absorption; Δ, ▼, and \\\\\ - electrical conductivity; dotted region - DTA and dilatometry; ///// - magnetic permeability.

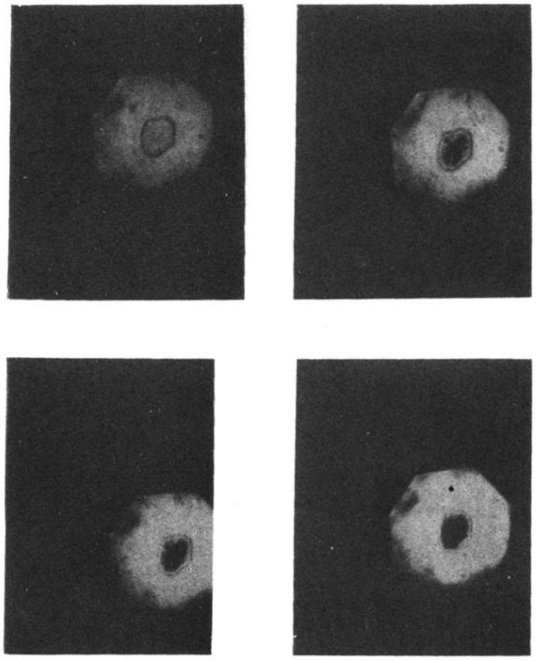

FIG. 7. Microphotographs of CuCl pressed between the anvils of an ungasketed diamond-anvil pressure cell. The pressure is estimated to be about 10 GPa near the center and drops off to ambient at the periphery; (a) immediately after pressurization, (b) after 1 h, (c) after 3 h, and (d) after 24 h.