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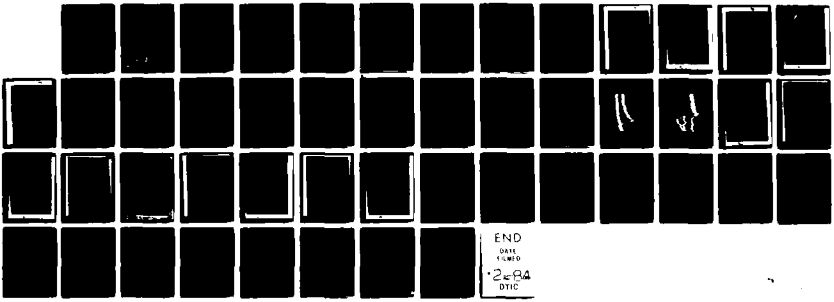

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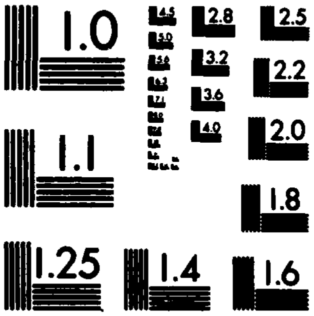

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A STUDY OF PHASE TRANSITIONS

FINAL REPORT

ISSAI LEFKOWITZ

NOVEMBER 25, 1983

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The diamagnetic transition in CuCl has been verified, and materials studies have been carried out to determine the conditions under which this transition, which may per precursive to high temperature superconductivity, may be found. A photoactivated, defect induced, dielectric anomaly has been detected in CuCl, and the relationship of the anomalies to the superdiamagnetism has been explored. Equilibrium measurements of superdiamagnetism and the diamagnetic transition on samples of CuCl epitaxially gron on single crystals of silicon have been carried out

TABLE OF CONTENTS

Statement of Problem

This program was devoted to the study of phase transitions in inorganic solids by measuring dielectric properties and magnetic properties as a function of temperature on powdered samples and single crystals. Phenomena occuring as a result of various light stimulated techniques, as well as other experimental conditions such as substrate, molten salt composition, external magnetic fields, were also studied systematically.

Specifically, the research program was concerned with the phase diagram of CuCl, with special emphasis being placed on the properties of excitons and plasmons in samples with controlled defect structures. It has been postulated that unusual crystalline forms of metal halides may result by epitaxial growth on various substrate. An unusual crystalline form of CuCl produced by epitaxial growth on silicon single crystals was found to have properties similar to the chemically inert form of CuCl that has been reported.

In addition, the time response limits of liquid crystal systems in electrooptic applications were explored.

Summary of Important Results

Magnetic measurements were carried out on disordered CuCl in the temperature range 77 to 280 K under applied presures of 5 kbar (see Appendix I). Anomalous increases in diamagnetis were observed between 120 and 230 K. The diamagnetic anomaly may be explained in terms of an exciton model in which the electrons, as well as the interactions between them, stem from excitonic states. Unfortunately, it was not possible to reproduce the results consistently.

A new series of measurements were made on CuCl specimens grown on single crystal wafers of silicon, specifically on the (111) face. The (111) face was selected for epitaxial growth since d_{111} of silicon is 3.141 Å and d_{111} of CuCl is very similar, being 3.121 Å. Samples were produced under various experimental conditions, and magnetic measurements made on several samples exhibited giant diamagnetic anomalies near 110 K. These measurements represent the first equilibrium measurements of the diamagnetic transition (see Appendix II).

The theory of deep impurity levels was extended to semiconductors with d electrons, and major chemical trends were predicted for a large number of substitutional impurities in CuCl (See Appendix III). Deep levels were found for S and Se impurities on the Cl site, but not for Ag or Au on the Cu site, in agreement with experiment. The theory also predicted that there would be no deep level for isolated O on the Cl site, a result which supports the conclusion that the observed O-related defect is not a simple subsititdional impurity.

Dielectric measuremnts were made on optically irradiated single crystals and composite samples of CuCl prepared and stored under carefully controlled conditions. These measuremnts revealed anomalies in both the capacitance and tan δ at 220 K. The results correlate with the earlier reports of anomalous diamagnetism at 110 K (and higher) in CuCl (see Appendix IV). The observation supports the existence of a low frequency (soft) phonon mode in CuCl-Cu^0 precipitate composite which could provide a mechanism for hight temperature superconductivity.

It has long been believed that LC panels could not respond faster than 25-50 milli-seconds. Our work (and work by Noel Clark) showed this to be incorrect. We used a nematic system, and Clark used a smectic LC system, but micro-second response time was found in both cases. These results have important implications for optical correlation applications of LC Systems.

LIST OF PUBLICATIONS AND REPORTS:

Lefkowitz, I.; Manning, J.S.; Bloomfield, P.E. "Diamagnetic Transition in Disordered CuCl", Phys. Rev. B, 1979, 20, 4506-4510.

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Ren, Shang-Yuan; Allen, Roland E.; Dow, John D.; Lefkowitz, I. "Theory of Deep Impurity Levels in CuCl", Phys. Rev. B, 1982, 25, 1205-1213.

Lefkowitz, I.; Estes, William E.; Hatfield, W.E.; Bloomfield, Philip E. "Evidence for Photoactivated Defect Induced Dielectric Defect Induced Anomalies in CuCl", submitted for publication.

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APPENDIX I

PHYSICAL REVIEW B VOLUME 20, NUMBER 11 1 DECEMBER 1979

Diamagnetic transition in disordered CuCl

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Recent work has discussed high-T_c superconductivity in terms of various excitonic high-density states and how the band structure of CuCl makes it a good candidate material. We have measured the magnetic state of disordered CuCl in the temperature range from 77 to 280 K using an ac mutual inductance technique at 17 Hz, and we have observed anomalous increases in diamagnetism at temperatures between 120 and 230 K. We believe that our observations provide totally independent corroborative evidence of the diamagnetic phase transition reported by Brandt *et al.* and Chu *et al.* Analyses of the data (on cooling and heating) in light of observations in inhomogeneously heated (radioactive) superconductors lends credence to the conclusion that the observed anomalies are a special form of superconductivity.

I. INTRODUCTION

Little[1] and Ginzburg[2] have pointed out that since the transition temperature T_c is proportional to the Debye temperature Θ_D, that if a hole exciton mass were substituted for the atomic mass (exciton mechanism), then a T_c of 180 K would be possible. These ideas have been extensively developed by Little[1] and Ginzburg,[2] as well as Allender, Bray, and Bardeen.[3] Rusakov[4] has discussed CuCl in light of these exciton-state concepts, and Abrikosov[5] has applied the Wigner excitonic metallic-lattice interpretation to the experiment of Brandt, Kuvschinnikov, Rusakov, and Semenov.[6]

Brandt *et al.*[6] have reported susceptibility measurements on polycrystalline CuCl at various hydrostatic pressures up to 10 kbar, for temperatures between 4.2 and 350 K. Their results under certain conditions, such as a rapid cooling rate (greater than 20 K/min), indicate a transition into a very diamagnetic state ($\chi = -0.8$) at temperatures of 170 K and less. This strong diamagnetic transition, which in some cases was accompanied by an increase of four to six orders of magnitude in electrical conductivity, was interpreted as evidence of some type of superconductive transition.

Chu *et al.*[7] in a thorough study of CuCl have also reported a diamagnetic anomaly above 90 K over a temperature range of 10–20 K in rapidly warmed samples. Further, they have shown a sharp increase of conductivity and an *associated differential thermal* analysis (DTA) signal accompanying the diamagnetic anomaly, drawing the conclusion that if a small amount of superconductive second phase had been formed, the measurements could easily be understood.

In this paper we report our independent investigation into the existence of a diamagnetic anomaly in CuCl through measurements at 17 Hz.

Cupric chloride powder was converted to cuprous chloride powder using standard chemical techniques.[8] In addition, vapor transport techniques were applied to purify the samples. The CuCl was placed into a platinum crucible and heated in an overpressure of argon or helium until the powder melted. If heated in vacuum, it would sublimate. If heated in a nitrogen atmosphere, the samples would turn slightly blue. When the CuCl was melted, the bell jar was raised and liquid nitrogen was poured over the samples so as to rapidly quench the samples. This procedure yielded a disordered glassy-like material; i.e., amorphous type samples. Under cross-polarizers no single crystals were seen in the samples. The CuCl samples studied were disordered, diamagnetic at room temperature, and transparent or cloudy. The samples were often colorless, but sometimes had a blue or gray color which, under a microscope, appeared as blue or black flecks in a background of transparent or cloudy white material.

In order to check for magnetic impurities in the

CuCl, two samples were tested with a vibrating sample magnetometer. These measurements were made in a field of 10000 G, at a frequency between 80 and 90 Hz. A dark blue sample at atmospheric pressure exhibited a temperature-independent diamagnetism of less than 10^{-7} emu/g, or 5×10^{-6} in SI (*Système International*) units. A transparent, light blue sample at atmospheric pressure was slightly diamagnetic at room temperature, but became weakly paramagnetic below 20 K, probably indicating the presence of a small amount of a paramagnetic impurity. Brandt *et al.*[6] reported a diamagnetic susceptibility at room temperature of 5×10^{-6} in SI units; this value was independent of pressure up to 8 kbar.

Uniaxial pressure was applied to the CuCl samples between boron carbide anvils approximately 6.5 mm in diameter. The actual pressure was applied by means of a calibrated hydraulic press. The calibration of the system came from earlier work done using the anvils and hydraulic loading in measurements of the pressure dependence of Mössbauer spectra. There were enough differences that the calibration of pressure has a 10% uncertainty in the absolute value reported herein. Changes as a function of temperature in the magnetic properties of CuCl under pressure were measured by an ac mutual inductance system consisting of concentric primary and secondary coils inside a stainless-steel pressure cell. The anvils and the sample formed the core of the coils. An ac current at 17 Hz through the primary created a magnetic field of less than 10 G within the core. The induced voltage in the secondary was monitored with a lock-in amplifier, which selected the component out of phase with the current in the primary. The sample temperature was determined by the use of a liquid-nitrogen referenced, copper-Constantan thermocouple located inside the pressure cell. The pressure cell was cooled rapidly by immersion in a Dewar of liquid nitrogen, at a rate of about 30 K/minute. The secondary voltage and the thermocouple voltage were monitored while the cell was warmed from 77 K to room temperature. The background secondary voltage of about 220 mV was determined from 12 runs with a "dummy" paper sample or no sample between the anvils. The background was slightly temperature dependent, with a 2% decrease from room temperature to 77 K, and showed a reproducibility to within ±0.10 mV at 100 K, and ±0.05 mV at 150 K, when the secondary voltage is normalized to a constant value at 200 K. A change in the induced secondary voltage beyond background drift indicates a change in the susceptibility of the sample. In particular, a positive deviation from background implies increased diamagnetism or lessened paramagnetism. The sensitivity of the coil to changes in the susceptibility of the sample was calibrated from test runs with $Pb_{40}Sn_{60}$ solder. The positive deviation of the secondary voltage from background when this sample became superconducting was approximately 200 mV/cm^3, due to the susceptibility change from $\chi \sim 0$ to $\chi = -1$ (in SI units). We estimate this ac mutual inductance system can detect superconductivity in a sample as small as 20 mg.

Approximately two dozen samples of CuCl have been studied under pressure. Samples were measured at different times after preparation and evidence for the rapid change of the freshly made samples in the presence of humidity and light were clearly apparent. Subsequent to the initial measurements, samples were stored in a soft vacuum and in the dark. The obvious degradation of the samples showing the anomalies prevented long-term storage or subsequent analysis of the relevant parameters for the onset of the diamagnetic anomalies. Samples stored longer than three days did not show any anomalies. Diamagnetic anomalies have been observed for two blue-flecked samples. In both cases the samples were examined for susceptibility anomalies two days after preparation.

Figure 1 indicates the deviation from background voltage observed for a CuCl sample under 5 kbar pressure. This sample was warmed by removing the pressure cell from the cryostat into the laboratory and heating the outside of the cell with hot air. This procedure provided rapid heating. As was observed on the thermocouple, the pressure cell and sample were warmed from 77 K at the following approximate rates: 25 K/minute between 77 and 100 K; 12 K/minute between 100 and 150 K; and 6 K/minute above 150 K. Thus, 10 minutes were taken to heat the sample from 77 to 180 K. The secondary voltage concurred with the background except between 120

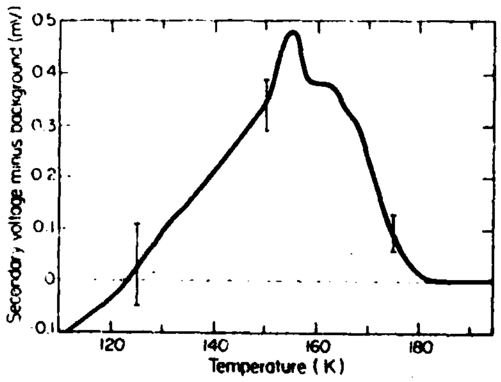

FIG. 1. This figure shows the deviation of the secondary voltage beyond background drift as a CuCl sample was warmed under 5 kbar pressure. The positive deviation indicates increased diamagnetism. The error bars indicate uncertainty in the background. The secondary voltage deviated from the background only between 120 and 180 K.

and 180 K, where a deviation as large as 0.5 mV was observed in the direction of increased diamagnetism. The error bars in this figure indicate the uncertainty in the background drift. The CuCl samples were in the shape of discs 0.07 mm thick and 6.5 mm in diameter, with a total volume of 0.002 cm^3. For a sample of this volume, the deviation in induced voltage could be explained by 65% (±25%) of the sample volume becoming superconducting. The uncertainty in estimating the superconducting fraction of the volume arises from difficulty in measuring the sample thickness, the uncertainty in the background drift, and errors in the sensitivity calibration.

For another CuCl sample, a diamagnetic anomaly was observed during three consecutive warming cycles, twice at 5 kbar pressure and once at 10 kbar. We noted no increase in diamagnetic anomaly occurring with increase in pressure. This sample was studied a few weeks earlier than the sample reported in Fig. 1. At that time dry helium gas was flowed through the cryostat to warm up the sample. This provided a much slower heating rate so that between one and two hours were needed to heat the sample from 77 to 240 K. The secondary voltage then had a behavior similar to data of Fig. 1 but it exhibited jumps or discontinuities in value. However its slope $\Delta V/\Delta T$ was continuous and more reliable. Therefore from our data of V_{sec} and V_{bkg} we measured the slope of V_{sec} and V_{bkg} and in Fig. 2 we plot the slope (in μV/K) of the induced secondary voltage, minus the background, as a function of temperature for this CuCl sample under 5 and 10 kbar pressure. The peaks of $\Delta V_{sec}/\Delta T$ minus $\Delta V_{bkg}/\Delta T$ show that the slope of V_{sec} had a maximum at ~150 K and a minimum at ~185 K while its zero crossing indicates that V_{sec} was maximum at ~170 K. This behavior agrees roughly with the direct measurement of V_{sec} shown in Fig. 1 for a different sample.

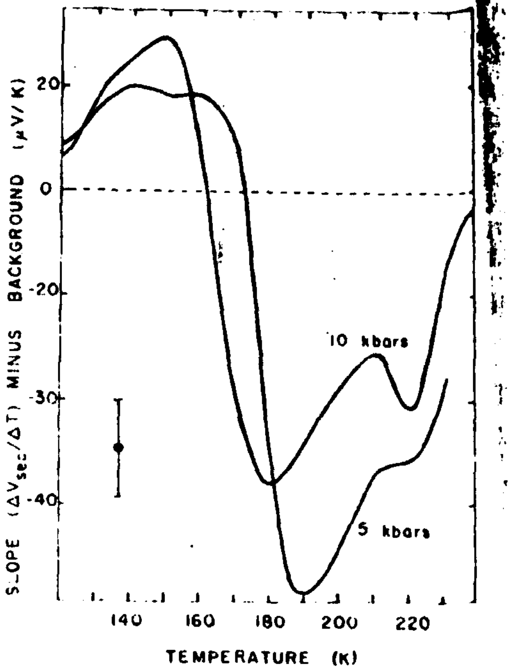

FIG. 2 This figure shows the change in induced secondary voltage per Kelvin as a different sample (than shown in Fig. 1) of CuCl under 5 and 10 kbar is warmed from 77 K. $\Delta V_{sec}/\Delta T$ minus $\Delta V_{bkg}/\Delta T$ is proportional to $\Delta\chi/\Delta T$. Below 120 K and above 240 K $\Delta V_{sec}/\Delta T$ did not differ from the background $\Delta V_{bkg}/\Delta T$. The larger value for the minimum at ~185 K over the maximum at ~150 K shows that V_{sec} (or χ) vs T has a steeper slope on the high-temperature side of its peak. This behavior concurs with the data (for a different sample) shown in Fig. 1.

II. DISCUSSION

Comparing the published data of the diamagnetic temperature dependences on warming and cooling with the present data is rewarding.

(i) All three groups report greatest success when rapidly temperature cycling the CuCl samples and report "poor" thermal contact between sample and the bath.

(ii) Brandt *et al.*[6] observed large magnitude periodic oscillations [Fig. 3(a)] in the ac diamagnetic susceptibility on cooling but not on warming.

(iii) The data reported by Chu *et al.*[7] and the present authors do not reveal any periodic oscillations on warming[9] but do show diamagnetic susceptibility displacements over a broad temperature range.

It is instructive to compare these results with recent work on an alloy of the radioactive superconductor americium [Fig. 3(b)]. In this study Olsen[10] reports that when this alloy is rapidly temperature cycled and the sample is in poor thermal contact with the bath, large magnitude diamagnetic susceptibility oscillations are observed [Fig. 3(b)]. These oscillations are more generally observed in the radioactive metal americium on warming than cooling. The following interpretation of such oscillations are put forth: The radioactive metal[11] self-heats (radiation 6.8 mW/g) and drives the "central" bulk normal leaving a superconductor as an interface (a thermal barrier therefore) between the bath and the warm "normal" metal center. Then in turn the temperature is lowered and leads to a new onset of a superconducting state and thus to flux exclusion by the diamagnetic state. Smith and Haire[11] in fact note that such oscillations, arising from a superconducting region that forms and subsequently collapes, are used to demonstrate bulk superconductivity in their samples. The effects occur when the samples are in poor thermal contact with the bath during rapid temperature cy-

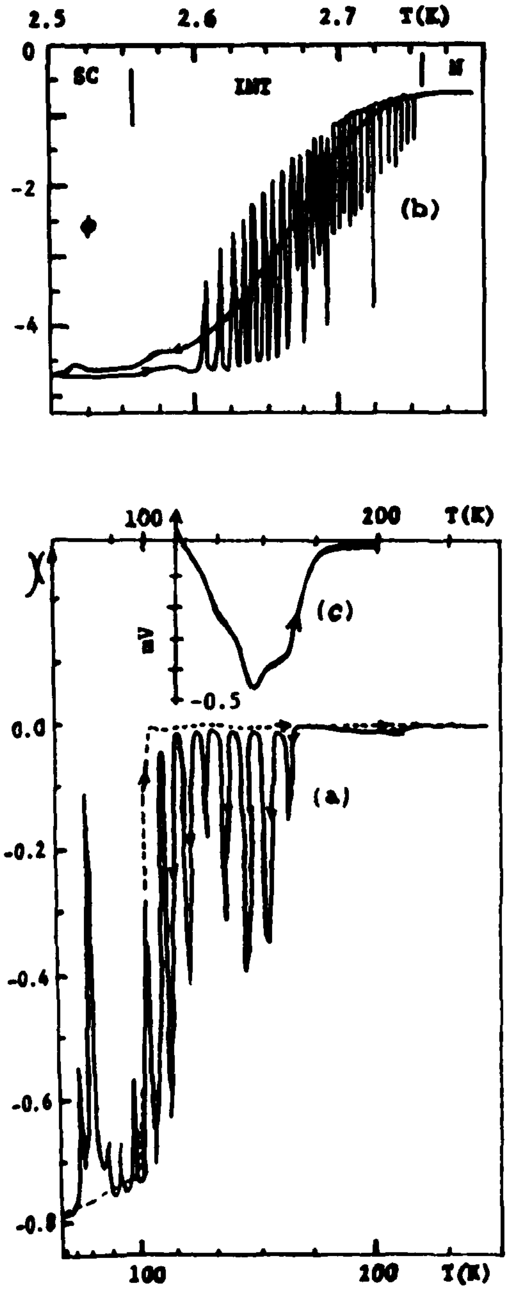

FIG. 3. Oscillatory susceptibility behavior. (a) the differential magnetic susceptibility observed at 20 Hz in CuCl redrawn from Brandt *et al.*, Ref. 6, (b) negative of phase change observed in secondary coil during 100 Hz susceptibility measurement in americium redrawn from Olsen. (Ref [illegible]. SC: superconducting. INT: intermediate state. N: normal. (c) work reported herein redrawn on the same (logarithmic) temperature scale as Brandt *et al.* (Ref. 6).

cling and can be minimized or removed by good thermal coupling to the bath.

In the case of radioactive material the "self-heating" provides the thermal energy to drive the "center" of the solid normal and provides the conditions for oscillation.

In both the americium and CuCl cases the oscillating diamagnetism is rate dependent; there is a diffusion of the internal heat through the external superconducting sheath as a function of time when the material is in a bath having a temperature below T_c in the Am case; but in the CuCl case only a thermal lag due to an inhomogeneous temperature distribution within the sample can provide the thermal energy for the oscillatory behavior; i.e., a higher temperature in one part versus another part of the sample. Therefore in the CuCl one should observe the oscillations on cooling but not on warming when uniformly heated over the surface (due to sporadic thermal contact).

That the number of oscillations has been reported[6] to be linearly dependent on temperature can be understood by the temperature change being linearly proportional to time. The work herein [Fig. 1(b)], as well as that of Chu *et al.*,[7] shows a diamagnetic displacement without evidence of oscillation.[9]

In summary, we observed increased diamagnetism in CuCl under 5 and 10 kbar pressure, between 120 and 180 K. Thus we have confirmed in part the observations of Brandt *et al.*,[6] and Chu *et al.*[7] Our samples were independently and differently obtained, purified, and quenched. Our method of pressurization was unidirectional, not hydrostatic. Our data was taken during warming cycles, not cooling. We saw no periodic diamagnetic oscillations when using a three-second time constant for the amplifier output, which corresponds to averaging over less than 1 K intervals. Brandt *et al.*[6] observed diamagnetic jumps of the magnetic susceptibility with a periodicity of 9 K between 170 and 100 K. The diamagnetic anomaly we observed was not stable below a critical temperature, but appeared only above 120 K.

Finally, we note that Lefkowitz, Yoffe, Lowndes, and Martin[12] reported dielectric anomalies in the thallous halides (Curie-Weiss behavior in the capacitance and conductance) associated with an instabililty in a light populated exciton system and have identified these exciton states in some detail.[13] The same phenomena have recently been found in CuCl.[14] Measurements of the temperature dependence of ϵ_0 in CuCl (at 1 kHz to 100 kHz on a capacitance bridge) gave values expected (~8–10) with a slowly decreasing ϵ_0 below ~20 K. However similar to the previously observed behavior in the thallous halides, ϵ_0 was enhanced by a factor of ~50 by direct light stimulation of the exciton population with Curie-Weiss behavior below ~ 20 K.[14]

On the basis of the observed thallous halide and cuprous chloride low-temperature electromagnetic anomalies an exciton model of superconductivity has been developed in which the electrons, as well as the attractions between them, stem from the excitonic states.[15]

ACKNOWLEDGMENTS

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APPENDIX II

DIAMAGNETIC ANOMALIES IN EPITAXIAL FILMS OF CuCl ON SILICON

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DIAMAGNETIC ANOMALIES IN EPITAXIAL FILMS OF CuCl ON SILICON

ABSTRACT

We wish to report the first equilibrium measurements of superdiamagnetism and diamagnetic transition on samples of CuCl.Studies were made on samples formed by epitaxial single crystal growth of CuCl on silicon single crystals.The results correlate quite well with earlier reports of superdiamagnetism in CuCl made under non-equilibrium conditions. Correlation with EPR data is included. The forms of the samples used in this study are similar to those that have been considered as candidates for high temperature superconducting systems by several investigators. A recent calculation of Takada suggests that a paired state is most likely to occur in a one- or two-dimensional system, but not in a three-dimensional system. Some of the properties of our samples suggest that this may very well be the case in these systems.

Oct. 1982

INTRODUCTION

The question of high temperature superconducting systems has led to controversy and the consensus is that such a state cannot exist above 30 K. Recent measurements of superdiamagnetism in CuCl (1-3) and cadmium sulfide (4,5) have provided experimental evidence suggesting that a high temperature superconducting state can, in fact, exist. Ginzburg (6) has considered the experimental evidence and has suggested that low-dimensional systems be considered as candidates for high temperature superconductors and, more recently, Takada (7) in a calculation using the XYZ model, has shown that the paired state is possible in one and two dimensions, but probably not in three dimensions for a polaron system. We wish to report the first equilibrium measurements of superdiamagnetism on samples of CuCl which have been epitaxially grown on silicon and whose form leads to the possibility of a system like those discussed by Takada and Ginzburg.

EXPERIMENTAL AND RESULTS

Thin films of CuCl have been grown on undoped or phosphorus doped silicon substrates by epitaxial growth techniques under conditions to be described elsewhere. Typical thickness of the CuCl was a few thousand Angstroms on 270 μm silicon blanks. These films have been characterized by x-ray diffraction and optical studies. The films appear to be formed reproducibly and are stable under a variety of environmental and experimental conditions. X-ray diffraction of CuCl on (111)-plane of silicon substrates show D_{111} CuCl = 3.121 Å and D...silicon = 3.141 Å. In addition, a weak D...T at 3.265 Å is observed which may correspond to an interfacial CuCl region that is compressed radially i.e., expanded normal to the epitaxial plane. The latter may indicate that the CuCl is highly ordered, and structurally epitaxial at the interface to silicon. Optical polarization experiments on the transparent CuCl film confirm a highly strained interfacial region (less than 1/20 of the CuCl thickness) when viewed with transmitted light parallel to the interface. In addition, when strong light is focused on the edge of the film, light is transmitted only through the stress-strain region, and interference figures are observed with white light. Similarly, scanning electromicroscopy shows an anomalous electron scattering effect, with the focus, being the image of this interface region. The samples and the silicon blanks have been checked by EPR to contain paramagnetic impurities.

Magnetic susceptibility data were collected using a Princeton Applied Research Model 155 vibrating-sample magnetometer. The magnetometer was initially calibrated against $HgCo(NCS)_4$, and the calibration was checked against a Ni-sphere in a saturation field. The total sample masses were very small (0.008 - 0.03 g) and the CuCl layer volume ranged from 1.5 to 6×10^{-6} cm^3. Samples were packed into a lucite sample holder without using glue or grease. The liquid nitrogen dewar and enclosing jacket were set up carefully to avoid any mutual contact, or contact to the pick-up coils of the VSM. Great care was taken to make certain of the saddle point position of the sample (position of maximum sensitivity), and numerous measurements were made on the empty sample holder, standard samples, as well as the sample holder with a silicon blank. The jacket enclosing the sample was evacuated before the experimental measurements, then it was filled with gaseous helium, which was kept under small pressure and used as a temperature exchange gas. A typical measurement would take about 40 minutes to go from liquid nitrogen (77 K) to room temperature. To extract the effect of sample holder and silicon from the experimental data, the background effects were recorded before a sample measurement. The data indicates a diamagnetic behavior of the lucite, i.e. a linear increase of $|\chi_{dia}|$ with magnetic field, and some decrease of the $|\chi_{dia}|$ in 77 - 300 K temperature range due probably to thermally activated paramagnetic centers in the sample holder material. The silicon seems to exhibit a very weak paramagnetic shift as the effect of doping, but this paramagnetism is dominated by the lucite sample holder diamagnetism.

Anomalies of $\chi(T)$ have been observed on two different samples, with CuCl thickness of about 2000 Å on Si (111)-plane. The sample coded B1, which has been grown on undoped silicon showed an anomalous diamagnetic susceptibility shift at T=105 K, as presented in Fig.1 together with the background effect. The mass of CuCl of the sample was 7×10^{-6} g. The effect was independent on the orientation of the sample with respect to the magnetic field of the magnetometer, and slowly vanished with time. After 24h the effect vanished completely, and trials to recover the effect by using an electric field (up to 2.5 kV/cm) and strong white light irradiation did not give positive results. A magnetization study indicated pure diamagnetic behavior of the relaxed sample, i.e., a linear response in the magnetic field up to 15000 G.

The sample coded #1 showed the anomalous decrease in susceptibility value at about T=130 K. The sample was grown on P-doped silicon. The mass of the CuCl layer was about 2.4×10^{-5} g. The diamagnetic transition at T=130 K is presented in Fig. 2. The effect is strongly time dependent and vanishes after a few hours. The $\chi(T)$ plots in Fig. 2 have been recorded in about 20 minute intervals. This effect being a drop of - 0.44 emu/cm^3 in susceptibility, may be due to a detrapping processes of charges by thermal excitation similarly to that observed in CuCl single crystal by Chu, et al. (2) at higher temperatures.

Another possibility is an evaporation of oxygen molecules which have been condensed on the surfaces of the sample and/or sample holder at low temperatures, but we discount this since this effect was not seen on blank runs. The anomaly can be related also to a valency state transition between Cu(II) and Cu(I) ions similarly to that observed in nonstoichiometric Cu Se system (8). It is arguable that Cu(II) ions could exist in the CuCl layer as an impurity or as a result of the spontaneous disproportionation processes known in single crystals of CuCl (9), but Cu(II) would have to be present in very small amounts because our EPR studies did not show a signal from Cu(II) in the samples.

The diamagnetic anomaly in B1-sample correlates rather well with those have been reported earlier (Fig. 3). The diamagnetic shift is calculated to be -0.079(20) emu/cm^3 thus corresponding to the maximal diamagnetic susceptibility $\chi_{dia}^{max} = (4\pi)^{-1}$ of the sample. These results suggest an appearance of the superconducting state in the sample at the same temperature as has been reported by Brandt, et al. (1) for CuCl single crystal.

DISCUSSION

The results described above for the B1-sample are the first experimental reports of a diamagnetic shift in CuCl at equilibrium with nearly complete Meissner exclusion . The results correlate in temperature rather well with the earlier reports. The EPR data also suggest some correlation between purity of the substrate and magnetic sample properties. The samples which display EPR lines from Fe(III) impurities in g= 4 region, do not show magnetic anomalies.

Numerous models that have been put forth to explain high temperature superconducting systems, but we fell that insufficient experimental data exist at this time to support conclusions about the various models either positively or negatively. However, some experimental facts should be noted. CuCl is an incipiently unstable material. The work of Boffman, et al. (10), which has been repeated recently by Merlin, et al. (11), which is always quoted by those who work with the light scattering properties of CuCl, and all conclude that there are two extra modes of vibration at TOLO mode that is symmetry forbidden in these materials. Lefkowitz, et al. (12) have shown that light irradiation introduces a defect mode which exhibits itself as a dielectric anomaly that correlates with the earlier reported diamagnetism.

These experimental results provide an impetus for the reconsideration of the earlier models of Ginzburg (6) and, they may provide an experimental verification of the model that was discussed in detail by Takada (7).

ACKNOWLEDGEMENT. This research was supported in part by the Army Research Office.

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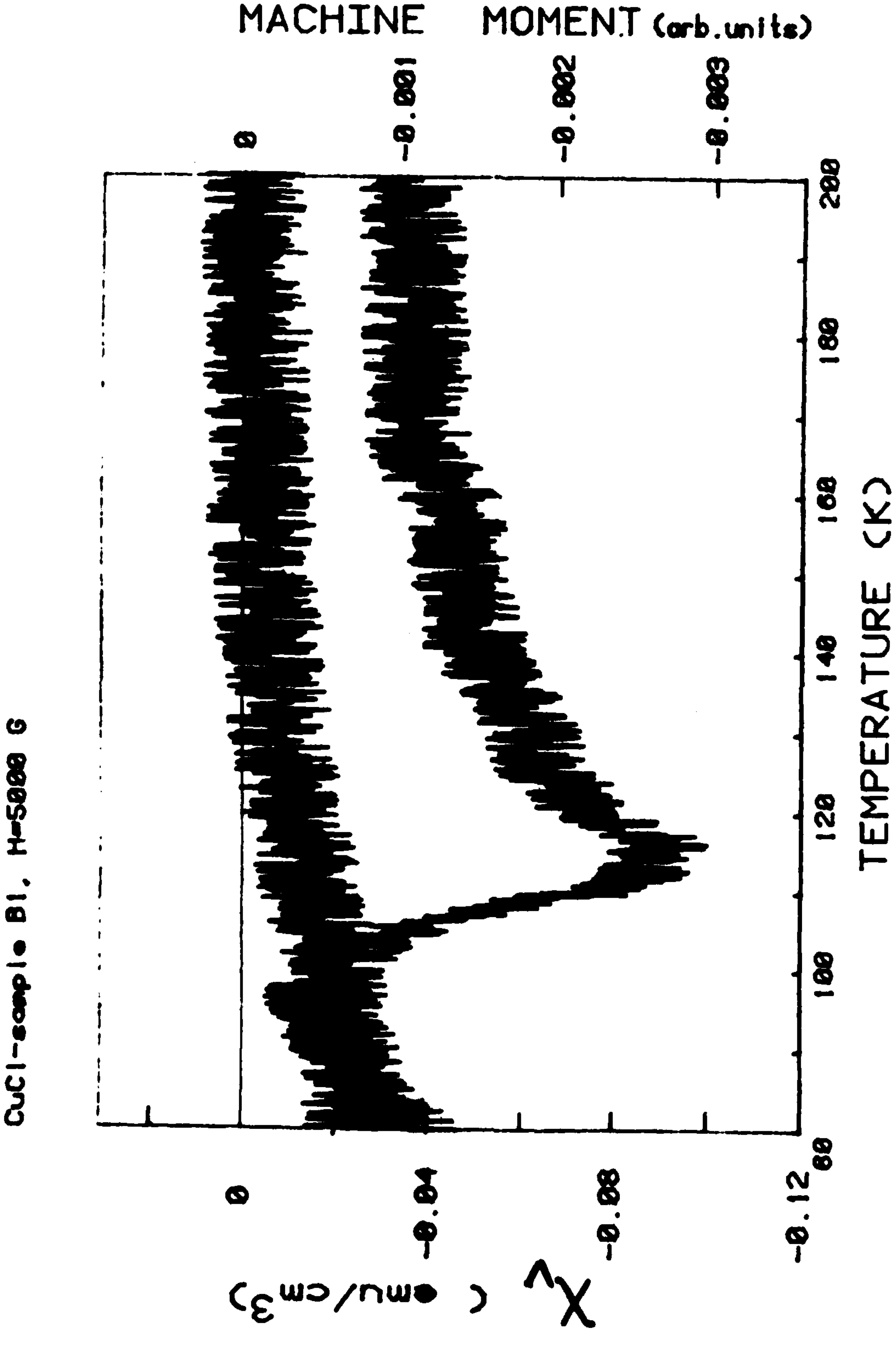
FIGURES

Fig.1. Diamagnetic anomaly in B1-sample of CuCl on (111)-plane of undoped Si observed in H=5000 G. The upper plot represents the bacground signal recorded with sample holder and silicon blank.

Fig.2. Paramagnetic-diamagnetic transition in #1-sample of CuCl on (111)-plane of phosphorus doped silicon as observed in H=8000 G. Paramagnetic state vanishes in time and the three plots were recorded in about 20 min. intervals.

Fig.3. Summary of diamagnetic anomalies observed in CuCl single crystals by Brandt, et al. (1), Chu, et al. (2), Lefkowitz, et al.(3), and in CuCl layer on Si as reported in this paper.


CuCl-sample B1, H=5000 G
MACHINE MOMENT (arb.units)
0
-0.001
-0.002
-0.003
TEMPERATURE (K)
80
100
120
140
160
180
200
χ_v (emu/cm^3)
0
-0.04
-0.08
-0.12

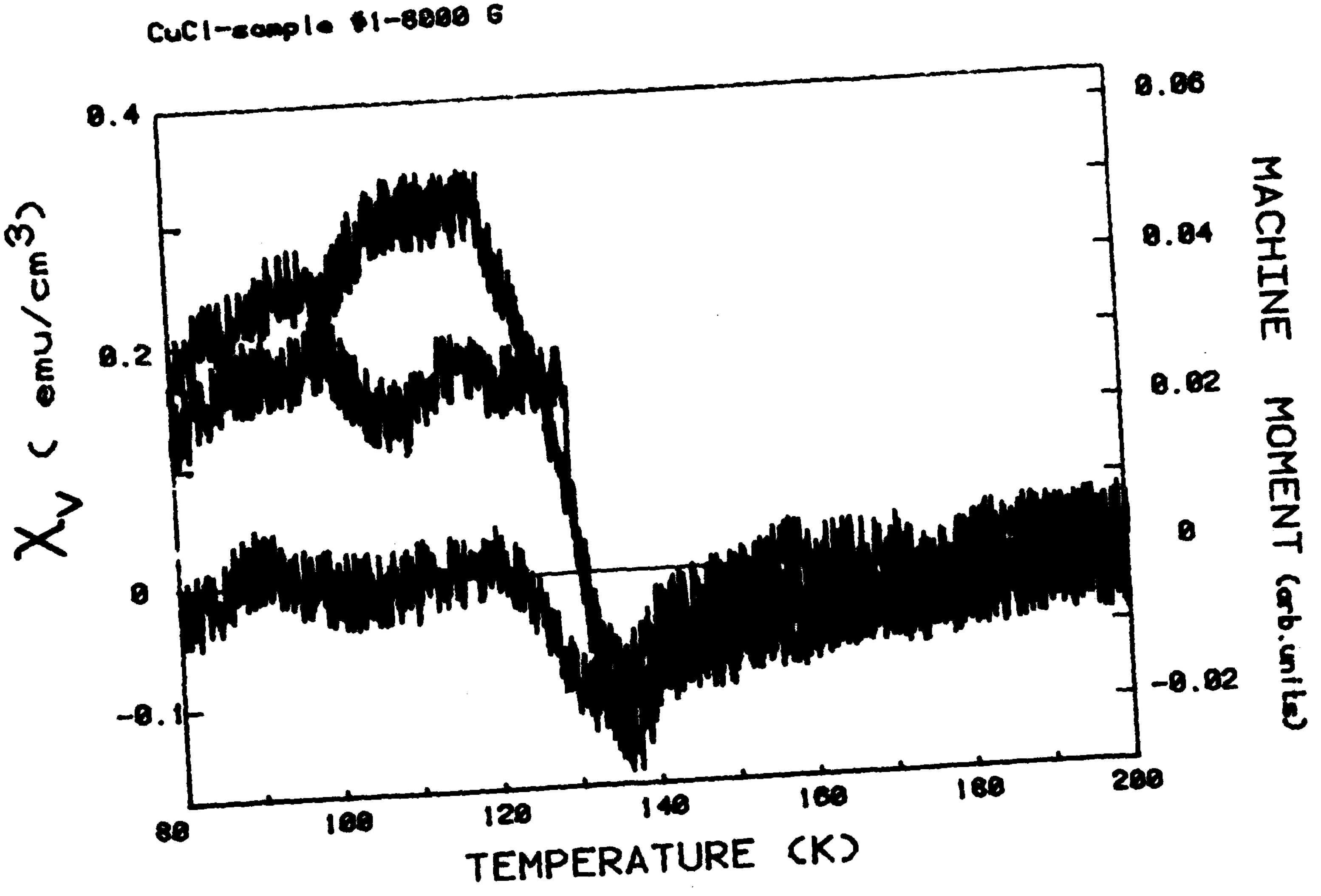

CuCl-sample #1-8000 G
χ_v (emu/cm^3)
0.4
0.2
0
-0.1
MACHINE MOMENT (arb.units)
0.06
0.04
0.02
0
-0.02
80
100
120
140
160
180
200
TEMPERATURE (K)

Fig 2

APPENDIX III

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Theory of deep impurity levels in CuCl

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The theory of deep impurity levels is extended to semiconductors with d electrons. The major chemical trends are predicted for a large number of substitutional impurities in CuCl. Deep levels are found for S and Se impurities on the Cl site, but not for Ag or Au on the Cu site, in agreement with experiment. The theory also predicts no deep level for isolated O on the Cl site, thus supporting the conclusion that the observed O-related defect is not a simple substitutional impurity.

I. INTRODUCTION

CuCl has been reported to exhibit an anomalous diamagnetism that is reminiscent of superconductivity[1-3] and possibly associated with defects.[4] The importance of defect states is further emphasized by the occurrence of a broadened z_3 exciton line[5] in the same temperature region in which the diamagnetism is observed. This broadening has been variously related to defect states, free electron effects,[5] a defect-stabilized plasma state,[6] or a modified phonon spectrum.[4] In order to provide some theoretical guidance for experiments involving defects in CuCl,[4,7] we have extended the theory of substitutional impurities[8-10] to include d electrons on the cation site. We focus on the deep levels—i.e., the levels that are bound within the fundamental band gap predominantly by the central-cell defect potential.

The theory of impurities in sp^3-bonded covalent materials, as enunciated by Hjalmarson *et al.*,[8] contains two basic ingredients: (i) an empirical tight-binding model of the host electronic structure that incorporates experimental information, chemical trends, and the relevant features of theoretical energy bands, and (ii) a defect potential whose off-diagonal matrix elements in the tight-binding basis are determined by Harrison's d^{-2} scaling rule[11] and whose diagonal matrix elements V_l are determined by the differences in impurity and host atomic energies:

$$V_l = \beta_l (E_l^i - E_l^h) . \tag{1.1}$$

Here E_l^i and E_l^h are impurity and host orbital energies for states of angular momentum l, and are converted into "orbital energies within the solid" by the constant factor β_l.

In this paper, we generalize the theory of Hjalmarson *et al.* to include d-electron orbitals on the cation site. This immediately leads to two changes: (i) The host Hamiltonian H_0 involves five d orbitals on the cation site, as well as one s orbital and three p orbitals on each site, and (ii) the defect potential matrix for Cu substitutional impurities is also augmented by matrix elements involving d orbitals.

II. THE MODEL

Our 13-state tight-binding host Hamiltonian is shown in Appendix A. Its parameters, given in Table I, were determined by a fitting procedure described in Appendix B. The resulting band structure is displayed in Fig. 1, together with the results of a psuedopotential calculation by Kleinman and Mednick.[12] The bands of Kunz *et al.*[13] and of Zunger and Cohen[14] are similar to those of Kleinman and Mednick.

The primary requirement of a successful tight-binding model is that it adequately reproduces the projected densities of states—not just the energy bands. It is these densities of states, for anion s and p electrons and for cation s, p, and d electrons, that determine the defect levels in accordance with Eqs. (3.2) and (3.3). We imposed the following re-

TABLE I. Parameters of the tight-binding model in eV. With these parameters the charges on the Cu and Cl ions are, respectively, $+0.59|e|$ and $-0.59|c|$.

$E(s,c)$	$E(s,a)$	$E(p,c)$	$E(p,a)$	$E(d,c)$	$E'(d,c)$	$V(x_c,yz_c)$	
2.80	−15.15	9.00	−3.75	−1.25	−1.90	0	
$V(s,s)$	$V(x_a,s_c)$	$V(s_a,x_c)$	$V(x,x)$	$V(x,y)$	$V_{sd\sigma}$	$V_{pd\sigma}$	$V_{pd\pi}$
−2.877	4.841	2.866	0	0	−1.980	−5.085	1.220

quirements in fitting our tight-binding model: (i) The band gap is 3.25 eV.[15] (ii) The Cu 3*d* bands lie above the Cl 3*p* bands,[16] and the widths of these bands[17] are approximately the observed widths. (iii) The four main peaks observed in x-ray photoemission[16] have their observed positions. (iv) The top of the highest valence band is 75% Cu 3*d* and 25% Cl 3*p*.[16] (v) The charge on the Cu ion is positive. (vi) The remaining important features in the pseudopotential bands of Refs. 12 – 14 are adequately reproduced.

The resulting tight-binding Hamiltonian yields densities of state for the upper valence bands that are in good agreement with the available photoemission data, as shown in Table II and Fig. 2. It also produces bands that are in reasonable agreement with the pseudopotential calculations (Fig. 1).

III. METHOD OF CALCULATION

The change in the tight-binding Hamiltonian resulting from the introduction of an impurity or vacancy is the defect potential $V \equiv H - H_0$. If we neglect lattice relaxation, the defect potential is diagonal[8] because Harrison's scaling rules[11] imply that the off-diagonal matrix elements of H and H_0 are equal.

Following the approach of Hjalmarson *et al.*, we take the on-site diagonal defect potential for isoelectronic defects to be given by Eq. (1.1).[18] The Hjalmarson *et al.* model was originally developed for studying isoelectronic defects in highly covalent materials; its application to charged centers in more ionic materials requires a modification of the expression for V to account for the different ionic

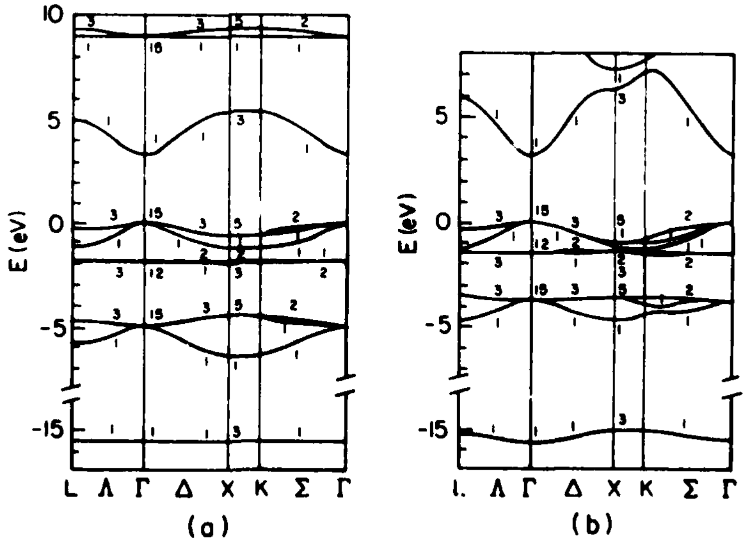

FIG. 1. Band structure of CuCl: (a) calculated from the Hamiltonian of Appendix A and Table I, (b) calculated by Kleinman and Mednick (Ref. 12).

TABLE II. Experimental features fit in determining the empirical CuCl Hamiltonian.

	Experiment	Theory
Order of valence bands	Cu 3*d* higher than Cl 3*p*[a]	Cu 3*d* higher than Cl 3*p*
Cu 3*d* character at top of valence band	75%[b]	75%
Cl 3*p* character at top of valence band	25%[b]	25%
Band gap (eV)	3.25[c]	3.25
Photoemission peaks (eV)		
A	0.8–1.4[b]	0.6
B	1.9–2.6[b]	1.9
C	4.9–5.2[b]	4.8
D	6.0–6.3[b]	6.4
Width of lower band (eV) (Cl 3*p*)	2.4[a]	2.4
Width of upper band (eV) (Cu 3*d*)	1.7[a]	2.0

[a] Reference 17.
[b] Reference 16.
[c] Reference 15.

charges. This modification we term ΔV_l; it is expected to have the same sign as the correction Eq. (1.1) would experience if ionic energies were used in place of atomic energies. Crude estimates of ΔV_l for singly charged defects in an ionic host such as CuCl indicate that it is of the order of 4 eV.[19] We shall see independently that a value of $\Delta V_p = 3.5$ eV produces S and Se levels in agreement with the data.

The defect potential for an anion-site defect is thus a diagonal 4×4 matrix with one element V_s and three elements V_p. For a cation-site defect, it is a 9×9 matrix with one element V_s, three elements V_p, three elements V_d, and two elements V_d'. (We do not assume that the d_{xy} and $d_{y^2-z^2}$ defect potentials are equal.) In each case we have

$$V_l = \beta_l (E_l^I - E_l^h) + \Delta V_l \ . \tag{3.1}$$

Since the defect potential is localized, it is appropriate to use the Green's-function method to compute the defect energy levels. This method produces a secular equation in a localized basis that involves only those basis functions within the defect space[8–10]:

$$\det[1 - G_0(E)V] = 0 \ , \tag{3.2a}$$

where we have

$$G_0(E) \equiv (E - H_0)^{-1} \ . \tag{3.2b}$$

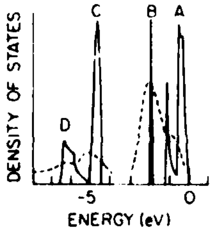

FIG. 2. Valence-band density of states calculated the host Hamiltonian of this paper (solid curve), in rison with the deconvoluted x-ray-photoelectron-oscopy spectra obtained by S. Kono *et al.* as cited f. 16 (dashed curve).

For the anion site, this 4×4 problem reduces to four 1×1 problems, yielding one A_1 (*s*-like) and three degenerate T_2 (*p*-like) defect states. For the cation site, Eq. (3.2) is a 9×9 problem. Our decoupling of the cation *p* and *d* orbitals (see Appendix B) reduces Eq. (3.2) to nine scalar problems, yielding one A_1 (*s*-like), three T_2 (*p*-like), another three T_2 (d_{xy}-like), and two E ($d_{y^2-z^2}$-like) states.

Each eigenvalue problem has the form

$$\frac{1}{V_{\lambda b}} = G_{\lambda b}(E) = \int \frac{D_{\lambda b}(E')dE'}{E - E'} \ . \tag{3.3}$$

where

$$\lambda = A_1(s),\ T_2(p),\ T_2(d_{xy}),\ \text{or}\ E(d_{y^2-z^2}), \tag{3.4}$$

and b means "anion" or "cation."

Here $D_{\lambda b}$ is the contribution of the λ-symmetric irreducible representation to the local density of states on the b site:

$$\begin{aligned} D_{\lambda b}(E) &= \langle \lambda b \mid \delta(E - H_0) \mid \lambda b \rangle \\ &= \sum_{n\vec{k}} \langle \lambda b \mid n\vec{k} \rangle \langle n\vec{k} \mid \lambda b \rangle \delta(E - E_{n\vec{k}}) . \end{aligned} \tag{3.5}$$

IV. RESULTS

The predictions for deep levels associated with isolated substitutional impurities are given in Figs. 3–8. The predicted level for a given impurity is obtained from the intersection of the calculated curve with a vertical line representing the isoelectronic impurity potential.

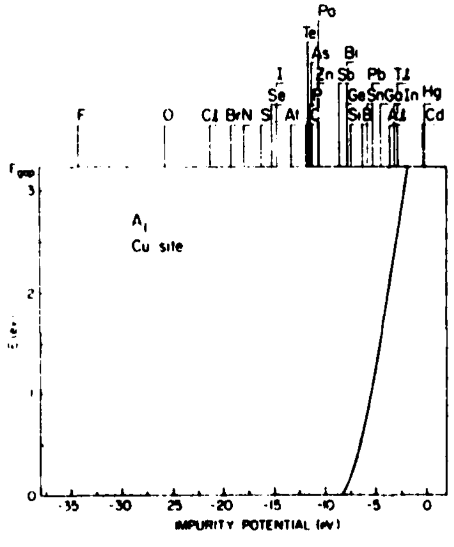

FIG. 3. Energies in eV of the A_1 (s-like) substitutional defect levels predicted for impurities at the Cu site in CuCl. The abscissa is the defect potential; each impurity has a tic at its potential. All transition-metal potentials are between −2 and +2 eV; hence these defects are not predicted to produce A_1 deep traps. No A_1 deep levels are predicted to lie within the band gap for the isoelectronic impurities Ag and Au.

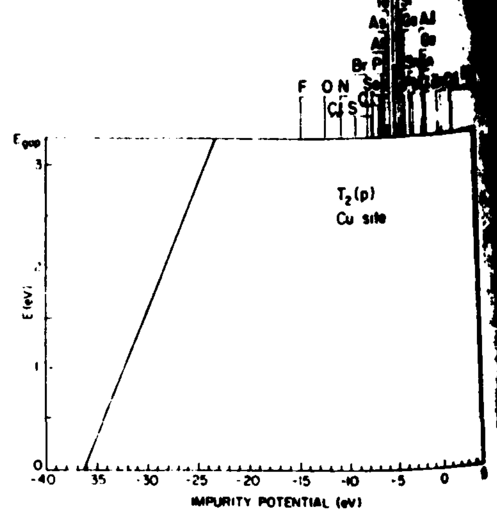

FIG. 4. Energies of the T_2 (p-like) substitutional defect levels predicted for impurities at the Cu site in CuCl. T_2 p-derived levels in the gap are not predicted for any of the impurities.

These predictions should be viewed within the context of the goals of the theory. They represent a global view of the expected chemical trends in the defect data, and should be corrected for the different charge states of the defect levels, and, possibly, lattice relaxation. (The present calcula-

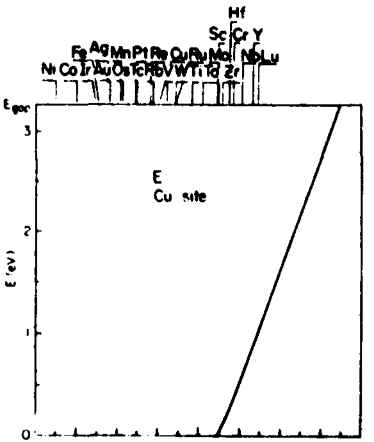

FIG. 5. Energies of the E-symmetric ($d_{y^2-z^2}$-like) defect levels predicted for impurities at the Cu site in CuCl. Notice that Ag and Au do not produce d-like E defect levels in the gap when on the Cu site.

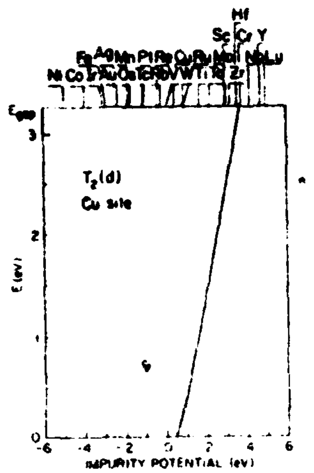

FIG. 6. T_2-symmetric (d_{xy}-like) defect levels for the Cu site. Note that Ag and Au again do not produce levels in the gap.

tions predict the neutral defect levels, and corrections to these levels for the different charge states can be estimated using simple electrostatic arguments.) Since the purpose of the theory is to predict trends, predictions of relative orderings of energy levels produced by different defects should be even more reliable than the theoretical energies of individual defects.

The predictions of the theory agree with the major experimental facts of which we are aware: (i) S and Se substituting for Cl are known to produce deep levels in CuCl,[20,21] with the Se level being 0.32 eV above the S level; (ii) searches for deep traps associated with Ag or Au substituting for Cu have been unsuccessful[22]; and (iii) an O-related level has been identified[20] which, unlike the S and Se levels, is not associated with the tetrahedral symmetry of a simple substitutional defect.

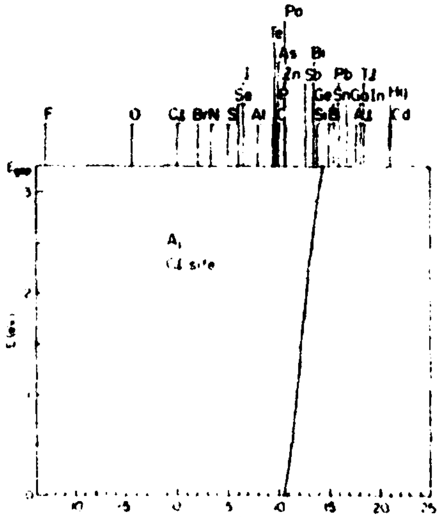

FIG. 7. Energies of the A_1 defect levels predicted for impurities on the Cl site of CuCl.

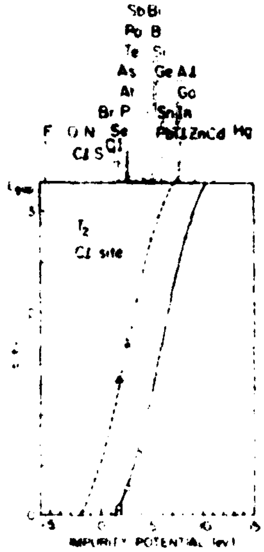

FIG. 8. Energies of the T_2 defect levels predicted for impurities on the Cl site of CuCl. The solid line is the uncorrected theory; the points marked with open squares are the uncorrected predictions for S, Se and Te levels. The solid circles represent the experimental results for S and Se (after Ref. 20). The dashed line represents the corrected theory for acceptors, with the correction being determined by the S datum; the open triangles are the corrected predictions for S, Se, and Te.

The experimental S and Se impurity levels have the same ordering as in the uncorrected predictions of Fig. 8, but are somewhat higher in absolute energy than predicted. As mentioned in Sec. III, the uncorrected predictions are for isoelectronic impurities [Eq. (1.1)], whereas the S and Se impurities are expected to have an extra electron in comparison with the replaced Cl atom. (Roughly speaking, S^- and Se^- replace Cl^-.) Allowance for the fact that S is not isoelectronic to Cl, through modification of the defect potential as prescribed in (3.1), brings the theory into improved agreement with the data. By choosing the defect potential modification ΔV_p such that the S datum is reproduced, we find a reasonable value $\Delta V_p = 3.5$ eV. The correction ΔV_p contains not only the atomistic correction discussed above, but the long-range polarization energy, which systematically alters the levels of the S, Se, and Te defects. We then predict a Se level in excellent agreement with the observed value, as indicated in Fig. 8. Such agreement is, of course, expected of a theory that is intended to predict trends in impurity levels more reliably than absolute energies.[8]

The theory predicts that the defect levels associated with Ag or Au on the Cu site all lie within the bands and outside of the fundamental band gap. Thus it explains why no deep levels have been observed for these impurities.[22]

An especially interesting prediction of the model is that isolated O on a Cl site should not produce a deep trap, but its isoelectronic mates S and Se should. The reason for this is that O attracts electrons more strongly than Cl, whereas S and Se are weaker. The O levels should *therefore* lie below the corresponding Cl levels, outside the gap, whereas the S and Se levels should lie above Cl, within the gap. Thus, in a natural way, the theory supports the interpretation that the O-related defect, with a level 1.08 eV above the valence band,[20] is not a substitutional impurity like S and Se, but is instead an extended defect of nontetrahedral symmetry. The present work, therefore, lends indirect support to the work of Kunz *et al.*,[13] who have proposed that a complex consisting of O^{-2} and a vacancy produces a level near the conduction-band edge.

Finally, when it substitutes for Cl, the impurity Te should produce a T_2-symmetric defect level at about 2.20 eV above the valence-band edge. Observation of this level would provide gratifying confirmation of the present theory.

ACKNOWLEDGMENTS

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APPENDIX A

The 13-orbital tight-binding Hamiltonian has the form as shown in Table III, where we have

$$g_0 = \cos q_1 \cos q_2 \cos q_3 - i \sin q_1 \sin q_2 \sin q_3 \,, \quad \text{(A1a)}$$

$$g_1 = -\cos q_1 \sin q_2 \sin q_3 + i \sin q_1 \cos q_2 \cos q_3 \,, \quad \text{(A1b)}$$

$$g_2 = -\sin q_1 \cos q_2 \sin q_3 + i \cos q_1 \sin q_2 \cos q_3 \,, \quad \text{(A1c)}$$

$$g_3 = -\sin q_1 \sin q_2 \cos q_3 + i \cos q_1 \cos q_2 \sin q_3 \quad \text{(A1d)}$$

with

$$\vec{q} = \frac{a}{4}\vec{k}$$

and

$$V(s_a, xy_c) = \frac{1}{\sqrt{3}} V_{sd\sigma} \,, \quad \text{(A2a)}$$

$$V(x_a, xy_c) = \tfrac{1}{3} V_{pd\sigma} + \frac{1}{3}\frac{1}{\sqrt{3}} V_{pd\pi} \,,$$

$$V(x_a, yz_c) = \tfrac{1}{3} V_{pd\sigma} - \frac{2}{3}\frac{1}{\sqrt{3}} V_{pd\pi} \,, \quad \text{(A2b)}$$

TABLE III. 13-orbital tight-binding Hamiltonian matrix.

	s_a	s_c	x_a	y_a	z_a	x_c	y_c
s_a	$E(s,a)$	$V(s,s)g_0^*$	0	0	0	$-V(s_a,x_c)g_1^*$	$-V(s_a,x_c)g_2^*$
s_c	$V(s,s)g_0$	$E(s,c)$	$V(s_c,x_a)g_1$	$V(s_c,x_a)g_2$	$V(s_c,x_a)g_3$	0	0
x_a	0	$V(s_c,x_a)g_1^*$	$E(p,a)$	0	0	$V(x,x)g_0^*$	$V(x,y)g_3^*$
y_a	0	$V(s_c,x_a)g_2^*$	0	$E(p,a)$	0	$V(x,y)g_3^*$	$V(x,x)g_0^*$
z_a	0	$V(s_c,x_a)g_3^*$	0	0	$E(p,a)$	$V(x,y)g_2^*$	$V(x,y)g_1^*$
x_c	$-V(s_a,x_c)g_1$	0	$V(x,x)g_0$	$V(x,y)g_3$	$V(x,y)g_2$	$E(p,c)$	0
y_c	$-V(s_a,x_c)g_2$	0	$V(x,y)g_3$	$V(x,x)g_0$	$V(x,y)g_1$		$E(p,c)$
z_c	$-V(s_a,x_c)g_3$	0	$V(x,y)g_2$	$V(x,y)g_1$	$V(x,x)g_0$	0	0
x_cy_c	$V(s_a,xy_c)g_3$	0	$-V(x_a,xy_c)g_2$	$-V(x_a,xy_c)g_1$	$-V(x_a,yz_c)g_0$	0	0
y_cz_c	$V(s_a,xy_c)g_1$	0	$-V(x_a,yz_c)g_0$	$-V(x_a,xy_c)g_3$	$-V(x_a,xy_c)g_2$	$V(x_a,yz_c)$	0
z_cx_c	$V(s_a,xy_c)g_2$	0	$-V(x_a,xy_c)g_3$	$-V(x_a,yz_c)g_0$	$-V(x_a,xy_c)g_1$	0	$V(x_a,yz_c)$
$y_c^2-z_c^2$	0	0	0	$-V(y_a,y^2-z_c^2)g_3$	$V(y_a,y^2-z_c^2)g_2$	0	0
$3z_c^2-r_c^2$	0	0	$2V(x_a,3z^2-r_c^2)g_1$	$-V(y_a,3z^2-r_c^2)g_2$	$-V(y_a,3z^2-r_c^2)g_3$	0	0

$$V(y_a,y^2-z_c^2)=\frac{1}{\sqrt{3}}V_{pd\pi}\,,$$

$$V(y_a,3x^2-r_c^2)=-\tfrac{1}{3}V_{pd\pi}\,. \qquad \text{(A2c)}$$

APPENDIX B

As discussed in the text, our first priority in fitting the tight-binding Hamiltonian is to reproduce the available experimental data. A second priority is to fit the remaining important features of the bands obtained in the pseudopotential calculations of Refs. 12 and 14.

We first take

$$V(x_c,yz_c)=0\,. \qquad \text{(B1)}$$

There are three reasons for doing this: (i) Preliminary fits indicated that this parameter should have a small value, of the order of 0.1 eV. This is to be expected because the coupling vanishes in the free Cu atom. (ii) Equation (B1) reduces the band fitting to an entirely linear procedure, with none of the ambiguities that can plague nonlinear fits. (iii) The impurity problem is reduced to the solution of scalar equations. With $V(x_c,yz_c)\neq 0$, the impurity problem on the cation site involves three 1×1 secular equations (corresponding to s, $d_{y^2-z^2}$, and $d_{3z^2-r^2}$ electrons) and three 2×2 equations (corresponding to p_x and d_{yz}, p_y and d_{xz}, and p_z and d_{xy} electrons). But with $V(x_c,yz_c)=0$, the p and d electrons are decoupled, and this problem reduced to nine 1×1 problems.

The matrix elements $E(s,c)$, $E(s,a)$, $E(p,c)$, $E(p,a)$, $E(d,c)$, $E'(d,c)$, $V(s,s)$, $V(x,x)$, $V(x_c,yz_c)$, and $V(x_a,yz_c)$ are determined by fitting information about the band structure at Γ, the center of the Brillouin zone. According to group theory, there are three Γ_{15} states. Their energies are determined by the equation:

$$\begin{vmatrix} E(p,a)-E & V(x,x) & -V(x_a,yz_c) \\ V(x,x) & E(p,c)-E & 0 \\ -V(x_a,yz_c) & 0 & E(d,c)-E \end{vmatrix}=0\,. \qquad \text{(B2)}$$

Experimentally[16] the wave function at the top of the valence band (Γ_{15}) is composed of 25% Cl $3p$, 75% Cu $3d$, and a negligible percentage of Cu $4p$. To eliminate the Cu $4p$ contribution at the valence-band maximum, we first choose $V(x,x)=0$. The remaining off-diagonal parameter $V(x_a,yz_c)$ is then fixed by requiring that the 25% Cl $3p$ and 75% Cu $3d$ character be reproduced. The diagonal matrix elements $E(p,a)$ and $E(d,c)$ are chosen so that the energy at the top of the valence band is zero and the lower Cl $3p$-like valence band (also Γ_{15}) occurs at -5 eV, in agreement with photoemission data. This leaves $E(p,c)$ to be determined.

The matrix element $E'(d,c)$ can be determined by the position of peak B of the photoemission data (Fig. 2), which corresponds to the Γ_{12} valence band. The matrix elements $E(s,c)$, $E(s,a)$, and $V(s,s)$ determine the bottoms of the conduction band and the lowest valence band, both of which are Γ_1. The bottom of the conduction band is given by the experimental band gap (3.25 eV), and the bottom of the lowest valence band is taken from the calculation of Kleinman and Mednick. The third of these parameters is fixed by requiring the lowest valence band to have 90% Cl $3s$ charac-

TABLE II. *(Continued.)*

z_c	x_cy_c	y_cz_c	z_cx_c	$y_c^2-z_c^2$	$3z_c^2-r_c^2$
$-V(s_a,z_c)g_1^*$	$V(s_a,xy_c)g_1^*$	$V(s_a,xy_c)g_1^*$	$V(s_a,xy_c)g_1^*$	0	0
0	0	0	0	0	0
$V(x,y)g_1^*$	$-V(x_a,xy_c)g_1^*$	$-V(x_a,yz_c)g_0^*$	$-V(x_a,xy_c)g_1^*$	0	$2V(y_a,3x^2-r_c^2)g_1^*$
$V(x,y)g_1^*$	$-V(x_a,xy_c)g_1^*$	$-V(x_a,xy_c)g_1^*$	$-V(x_a,yz_c)g_0^*$	$-V(y_a,y^2-z_c^2)g_1^*$	$-V(y_a,3x^2-r_c^2)g_1^*$
$V(x,x)g_0^*$	$-V(x_a,yz_c)g_0^*$	$-V(x_a,xy_c)g_1^*$	$-V(x_a,xy_c)g_1^*$	$V(y_a,y^2-z_c^2)g_1^*$	$V(y_a,3x^2-r_c^2)g_1^*$
0	0	$V(x_c,yz_c)$	0	0	0
0	0	0	$V(x_c,yz_c)$	0	0
$E(p,c)$	$V(x_c,yz_c)$	0	0	0	0
$V(x_c,yz_c)$	$E(d,c)$	0	0	0	0
0	0	$E(d,c)$	0	0	0
0	0	0	$E(d,c)$	0	0
0	0	0	0	$E'(d,c)$	0
0	0	0	0	0	$E'(d,c)$

ter, as calculated by Zunger and Cohen.[14]

The matrix element $E(p,c)$ is fitted to the previously calculated results for the highest conduction bands (Γ_{15}) at Γ.[12,14] The remaining matrix elements are determined by fitting previously calculated results at the X point. In our model, the secular equations at the X point are

$$\begin{vmatrix} E(s,c)-E & iV(x_a,s_c) & 0 \\ iV(x_a,s_c) & E(p,a)-E & i\tfrac{2}{3}V_{pd\pi} \\ 0 & -i\tfrac{2}{3}V_{pd\pi} & E'(d,c)-E \end{vmatrix} = 0\,, \quad \text{(B4)}$$

for X_1,

$$E'(d,c)-E=0\,,$$

for X_2,

$$\begin{vmatrix} E(s,a)-E & iV(x_c,s_a) & iV_{sd\sigma}/\sqrt{3} \\ -iV(x_c,s_a) & E(p,c)-E & 0 \\ -iV_{sd\sigma}/\sqrt{3} & 0 & E(d,c)-E \end{vmatrix} = 0\,,$$

for X_3, and

$$\begin{vmatrix} E(p,c)-E & iV(x,y) & 0 \\ -iV(x,y) & E(p,a)-E & i\left(\frac{1}{3}V_{pd\sigma}+\frac{1}{3}\frac{1}{\sqrt{3}}V_{pd\pi}\right) \\ 0 & -i\left(\frac{1}{3}V_{pd\sigma}+\frac{1}{3}\frac{1}{\sqrt{3}}V_{pd\pi}\right) & E(d,c)-E \end{vmatrix} = 0 \quad \text{(B7)}$$

for X_5. From these equations, the off-diagonal matrix elements can be determined directly:

$$[V(x_a,s_c)]^2 = -\frac{[E(s,c)-X_1(1)][E(s,c)-X_1(2)][E(s,c)-X_1(3)]}{E(s,c)-E'(d,c)}\,, \quad \text{(B8)}$$

$$(\tfrac{2}{3}V_{pd\pi})^2 = -\frac{[E'(d,c)-X_1(1)][E'(d,c)-X_1(2)][E'(d,c)-X_1(3)]}{E(s,c)-E'(d,c)}\,, \quad \text{(B9)}$$

$$[V(x_c,s_a)]^2 = -\frac{[E(p,c)-X_3(1)][E(p,c)-X_3(2)][E(p,c)-X_3(3)]}{E(p,c)-E(d,c)}\,, \quad \text{(B10)}$$

$$(V_{sd\sigma}^2/3) = -\frac{[E(d,c)-X_3(1)][E(d,c)-X_3(2)][E(d,c)-X_3(3)]}{E(p,c)-E(d,c)}\,, \quad \text{(B11)}$$

$$[V(x,y)]^2 = -\frac{[E(p,c)-X_5(1)][E(p,c)-X_5(2)][E(p,c)-X_5(3)]}{E(p,c)-E(d,c)}\,, \quad \text{(B12)}$$

and

$$\left(\frac{1}{3}V_{pd\sigma}+\frac{1}{3}\frac{1}{\sqrt{3}}V_{pd\pi}\right)^2 = -\frac{[E(d,c)-X_5(1)][E(d,c)-X_5(2)][E(d,c)-X_5(3)]}{E(p,c)-E(d,c)}\,. \quad \text{(B13)}$$

Here $X_i(j)$, with $i=1$, 3, and 5 and $j=1$, 2, and 3, are the three energy values of the X_i representation. We choose the $X_i(j)$ employing the following two conditions: (i) they should give a band structure which is in good agreement with previous calculations, and (ii) the tight-binding Hamiltonian should give a positive charge on the Cu site. Table I presents the parameters determined by this scheme.

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APPENDIX IV

EVIDENCE FOR PHOTOACTIVATED DEFECT INDUCED DIELECTRIC ANOMALIES IN CuCl

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ABSTRACT

Dielectric measurements of optically irradiated single crystal and composite samples of CuCl prepared and stored under carefully controlled conditions have revealed anomalies in both the capacitance and tan δ at 220K. At low temperature the capacitance shows a peak versus increasing integrated photon flux which is interpreted as increasing photo-induced Cu^0 defect precipitate. The results are reproducible and correlate with earlier reports of anomalous diamagnetism (high temperature superconductivity precursor) in CuCl. The observation of a large low frequency dielectric constant in CuCl supports the existence of a low frequency (soft) phonon mode in the CuCl-Cu^0 precipitate composite which could provide a mechanism for high temperature superconductivity.

Recent theoretical[1] and experimental[2,3,4] studies on copper chloride (CuCl) have suggested that this material may be a prime candidate for the prototype of a high temperature superconductor. Lefkowitz and Bloomfield[5] have speculated that BCS pairing of electrons can be obtained from their interaction with the (softening) of the phonon mode associated with the aggregates of islets of copper (Cu^0) formed about impurities and defects in the CuCl lattice. Magnetic studies by several groups[2,3,4] have shown large diamagnetic shifts in the susceptibility of CuCl near 150K, and these diamagnetic shifts are suggestive of a transition to a superconducting-like state. These results are very sample dependent but have been duplicated by the original groups (private communications from [2,3,4]).

We have studied the dielectric properties as a function of photon flux and temperature of well characterized and carefully stored single crystal and pressed composite samples of CuCl. The results of these studies are reported herein.

Photochromism is a well-known phenomenon in CuCl.[1] It is commonly accepted that free copper is formed by the oxidation reduction disproportionation reaction[1]

$$2\ Cu^{1+} = Cu^{2+} + Cu^{0}.$$

This reaction is stimulated by ultraviolet irradiation of CuCl samples especially when small particles of copper already exist in the crystal. Most samples of CuCl contain free Cu^0 as evidenced by their emission spectra under laser irradiation.[6] We have used the UV irradiation technique to change the density of Cu^0 in the samples studied in this work. After irradiation the enhanced Cu^0 density (increase in number and larger sized visible islets) could be observed under microscopic examination (micron sized particles appeared which were not visible before irradiation). The dielectric properties of the CuCl samples prepared were studied as a function of temperature and photon flux (and hence as a function of defect density, the defects consisting of free Cu^{1+}, Cu^{2+}, and Cu^0).

The samples employed were prepared under very stringent experimental conditions. Pure CuCl was prepared by the reduction of ACS reagent grade $CuCl_2 \cdot 2H_2O$ with ACS reagent grade copper metal in constant boiling HCl under an argon shroud to maintain an oxygen free environment. White crystals of CuCl were precipitated by dilution of the acidic reaction mixture to about 4 M HCl. The CuCl crystals were collected on a sintered (porous) glass funnel under argon; excess liquid was removed by passing an argon stream over the crystals; and the crystals were dried in a vacuum desiccator. The reaction product was sublimed under red light at 400-500°C at about 10^{-4} torr for final purification. The samples were stored under soft vacuum. Purity and identity of the materials were determined by X-ray diffraction techniques and electron paramagnetic resonance. Optically transparent electrodes of gold were vacuum evaporated on the samples which had been formed into (1 cm diam.) pressed discs. The single crystals that were used for the measurements were grown by a flux method into 1 cm diam. discs using the CuCl prepared by the methods just described. Gold electrodes were also evaporated on these specimens in order to make good electrical contacts with the crystal. Photodielectric measurements were performed using a high pressure, high intensity xenon lamp in conjunction with a grating monochromator. The exciting radiation was varied for some measurements; but most experimental measurements were made at 391 nanometers. Infrared radiation was blocked by filtering the radiation through a water bath. Capacitance data were obtained as a function of frequency (0.240 kHz to 20 kHz) and temperature (25-300K) using both an automatic self-balancing RLC bridge and a standard hand-balanced bridge. The self-balancing bridge was used in a 4-arm network configuration while the hand-balanced bridge was used in a 3-arm network configuration. Temperature variation of the samples was achieved by a closed-cycle refrigerator. Quartz specimens of similar dimensions with gold electrodes deposited under the same evaporation conditions were used to check the calibration of both bridges as the measurements were made. Two types of studies are reported herein: (i) dielectric properties at low temperature as a function of integrated light flux (i.e., as a function of defect density), (ii) dielectric properties as a function of temperature with constant defect density. Several hundred measurements have been made and all show similar features to that presented in Fig. 1 and Fig. 2 under similar conditions. Under constant light flux the dielectric properties, as shown in Fig. 1, are a function of time with the sample temperature held at 46K. The measurement shows a slow increase in capacitance for the first two hours. The two anomalies at 210 minutes and at about 270 minutes occurred when a DC magnet was twice brought (about 8 cm) toward and away from the sample with the magnetic flux lines approximately parallel to the sample surface (only one orientation was possible). The large dielectric anomaly at about 350 minutes occurred on continuous irradiation.

In order to study the temperature variation of the dielectric properties of the CuCl system under reasonably constant composite density, we utilized the following experimental configuration: Half of the single crystal surface was irradiated and the other half of the crystal, onto which the probe electrodes had been placed, was kept shadowed by an opaque mask. Repeated measurements using this configuration yielded results such as those shown in Fig. 2 for a typical run. The lower curve (□) represents a control run in which the dielectric properties were measured on an annealed crystal which was kept in the dark, while the upper curve (experimental points denoted by +) readily reveals a dielectric anomaly. The large sharp peak in both capacitance and tan δ is centered near 220K. As a function of time no dielectric anomaly is seen in these continually semi-illuminated samples if the temperature is held constant. Thus we conclude that constant equilibrium defect density has been attained in the unilluminated half of the sample.

Measurements made on samples which had long irradiation periods invariably exhibited features very similar to those depicted in Fig. 2. In the case of the pressed powder samples, increases in the dielectric constant were observed for 3-4 days following irradiation. When the experiment is repeated, features similar to those shown in Fig. 2 were always found in the samples. When the single crystal samples were brought up to room temperature, kept in the dark, and warmed to slightly above 60°C, the dielectric properties would revert to those shown in the control run. Independent evidence for the reproducibility of the phenomena described above was provided by measurements made at Bell Labs on pressed powder samples in a Deep Level Trap Spectrometer.[7]

In summary, a reproducible light induced dielectric anomaly at about 200K is observed in both pressed powder samples and single crystal samples. Measurements on the pressed powder samples show a dielectric anomaly which is broader and shows greater variation from sample to sample than do the single crystal samples.

The fractional changes reported here are large. If one considers that the 391 nm light is virtually completely absorbed by the surface, and does not penetrate the bulk, the measured dielectric properties have been changed dramatically. It is well-known that CuCl is a photochromic material and that Cu^0 forms as a result of light irradiation.[1] When light is shone on CuCl, a range of valency states is photoactivated. These states include electron-hole pairs, Cu^{1+}, Cl^-, and for large integrated photon flux free Cu^0 (from the disproportionation reaction) as a precipitate (most likely into dislocation planes[8]). We have shown that dielectric anomalies occur both as a function of integrated light intensity (which we assume increases the defect density) at constant temperature and that at constant density as a function of temperature, this latter anomaly (at approximately 200K) being correlated with previously reported dramagnetic shifts.[2,3,4]

There is no evidence for a classical structural phase transition in this temperature region (no structural change evidenced in examination under cross-polarizers or X-ray, or thermal neutron diffraction studies at 150K-250K) although the incipient instability of the CuCl lattice has been well documented.[9,10] Vardeny and Barfman[9] observe changes in light scattering spectra at these temperatures, and by analyzing their data and previous thermal neutron scattering data within the framework of a lattice dynamical model, they theorize that the CuCl lattice is incipiently unstable to a statistical displacement of the Cu atoms into the (111)-direction. Early measurements on exciton states in CuCl by Ueta and Gota[10] identified three different band structures and hence three different types of (structurally identical) CuCl crystals. Even under carefully controlled growth conditions if the samples are exposed to light and not stored under inert conditions, the material can have widely different properties. In fact exposure to too much oxygen or water vapor or light can fully deteriorate the samples. It is clear that in the case of the diamagnetic studies,[2,3,4] little was characterized besides structure and purity of the starting material; thus variability of results were to be expected.

The dielectric anomalies that we have observed in CuCl have a precedent in the structurally similar alkali halides. Sievers[11] originally showed that a soft defect mode in an alkali halide can give rise to a dielectric anomaly. Sack and Moriarti[12] have reported a dielectric anomaly at 15K when CN^-, NO_2^- and even Li^+ are added to KCl and related this directly to the dipolar properties of the defect system. Kanzig, et al.,[13] added impurities to alkali halide crystals and claimed ferroelectric behavior. This behavior was ascribed to dipolar properties of the impurities that were added to the KCl used in the experiments. Both Grannan, et al.,[14] and Fiory[15] observed an increase in dielectric constant as a function of defect density, the defects being introduced via substitutions of polar molecules and atoms (Li, OH, F, CN) and via noble metal seeding into the alkali halides. Fiory[15] also reports a decrease in the dielectric constant at very high defect densities and a dielectric anomaly as a function of temperature; he has discussed this in terms of the dipolar interactions of the impurities. Narayanamurti[16] reported frequency satellites; i.e., soft defect modes when KCN was added to KCl and KBr and noted anomalous strong coupling of the defect modes to the host phonons.

In conclusion we have observed a maximum in the dielectric properties of irradiated CuCl when either: (i) the temperature is held fixed (46.5K) and the integrated photon flux is increasing (time of exposure and density of photoactivated defects increasing) while the dielectric constant increases (by 300%) or (ii) the defect density is held at a low equilibrium level and the temperature is increasing while the dielectric constant increases (by 200%). Inspection of the highly irradiated samples revealed visible increases in the free copper density. We have sought an explanation for the observed dielectric anomalies. First we ruled out simple photoconduction because of the temperature dependence of the phenomena. Comparing our data to the previous studies on defect (polarization) centers in the alkali halides and keeping in mind that anomalies in the phonon spectra of CuCl occur in the same temperature region[6,9] as our observation (ii) above, we are led to interpret our results in terms of weak long range interactions between polarizable defects. We correlate the observed low frequency dielectric anomaly in CuCl with the softening of a vibrational mode associated with the optically enhanced polarizable Cu^0 defects in the CuCl lattice.

The proposed existence of a photoactivated defect induced soft mode phase in CuCl not only provides a ready interpretation for the herein reported dielectric anomaly; but it also provides the high dielectric constant and low frequency optical mode which serves as input to our theoretical treatment of high temperature superconductivity.[5] This calculation[5] follows that of Hurault[17] and Ginzberg[18] except that we introduce a mechanism for a large low frequency dielectric constant (observation reported herein). That is, Ginzberg extended Hurault's model of a heterogeneous superconductor of conducting particles embedded in an insulator. Both authors[17,18] introduced superconductivity of conduction electrons in the seeded metal particles via their interaction through excitons inherent to the insulating host. We proposed[5] a model based on new phonon branches occurring in an inhomogeneous system consisting of metallic-Cu particles surrounded by a hole plasma embedded in the CuCl matrix, the non-localized electrons interacting via the oscillations of the polarizable system.

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Figure Captions

Figure 1. Capacitance versus time for a single crystal sample held at 46.5K under 391 nanometer radiation. The extra two small peaks observed at about 190 and 250 minutes were due to DC magnetic excitation. Note that the abscissa is marked off in units of 33.33 minutes; however, the computer print-out of the 200.0-400.0 legend is not aligned correspondingly.

Figure 2. Dielectric constant of dark probed half of sample versus temperature for a single crystal sample with unprobed half of sample surface:
(a) in the dark (□); (b) under 391 nanometer radiation (+). Note that the abscissa is marked off in units of 30.0K; however, the computer legend print-out is incremented by 50.0K; thus only 0.0, 150.0, and 300.0 correspond to marks on the abscissa.

LME