

Pressure-induced phase transitions and shifts in the absorption edge of CuCl

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The dependence of the optical absorption edge on hydrostatic pressure has been investigated in CuCl up to 15 GPa. The absorption edge shifts abruptly at 4.8 and 9.0 GPa, as reported by Edwards and Drickamer, due to phase transitions from zinc blende \rightarrow tetragonal \rightarrow NaCl-type structure. From the shape of the absorption edge we conclude that in the zinc-blende and tetragonal phases, the lowest energy gap is direct and in the NaCl type it is indirect. In all the three phases the absorption edge shifts to higher energy with pressure at the rates: zinc blende, 1.78×10^{-2} eV/GPa; tetragonal, 2.1×10^{-2} eV/GPa; and NaCl type, 4.3×10^{-2} eV/GPa. These values yield -1 , -1.65 , and -5 eV for the deformation potentials of the gaps in the three phases, respectively. We compare our experimental values of these deformation potentials with the calculated ones for the zinc-blende phase. The energy gaps and deformation potentials for AgCl are discussed to obtain some insight into the electronic band structure of the NaCl phase of CuCl. Our data have revealed the new fact that the lowest energy gap (indirect gap) in the NaCl phase of CuCl is ~ 3.0 eV, which is lower than that in the zinc-blende phase. This is consistent with the behavior of other zinc-blende-type compounds undergoing a similar transition.

INTRODUCTION

The effect of high pressure on the optical absorption edge of CuCl was first investigated by Edwards and Drickamer¹ in 1961. These authors reported two abrupt changes: a large red shift (2000 cm^{-1}) near 4 GPa and a blue shift of similar magnitude near 12 GPa. Subsequent high-pressure x-ray studies²⁻⁴ have established that the zinc-blende form of CuCl transforms to a tetragonal structure near 4.8 GPa and the latter to the NaCl-type structure near 9 GPa. Evidently the abrupt shifts in the optical absorption edge of CuCl reported by Edwards and Drickamer¹ are related to these phase transitions. This connection has recently been verified by Piermarini *et al.*,⁴ by a combination of qualitative optical microscopic observations with high-pressure structure determinations in a diamond anvil cell. However, quantitative measurements of the shift in the absorption edge with good pressure calibration are lacking. Such measurements appeared worthwhile to us for a number of reasons: firstly, to establish the nature of the energy gap in the different high-pressure phases (direct or indirect); secondly, to compare the pressure coefficient of the energy gap of the zinc-blende phase with the deformation potential predicted in recent band-structure calculations; and thirdly, to see if there is any optical evidence for the insulator-metal transition which has been claimed in some recent publications to occur around 4 GPa (Ref. 5).

EXPERIMENTS

Single crystals of CuCl were prepared by the following procedure. CuCl powder of analytical grade from Merck was thoroughly washed in methanol containing 5% HCl and 2% dilute H_2SO_4 , and subsequently dried at 150°C for 24 h in inert atmosphere. The purified powder was melted in nitrogen atmosphere and slowly cooled to room temperature over a period of 72 h. The resulting material was distilled repeatedly in a sealed quartz tube, and large single crystals of 2 to 3 cm linear dimensions were obtained by sublimation growth over a period of 3-4 months.

High-pressure optical absorption data to 15 GPa were taken in a gasketed diamond anvil cell.^{6,7} The 200- μm aperture in the gasket was filled with a small crystal chip of CuCl. When pressed between the diamonds, the CuCl filled the entire aperture by flowing plastically and transmitted light freely. A small ruby chip (about 20 to 30 μm in size) was embedded in CuCl for pressure calibration. We did not use alcohol as a pressure transmitting fluid in the measurements reported here. Several attempts to perform measurements with the samples in alcohol did not yield reproducible results. We find from the shape of the R_1R_2 lines of ruby that the pressure distribution is nearly hydrostatic with the above arrangement; no sign of broadening of the R_1R_2 lines was observed up to 10 GPa. Two Beck objectives with Cassegrain mirror optics were used to focus the light to a

fine spot and to collect the light transmitted through the diamond cell. A 100-mm focal-length quartz lens placed at the appropriate distance next to the second Beck objective focused the transmitted light onto the slit of a Spex double monochromator. Conventional photomultiplier tube and electronics were used to measure the intensity of the light transmitted, with and without the sample, in the diamond cell.

The first-order transitions in CuCl, from the zinc-blende to the tetragonal phase near 4.5 GPa and from tetragonal to the NaCl-type structure near 8.0 GPa can be observed visually with a low-power microscope.⁴ At the zinc-blende to tetragonal transition, the transparent crystal is filled with dark brown filaments, which clear up as the pressure is increased slightly above the transition pressure. In the tetragonal phase the crystal appears slightly yellowish. At the tetragonal to NaCl-type transition, a bluish filamentary structure appears, which clears up when the crystal is fully transformed to the NaCl phase. These anomalies in the transmitted light are probably connected with the scattering of light at the boundaries of the two types of phases in the mixed phase region. When the pressure medium is hydrostatic, the transmission disappears and reappears abruptly⁴ at the transition points.

RESULTS

In Figs. 1 and 2 are shown the absorption data obtained in the region of stability of the zinc-blende, tetragonal, and NaCl-type phases. In Fig. 1 the transmission I/I_0 , where I_0 is the incident intensity without the sample and I with the sample, is plotted against photon energy. In Fig. 2 are shown the absorption coefficients plotted against photon energy for the three phases. The thickness of the sample was measured after pressure release and found to be $\sim 30 \mu\text{m}$. This value was used to calculate the absorption coefficient. The bending over of the curves of Fig. 1 at high values of the ordinate is produced by scattered light or light leakage in the sample and cell.

The absorption edge for the zinc-blende and tetragonal phases is well defined and sharp, whereas it is not for the NaCl phase. From this we conclude that in the former two phases the smallest energy gap is a *direct one* while in the latter phase it is *indirect*. In the tetragonal phase, of course, the edge is expected to be dichroic; probably we only see the lower-energy component, as the sample must have a random orientation. In all cases there is a weak absorption tail to the edge, but we attribute this to impurities or defect states in the crystal. In Fig. 3 we plot the energy

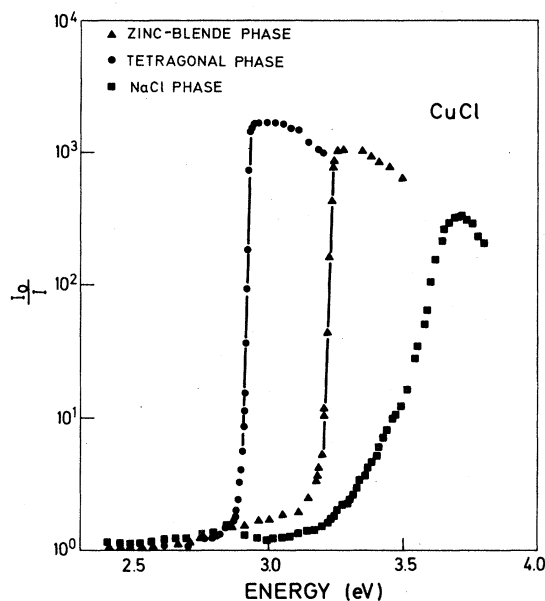


FIG. 1. Absorption edge of the zinc-blende, tetragonal, and NaCl-type phases of CuCl. The data of the three phases were obtained at 3.8, 5.8, and 13.2 GPa, respectively.

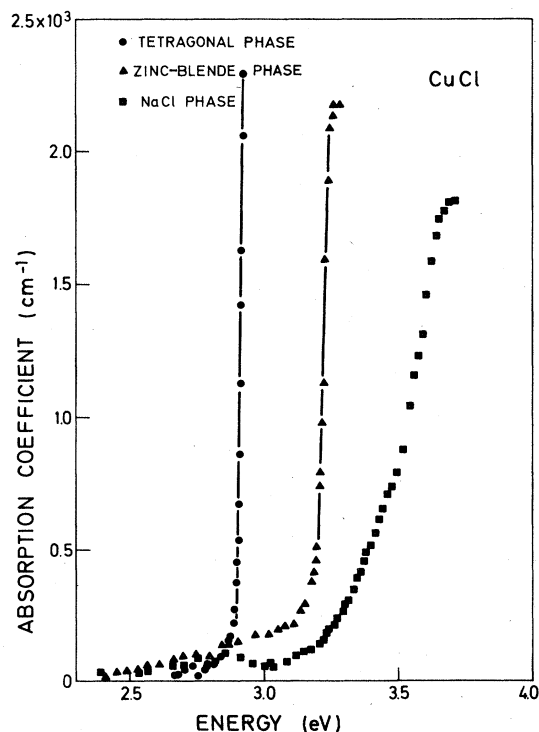


FIG. 2. Plot of the absorption coefficient α against energy for the zinc-blende, tetragonal, and NaCl-type phases at 3.8, 5.8, and 13.2 GPa, respectively.

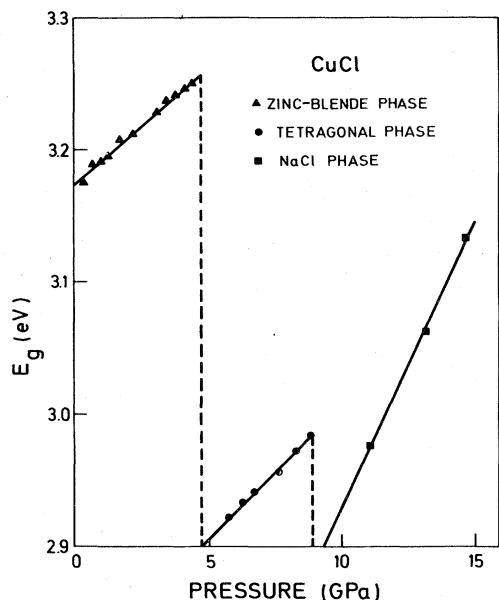


FIG. 3. Pressure dependence of the energy gap in CuCl. The decrease at about 4.8 GPa is due to the zinc-blende-tetragonal transition. The change near 9 GPa is due to the tetragonal NaCl-type transition.

gap as a function of pressure for all the three phases of CuCl. Many data points were obtained in the zinc-blende and tetragonal phases. We point out, however, that the point of maximum "reliable" absorption, limited by stray light in Fig. 2, lies for our samples at $\sim 2 \times 10^3 \text{ cm}^{-1}$, one order of magnitude below the peak of the exciton.¹⁵ We take this point, estimated to lie $\sim 80 \text{ meV}$ below the exciton peak, as our energy gap in the plot presented in Fig. 3 for the zinc-blende and the tetragonal phases. Despite the fact that the edges shown in Fig. 2 correspond to the lower tail of the exciton peak,¹⁵ we believe this definition of the edge will give correct pressure coefficients. In the case of the NaCl phase we have estimated the indirect gap by plotting the square root of the absorption coefficient (α) against energy and extrapolating the resulting straight line to zero absorption. The energy gap in the zinc-blende phase shifts to higher energy with pressure at the rate of $1.78 \times 10^{-2} \text{ eV/GPa}$. Again a blue shift is observed for the tetragonal phase at the rate $2.1 \times 10^{-2} \text{ eV/GPa}$. For the NaCl phase the indirect gap shifts blue at the rate of $4.3 \times 10^{-2} \text{ eV/GPa}$. We obtained just about the same value for the latter phase when the shifts with pressure of the absorption edge were taken at the absorption coefficient of 1×10^3 . The whole absorption edge shown in Fig. 2 for the rock-salt phase shifts uniformly with pressure.

DISCUSSION

The electronic band structure of CuCl in the zinc-blende phase has been investigated both experimentally and theoretically in many earlier studies.⁸ CuCl has a direct band gap of $3.2 \pm 0.1 \text{ eV}$ at room temperature (see Table I). The top of the valence band is derived primarily from Cu^+3d states ($\sim 75\%$ of the charge density for the $\Gamma_{15}(2)$ state, with $\text{Cl}3p$ states contributing 25%), while the conduction band at the center of the zone $\Gamma_1(2)$ is predominantly from $\text{Cu}4s$ states. There is a low-lying valence band $\Gamma_{15}(1)$ derived largely from $\text{Cl}3p$ states and a still lower $\Gamma_1(1)$ almost entirely of $\text{Cl}3s$ states.

The report of possible superconductivity⁵ in CuCl at high temperatures ($\approx 100 \text{ K}$) via the excitonic mechanism suggested by Abrikosov⁹ has stimulated new calculations of the electronic band structure of CuCl from first principles. In these calculations the motivation was largely to ascertain the possible existence of an indirect gap at energies lower than 1 eV , as proposed by Ruskov¹⁰ to satisfy the requirement of the Abrikosov mechanism. No evidence for such an indirect gap has been found in these recent calculations¹¹⁻¹⁴ and further, the gap remains direct even at reduced lattice parameters corresponding to 4.0 GPa; at pressures lower than 4.0 GPa diamagnetic and resistance anomalies have been reported.⁵

Of particular interest to this study are the calculated deformation potentials for the direct gap. We compare in Table II the calculated deformation potentials with the values obtained experimentally, including the present study. While all the values agree on the sign, there are differences in magnitude. Our experimental value is higher than those obtained by Edwards and Drickamer¹ and from the exciton measurements with pressure,^{15,16} but it falls within the limits of the theoretically predicted values. We believe that the present measurements have been obtained under more favorable conditions than previous ones (pressure more

TABLE I. Energy gaps in CuCl and AgCl.

		Zinc blende	Tetragonal	Rock salt
CuCl	direct	3.25	2.9 ^a	5.3 ^b
	indirect			3.0 ^c
AgCl	direct			5.5 ^d
	indirect			3.6 ^d

^a Measured in the present study at 5.0 GPa.

^b Estimated (see text).

^c Measured in the present study at 11.1 GPa.

^d Reference 17 (see also Ref. 27).

TABLE II. Deformation potentials for CuCl and AgCl in eV.

		CuCl				AgCl	
zinc blende		-1 ^a	-0.4 ^b	-0.3 ^c	-2.3 ^d	-2.2 ^e	NE ^f
tetragonal		-1.65 ^a					NE ^f
rock salt	indirect	-5 ^a					+0.65, ^g +0.51 ^g +0.1 ^h
	direct						-2.70, ^g -2.77 ^g -4.2 ⁱ

^a Present results obtained using the equation of state data of Piermarini et al.⁴

^b References 1 and 6.

^c Reference 14.

^d Reference 13.

^e Reference 12.

^f NE: Nonexistent.

^g Experimental values from Refs. 19 and 20.

^h Indirect edge, calculated theoretically, Ref. 18.

ⁱ Direct edge, calculated theoretically, Ref. 18.

hydrostatic and better known than in Ref. 1, pressure range larger than in Ref. 16 and, further, in the study reported in Ref. 16 the films were attached to quartz substrates and thus somewhat nonhydrostatically strained). Hence our data are likely to be closer to the true value for the deformation potential.

Unfortunately no band-structure calculations exist for the high-pressure phases of CuCl and hence we have no direct way of comparing the observed gaps and pressure coefficients with theoretical predictions. However, for the NaCl phase of CuCl we may anticipate the general features of the electronic band structure to be similar to those of AgCl.¹⁷ In AgCl the lowest conduction band is *s*-like (Ag⁺ 4*s* states) with a minimum at the Γ_1 point. In the valence band, the halogen *p* states lie above the Ag⁺ 4*d* states at $\vec{k}=0$. Contrary to the zinc-blende case, in the rock-salt structure with inversion symmetry, *p* and *d* states do not mix at $\vec{k}=0$ (Γ point). Away from Γ , however, *p* and *d*-like states mix, leading to a higher-lying maximum for the valence-band structure away from $\vec{k}=0$. The highest of these maxima are believed to be at L'_3 , nearly degenerate with maxima along Σ . Consequently AgCl has an indirect edge of ~3.7 eV ($\Gamma_1 - L'_3$). The direct edge ($\Gamma_1 - \Gamma_{15}$) occurs at an energy of 5.5 eV (see Table I).

Theoretical calculations for AgCl as a function of lattice parameter¹⁸ indicate that while the direct gap shifts blue with pressure, the indirect gap shifts slightly red.^{19,20} The data for AgCl obtained in the calculations and the results of present measurements on the NaCl phase of CuCl are shown in Table II. Our data for the NaCl phase of CuCl clearly indicate a blue shift, at variance with the

situation in AgCl. We should point out, however, that in rock-salt-type CuCl and *p* (Γ_{15}) and *d* ($\Gamma_{25'}$) valence band are supposed to be reversed with respect to their order in AgCl.⁸

The various mechanisms which cause states to shift in energy with pressure are the following¹⁸: intrinsic broadening, change in hybridization (e.g., *p-d*), and change in Madelung energy. In the case of AgCl the Γ_{15} valence state is nonhybridized and largely halogen *p*-like. Decreasing the lattice parameter leads to a relative lowering in energy of Γ_{15} due to the change in the Madelung energy. The Γ_1 conduction state, which is derived largely from Ag *s*-like states, rises in energy relative to Γ_{12} as the lattice contracts. Hence the $\Gamma_1 - \Gamma_{15}$ -energy separation is strongly affected by a change in the lattice constant, accounting for the large blue shift of the direct gap, calculated and observed for AgCl.¹⁷⁻²⁰ On the other hand, the valence-band edge at L'_3 tends to move away from Γ_{15} as the lattice contracts and the *p-d* hybridization increases. It thus tends to move more in step with Γ_1 , resulting in a smaller deformation potential for the indirect gap, or even possibly a sign reversal (red shift).¹⁹⁻²⁰ The explanation for the different behavior of the indirect edge of the NaCl phase of CuCl from that of AgCl has to await results of band-structure calculations.

Perhaps the most striking difference between our results and those of Edwards and Drickamer¹⁹ concerns the NaCl phase of CuCl. Whereas the plot of Edwards and Drickamer of the energy gap as a function of pressure indicates a sharp rise in the gap in going from the tetragonal to the NaCl phase, by about the same magnitude as the sharp decrease in the zinc-blende to the tetragonal phase transition, our plot shows a small drop in the en-

ergy gap at the tetragonal to the NaCl phase transition. Such a behavior, the result of our having defined the gap as the point at which $\alpha = 0$, would be consistent with the behavior of other semiconductors which undergo the zinc-blende to NaCl transition.^{21,22} Further, our data demonstrate that the lowest energy gap in the NaCl phase is indirect. The magnitude of the absorption coefficient shown for this phase in Fig. 2 is similar to that observed for AgCl in the same energy range above the indirect edge.²³ By using the tight-binding parameters of Ref. 24 for zinc-blende CuCl and the Hamiltonian of Ref. 25 we estimate the direct gap of the NaCl phase of CuCl to be about 5.3 eV. Unfortunately neither do our data extend into the ultraviolet (the diamond windows cut off at 4.5 eV) nor is the thickness of our sample appropriate to see this direct edge.

We have not seen any optical evidence for a metal-insulator transition in CuCl up to a pressure of 15 GPa, but we observed darkening of the sample when exposed to laser radiation (e.g., 5146 Å) while carrying out pressure experiments on the zinc-blende phase, as reported by Chu *et al.*²⁶ However, such darkened areas cleared up when the crystal transformed to the tetragonal or the NaCl phase. Evidently, exposure to high-intensity light causes some damage to the crystal (possibly segregation of Cu clusters) in the zinc-blende phase, which does not occur in the high-pressure phases. Also, darkening which was seen while the

phase transition was taking place, cleared up immediately after the transition was completed.

SUMMARY AND CONCLUSIONS

In summary our findings are as follows: (1) The energy gap of CuCl is direct in the zinc-blende and tetragonal phases and indirect in the NaCl phase. (2) The deformation potential for the direct gap in the zinc-blende phase agrees in sign with the theoretical calculations and other experiments but has a value higher than any measured hitherto. (3) The deformation potential for the indirect gap in the NaCl phase has the opposite sign to the theoretically calculated value for the indirect gap in AgCl. (4) The lowest energy gap in the NaCl phase of CuCl is smaller than that of the zinc-blende phase, which is consistent with the behavior of similar compounds exhibiting this transition. (5) There is no evidence for a metal-insulator transition.

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