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Deformation Potentials for Excitons in Cuprous Halides[†]

J. B. Anthony* and A. D. Brothers

Department of Physics, Benedictine College, Atchison, Kansas 66002

and

D. W. Lynch

Department of Physics and Institute for Atomic Research, Iowa State University, Ames, Iowa 50010

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The hydrostatic-pressure shifts of the $Z_{1,2}$ and Z_3 exciton peaks were measured in thin films of cubic CuCl, CuBr, and CuI at 90 K. That of the E_1 peak in CuI also was measured. The deformation potentials of all Z excitons and of the E_1 exciton in CuI, about -1 eV, are more than twice those of the Z excitons in CuCl and CuBr. This suggests the two valence bands in CuI may be considerably more mixed than in CuCl and CuBr.

I. INTRODUCTION

The cuprous halides, CuCl, CuBr, and CuI, are insulators whose band structures have been considered to be related to those of the group-IV, -III-V, and -II-VI cubic semiconductors, when account is taken of the increased ionicity.^{1,2} They are cubic (zinc-blende structure) below about 640 K.³⁻⁵ Cardona² measured the absorption spectra of these compounds and found two sharp peaks at low energy and a stronger peak at higher energy. Up to that time, it was believed that the valence band was largely composed of halogen- p -like functions. The splitting of the two lowest-energy peaks was interpreted as a spin-orbit splitting, since it increased from chloride to bromide to iodide, but because it was smaller than the spin-orbit splitting of the halogen, an appreciable Cu- $3d$ component was believed to be present in the valence band. The positions of the band edges could not be reconciled with predictions from the gaps in III-V and II-VI compounds.²

Song^{6,7} calculated energy bands for CuCl. He found that there were two valence bands, with a gap of about 2 eV between them (Fig. 1). At the center of the zone, the uppermost band is derived primarily from Cu⁺- $3d$ levels ($\sim 80\%$ of the charge density for the Γ_{15} state) while the lower is predominantly from Cl⁻- $3p$ levels ($\sim 80\%$ for the lower Γ_{15}). He showed that only the lower band was to be associated with the valence band in cubic semiconductors, and its position could be extrapolated with reasonable accuracy from band gaps in cubic semiconductors.

The exciton spectrum of CuCl consists of a sharp line called the Z_3 line, followed at higher energy by the $Z_{1,2}$ line, which often is split into two by strain.⁸ According to Song⁷ these originate from the spin-orbit-split Γ_{15} levels, Γ_7 and Γ_8 , respectively, both in the upper valence band (Fig. 1). The lower valence band gives a series of absorption structures, beginning with a peak called E_1 and extending into the vacuum ultraviolet.² The E_1 peak originates at the lower Γ_{15} level and corresponds to the lowest-energy direct exciton at Γ in the group-IV, -III-V, and -II-VI semiconductors.

The E_1 peak is stronger than the $Z_{1,2}$ and Z_3 peaks, and is "allowed," while the $Z_{1,2}$ and Z_3 peaks correspond roughly to dipole-forbidden atomic transitions, Cu⁺ $3d \rightarrow$ Cu⁺ $4s$, that are allowed at $\vec{k} = 0$ by the admixture of Cl⁻ $3p$ wave functions. CuBr presumably has a similar set of valence bands, and so might CuI, but in both of these, the $Z_{1,2}$ line is at lower energy than the Z_3 line,² indicating a reversal of sign of the spin-orbit parameter. The gap between the lower and upper valence bands may diminish in CuBr and CuI. (The $Z_{1,2} - E_1$ separations diminish.) The two valence bands then would become more mixed in atomic-wave-function character. (In AgCl, the Cl⁻ $3p$ and Ag⁺ $4d$ states completely mix, except at a few points, into one complicated valence band.^{9,10} Extensive mixing should make the $Z_{1,2}$ and Z_3 absorption peaks stronger with respect to the E_1 peak, but this does not seem to be the case.²

Measurements of the hydrostatic-pressure coefficient of band gaps have shown that, within a group of materials of identical crystal structure and simi-

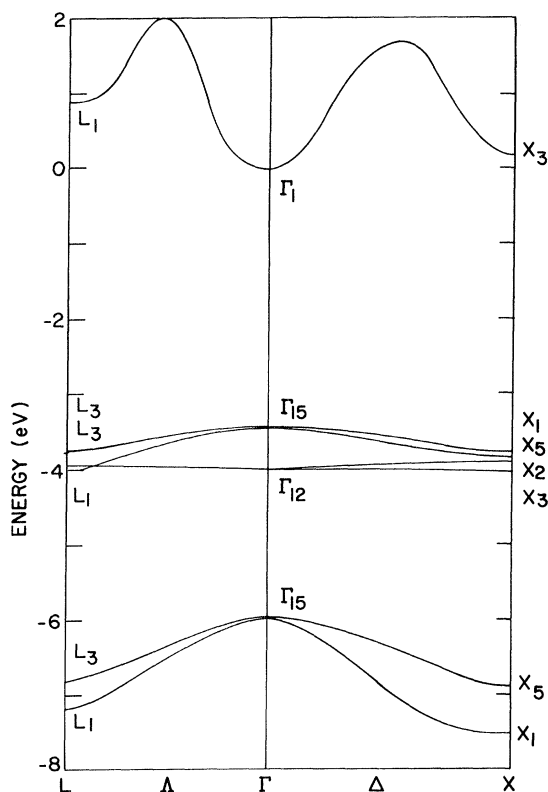


FIG. 1. Conduction band and two highest valence bands as calculated for CuCl by Song (Ref. 7).

lar binding, the band gaps vary with pressure, or volume, with coefficients depending only on the symmetries of the states at the edges of the gaps. For example, in group-IV and -III-V semiconductors, the values of $(\partial E/\partial P)_T$ are dependent primarily on the symmetry of the states and not on the nature of the atoms.¹¹ In alkali and silver halides, the deformation potential $(\partial E/\partial \ln V)_T$ seems to be better than $(\partial E/\partial P)_T$ for characterizing energy gaps, and it too seems to depend primarily on the symmetry of the states at the gap edges.¹² Recent work^{13,14} indicates that the $\Gamma_{15} - \Gamma_1$ transition in

II-VI compounds is not characterized by nearly constant values of $(\partial E/\partial P)_T$ or of $(\partial E/\partial \ln V)_T$, so extrapolation to the cuprous halides is not possible.

II. EXPERIMENTAL

Thin films of cuprous halides were evaporated on quartz substrates at room temperature. Film thicknesses were 500–2000 Å. The absorption spectra of these films showed only peaks characteristic of the cubic phase.² Upon cooling to liquid-nitrogen temperature, these peaks became sharper, indicating that differential contraction between film and substrate was not badly straining the films. A film of CuBr on a Pyrex substrate gave results indistinguishable from those obtained on quartz.

Spectra were run on a Cary-14 spectrophotometer with the samples at 90 K in a previously described^{15,16} high-pressure cell using helium as a pressure fluid. Data were taken in the range 1.0–3.5 kbar. The experimentally observed pressure shifts of the exciton peaks are given in Table I. Our values for the positions of the $Z_{1,2}$ and Z_3 peaks are not in good agreement with those of Cardona,² but are quite close to those in more recent work on films and single crystals.^{17–23} Typical scatter of the data about a straight line (Fig. 2) was a few percent, but sample-to-sample differences in the values of $(\partial E/\partial P)_T$ of about 10% occurred.

Edwards and Drickamer²⁴ have measured $(\partial E/\partial P)_T$ of the absorption edge of polycrystalline slabs, using the shift of the energy at which the absorption coefficient was 15 cm^{-1} in CuCl. They obtained $(\partial E/\partial P)_T = +0.7 \times 10^{-6} \text{ eV bar}^{-1}$ for CuCl, substantially in agreement with our value for the first exciton peak; approximately zero for CuBr; and $-4.1 \times 10^{-6} \text{ eV bar}^{-1}$ for CuI. The latter disagrees with our result in sign as well as magnitude. They also observed a peak at 3.3 eV in CuCl ($Z_{1,2}$, Z_3 , presumably) and found its pressure shift to be $+0.74 \times 10^{-6} \text{ eV bar}^{-1}$, in agreement with the absorption edge value.

We have converted our values of $(\partial E/\partial P)_T$ to deformation potentials via the equation

TABLE I. Excitons in cubic cuprous halides.

	CuCl	CuBr	CuI
Peak positions at 90 K (eV) ^a (0 bar)			
$Z_{1,2}$	3.288	2.979	3.060
Z_3	3.220	3.123	3.694
E_1	(6.45)	(5.60, 5.48)	5.10, 4.8
$(\frac{\partial E}{\partial P})_T$ in $10^{-6} \text{ eV bar}^{-1}$			
$Z_{1,2}$	+0.9	+0.4	+2.9
Z_3	+0.9	+0.9	+4.0
E_1

^a Figures in parentheses from Ref. 2.

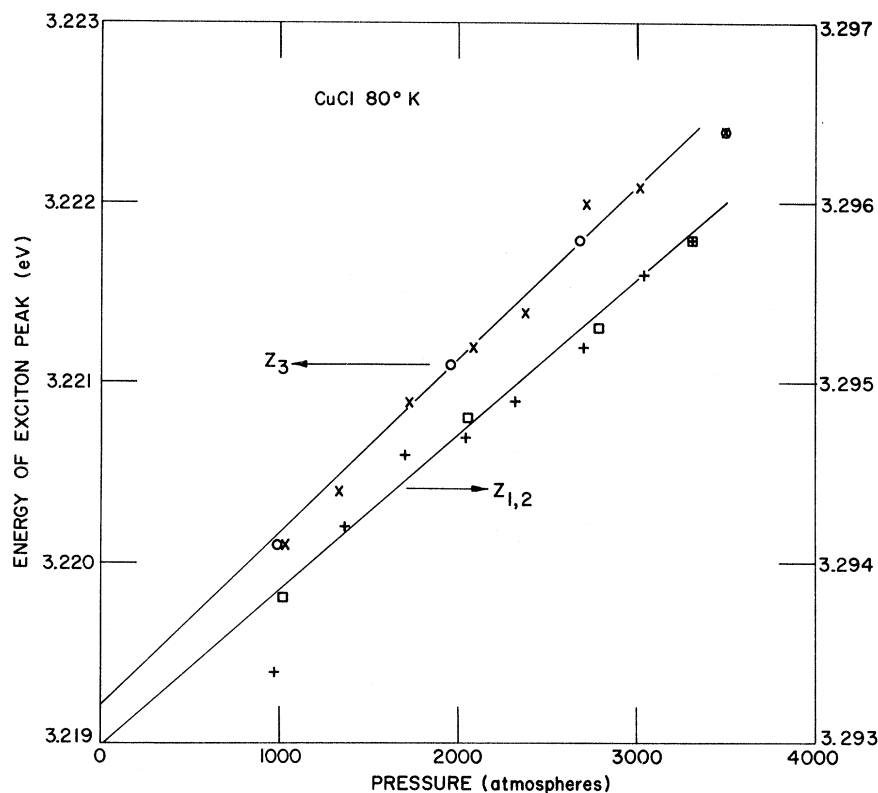


FIG. 2. Position of exciton peaks in CuCl at 90 K vs pressure. The film was 1200 Å thick. Circles (square) and crosses (plus) represent data taken with increasing and decreasing pressure, respectively. The lines are least-squares fits and have slopes of 8.94 and 4.61×10^{-7} eV/atm.

$$\frac{\partial E}{\partial(\ln V)} = K^{-1} \left(\frac{\partial E}{\partial P} \right)_T, \quad (1)$$

where K is the compressibility, for which Bridgman's values²⁵ were used (Table II).

III. DISCUSSION

One sees immediately that the deformation potentials (or pressure shifts, since the compressibilities vary by less than 20%) for the first exciton peaks in CuCl and CuBr are essentially the same, while that for CuI is considerably larger. The higher-energy exciton peak involves a hole in the lower (spin-orbit-split) part of the valence band. Since both holes are in states derived from the upper Γ_{15} level in Fig. 1, they are expected to have charge densities with the same spatial symmetry, so that similar pressure or volume shifts are expected on either an ionic or covalent²⁶ model. Both peaks in CuCl and CuBr have essentially the same pressure shifts, while they appear to be different for CuI. (When errors, previously estimated as 10%, are considered, the two pressure coefficients, in units of 10^{-6} eV bar⁻¹, are 2.9 ± 0.3 and 4.0 ± 0.5 for the $Z_{1,2}$ and Z_3 peaks, respectively, in CuI.) The small shifts for CuCl and CuBr are manifestations of the fact that the transitions are quite localized on one ion. A peak in CuI at 3.18 eV has been interpreted by Ueta *et al.*¹⁸ as an exciton bound

at an imperfection. It has been observed in films and in single crystals. Its temperature and pressure coefficient are similar to those for the free exciton Z_3 and $Z_{1,2}$ peaks.

The E_1 exciton in CuCl originates from a different valence band, separated from that for the $Z_{1,2}$ and Z_3 excitons by a distinct gap, as is probably true for CuBr and CuI.⁷ Unfortunately the E_1 exciton could not be measured in CuCl in the present work, being at too short a wavelength. While the E_1 peak in CuBr (actually a doublet) was in our wavelength range, the data scattered too badly for us to estimate $(\partial E/\partial P)_T$. In CuI the E_1 doublet was not well resolved. The average shift of the pair with pressure is given in Table I. The value of $(\partial E/\partial P)_T$ for the E_1 exciton is not in agreement with that for the $\Gamma_{15} - \Gamma_1$ transition in group-IV and -III-V semiconductors,¹¹ $+12 \times 10^{-6}$ eV bar⁻¹, nor is the deformation potential. The pressure shift of the E_1 exciton in CuI is unlike that of the $Z_{1,2}$ and

TABLE II. Deformation potentials (eV) for excitons in cubic cuprous halides.

	CuCl	CuBr	CuI
$Z_{1,2}$	-0.4	-0.2	-1.0
Z_3	-0.4	-0.3	-1.4
E_1	-1.1

Z_3 excitons in CuCl and CuBr, but quite close to that of the $Z_{1,2}$ and Z_3 peaks in CuI. The holes in the valence bands (in CuCl) are partially localized about different ions: Cu^+ for $Z_{1,2}$ and Z_3 and Cl^- for E_1 . Such similarities in $(\partial E/\partial P)_T$ for $Z_{1,2}$ and Z_3 and E_1 excitons in CuI are unexpected, and may be fortuitous, but they could arise if the gap between the uppermost valence bands is missing, or is very small, and the ten Cu^+3d electrons and six $\Gamma-5p$ electrons form, or almost form, one broad valence band complex with critical points similar to those in CuCl and CuBr. In this way the exciton spectrum would persist, but with altered $(\partial E/\partial P)_T$ values for all excitons, as observed. Better evidence is needed before this description of the valence bands in CuI can be accepted.

It would be of value to relate the observed exciton peak shifts to those of the band gap. This requires an estimate of the pressure dependence of the exciton binding energy B . For Wannier excitons $(\partial B/\partial P)_T \approx -2B(\partial \ln \epsilon/\partial P)_T$, where ϵ is an effective dielectric constant. For CuCl, Nikitine *et al.*²⁷ find $B = 0.189$ eV and $\epsilon = 5.41$, between the optical and static dielectric constants of 3.8 and 7.4. Unfortunately $(\partial \epsilon/\partial P)_T$ is not known, nor is $\partial \epsilon/\partial T$ from which an estimate of $(\partial \epsilon/\partial P)_T$ could be made. For alkali halides, $(\partial \ln \epsilon/\partial P)_T$ is about²⁸ $(5-10) \times 10^{-6} \text{ bar}^{-1}$, leading to $(\partial B/\partial P)_T \approx -(2-4) \times 10^{-6} \text{ eV bar}^{-1}$, much larger than our observed shift. This value is probably an upper limit for the binding-energy pressure shift, but it is so large we cannot equate even roughly the exciton pressure shift with that of the band gap.

From values of $(\partial E/\partial T)_P$, the observed temperature shift, and $(\partial E/\partial P)_T$, the measured pressure shift, one can determine what part of the former arises from thermal expansion, and what part, $(\partial E/\partial T)_V$, from the electron-phonon interaction via the equation

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V - \frac{3\alpha}{K} \left(\frac{\partial E}{\partial P}\right)_T. \quad (2)$$

α is the linear-expansion coefficient and K is the compressibility. Good values for $(\partial E/\partial T)_P$ for the cuprous halides unfortunately do not exist. $(\partial E/\partial T)_P$ is zero at 0 K, and increases in magnitude with increasing temperature, reaching a constant value above a temperature characteristic of the phonon spectrum. α also behaves similarly while

K and $(\partial E/\partial P)_T$ are relatively temperature independent. Kaifu *et al.*²² have shown that $(\partial E/\partial T)_P$ is constant, $+2.5 \times 10^{-4} \text{ eV K}^{-1}$ between 10 and 90 K for the Z_3 peak in CuCl. Cardona's average $(\partial E/\partial P)_T$ between 4 and 300 K is about half this, indicating a possible change in $(\partial E/\partial T)_P$ above 90 K. (The positive sign is not often found in solids.) One would like to use values of $(\partial E/\partial T)_P$ and α at a temperature high enough that both are sensibly constant. Because $(\partial E/\partial P)_T$ is so small for the Z_3 peak in CuCl, $(\partial E/\partial T)_V$, when evaluated from the above formula using the 3α value given by Mayer,²⁹ turns out to be positive with either Cardona's or Kaifu's value of $(\partial E/\partial T)_P$. $(\partial E/\partial T)_V$ is expected to be negative on a simple model, but exceptions exist.³⁰ In the case where $(\partial E/\partial T)_V$ is positive, its interpretation in terms of the temperature dependence of the electron-lattice coupling is quite complicated.³¹ Whether such a positive value of $(\partial E/\partial T)_V$ really exists for CuCl (and CuBr) must await further measurements of $(\partial E/\partial T)_P$ on single crystals above 90 K. It is interesting to note that for the $Z_{1,2}$ peak in CuI, $(\partial E/\partial T)_P$ is about zero between 4 and 80 K,²⁰ leading to a small negative value of $(\partial E/\partial T)_V$.

IV. SUMMARY

The exciton deformation potentials we have measured for cuprous halides cannot be interpreted fully without accurate knowledge of the temperature dependence of the exciton-peak position. (Data at 4, 78, and 300 K are probably insufficient.) They cannot be related to the band-gap deformation potentials because the pressure dependence of the exciton binding energy may be comparable to, or even larger than, the small observed exciton deformation potentials. A rough estimate of the pressure shift of the exciton binding energy can be made when the pressure (or temperature) dependences of the static and optical dielectric constant are available. Despite this, it is clear that the exciton in CuI is in one way dissimilar from that in CuCl and CuBr.

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*Present address: Department of Physics, Lehigh University, Bethlehem, Pa. 18015.

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Elastic Constants of RbF from 300 to 4.2 K*

C. R. Cleavelin, D. O. Pederson, and B. J. Marshall

Department of Physics, Texas Tech University, Lubbock, Texas 79409

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The adiabatic elastic constants have been measured in single crystals of rubidium fluoride over the temperature range of 300 to 4.2 K to investigate a discrepancy with neutron scattering data. The values of the elastic constants at 0 K, extrapolated from 4.2 K, are $C_{11} = 6.527$, $C_{44} = 0.952$, and $C_{12} = 1.255$ in units of 10^{11} dyn/cm². The Debye characteristic temperature at 0 K (Θ_D) as calculated from the elastic constants is $\Theta_D = 221.0$ K. A summary of Debye temperature values calculated from elastic constant data at 0 K is presented for all previously measured face-centered-cubic alkali halides.

INTRODUCTION

Recently Raunio and Rolandson¹ have obtained the phonon dispersion relations for RbF by using inelastic scattering of thermal neutrons. The elastic constants of RbF were calculated at 80 K by utilizing the dispersion curves for small wave vectors. A comparison of these elastic constants with those obtained from an extrapolation of Haussühl's² room-temperature thermoelastic constants showed acceptable agreement for C_{44} and C_{12} but not for C_{11} .

Because of the large discrepancy in the two calculated values of C_{11} , we have measured the temperature dependence of the elastic constants of RbF from 300 to 4.2 K.

EXPERIMENTAL

The single-crystal specimens used in these

measurements were approximately cylindrical with a diameter of 1.6 cm and a length of 2.5 cm. The crystals were obtained from Semi-Elements Inc. with the end faces of one crystal oriented perpendicular to the [100] axis and the end faces of the other oriented perpendicular to the [110] axis. The orientations were checked in this laboratory by means of x-ray Laue backreflections. Since RbF is extremely hygroscopic, preparation of the crystal was accomplished in a helium atmosphere. The crystals were aligned to within 1° of the desired directions. The end faces were polished parallel to within ± 0.001 cm.

Because of the symmetry of a cubic crystal, there are only three independent elastic constants: C_{11} , C_{44} , and C_{12} .³ To obtain C_{11} and C_{44} one simply measures the velocities (V) of 10-MHz longitudinal