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Photoelasticity of the cuprous halides

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We present our acousto-optic measurements of the photoelastic tensor of the cuprous halides, CuCl, CuBr, and CuI. The data include the magnitudes and signs of the coefficients and their optical wavelength dependence. Several distinct trends are observed as a function of ionicity both within the halides and in the isoelectronic and isostructural sequence Ge, GaAs, ZnSe, CuBr. Particularly interesting results are found for the infinite-wavelength limits. We find that p_{44} is very nearly the same in all the materials considered, whereas $(p_{11} - p_{12})/2$ grows monotonically on going from Ge to CuBr; $(p_{11} - p_{12})/2$ is approximately equal to p_{44} in the halides, indicating isotropy of the direct photoelastic tensor. The hydrostatic coefficient goes monotonically from a large negative value in Ge to a positive value in the halides—the only known tetrahedrally coordinated binary semiconductors to have positive coefficients. We believe this implies that the deformation potential of the average optical gap is nearly zero.

The cuprous halides CuI, CuBr, and CuCl are members of the family of tetrahedrally coordinated A^nB^{8-n} binary semiconductors. Within the context of this family, the halides manifest many extreme properties. Phillips[1] has pointed out that increasing ionicity weakens the stability of the tetrahedral coordination. A Phillips ionicity of ~0.78 seems to separate the four-coordinated from six-coordinated binary compounds. (As pointed out by Pantelides[2] and others, the zinc-blende and rock-salt structures are, in fact, quite similar; both have fcc Bravais lattices but the AB basis direction is sheared from [111] in zinc blende to [100] in rocksalt.) The ionicity of the cuprous halides places them just below this transition. In fact, the more ionic CuF is not known to exist in a four-coordinated structure. The incipient structural instability is rather dramatically demonstrated by the large softening of the reduced shear and bulk moduli relative to the other tetrahedrally coordinated materials.[3,4] Moreover, at elevated temperatures (~350 °C) CuI and CuBr become superionic conductors.[5] Other extreme values have been found for the piezoelectric[3] and nonlinear optical[6] coefficients. In this paper we report the results of our measurements of the photoelastic coefficients. They too show that the cuprous halides are extremal members of the four-coordinated family. For example, the cuprous halides are the only materials in the family known to have positive values for the "hydrostatic" photoelastic coefficient.

The strain-induced change in the optical susceptibility of a material is called the photoelastic effect. The photoelastic tensor p is defined by the linear relation

$$(\Delta\epsilon^{-1})_i = p_{ij}e_j, \qquad (1)$$

where e is the strain (cf. Nye[7] for explanation of the contracted tensor notation). For cubic materials there are three independent coefficients p_{11}, p_{12}, and p_{44} or equivalently an effective hydrostatic coefficient $\frac{1}{3}(p_{11} + 2p_{12})$ and two purely shear coefficients $\frac{1}{2}(p_{11} - p_{12})$ and p_{44}.

The three acousto-optic techniques for measuring the absolute magnitudes,[8] signs,[9] and relative dispersion[10] of the photoelastic coefficients have been described elsewhere. The photoelastic magnitude and dispersion are derived from measurements of the acousto-optic scattering cross sections, which in turn depend on the quantity $p^2n^6/\rho v^3$. Here p and n are the photoelastic coefficient and refractive index at a given optical wavelength and ρ and v are the density and acoustic-mode velocity, respectively. We have used values of $n(\lambda)$ interpolated from the data of Chemla *et al.*[11] and v from Hanson *et al.*[3] We have used our measured values of ρ, which agreed with the x-ray values to better than 0.1% ($\rho_{\text{x ray}} > \rho_{\text{meas}}$). The samples were prepared by the traveling-solvent technique.[12] Longitudinal- and shear-mode pulses were transmitted along the [100] direction. The acoustic faces were prepared parallel to (001) planes to better than 1°. It might be noted here that to obtain sufficiently good Laue x-ray patterns for sample alignment, an etch had to be used to remove the surface-damaged layer. A fresh dilute HNO_3 etch was used for this purpose.

The results of the individual photoelastic coefficients normalized to the value at 633 nm, are

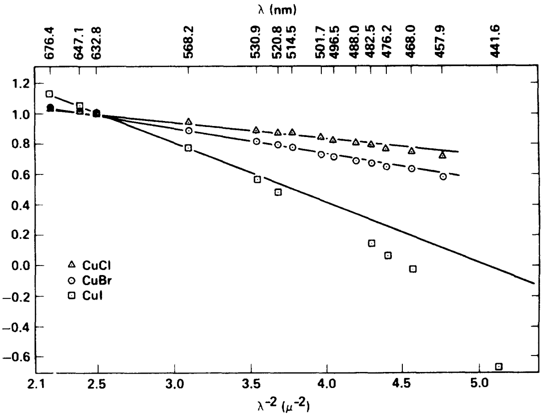

FIG. 1. Dispersion of p_{11} normalized to the value at 633 nm.

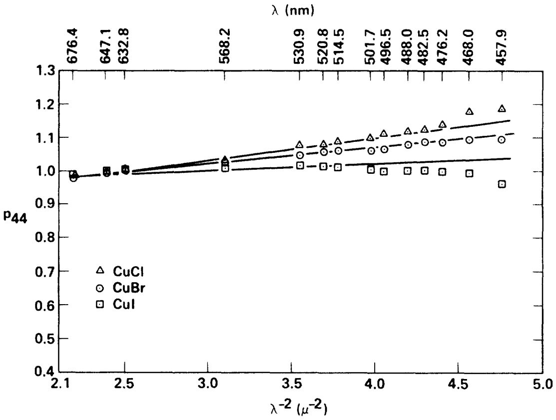

FIG. 3. Dispersion of p_{44} normalized to the value at 633 nm.

shown in Figs. 1–5. Each point is the average of many runs at different positions in the sample and different acoustic frequencies. The reproducibility is of the order of the symbol size. In Table I we present the values of the individual coefficients at 633 nm. We also give, for comparison, the piezobirefringence data of Schwab and Robino[13] also measured at 633 nm. (Note that an erroneous typographical shift in the decimal of the data of Ref. 13 has been corrected here.) The straight line drawn for each set of points is the least-squares fit of the values of p vs λ^{-2} for $\lambda \geq 568.2$ nm. Because of time-reversal invariance of the Hamiltonian, no odd powers occur in an expansion of p in terms of energy (or $1/\lambda$). Therefore, for energies well below the lowest absorption edge, $(\lambda_a/\lambda)^2$ is small and the quadratic term dominates the dispersion. Calculation of the coefficient of this quadratic term requires accurate knowledge of the pressure dependence of the band structure throughout the Brillouin zone. Such a calculation has not been performed for the cuprous halides.

For the isoelectronic sequence Ge,[14] GaAs,[14] and ZnSe,[15] the dispersion in $p_{11}-p_{12}$ and p_{44} has been shown to deviate strongly from the linear behavior as the absorption edge is approached. The deviation occurs consistently at lower energies for $p_{11}-p_{12}$ than for p_{44}. In all cases the coefficients go through zero and seem to be diverging at the absorption edge. Continuing in the isoelectronic sequence to CuBr (and for the cuprous halides in general) the same characteristics appear to be valid; although, in this study the downward deviation in p_{44} is quite weak, and clear only in CuI. For Ge and GaAs Higginbotham *et al.*[14] have demonstrated that the sign of $p_{11}-p_{12}$ and p_{44} at zero energy is determined by the strain dependence of the E_2 gap. The contribution of the E_0 and E_1 gaps at low energy are much weaker and of opposite sign. The E_0 contribution, however, becomes resonant near the absorption edge with the same frequency dependence for both shear coefficients but with p_{44} having the smaller weighting.

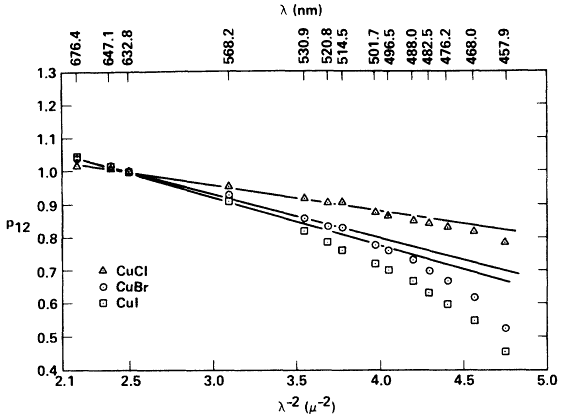

FIG 2. Dispersion of p_{12} normalized to the value at 633 nm.

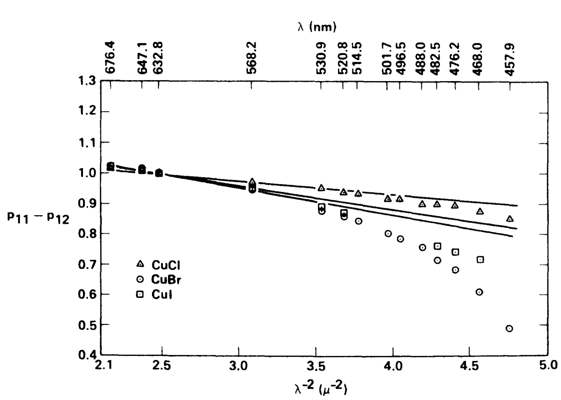

FIG. 4. Dispersion of p_{11}-p_{12} normalized to the value at 633 nm.

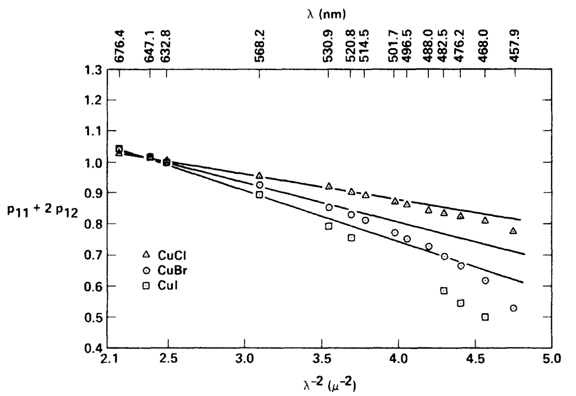

FIG. 5. Dispersion of $p_{11}+2p_{12}$ normalized to the value at 633 nm.

The zero crossing thus occurs nearer the edge for p_{44} than for $p_{11}-p_{12}$. Because ZnSe and the cuprous halides appear to manifest the same general behaviors below their absorption edges, and lacking any detailed pressure-dependent band-structure calculations, we make the following hypotheses. For the entire isoelectronic sequence the E_2 gap dominates the zero-energy limit of the photoelastic coefficients. Further, the strong dispersion below the edge is dominated by the strain dependence of (or excitonic effects associated with) E_0, which is opposite to that of E_2.

It is particularly interesting to investigate the results of the data extrapolated to zero energy. In Table II we have presented our data for the two shear coefficients $\frac{1}{2}(p_{11}-p_{12})$ and p_{44}, and the average hydrostatic coefficient $p_h \equiv \frac{1}{3}(p_{11}+2p_{12})$ a scalar quantity, which from Eq. (1) is

$$p_h = -\frac{\epsilon-1}{3\epsilon^2}\frac{d\ln(\epsilon-1)}{d\ln r}, \tag{2}$$

where r is the interatomic distance. We have also included for comparison, data for Ge, GaAs, and ZnSe. The ZnSe piezobirefringence data of Ref. 15 marked a in the table, were taken in the highly dispersive region between 2.2 and 2.7 eV. Our extrapolation to zero energy is therefore quite uncertain. The hydrostatic coefficient in ZnSe, marked b, was derived from uniaxial stress measurements in polycrystalline ZnSe at 633 nm.[16] (The parentheses in the table signify that data are indicative, but not necessarily accurate, approximations to the low-energy limit.) Use of measurements on polycrystalline samples should be acceptable here because the effective hydrostatic term is a scalar invariant of the photoelastic tensor. GaAs entries marked c and e are piezobirefringence data extrapolated to zero energy and 1.08 eV, respectively; the latter is presented for comparison with the acousto-optically measured data,[17] marked f. The hydrostatic term, marked d, was taken from data by DeMeis.[18] The Ge entries, marked g, are our own acousto-optic data measured at 0.37 eV, and believed, for the present purposes, to be quite good approximations to the zero-energy values. Entries marked h and i are similar to those marked c and e.

TABLE I. Photoelastic coefficients of the cuprous halides at 633 nm. (Parenthetical results are data from Ref. 13.)

	p_{11}	p_{12}	p_{44}	$\frac{1}{2}(p_{11}-p_{12})$	$\frac{1}{3}(p_{11}+2p_{12})$
CuCl	+0.120	+0.250	−0.082	−0.065	+0.207
			(−0.080)	(−0.056)	
CuBr	+0.072	+0.195	−0.083	−0.062	+0.154
			(−0.078)	(−0.057)	
CuI	+0.032	+0.151	−0.068	−0.060	+0.111
			(−0.064)	(−0.075)	

TABLE II. Zero-energy values of photoelastic coefficients of the cuprous halides.

	$\frac{1}{2}(p_{11}-p_{12})$	p_{44}	$\frac{1}{3}(p_{11}+2p_{12})$
CuCl	−0.068	−0.067	+0.273
CuBr	−0.074	−0.067	+0.198
CuI	−0.070	−0.061	+0.152
ZnSe	−0.05 to −0.15 [a]	−0.07 to −0.18 [a]	(−0.06 [b])
GaAs	−0.033 [c]	−0.080 [c]	−0.10 [d]
	(−0.014 [e])	(−0.058 [e])	
	(−0.013 [f])	(−0.072 [f])	(−0.15 [f])
Ge	−0.013 [g]	−0.074 [g]	−0.141 [g]
	−0.014 [h]	−0.081 [h]	
	−0.012 [i]	−0.076 [i]	

[a] Reference 15 (extrapolated from data taken between 2.2 and 2.7 eV).

[b] Reference 16 (data at 633 nm only).

[c] Reference 14 (data extrapolated to infinite wavelength).

[d] Reference 18 (data extrapolated to infinite wavelength from data above 0.3 eV).

[e] Reference 14 (data at 1150 nm).

[f] Reference 17 (data at 1150 nm).

[g] D. K. Biegelsen and J. C. Zesch [(unpublished); data at 3390 nm].

[h] Reference 14 (data at 3390 nm).

[i] Reference 14 (data extrapolated to infinite wavelength).

Several trends in the long-wavelength photoelastic coefficients can be seen. One trend is the increase in magnitude of $\frac{1}{2}(p_{11}-p_{12})$ with ionicity. Another is the seeming constancy of p_{44}. Moreover, for the cuprous halides, $p_{44} \simeq \frac{1}{2}(p_{11}-p_{12})$, indicating an unexpected isotropy of the direct photoelastic tensor. (We specify direct here to denote that the second-order piezoelectric–electro-optic contribution has been experimentally excluded.)

The most striking trend is the monotonic algebraic increase with ionicity of the hydrostatic photoelastic coefficient, both isoelectronically and within the CuX family. In fact, the cuprous halides are the only tetrahedrally coordinated binary semiconductors known to have positive coefficients. The zero crossing may be quite accidental; however, the coincidence of this crossing with, for example, the superionic conductivity and the coordination near instability of the cuprous halides, leads one to suspect an underlying balance between strain-induced changes in short-range and long-range energies for these materials.

We will present here a plausibility argument to explain the trend in the long-wavelength hydrostatic coefficients. To begin, let us consider the band structures of the isoelectronic sequence Ge, GaAs, ZnSe, and CuBr. The virtual transitions which dominate the low-energy optical dielectric response occur between the (anion) p-like valence band and the (metal) s-like conduction band. Moving from Ge outward, the gap increases and the p-like band narrows.[19] At the same time, the metal d-electron energy rises towards that of the top valence p band. In CuBr the d band actually lies above the top p band and the p-d mixing is appreciable.[20] The band of partially screened p electrons is here quite narrow, looking quite localized and ionic. In considering the cuprous halides we note that the ionic radius of Cl^- is smaller than that of I^- so that the Cu-Cu overlap is greater in CuCl than in CuI. Similarly the halogen p orbitals overlap less and are more heavily screened. This manifests itself in the average p mixing into the d band[20]: CuCl (9%), CuBr (14%), and CuI (18%). Since the d-s gap remains nearly constant for the three materials, the "effective p band" is lowered in CuCl relative to CuI. The fact that $\epsilon(0)$ in CuCl is considerably lower than in CuI tends to corroborate the idea that the effective optical gap (E_p) is largest in CuCl. If we assume a Penn-like model[1] for $\epsilon(0)$, we have

$$\epsilon(0) - 1 \propto N/E_p^2, \tag{3}$$

where N is the number of valence electrons per atomic volume. From Eqs. (2) and (3) we find

$$p_h(0) = \frac{\epsilon - 1}{3\epsilon^2}\left(3 + \frac{d\ln E_p^2}{d\ln r}\right). \tag{4}$$

TABLE III. Scaled deformation potentials of average gaps. Calculated from the experimental values of p_n using Eqs. (4) and (5).

	Uniform-charge limit	Point-ion limit
CuCl	+ 1.1	−0.8
CuBr	+ 0.1	−1.4
CuI	− 0.3	−1.8
ZnSe	− 4.3	−3.5
GaAs	− 6.6	−3.8
Ge	−10.2	−4.2

The hydrostatic coefficient thus has an explicit positive volume dependence and an implicit term which is essentially the deformation potential of the average gap, divided by the gap. We would expect that the scaled deformation potential would be least (most nearly positive) in CuCl because here the effective gap is greatest and the p-d mixing smallest. In Table III we have listed the values for $(d\ln E^2)/(d\ln r)$ calculated from the experimental data for p_h. The monotonic trend in p has translated into a monotonic trend in scaled deformation potentials. The zero crossing here is model dependent and not quantitatively meaningful. In fact, a more complete model would include a local-field correction factor, which changes from the covalent elemental member to the ionic halides. If we write $E_{\mathrm{local}} = E + 4\pi\gamma P$, where $\gamma = 0$ for a uniform charge distribution and $\gamma = \frac{1}{3}$ for a cubic array of point dipoles (extreme ionic limit), then for the hydrostatic photoelastic coefficient we find

$$p_h(0) = \frac{(\epsilon - 1)[1 + \gamma(\epsilon - 1)]}{3\epsilon^2} \times \left(3 + \frac{d\ln E^2}{d\ln r} - \frac{\epsilon - 1}{1 + \gamma(\epsilon - 1)}\frac{d\gamma}{d\ln r}\right). \tag{5}$$

The last term in parentheses is expected to be negligible compared to 3. What remains is the same as Eq. (4) multiplied by $[1 + \gamma(\epsilon - 1)]$. The values of $(d\ln E^2)/(d\ln r)$ found in the ionic limit are also shown in Table III. Since γ is expected to change from near zero in Ge to a value less than $\frac{1}{3}$ in CuCl, we estimate that the correct value for $(d\ln E^2)/(d\ln r)$ is very nearly zero in the halides. Our conjecture is that the approach to zero of the deformation potential is an indication of the incipient structural instability.

In summary, we have presented our measurements of the photoelastic coefficients of the cuprous halides. We have found that the long-wavelength photoelastic response of the halides is particularly noteworthy in the context of the tetrahedrally coordinated binary semiconductors in that the tensor is nearly rotationally invariant and the deformation potential of the average gap is nearly zero.

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