

Dispersion of Piezo-optic Constants of Some Alkali Halides in the Ultraviolet Region. II. Deformation Potential Constants of the Valence Band

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Expressions are developed for the deformation-induced changes in polarizability in terms of fundamental frequency shifts and oscillator strength changes using the Lorentz model. The peaks in the absorption spectrum of the alkali halides are identified with exciton transitions associated with the conduction and valence band levels following recent band structure calculations. The large dispersion of piezo-optic coefficients near the absorption edge in KBr and KI is ascribed to the first low lying exciton peak, which is associated with the transition $\Gamma_8^- - \Gamma_6^+$ at $\mathbf{K}=0$ in the Brillouin zone. The piezo-optic data are used to evaluate the deformation potential constants of the valence band at $\mathbf{K}=0$ for KBr and KI.

Introduction

Cubic crystals are isotropic in their optical properties. The index of refraction is one such property and is determined by the electronic polarizability of the atoms which is a function of the optical frequency and increases with increasing frequency as the absorption region of the solid is approached. The absorption lines of this region result from electronic excitations (transitions). A detailed study of the position and intensities of these lines in alkali halides has been carried out by a number of workers (Hilsch & Pohl, 1930; Schneider & O'Bryan, 1937; Eby, Teegarden & Dutton, 1959; Teegarden & Baldini, 1967).

An isotropic stress deforms a solid without altering its symmetry. The deformation causes a shift in the position and a change in the intensity of the absorption lines, thus altering the electronic polarizability of the solid. Deformation due to a uniaxial stress has a similar effect and in addition may split some of the lines. Under uniaxial stress each split component contributes to the electronic polarizability. If the resultant polarizabilities for light polarized in directions parallel and perpendicular to the stress are not equal, piezo-birefringence will result. The correspondence between the nature of the absorption-peak splitting and the piezo-birefringence in its neighbourhood, first pointed out by Kaplyanskii & Lozovskaya (1966), has since been confirmed in several semiconductors (Ge: Riskaer & Balslev, 1966; ZnSe: Dubenskii, Kaplyanskii & Lozovskaya, 1967; GaAs: Feldman & Horowitz, 1968).

From a knowledge of the energy bands of the solid and the deformation-induced changes in them an estimate can be made of the magnitude of the piezo-birefringence. Riskaer & Balslev (1966) have explained the dispersion of birefringence near the interband edge of Ge in terms of the known deformation potential constants of the valence band at $\mathbf{K}=0$. Conversely, experimental data on piezo-birefringence in the wave-

length region close to an absorption line may be used to evaluate the deformation-induced shift and splitting of the energy level involved in that transition. In this paper the determination of the deformation potential constants of the valence band at $\mathbf{K}=0$ in KBr and KI using the piezo-birefringence data of part I (Rahman & Iyengar, 1970) will be discussed.

The absorption spectrum and deformation potential constants

Beyond the absorption edge in alkali halides there exists an absorption region characterized by well-marked peaks where the electronic excitation may be identified with exciton transitions (Phillips, 1964). Recent band-structure studies (see Knox & Teegarden, 1968) provide a sound basis for assigning the transitions to energy levels at appropriate points in the Brillouin zone (BZ). The first peak close to the absorption edge is unambiguously assigned to an exciton associated with the highest valence band Γ_8^- and the lowest conduction level Γ_6^+ , at $\mathbf{K}=0$ in the BZ. [For the assignments of the remaining peaks, see Teegarden & Baldini (1967).] The discussion in this paper will be confined mainly to the first exciton peak.

The valence band has *p*-like symmetry with a total angular momentum quantum number $J=\frac{3}{2}$ and the conduction band Γ_6^+ is *s*-like with $J=\frac{1}{2}$. According to Kleiner & Roth (1959) a uniaxial strain parallel to [100] or [111] splits the Γ_8^- -level into two sublevels characterized by magnetic quantum numbers $M_J = \pm\frac{3}{2}$ and $M_J = \pm\frac{1}{2}$ respectively. The conduction level is not split but its energy is shifted. The energy spacing $2\varepsilon_0$ between the two sublevels $M_J = \pm\frac{3}{2}$ and $M_J = \pm\frac{1}{2}$, is given by

$$\begin{aligned} 2\varepsilon_0 &= \frac{4}{3} \cdot D_u \cdot e \quad \text{for } e \parallel [100] \\ 2\varepsilon_0 &= \frac{4}{3} \cdot D'_u \cdot e \quad \text{for } e \parallel [111] \end{aligned} \quad (1)$$

and the shift of the centre of gravity of the split va-

lence levels with reference to the conduction level is given by

$$\delta E_g = (D'_u - D'_c) \cdot dv/v, \quad (2)$$

where D'_u and D'_c are a measure of the energy changes of the valence band for uniaxial strains parallel to [100] and [111] and D'_c and D'_u describe the changes in the conduction and valence band energies due to volume strain dv/v .

In the interband approximation of Kleiner & Roth the splitting and the shift of the centre of gravity of the exciton peak are also given by expressions (1) and (2).

The strain-polarizability coefficients and the Lorentz model

In the undeformed state, the refractive index of the solid, n , is a function of its density ρ and its polarizability α :

$$n = n(\rho, \alpha). \quad (3)$$

Differentiating expression (3) and using the well-known Lorentz-Lorenz formula for the refractive index to evaluate the derivatives $\left(\frac{\partial n}{\partial \rho}\right)_\alpha$ and $\left(\frac{\partial n}{\partial \alpha}\right)_\rho$, one arrives at the following:

$$\left(\frac{dn}{e}\right) = L(\lambda - 1), \quad (4)$$

where dn is the change in the refractive index due to a strain e ,

$$L = (n^2 - 1)(n^2 + 2)/6n$$

and

$$\lambda = \frac{d\alpha}{\alpha \cdot e}$$

is the strain-polarizability coefficient.

The changes in the refractive index dn_{\parallel} and dn_{\perp} for light polarized parallel and perpendicular to the strain axis, can be written in terms of the corresponding strain-polarizability coefficients, λ_{\parallel} and λ_{\perp} , so that the piezo-birefringence is given by

$$\frac{\delta n}{e} = (n_{\parallel} - n_{\perp})/e = L(\lambda_{\parallel} - \lambda_{\perp}). \quad (5)$$

One can now treat the solid as an assembly of oscillators, with fundamental frequencies ν_i and oscillator strengths f_i , according to the classical theory of Lorentz, and express the polarizability $\alpha(\nu)$ for the frequency ν of the incident radiation as

$$\alpha(\nu) = \sum_i \frac{C f_i}{\nu_i^2 - \nu^2}$$

where C is a constant.

For a single oscillator, of frequency ν_0 , the Lorentzian expression yields, on differentiation

$$\lambda(\nu) = N - K(\nu) \cdot M, \quad (6)$$

where

$$\lambda(\nu) = \frac{d\alpha}{\alpha \cdot e}, \quad N = \frac{df_0}{f_0 \cdot e}, \quad M = \frac{d\nu_0}{\nu_0 \cdot e}, \quad K(\nu) = \frac{2\nu_0^2}{\nu_0^2 - \nu^2},$$

ν_0 = the fundamental frequency and f_0 = the strength of the oscillator.

Expressions for the strain-optical coefficients in terms of deformation potential constants

The strain-induced frequency shifts $d\nu_0$ of the Lorentzian oscillators may now be correlated with the energy changes in the associated exciton transitions. Each one of the two split components of the exciton peak will contribute to the strain-polarizability coefficients λ_{\parallel} and λ_{\perp} in the deformed state. These contributions will be governed by selection rules for the transitions in polarized light from the split valence levels with $M_J = \pm \frac{3}{2}$ or $M_J = \pm \frac{1}{2}$ to the exciton level ($J = \frac{1}{2}$). The rules for these energy levels have been worked out (see Kaplyanskii, 1964; Riskaer & Balslev, 1966). Riskaer & Balslev have given normalized matrix element coefficients (m) determining the intensities of transitions for light polarized parallel and perpendicular to the strain. Using these coefficients, the contribution of the split exciton peaks to the strain-polarizability λ_{\parallel} and λ_{\perp} can be written:

$$\left. \begin{aligned} [\lambda_{\parallel}]_r &= m_{\parallel}^{3/2} \cdot \lambda_{3/2} + m_{\parallel}^{1/2} \cdot \lambda_{1/2} \\ [\lambda_{\perp}]_r &= m_{\perp}^{3/2} \cdot \lambda_{3/2} + m_{\perp}^{1/2} \cdot \lambda_{1/2} \end{aligned} \right\}, \quad (7)$$

where $\lambda_{3/2}$ and $\lambda_{1/2}$ are the strain-polarizability coefficients for the split exciton peaks due to transitions from the $M_J = \pm \frac{3}{2}$ and $M_J = \pm \frac{1}{2}$ valence levels. The superscripts indicate the valence level and the subscripts, the polarization of light. The subscript r to the strain-polarizability coefficients denotes the contribution of the $\Gamma_8^- - \Gamma_6^+$ exciton. The m values as given by Riskaer & Balslev are:

$$m_{\parallel}^{3/2} = 0, \quad m_{\parallel}^{1/2} = 1, \quad m_{\perp}^{3/2} = \frac{3}{4}, \quad m_{\perp}^{1/2} = \frac{1}{4}.$$

With substitution of these values, expressions (7) reduce to

$$\left. \begin{aligned} [\lambda_{\parallel}]_r &= \lambda_{1/2} \\ [\lambda_{\perp}]_r &= \frac{3}{4} \cdot (\lambda_{3/2} + \frac{1}{3} \cdot \lambda_{1/2}) \end{aligned} \right\}. \quad (8)$$

and

$$[\lambda_{\parallel} - \lambda_{\perp}]_r = -\frac{3}{4} \cdot (\lambda_{3/2} - \lambda_{1/2})$$

Using equation (6) $\lambda_{3/2}$ and $\lambda_{1/2}$ can be expressed in terms of the relative oscillator strength and fundamental frequency changes:

$$\begin{aligned} [\lambda_{\parallel} - \lambda_{\perp}]_r &= \\ &= -\frac{3}{4} [(N_{3/2} - N_{1/2}) - K(\nu) (M_{3/2} - M_{1/2})]. \end{aligned} \quad (9)$$

Assuming that for positive values of D'_u and D'_c the energy of the $M_J = \pm \frac{3}{2}$ level is greater than that of the $M_J = \pm \frac{1}{2}$ level for a positive (*i.e.* extensional) strain (Hensel & Feher, 1963), the relative changes in the fundamental frequency can be written

$$M_{3/2} = \frac{\delta E_g - \varepsilon_0}{E_0 \cdot e}; \quad M_{1/2} = -\frac{\delta E_g + \varepsilon_0}{E_0 \cdot e}, \quad (10)$$

where E_0 is the energy of the exciton peak in the undeformed state. Using equations (8), (9), (10), (1) and (2) one obtains

$$\left. \begin{aligned} [\lambda_{\parallel} - \lambda_{\perp}]_R^{100} &= \frac{3}{4}(N_{1/2} - N_{3/2}) - \frac{K(v)}{E_0} \cdot D_u \\ [\lambda_{\parallel} - \lambda_{\perp}]_R^{111} &= \frac{3}{4}(N_{1/2} - N_{3/2}) - \frac{K(v)}{E_0} \cdot D'_u \\ [\lambda_{\parallel} + 2\lambda_{\perp}]_R &= \frac{3}{2}(N_{1/2} - N_{3/2}) - \frac{K(v)}{E_0} \cdot (D_a^c - D_a^g) \end{aligned} \right\} (11)$$

where the superscripts 100 and 111 refer to the strain directions [100] and [111] respectively, and in the third equation λ_{\parallel} and λ_{\perp} refer to the cases of strain parallel to [100] or [111].

Using equations (5) and (11) and the well-known relations between piezo-birefringence and the strain-optical coefficients (Nye, 1957) the following expressions are obtained:

$$\left. \begin{aligned} (\delta n)_R^{100} &= \frac{n^3}{2} (p_{11} - p_{12}) = \frac{3}{4}L(N_{3/2} - N_{1/2}) \\ &\quad + \frac{L \cdot K(v)}{E_0} \cdot D_u \\ (\delta n)_R^{111} &= \frac{n^3}{2} (2p_{44}) = \frac{3}{4}L(N_{3/2} - N_{1/2}) + \frac{L \cdot K(v)}{E_0} \cdot D'_u \\ (\delta n)_R^i &= \frac{n^3}{2} \left(\frac{p_{11} + 2p_{12}}{3} \right) = L - \frac{L}{2} (N_{1/2} + N_{3/2}) \\ &\quad + \frac{L \cdot K(v)}{E_0} (D_a^c - D_a^g) \end{aligned} \right\} (12)$$

where $(\delta n)_R^{100}$ and $(\delta n)_R^{111}$ are the piezo-birefringences contributed by the $\Gamma_8^- - \Gamma_6^+$ exciton for strains parallel to [100] and [111] respectively, for a compressive strain, and the contribution to the change in refractive index for isotropic strains is $(\delta n)_R^i$.

Results

Fig. 1 shows the $(\lambda_{\parallel} - \lambda_{\perp})$ versus $K(v)$ curves for KBr and KI. In evaluating $K(v)$ the wavelengths as given by Hilsch & Pohl (1930) for the first low-energy exciton peaks for KBr and KI, viz. $187m\mu$ and $219m\mu$ respectively, at room temperature, have been used. The curves tend to become linear for large values of $K(v)$, indicating that the first peak plays a major part in determining the birefringence [cf. equation (11)]. The deformation potential constants D_u and D'_u for KBr and KI were evaluated from the linear parts of the curves. The constant $(D_a^c - D_a^g)$ was similarly evaluated from $n^3/2 (p_{11} + 2p_{12})$ versus $L \cdot K(v)$ curves (L has negligible dispersion in this wavelength region). The results are given in Table 1.

Table 1. Deformation potential constants of the Γ_8^- valence band at $\mathbf{K}=0$ in KBr and KI

Units: eV per unit strain.

Crystal	D_u	D'_u	$D_a^c - D_a^g$
KBr	-0.133	+0.344	-0.066
KI	-0.209	+0.137	-0.084

Discussion

(1) The signs of the deformation potential constants D_u and D'_u determine the arrangement of the polarized split-exciton peaks. A positive constant would mean that the energy of the $M_J = \pm \frac{1}{2}$ valence level is higher than that the $M_J = \pm \frac{3}{2}$ level, in the case of a compressive strain. The energy of transition from the $M_J = \pm \frac{1}{2}$ level [active for light polarized parallel to the strain, equation (8)] is hence lower than the transition energy from the level $M_J = \pm \frac{3}{2}$. For a positive deformation potential constant, therefore, the low energy component of the split exciton peak will be active in light polarized parallel to the strain. As discussed by Kaplyanskii & Lozovskaya (1966), this results in a positive piezo-birefringence and a 'normal' dispersion $\left(\frac{d}{d\lambda} (\delta n) < 0 \right)$. The reverse is true when the deformation potential constant is negative: close to the exciton peak (δn) is negative and its dispersion is 'anomalous'. The above discussion is supported by the following expressions obtained from equation (12):

$$\begin{aligned} (\delta n)_{v \rightarrow v_0} &= + \frac{L}{E_0} \cdot K(v) \cdot D \\ \frac{d}{d\lambda} (\delta n) &= - \left| \frac{L}{E_0} \cdot \frac{dK(v)}{d\lambda} \right| \cdot D, \end{aligned}$$

where D is the relevant deformation potential constant, D_u or D'_u . $\left(\frac{dK(v)}{d\lambda} \right)$ has a negative sign.

The signs of the deformation potential constants given in Table 1 are consistent with the above discussion.

It may be pointed out that D_u and D'_u have different signs, giving rise to 'anomalous' dispersion of piezo-birefringence for strain parallel to [100], and 'normal' dispersion for strain parallel to [111] for KBr and KI. This is in contrast to observations, near the band edge, in the semiconductors Ge (Riskaer & Balslev, 1966), GaAs (Feldman & Horowitz, 1968) and ZnSe (Dubenskii *et al.*, 1967), where both D_u and D'_u are positive and the dispersion of piezo-birefringence near the band edge is 'normal' for both [100] and [111] directions of strain.

Laiho & Korpela (1968) have studied the piezo-optic birefringence of Rb and Cs halides near the absorption edge. Rb halides behave very much like K halides, while for the Cs halides, the behaviour is just

the reverse: $\frac{d}{d\lambda} (\delta n)^{100}$ is positive and $\frac{d}{d\lambda} (\delta n)^{111}$ is negative. This difference may be attributed to the symmetry character of the excitons at low energies. The first low energy exciton in K and Rb halides is associated with a p -like valence level and s -like conduction level (s -exciton). At slightly higher energies, excitons associated with p -like valence levels and d -like conduction levels are found (d -excitons). It is suggested that the d -excitons, which are very close to the absorption edge in Cs halides (Teegarden & Baldini, 1967) have deformation potential constants with signs opposite to the corresponding constants of the s -excitons, giving rise to a piezo-optic behaviour opposite to that found in K and Rb halides.

(2) The existence of the d -excitons at higher energies also explains the sign reversal of piezo-birefringence in K and Rb halides, as the contribution from these d -excitons may eclipse that due to the low energy s -excitons at longer wavelengths. Experiments on NaI could serve as a check on this line of reasoning, for the d -excitons in NaI (if they exist at all) must be at much higher energies (> 10 eV, Kunz, 1966) and sign reversals of piezo-birefringence may not occur in the near ultraviolet or the visible region.

(3) The temperature dependence of the first low energy exciton peak in KI has been studied by several workers (see Roessler & Walker, 1967). The energy shift is -8.5×10^{-4} eV. $^{\circ}\text{K}^{-1}$, which is linear between

20 and 900 $^{\circ}\text{K}$. Using the value of $D_a^c - D_a^v$ ($= \frac{\delta E_g}{dv/v}$) from Table 1, and the thermal expansion coefficient of KI (Krishnan, 1958), the stress-induced part of the energy shift was calculated as -0.10×10^{-4} eV. $^{\circ}\text{K}^{-1}$. Hence the pure temperature effect for the first peak is -8.4×10^{-4} eV. $^{\circ}\text{K}^{-1}$. This shows that the electron-phonon interaction is quite large for states near the valence and conduction band edges in KI.

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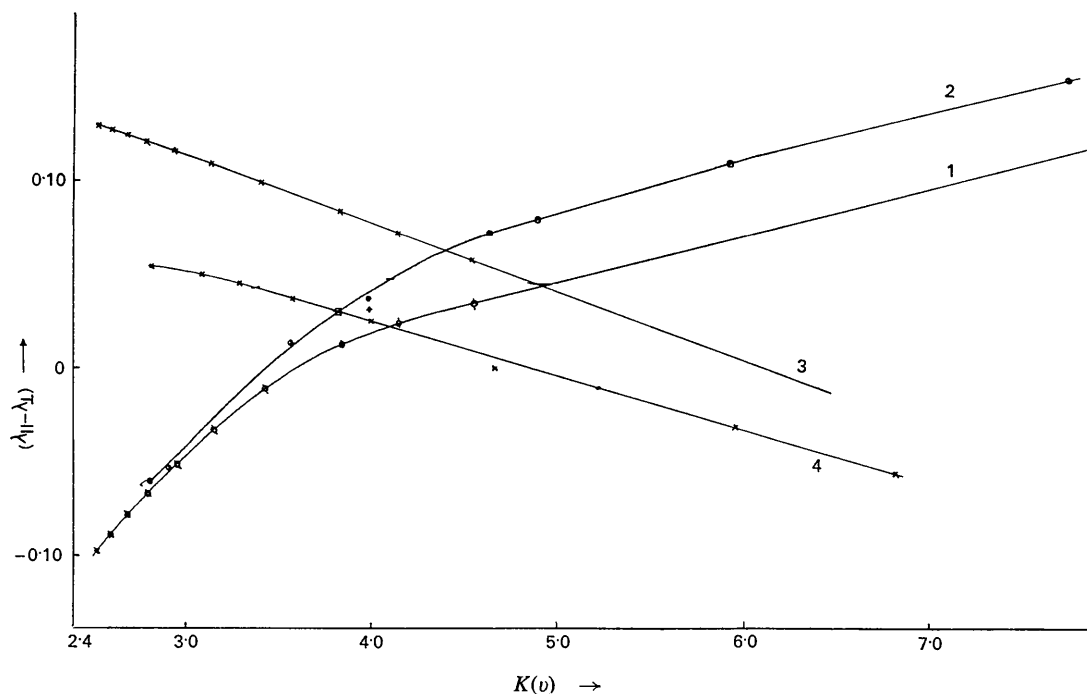


Fig. 1. Strain-polarizability coefficients versus $K(v) = 2v_0^2/(v_0^2 - v^2)$, for KBr and KI. $(\lambda_1 - \lambda_2)$ for strain parallel to [100]: 1-KBr, 2-KI; $(\lambda_1 - \lambda_2)$ for strain parallel to [111]: 3-KBr, 4-KI.

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Lattice Parameters and Thermal Expansion of Zinc Telluride and Mercury Selenide

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The lattice parameters of zinc telluride and mercury selenide were measured with a Unicam 19 cm high-temperature powder camera; the following equations represent the results: ZnTe, $a_t = 6.1016 + 54.63 \times 10^{-6}t + 6.82 \times 10^{-9}t^2 + 5.28 \times 10^{-12}t^3$; HgSe, $a_t = 6.0854 + 28.61 \times 10^{-6}t + 4.93 \times 10^{-9}t^2 + 3.74 \times 10^{-12}t^3$. The expressions for thermal expansion coefficients are also given.

Introduction

Previous work on the microscopic thermal expansion of zinc telluride and mercury selenide has not been very extensive. Novikova & Abrikosov (1963) determined the macroscopic thermal expansion of zinc telluride (sphalerite type structure) from 20 to 340°K with a silica dilatometer. They showed that the thermal expansion, α , changes sign at 46°K. Zhdanov, Lukina & Novikova (1966) measured the coefficient of thermal expansion of mercury selenide in the temperature range 20° to 500°K with a quartz type of dilatometer. The microscopic data of thermal expansion of zinc telluride at elevated temperatures have been published by Holland & Beck (1968) who determined the lattice parameters without the use of any graphical or analytical methods, which certainly gives better results. In the present investigations we have used a 19 cm Unicam High-Temperature Powder Camera. The lattice parameters were calculated by Cohen's (1936) analytical method with Nelson & Riley's (1945) extrapolation function.

Experimental

For diffraction work, fine quartz capillaries of inner diameter 0.3 mm were chosen. At each temperature the photographs were taken three times and care was taken to reproduce the same temperature within $\pm 2^\circ\text{C}$. The methods of calibration of the thermocouple and

evaluation of lattice parameters and thermal expansion coefficients were the same as those described by Singh (1968).

Results and discussion

Zinc telluride

Ultra-pure zinc telluride was annealed at 256°C for four hours and the well-resolved lines corresponding to reflexions 711, 642, and 731 (Cu $K\alpha$ radiation) were used for the derivation of the lattice parameters. These are tabulated in the first column of Table 1 and are expressed by the parabolic equation:

$$a_t = 6.1016 + 54.63 \times 10^{-6}t + 6.82 \times 10^{-9}t^2 + 5.28 \times 10^{-12}t^3,$$

where a_t is the lattice parameter in Å at $t^\circ\text{C}$. The expression for the thermal expansion coefficient α_t is given by:

$$\alpha_t = 8.95 \times 10^{-6} + 2.24 \times 10^{-9}t + 2.60 \times 10^{-12}t^2.$$

Table 1. *Lattice parameters and thermal expansion coefficients of zinc telluride*

Temperature (°C)	Lattice parameter, a (Å)		$\alpha \times 10^6$ (°C ⁻¹)
	Observed	Calculated	
35	6.1035	6.1035	9.03
103	6.1073	6.1073	9.21
167	6.1109	6.1109	9.40
256	6.1161	6.1161	9.70
352	6.1218	6.1219	10.06
445	6.1277	6.1278	10.46

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