

Natural birefringence in alkali halide single crystals

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The birefringence induced by spatial dispersion (BISD) of NaCl, KCl, RbCl, NaBr, KBr, RbBr, CsBr, NaI, KI, RbI, and CsI single crystals has been measured at room temperature near their fundamental absorption edge. The sign of the birefringence is negative ($n_{1\bar{1}0} < n_{001}$) for chlorides and iodides. For bromides no BISD has been obtained. By fitting the experimental results with a microscopic model one obtains the warping parameter ($\gamma_2 - \gamma_3$) of these compounds. $\gamma_2 - \gamma_3$ estimated from the available band calculation for the alkali halides does not agree with the abnormally high values measured for iodides and chlorides.

I. INTRODUCTION

Optical anisotropy induced by spatial dispersion, i.e., the dependence of the dielectric constant on the light wave vector has received a great attention in the last years,¹ special attention has been paid to semiconductor materials focusing mainly in problems related with polaritons and their influence in reflection Raman and Brillouin spectra.^{1,2}

Birefringence in cubic crystals is one of the easiest methods to study spatial dispersion. This effect has been mostly measured in zinc-blende-structure semiconductors³⁻¹⁰ and theoretically explained in terms of the warping of the Γ_8 valence band.⁴ Recently anisotropies in the reflectance spectrum on (110) faces of semiconductors induced by intrinsic (spatial dispersion) and extrinsic mechanisms of the surface has been also reported.¹¹ Birefringence induced by spatial dispersion (BISD) should be dependent on the ionicity of the bonds. Therefore small BISD effect should be expected in ionic materials such as alkali halides due to the flatness of their energy bands. However, results of BISD on KI have been recently reported¹² near the absorption edge of this material. The results have been explained in terms of the q -vector-induced splitting of the exciton which is well known to be a very strong dispersion center.

In this paper we report measurements of BISD on NaI, KI, RbI, CsI, NaBr, KBr, CsBr, NaCl, KCl, and RbCl single crystals at room temperature near their fundamental absorption edge. One obtains also the sign of the BISD by comparing with birefringence induced by mechanical stress in KCl and LiF single crystals.¹³ The results are much higher than those obtained from different band calculations. Moreover, the theory does not explain the dependence of the warping parameter with the cation in alkali halides.

II. THEORY

The theory of the BISD is in some aspects similar to that of piezobirefringence (PB). This similarity can be clearly appreciated as we develop the dielectric constant as

a function of the wave vector of q ,¹

$$\epsilon_{ij}(\omega, q) = \epsilon_{ij}(\omega) + i\gamma_{ijk}q_k + \alpha_{ijkl}q_kq_l, \quad (1)$$

where the third-order tensor γ_{ijk} responsible for the optical activity vanishes for crystals with inversion symmetry and also for zinc-blende- (ZB-) type materials. When a magnetic field is applied, Kramers degeneracy is lifted and therefore $\gamma_{ijk} \neq 0$ is induced.¹ Since q_kq_l has the same tensor properties as the mechanical stress tensor σ_{kl} , α_{ijkl} works like the piezo-optical (PO) tensor Q_{ijkl} , defined through

$$\Delta\epsilon_{ij} = Q_{ijkl}\sigma_{kl}, \quad (2)$$

where $\Delta\epsilon_{ij}$ is the birefringence associated with the PO effect.^{14,15} Therefore in crystals with cubic symmetry, α_{ijkl} has only three independent constants: α_{1111} , α_{1212} , and α_{1122} .¹³ When the light travels along the directions of higher symmetry, such as (100) and (111) directions, the crystal becomes uniaxial with the optical axis parallel to q . Therefore, no birefringence is induced. However, when the q vector is parallel to (110) direction, the crystal becomes biaxial with the dielectric constant as

$$\epsilon(q) = \epsilon(0) + \frac{q^2}{2} \begin{bmatrix} \alpha_{1111} + \alpha_{1122} & \alpha_{1212} & 0 \\ \alpha_{1212} & \alpha_{1111} + \alpha_{1122} & 0 \\ 0 & 0 & 2\alpha_{1212} \end{bmatrix}. \quad (3)$$

The birefringence for the light along (110) is

$$\Delta\epsilon = \epsilon_{1\bar{1}0} - \epsilon_{001} = 2n\Delta n = (\alpha_{1111} - \alpha_{1122} - 2\alpha_{1212})q^2/2. \quad (4)$$

In the microscopic theory developed by Yu and Cardona⁴ the BISD is explained in terms of the q -induced splitting of the valence band. This occurs because the heavy and light holes have different masses. In this way the effect of

the q -induced splitting on the valence band is similar to that of the uniaxial strain. At variance with the PB, which is governed by the deformation potential, in BISD the different effective masses along (111) and (100), or band warping, give rise to the q -induced birefringence.

For alkali halides the most prominent structure at the absorption edge is dominated by the excitons and the binding energy of that excitons is very high (~ 1 eV). Therefore, we could consider the Γ_8 exciton as responsible for the optical properties near the absorption edge. Consequently, we have considered the real part of dielectric constant being due to a single harmonic oscillator without damping pickup at Γ_8 exciton. Then, we can write

$$\epsilon = C_{\text{ex}} / [\omega_0^2(q) - \omega^2], \quad (5)$$

where $\omega_0(q)$ is the energy of exciton in function of the wave vector q , ω is the energy of the light, and C_{ex} is the oscillator strength of the exciton.

The q vector, as in the stress case, will split the Γ_8 exciton energies as well as modify C_{ex} . The splitting of the energy band ω_0 induces a more dispersive term than that of the change of C_{ex} that affects only the numerator of (5). Therefore, we will consider only the most dispersive term, i.e., the term that involves splitting in the exciton energy.

The effect of the spatial dispersion on the exciton binding energy and electron-hole exchange interaction¹⁶ will be neglected as in the microscopical theory of PO effect.¹⁷ From that one obtains

$$\Delta n = Dq^2 + \frac{C_{\text{ex}}}{\omega_0^3} (\gamma_2 - \gamma_3)_{\text{ex}} q^2 \frac{1}{(1-x^2)^2}, \quad (6)$$

where the first term considers the contribution of higher excitons and band-to-band transitions and $x = \omega/\omega_0$. The difference $(\gamma_2 - \gamma_3)_{\text{ex}}$ describes the warping of excitons band and is related to the warping of the valence band by^{18,19}

$$(\gamma_2 - \gamma_3)_{\text{ex}} = (\gamma_2 - \gamma_3)_{\text{band}} \beta_h^2, \quad \beta_h \simeq (1 + m_e^*/m_h^*)^{-1}. \quad (7)$$

The warping of the band $(\gamma_2 - \gamma_3)_{\text{band}}$ is defined as

$$(\gamma_2 - \gamma_3)_{\text{band}} = (\hbar^2/2m)[(m/m_{100}^*) - (m/m_{111}^*)], \quad (8)$$

where m_{100}^* and m_{111}^* are the effective masses of Γ_8 exciton along (100) and (111) directions, m_e^* is the electron mass, and m_h^* is the average hole mass.

III. EXPERIMENTAL DETAILS

The samples used were parallelepipeds with (110), $(1\bar{1}0)$, and (001) faces. Different thickness ranging from 1 to 3 cm depending on the strength of the BISD have been used. In order to avoid the influence of the residual strains in the crystals a careful annealing from about 500°C was done. Otherwise the BISD signal was overlapped by the birefringence induced by residual strains. The experiment was performed by measuring the light transmitted by the sample placed between two Brewster reflection polarizers. A deuterium light source and a

McPherson 0.3-m focal length and an S-1 photomultiplier were used. For wavelengths below 250 nm, the system was air evacuated in order to avoid the uv absorption of atmosphere. The light detected by the photomultiplier can be written as

$$\begin{aligned} I_{\theta}^{\parallel} &= I_0 [1 - \sin^2(2\theta) \sin^2(\delta/2)], \\ I_{\theta}^{\perp} &= I_0 \sin^2(2\theta) \sin^2(\delta/2), \end{aligned} \quad (9)$$

where I_0 is the incident light intensity and θ is the angle between the polarizer and the $(1\bar{1}0)$ axis of the sample. The \parallel and \perp superscripts hold for parallel and perpendicular polarizers; δ is the phase shift of the light between parallel and perpendicular polarization to the $(1\bar{1}0)$ axis given by

$$\delta = (2\pi t/\lambda)\Delta n, \quad \Delta n = n_{1\bar{1}0} - n_{001} \quad (10)$$

where t is the sample thickness and λ the wavelength of light in vacuum. From expression (9) it is not possible to obtain the sign of the BISD. For this purpose it is necessary to compare the BISD signal with that of a quarter-wave plate independent of light frequency in the uv region and with known fast axis. We have used a LiF and KCl single crystals oriented along the crystallographic directions and uniaxially stressed along the (001) direction. Under these circumstances they become uniaxial, with $n_{001} > n_{010}$ for KCl and $n_{001} < n_{010}$ for LiF and wavelength nondependent up to 5 eV.¹³

Figure 1 shows the light intensity recorded between

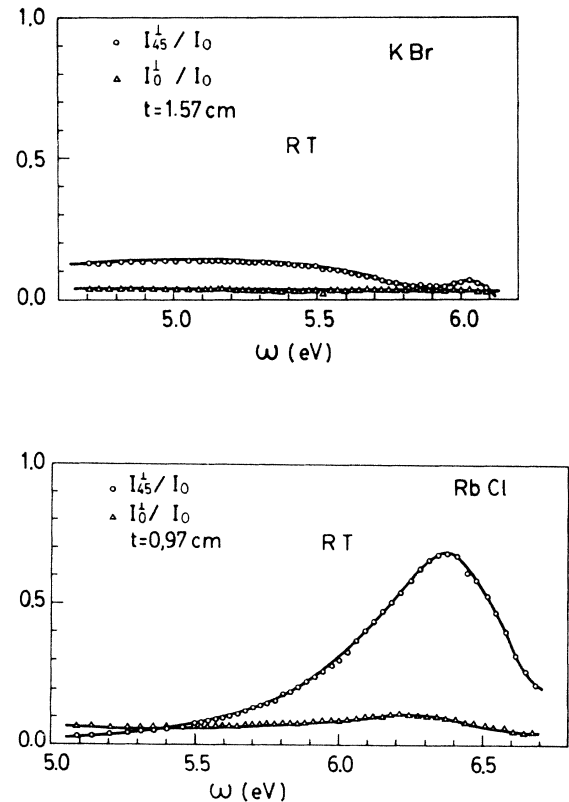


FIG. 1. Transmittance of KBr (upper part) and RbCl (lower part) samples placed at room temperature between crossed polarizers. The light travels along $[110]$ and the circles correspond to the polarization angle $\theta = 45^\circ$ and the triangles hold for $\theta = 0^\circ$ (see text). The solid lines are a guide for the eye.

crossed polarizers for $\theta=0^\circ$ and $\theta=45^\circ$ in two typical cases: RbCl and KBr. In the case of RbCl one observes quite different behavior for I_{45}^\perp/I_0 than that of I_0^\perp/I_0 . For $\theta=0^\circ$ no BISD is detected and therefore the signal is less dispersive than that of $\theta=45^\circ$ which is mainly due to BISD. The maximum of the curve does not reach the value $I_{45}^\perp/I_0=1$, probably due to some depolarization of the light by the sample. The signal of I_0^\perp in function of the light frequency could be due to residual strains or other sources of depolarization. In the case of KBr small differences between I_{45}^\perp and I_0^\perp appears. Therefore a small BISD effect is observed for this material. Similar results have been obtained for NaBr, RbBr, and CsBr even for sample thickness of about 3 cm in some of them. Figure 2 shows the results of I_{45}^\perp for CsI alone and with KCl or LiF uniaxial-strained induced compensator (USIC). When KCl-USIC is placed the maximum of the I_{45}^\perp is shifted to higher light energies at variance with LiF-USIC. This means¹¹ that BISD is $n_{1\bar{1}0} - n_{001} < 0$ for CsI. The same sign has been found for the iodide and chloride families. In the case of bromides no sign should be determined due to the smallness of the BISD.

IV. RESULTS AND DISCUSSION

The circles of Figs. 3 and 4 show $-(n_{1\bar{1}0} - n_{001})$ as obtained from experiments [see expression (9)] for alkali iodides, as a function of the light frequency close to their room-temperature absorption edge. Although $(n_{1\bar{1}0} - n_{001})$ is very small it has the same order of magnitude as that measured for silicon and zinc-blende-type semiconductors³⁻⁵ and shows strong dispersion near the exciton absorption peak as in cuprous halides.¹⁰ Figures 3 and 4 also show (solid lines) the fitting done with (5). Discrepancies between experiment and theory at higher-energy side of each curve close to the absorption edge could be safely due to errors in light detection by the strong absorption from the samples. Discrepancies at the lower part of the curves can be attributed to depolarization of the light probably due to residual strains. Figures 5 and 6 show $-(n_{1\bar{1}0} - n_{001})$ for NaCl, KCl, and RbCl as a function of the energy of the light at room temperature.

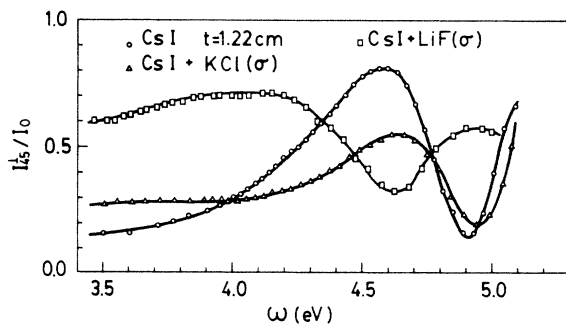


FIG. 2. Intensity of light transmitted by CsI (circles) and CsI with KCl uniaxial strained induced compensator (USIC) (triangles), and CsI with LiF-USIC (squares) placed between crossed polarizers. The solid line is a guide for the eye.

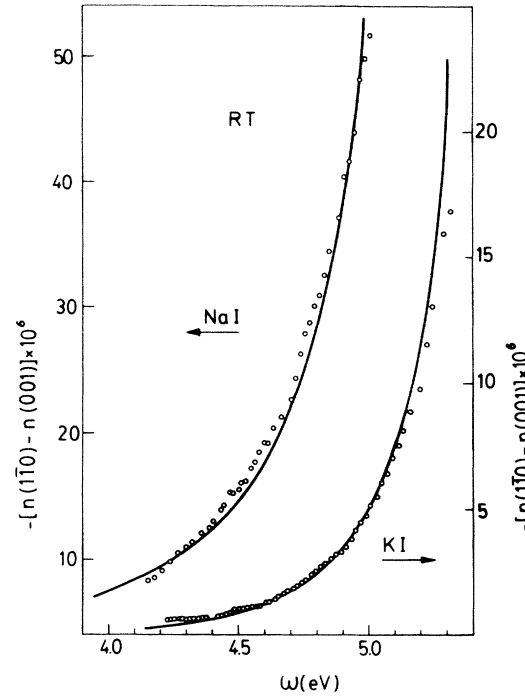


FIG. 3. BISD for NaI and KI as a function of photon energy. The solid lines are a fit with Eq. (6).

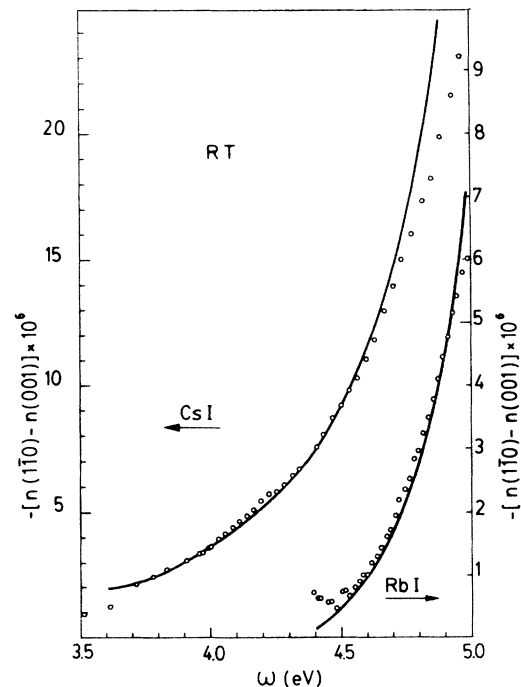


FIG. 4. BISD for CsI and RbI as a function of photon energy. The solid lines are a fit with Eq. (6).

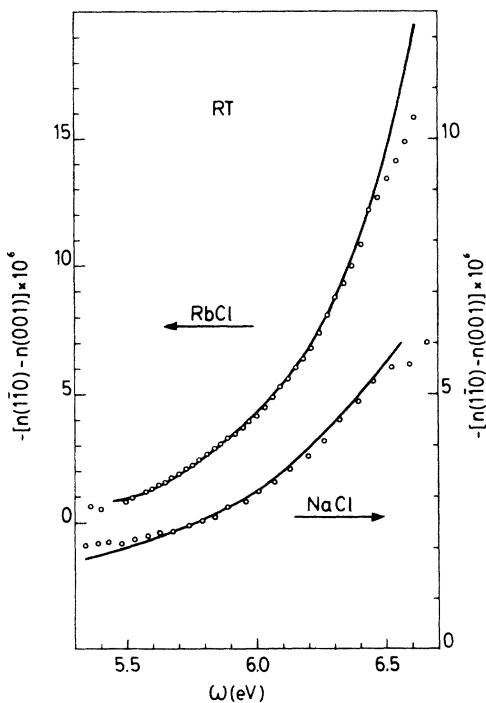


FIG. 5. BISD for RbCl and NaCl as a function of photon energy. The solid lines are a fit with Eq. (6).

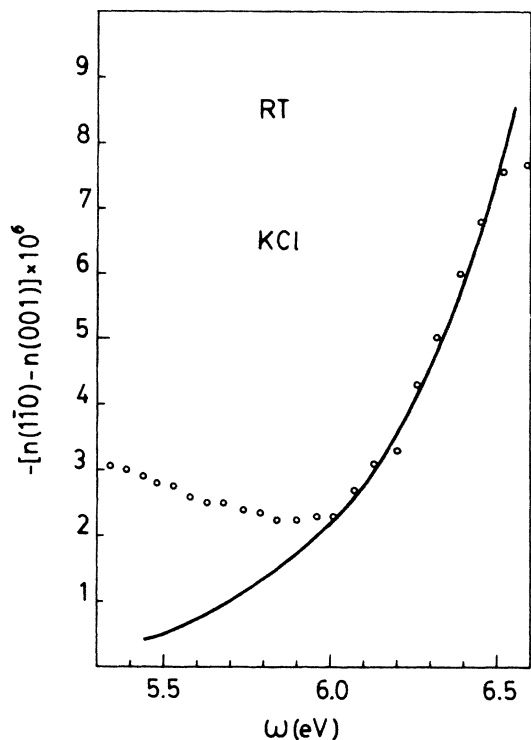


FIG. 6. BISD for KCl as a function of the photon energy. The solid lines are a fit with Eq. (6).

The continuous curve shows the theoretical fitting. The effect of the residual strains is stronger for NaCl and KCl than for RbCl. From the fits one obtains D and $(\gamma_2 - \gamma_3)_{ex}$ for the materials studied. These results are shown in Table I together with the oscillator strength C_{ex} and the energy of the Γ_8 exciton ω_0 . The BISD for alkali bromides is so small that it was not possible to obtain reliable results for $(\gamma_2 - \gamma_3)_{ex}$. A rough estimation indicates that $(\gamma_2 - \gamma_3)_{ex}$ for alkali bromides is at least one order of magnitude smaller than that of KI. This result holds for NaBr provided that its oscillator strength is comparable to that for other bromides. It is important to comment that the $(\gamma_2 - \gamma_3)$ values obtained for alkali halides with exception of bromides are comparable in absolute value with those measured for zinc-blende-type semiconductors. For instance the largest absolute value measured for ZB materials is $|\gamma_2 - \gamma_3|_{GaAs} = 0.9$, whereas $|\gamma_2 - \gamma_3|_{CsI} = 1.0$. These results are quite surprising because the main factor responsible for the warping parameter is the valence band that is flatter for alkali halides than those for ZB-type semiconductors. Consequently it should be expected stronger warping for them. From Table I one observes in chlorides and iodides, with the exception of NaI, a trend in the sense that warping parameter increases in absolute value as the cation becomes heavier. These results are surprising because, at first glance one argues that within the iodide (chloride) family the valence band should be equivalent for all compounds and comes from the iodine p level (chlorine p level).

A sort of theories have been devoted to deduce the band structure of alkali halides.²¹⁻²⁵ From that can be obtained the warping parameter for these materials. From the theory developed by Pantelides²⁶ based on the linear combination of atomic orbitals (LCAO) method, an analytic expression of the warping parameter for the valence band $(\gamma_2 - \gamma_3)_{band}$ can be obtained,

$$(\gamma_2 - \gamma_3)_{band} \approx -(V_p - V_\pi) / 12a_0^2(m_0/\hbar^2), \quad (11)$$

where V_p (V_π) is the p - (π -) bonding matrix element defined in Ref. 26, a_0 is the lattice constant and the other magnitudes have the usual meaning. As $V_\pi < \frac{1}{5}V_p$,²⁶ and the bandwidth W_V is related to V_p through $W_V = 7.5V_p$.²⁶ Then (11) becomes

$$(\gamma_2 - \gamma_3)_{band} \approx -(W_V/90)a_0^2(m_0/\hbar^2). \quad (12)$$

By using the data reported in Ref. 26 one obtains the same value of $(\gamma_2 - \gamma_3)_{band} = -0.14$ for all the alkali halides. One should note that $(\gamma_2 - \gamma_3)_{ex}$ can be related with the $(\gamma_2 - \gamma_3)_{band}$ through the relations (7) and (12):

$$(\gamma_2 - \gamma_3)_{ex} = -(W_V/90)a_0^2(1 + m_e^*/m_h^*)^{-2}m_0/\hbar^2. \quad (13)$$

From expression (13) and the values of a_0 and W_V reported in Ref. 26 one obtains $(\gamma_2 - \gamma_3)_{ex}$ reported in Table I. These values agree in sign with those measured, but, as expected from a simple model, does not explain the smallness of the bromide family and large values for NaI, CsI, and RbCl. Moreover, it does not explain the trend in

TABLE I. Exciton energies ω_0 and oscillator strengths C_{ex} . Experimental values of nondispersive term and $(\gamma_2 - \gamma_3)_{ex}$ obtained by fitting the BISD results with expression (6). Theoretical values of $(\gamma_2 - \gamma_3)_{ex}$, using Eq. (11) together with estimations of the warping parameter by band calculations together with β_h values.

	ω_0 (eV)	C_{ex} (eV) ²	D (10 ⁻⁸ eV ⁻²)	Experimental $(\gamma_2 - \gamma_3)_{ex}$	β_h	Theoretical this work $(\gamma_2 - \gamma_3)_{ex}$	Theoretical $(\gamma_2 - \gamma_3)_{ex}$
NaI	5.42 ^a	5.4 ^b	-25.2	-0.88	0.9 ^l	-0.11	
KI	5.63 ^a	5.9 ^c	3.2	-0.18	0.9 ^d	-0.11	-0.08, ^e -0.04 ^d
RbI	5.54 ^a	6.4 ^f	9.7	-0.22	0.9 ^l	-0.11	
CsI	5.62 ^a	6.7 ^f	-2.8	-1.00			
NaBr	6.50 ^a			<0.02	0.8 ^g	-0.09	0.006 ^g
KBr	6.62 ^a	6.6 ^c		<0.02	0.9 ^d	-0.11	-0.06, ^d 0 ^g
RbBr	6.44 ^a	7.1 ^f		<0.02	0.9 ^h	-0.11	
CsBr	6.65 ^a	6.7 ^f		<0.02	0.9 ^l	0.11	
NaCl	7.74 ⁱ	13.6 ⁱ	-3.0	-0.21	0.9 ^g	-0.11	-0.02 ^g
KCl	7.57 ^j	11.4 ^j	5.7	-0.26	0.9 ^{d,h}	-0.11	-0.06, ^h +0.013, ^g -0.01 ^g
RbCl	7.46 ^a	10.0 ^k	8.3	-0.43	0.9 ^g	-0.11	-0.07 ^d

^aReference 20.

^bReference 24.

^cReference 23.

^dReference 27.

^eReference 28.

^fReference 17.

^gReference 30.

^hReference 29.

ⁱReference 21.

^jReference 22.

^kReference 25.

^lReference 31.

$(\gamma_2 - \gamma_3)_{ex}$ as the ionic radius of the cation increases. The Table I also shows estimations of $(\gamma_2 - \gamma_3)_{ex}$ from the band calculations performed by different authors. We believe that agreement of these calculations with experiment like in KI or KCl cases for some of the works are fortuitous. For instance, estimations of $(\gamma_2 - \gamma_3)_{ex}$ based in the band structure done by Kunz³⁰ agrees with NaBr and KBr measurements. However, the same self-consistent calculations does not explain the $\gamma_2 - \gamma_3$ obtained for NaCl and KCl. From the relativistic calculation of band scheme by Onodera *et al.*,²⁸ for KI one obtains values of $\gamma_2 - \gamma_3$ that are closer to experimental values than those from other calculations.²⁷ We do not know the reason of those large values of $\gamma_2 - \gamma_3$ for iodides and chlorides and also for the experimental dependence of $\gamma_2 - \gamma_3$ on the ionic radius of the cation. Some authors have pointed out the importance of d bands of the cations for the alkali halide band theory with heavy cations. For instance, the band calculations by Onodera *et al.*²⁸ show d bands 1.2 eV above the s -like conduction band for KI. This band shows quite different curvature along (100) and (111) directions. The interaction between the d and p bands could be responsible for such a high warping parameter measured and therefore could explain the unusual large values of $\gamma_2 - \gamma_3$ in these materials.

V. CONCLUSIONS

In conclusion we have measured the BISD of alkali halides including its sign. By fitting the results obtained with a microscopical model enables us to obtain the warping parameter $(\gamma_2 - \gamma_3)_{ex}$ of the exciton that is negative and have values as large as those obtained in zinc-blende-type semiconductors. One also observes strong dependence of $(\gamma_2 - \gamma_3)_{ex}$ on the ionic radius of the cation. For alkali bromides (NaBr, KBr, RbBr, and CsBr) we have found no BISD. From band calculations by Pantelides²⁶ we obtain $(\gamma_2 - \gamma_3)_{ex} \approx -0.1$ for all the alkali halides. From other band calculations, it is not possible to explain the values of $(\gamma_2 - \gamma_3)_{ex}$ measured in chloride and iodide families. We suspect that the existence of d bands close to the s conduction band could be responsible for such large values. Theoretical effort in that way should be desirable.

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