# Exciton luminescence and polariton effects in alkali iodide crystals

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An investigation of the edge luminescence due to free excitons in KI and RbI has been made on bulk crystals and thin crystal plates of thicknesses from 10 to 0.1 $\mu$m at 11 K. In the thin samples, it is found that the edge luminescence line appears just around the absorption band attributed to the strain-induced spin-triplet states, both peaks showing the same thickness-dependent energy shift. From a close connection of these results with those obtained in unstrained bulk materials, the polariton model including the symmetry-breaking effect due to a finite exciton wave vector is invoked to account for the origin of the edge luminescence in alkali iodides. On the basis of the above arguments, the exchange energy $\Delta$ and the spin-orbit splitting $\lambda$ of excitons are evaluated; $\Delta = 20$ meV and $\lambda = 0.89$ eV for KI and $\Delta = 26$ meV and $\lambda = 0.78$ eV for RbI.

## I. INTRODUCTION

In some alkali halides, a sharp luminescence line has been observed in the edge region of the first exciton absorption band. This is called edge luminescence; it coexists with the broad luminescence, which has a large Stokes shift.[1] This fact reveals that the excitons in alkali halides exhibit both free and self-trapped states, separated by an adiabatic potential barrier due to the short-range nature of the exciton-phonon interaction.[2] The broad luminescence arising from self-trapped excitons generally consists of two different types of bands, one predominantly singlet, the other triplet in character. These features have been well accounted for on the basis of the close similarity between the electronic configurations of a self-trapped exciton and a diatomic rare-gas molecule.[3] On the other hand, although the sharp edge luminescence has been assigned to the free-exciton states from the spectroscopic point of view,[1] its nature is not yet fully understood.

Among several experimental means for investigating exciton states, the effect of uniaxial stress is of considerable interest. Uniaxially applied stress induces changes in the crystal symmetry, which can relax the selection rules in the optical spectra of excitons.[4,5] However, uniaxial stress experiments in alkali halides have been limited to date,[6,7] since the sample crystals are easily broken under high pressures. Recently we have succeeded in growing thin single crystals of alkali iodides inside a narrow gap between two parallel quartz plates. These thin crystals adhere to quartz plates. As a result, dilational strains appear in the plane of the sample because of the difference between the temperatures at which a sample was prepared and investigated and also because of the difference between the expansion coefficients of alkali iodides and quartz.[8] Since such strains cause a Poissonian deformation in the direction normal to the sample plane, they result in effects similar to those produced by uniaxial loads, and therefore, can be used in the studies of exciton states. In fact, we have found new structures appearing on the low-energy side of the exciton absorption band in thin KI and RbI crystals. They become intense and shift to lower

energy with decreasing crystal thickness; we attribute this to an increase of dilational strains, for thinner samples. From an analogy between these results and those obtained in uniaxially stressed semiconductors, the additional structures were attributed to strain-induced spin-triplet exciton states.[9,10]

In this paper we investigate the edge luminescence in such thin KI and RbI crystals. The thickness $d$ of samples ranges from about 10 to 0.1 $\mu$m. It is confirmed that the edge luminescence shows the same thickness-dependent peak shift which we observed for the triplet absorption band. These experimental data are extrapolated to the limit $1/d = 0$, in good agreement with those obtained in unstrained bulk crystals. From this it is pointed out that the finiteness of the exciton wave vector plays an important role in the occurrence of edge luminescence in alkali iodides. The polariton model is, furthermore, introduced to describe the coupling of exciton states with the electromagnetic radiation field. It is shown that the pure spin-triplet exciton state acts as an effective bottleneck for the polariton relaxation. On the basis of the above results we deduce the exchange interaction energy $\Delta$ and the spin-orbit splitting $\lambda$ of the excitons in these iodides from the Onodera and Toyozawa theory.[11]

## II. EXPERIMENTAL

Ingots of KI and RbI crystals were obtained from the Harshaw Chemical Co. and from the Crystal Growth Laboratory of the University of Utah, respectively. The method of preparation of thin samples was similar to that described in Ref. 12: Making use of surface tension, the melt was introduced into the narrow gap of a cell composed of two parallel quartz plates, and allowed to solidify. Bulk crystals cleaved from the ingot, or as-grown thin crystals within the cell, were mounted on the copper cold finger of a closed-cycle cryogenic refrigerator. An electric heater provided control of sample temperatures over a range of about 10 to 70 K; the temperature was measured with an Au:Fe-vs-Chromel thermocouple. The thickness

$d$ of thin samples was determined by an analysis of the Fabry-Perot interference fringes in the reflection spectra.[13]

For measurements of the edge luminescence, the uv light from a $D_2$ lamp was dispersed through a Bausch and Lomb grating monochromator and focused by a fused-silica lens on the sample surface. Luminescence was observed from the irradiated surface of samples by focusing it onto the entrance slit of a Nikon P250 monochromator equipped with a 600-grooves/mm grating blazed at 200 nm. The wavelength of the analyzing monochromator was calibrated to maintain accuracy within ±0.05 nm. The signal was detected by a Hamamatsu R106UH or R955 photomultiplier tube and then stored into a microcomputer, to improve the signal-to-noise ratio. The observed luminescence spectra were corrected for the dispersion of the monochromator and for the spectral response of the detecting systems.

## III. RESULTS

Luminescence spectra of KI and RbI were investigated in the edge region of the first exciton absorption band at 11 K. The edge luminescence observed in thin crystals had intensity comparable with that in bulk crystals, although it was somewhat sample dependent. Typical spectra are shown in Fig. 1, where the peak intensity is normalized to unity. In bulk crystals, sharp zero-phonon lines are found at 5.831 eV in KI and 5.728 eV in RbI, in quite good agreement with the previous experiment.[14] These lines are followed by one or more LO-phonon sidebands. The half-width (full width at half maximum) of the zero-phonon lines is about 4.5 meV, which roughly coincides with the spectral resolution of the analyzing monochromator used. In thin crystals, there appears the relatively broad luminescence band, with a tail toward the low-energy side. Like the edge luminescence in bulk crystals, this luminescence is strongly excited with uv light in the high-energy region of the first exciton band and exhibits a sharp decrease in intensity as the exciting photon energy is raised beyond the onset of the interband transition. As clearly seen in both cases of KI and RbI, the luminescence bands shift to lower energy and broaden, for thinner samples.[15] This low-energy shift is attributed to an increase of dilational strains with decreasing $d$. Furthermore, the increase of half-widths may be explained as a result of the strain-induced broadening and/or the thickness inhomogeneity of our samples. No other lumines-
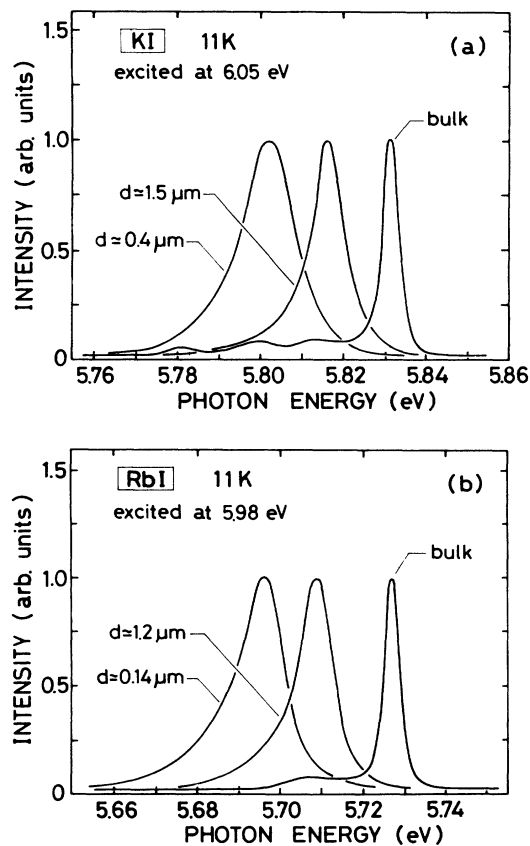


FIG. 1. Luminescence spectra observed in the edge region of the first exciton band at 11 K: (a) KI, excited at 6.05 eV, and (b) RbI, excited at 5.98 eV. Each spectrum is normalized at the maximum. $d$ is the crystal thickness, for thin samples.
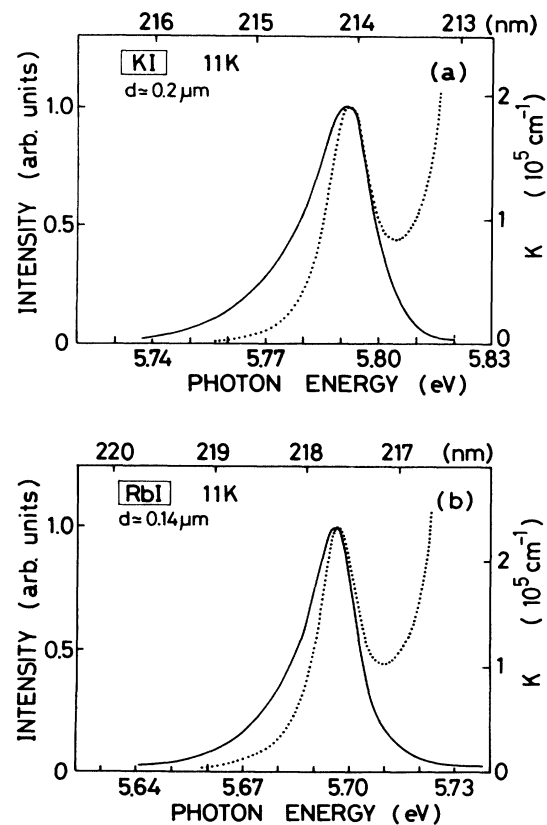


FIG. 2. Absorption spectra (dotted lines) and luminescence spectra (solid lines) at 11 K: (a) KI, $d = 0.2$ $\mu$m, and (b) RbI, $d = 0.14$ $\mu$m. The right-hand scale pertains to the absorption coefficient. The luminescence and absorption intensities are normalized at the maximum of the triplet band.

cence was observed in the spectral range investigated here.

In our previous experiments,[9,10] absorption and reflection spectra of thin crystals were measured in detail. Figure 2(a) is a combined result of the absorption spectrum (dotted line) and the luminescence spectrum (solid line) taken for a KI crystal with $d = 0.2$ $\mu$m. The absorption spectrum shows a well-defined peak on the low-energy tail of the first exciton band. This structure, which could not be observed in earlier experiments using bulk crystals or thin evaporated films, is associated with the spin-triplet exciton state allowed by thermal strains.[9,10] From this figure it is recognized that the edge luminescence appears just around the triplet absorption band. A similar situation was also found in the case of RbI; see Fig. 2(b).

In Fig. 3(a), peak positions of the edge luminescence (open circles) and the triplet absorption (solid squares) observed in KI crystals with different thicknesses are summarized as a function of $1/d$. For reference, maximum positions of the exciton band in reflection spectra are also indicated by solid circles. The data points at $1/d = 0$ correspond to the results obtained in bulk crystals. Continuous lines are simply drawn through the experimental points. Similar results for RbI are represented in Fig. 3(b). One can see that the triplet absorption appears when $d$ is decreased to ~0.5 $\mu$m and shifts to lower energy with further decrease in $d$. It is evident that the low-energy shift of the luminescence peak agrees well with that of the triplet absorption band. When $d > 0.5$ $\mu$m, the triplet absorption does not appear, but the edge luminescence can still be observed. Luminescence peaks vary sharply in the region of $d = 1-10$ $\mu$m, in parallel with the reflection maxima. Extrapolation of these data points to $1/d = 0$ leads to an energy position close to the luminescence peak in bulk crystals. This fact suggests that the edge luminescence in thin and bulk crystals is of the same origin.
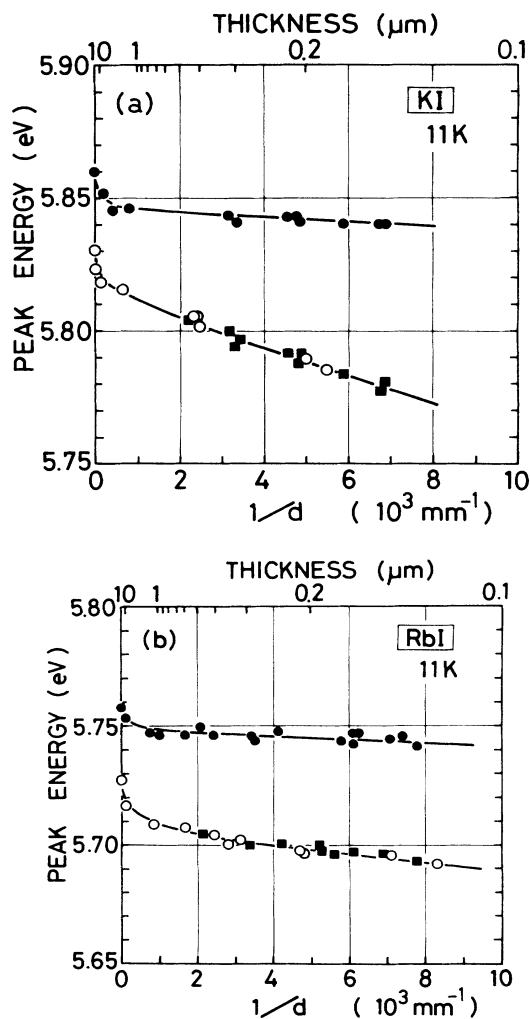


FIG. 3. Peak positions of the edge luminescence (open circles) and the triplet absorption (solid squares) as a function of $1/d$ in (a) KI and (b) RbI. Reflection maxima of the exciton band are also indicated by solid circles. All data were taken at 11 K. Continuous lines are simply drawn through the experimental points.
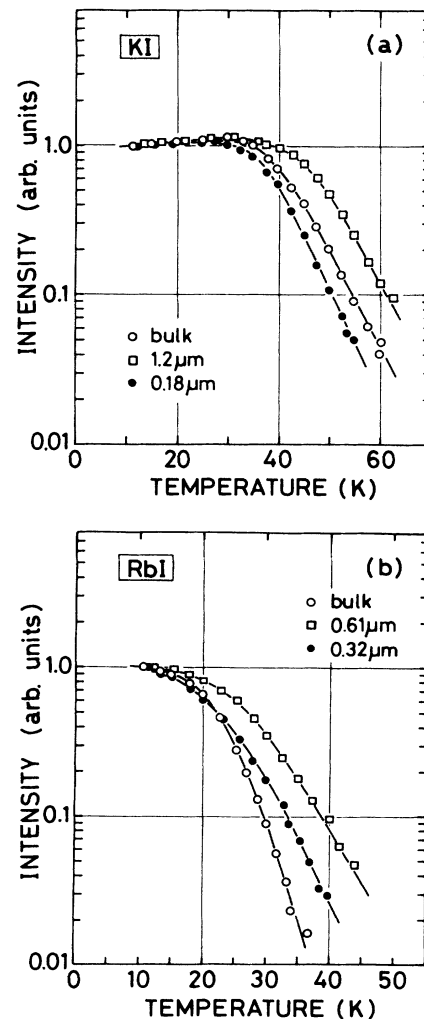


FIG. 4. Typical examples of the temperature dependence of the edge luminescence intensity: (a) KI, excited at 6.05 eV, and (b) RbI, excited at 5.98 eV. All curves are normalized to unity at 11 K.

We further examined the temperature dependence of the luminescence intensity. Typical examples of KI and RbI are shown in Figs. 4(a) and 4(b), respectively, where the luminescence intensity is plotted in a logarithmic scale against temperature. All curves are normalized to unity at 11 K. The temperature dependence varies somewhat from sample to sample. However, as a whole, the agreement between thin and bulk crystals may be regarded as satisfactory considering the sample-dependent crystal quality. Indeed, even in the case of bulk crystals,[16] it has been found that thermal quenching of the edge luminescence depends strongly on the samples used. Observed quenching temperatures are about 40 K in KI and about 20 K in RbI. These results are fairly consistent with the ones reported in Ref. 16.

## IV. DISCUSSION

An important point to be noted is that there is a strong similarity between both results for KI and for RbI; this strongly suggests the existence of common mechanisms in the luminescence processes. In the present experiments, the edge luminescence was observed in all the investigated samples whose thicknesses ranged from 10 to 0.1 $\mu$m. Since our thin crystals may contain several kinds of lattice imperfections, we have to worry about the contribution of excitons which might be bound to them. However, it is concluded that the components of edge luminescence observed here are not due to bound excitons but to free excitons, for the following reasons. (1) Their peak positions extrapolated to $1/d = 0$ agree well with those in bulk crystals (Fig. 3). (2) If they are due to bound excitons, free-exciton luminescence is also expected to appear on the high-energy side of the spectrum. However, such a symptom was not found (Fig. 1). (3) They are thermally quenched around 40 K in KI and 20 K in RbI, in agreement with those in bulk crystals (Fig. 4). This thermal quenching originates from relaxation of free excitons to self-trapped states over an activation barrier.[1,2]

As shown in Fig. 3, the edge luminescence is located in the vicinity of the absorption peak attributed to the triplet excitons. It is thus supposed that the triplet exciton state plays an important role for the luminescence processes. As is well known, the exciton ground states in alkali halides arise from $s$-like conduction and $p$-like valence bands at the $\Gamma$ point of the Brillouin zone. Because of spin-orbit interaction in the valence band, they split into the $\Gamma(\frac{3}{2},\frac{1}{2})$ exciton and the $\Gamma(\frac{1}{2},\frac{1}{2})$ exciton; here the first member in the parentheses indicates the angular momentum of a hole and the second that of an electron. Moreover, the electron-hole exchange interaction becomes important in alkali halides, as first pointed out by Onodera and Toyozawa.[11] Taking this into account, we have the exciton states with total angular momentum $J = 1$ and $J = 2$ at the interband edge $\Gamma(\frac{3}{2},\frac{1}{2})$, and with $J = 1$ and $J = 0$ at the interband edge $\Gamma(\frac{1}{2},\frac{1}{2})$. Here the two states with $J = 1$ are mixtures of the singlet and triplet states and are dipole active, corresponding to the halogen doublet observed in the optical spectra of excitons. The $J = 2$ and $J = 0$ states are pure spin-triplet and dipole-inactive states. These states are lower in energy than the $J = 1$

states because of the positive exchange energy. In Refs. 9 and 10, we assigned the triplet absorption band to the $J = 2$ state of the $\Gamma(\frac{3}{2},\frac{1}{2})$ exciton. As mentioned there, in the presence of thermal strains in thin crystal plates, the $J = 2$ state becomes mixed with the $J = 1$ state as a result of the relaxation of the selection rules, i.e., deformation-induced mixing.[5] Thus the oscillator strength is transferred from the dipole-active $J = 1$ state to the spin-triplet $J = 2$ state, which is consequently responsible for the luminescence process as well as the absorption process.[17]

Now the question arises: what mixing mechanisms exist between $J = 1$ and $J = 2$ states in bulk crystals? Possible candidates for this are finite electric field or strain field associated with phonons or residual strains. However, it seems to be a rather odd assumption that such strains should be present in all crystals prepared under different growth conditions. Moreover, the luminescence intensity did not show a remarkable increase with increasing temperature, and this is in contrast to an interpretation of the mixing as essentially due to phonons. Hence these mixing mechanisms seem to be less likely. The most likely one is the mixing mechanism associated with the exciton wave vector $\mathbf{k}$, the general treatment of which was developed by Cho.[18] Optically created excitons have finite values of the translational wave vector $\mathbf{k}$. This small but finite $\mathbf{k}$ can act as a perturbation which mixes the exciton states defined at $\mathbf{k} = 0$. Such a symmetry-breaking effect has proved to be the origin of many interesting anomalies in the exciton spectra of copper halides and II-VI compounds,[19] where the $\mathbf{k}$-linear term is allowed due to the lack of a center of inversion. In alkali halides, with inversion symmetry, the mixing between $J = 1$ and $J = 2$ states arises from the term quadratic in $\mathbf{k}$;[18,20] this term is de-
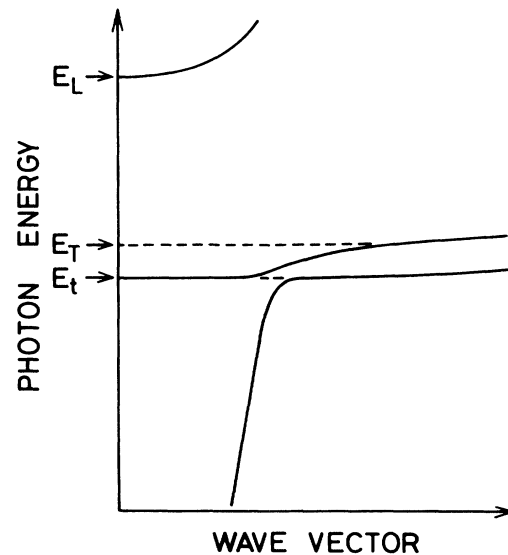


FIG. 5. Schematic representation of the dispersion curves of polaritons (solid lines) and excitons (dashed lines) in alkali iodides. The resonance energies of the longitudinal, transverse, and spin-triplet excitons are denoted as $E_L$, $E_T$, and $E_t$, respectively.

TABLE I. Experimental values of the exciton parameters of KI and RbI: $E_T$ is the resonance energy of the transverselike $J = 1$ state, $E_t$ the resonance energy of the triplet $J = 2$ state, $\delta_1 = E_T - E_t$, $\delta_2$ the energy separation of the halogen doublet, $\Delta$ the exchange energy, and $\lambda$ the spin-orbit splitting.

| | $E_T$ (eV) | $E_t$ (eV) | $\delta_1$ (meV) | $\delta_2$ (eV) | $\Delta$ (meV) | $\lambda$ (eV) |
|---|---|---|---|---|---|---|
| KI | 5.844[a] | 5.831 | 13 | 0.88[b] | 20 | 0.89 |
| RbI | 5.745[a] | 5.728 | 17 | 0.77[b] | 26 | 0.78 |

[a]Reference 23.
[b]Reference 28.

rived from the corresponding term in the valence-band Hamiltonian and leads to the so-called heavy and light excitons.[21,22] Consequently, the $J = 2$ state becomes allowed without any external perturbation; it couples spontaneously with the electromagnetic radiation field.

In order to describe the coupled exciton-photon system, we adopt the polariton dispersion curves calculated from an invariant expansion of the exciton Hamiltonian, including exchange interaction, up to second order in $\mathbf{k}$.[20] Figure 5 shows schematically the dispersion of polaritons (solid lines) and excitons (dashed lines). The resonance energy of the spin-triplet $J = 2$ state is denoted as $E_t$. Due to the dipole-dipole interaction, the $J = 1$ exciton states split into the longitudinal state $(E_L)$ and the transverse state $(E_T)$. According to recent experiments,[23,24] the longitudinal-transverse splitting is about 105 meV in both KI and RbI, corresponding to the broad exciton absorption band. The lowest curve is the lower polariton branch associated with the weakly allowed triplet excitons. The intermediate branch has the character of triplet excitons at small $\mathbf{k}$ but continues to the transverselike $J = 1$ excitons in the region with large $\mathbf{k}$. The uppermost curve is the usual upper branch of the intermediate one.

In the polariton picture, free-exciton luminescence is regarded as a result of the conversion of a polariton into external photons at the boundary of a crystal.[25] When polaritons are optically created at energies above $E_T$, they will be scattered on the transverselike $J = 1$ exciton branch through the exciton-phonon interaction. However, since the intermediate branch is a smooth function of $\mathbf{k}$, the polaritons on this branch easily relax to the spin-triplet state under subsequent scattering by phonons. Thus a large population of polaritons is realized on the triplet state, where a polariton is converted into the external luminescence. The edge luminescence peak is, therefore, reasonably assigned to the $J = 2$ exciton state, not the $J = 1$ state. A similar conclusion on the triplet nature of free-exciton luminescence has also been drawn from magnetoluminescence experiments in CuBr,[26] CdS, and CdSe.[27] Because of the higher-order perturbation due to the $\mathbf{k}$-quadratic term, the triplet excitons weakly couple with photons, so that the lower polariton branch shows a sharp bend in the knee region. This will explain why the edge luminescence has a very narrow half-width, in spite of the broad exciton absorption band.

On the basis of the above assignment, we can deduce the exchange energy $\Delta$ and the spin-orbit splitting $\lambda$ for the excitons in KI and RbI by using the Onodera-

Toyozawa formula.[11] When $\Delta \ll \lambda$, we have, to a good approximation,

$$\Delta = \tfrac{3}{2}\delta_1 , \tag{1}$$

$$\lambda = \delta_2 + \tfrac{1}{2}\delta_1 , \tag{2}$$

where $\delta_1 = E_T - E_t$ and $\delta_2$ is the energy separation of the halogen doublet in the exciton spectra. The present experiment yields $E_t = 5.831$ eV for KI and 5.728 eV for RbI. Also, we have $E_T = 5.844$ eV for KI and 5.745 eV for RbI, with an accuracy of $\pm 5$ meV, from the fitting of the dispersion curves with a theoretical formula of polaritons.[23] Concerning the values of $\delta_2$ in KI and RbI, identification of the doublet has represented a puzzle to many authors. However, recent measurement of magnetic circular dichroism spectra[28] provides clear evidence that the lowest two strong peaks correspond to the halogen doublet. According to this result, $\delta_2 = 0.88$ eV in KI and 0.77 eV in RbI. Substituting the above values into Eqs. (1) and (2), we thus obtain $\Delta = 20$ meV and $\lambda = 0.89$ eV for KI and $\Delta = 26$ meV and $\lambda = 0.78$ eV for RbI. These parameters are listed in Table I. It is worth noting that the present values of $\Delta$ are much larger than those in semiconductors, e.g., 2.1 meV (ZnSe) (Ref. 29) or 0.2 meV (CdS).[30] This is to be expected from the fact that the exciton radius is small in alkali halides, since the exchange energy is proportional to the probability of finding electron and hole on the same site.

We notice the reflection spectrum of KI measured by Petroff et al.[31] They found a small hump 10 meV below the reflection peak of the exciton band. This structure was interpreted as one LO-phonon sideband of the triplet $J = 2$ state becoming observable due to exciton-phonon interaction. Based on this assignment, they obtained the value $\Delta = 43$ meV by taking the peak energy of the exciton band as $E_T$ to estimate $\delta_1$. In the present estimates, our values of $E_T$ are situated slightly to the low-energy side of the reflection peaks.[23] If peak positions are taken as $E_T$, then we deduce $\Delta = 44$ meV for KI and 46 meV for RbI. This value of KI agrees well with the one obtained by Petroff et al. Although the agreement is quite satisfactory, it must be pointed out that their assignment of the triplet exciton band seems to be somewhat questionable, both in the experimental[10] and theoretical[32] points of view.

In summary, we investigated the edge luminescence due to free excitons by using thin and bulk crystals of KI and RbI. As for semiconductors, we attributed edge lumines-

cence in ionic materials to symmetry-breaking associated with the exciton wave vector. The bottleneck for the polariton relaxation was reasonably supposed to lie on the pure spin-triplet state of the $\Gamma(\frac{3}{2},\frac{1}{2})$ exciton. In addition, we were able to obtain the values of the exchange interaction energy and the spin-orbit splitting energy for the excitons in KI and RbI crystals.

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