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Optical properties and electronic structure of alkali halides by thermoreflectivity

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We report detailed measurements of thermoreflectivity spectra of NaCl, KCl, RbCl, NaBr, KBr, RbBr, NaI, KI, and RbI in the 5–9-eV region at several temperatures. Through an analysis of the thermoreflectivity line shapes and temperature coefficients, we try to find a general interpretation of the optical-spectra structures for all crystal families in terms of Γ, L, and X transitions, on the basis of present understanding of band calculations. The spin-orbit splitting of the Γ exciton is determined to be 0.13 ± 0.02 eV in chlorides, 0.49 ± 0.02 eV in bromides, and 1.10 ± 0.02 eV in iodides.

INTRODUCTION

In the last few years a remarkable effort has been made in interpreting the fundamental optical properties of alkali halides in terms of excitonic or band-to-band transitions.

Absorption and reflectivity spectra are now well available. The improvement of the spectroscopic techniques allowed the reflection spectra of many alkali halides to be measured with great accuracy, high resolution, and at very low temperatures.[1]

Years ago, Phillips proposed that the fundamental spectral of alkali halides had to be interpreted in terms of energy bands, as in semiconductors.[2] Connection with the band structure of rare-gas solids has also been suggested, by considering alkali halides as a slightly more complex version of rare-gas solids.[3-6] More recently, several calculations on electronic band structure were performed.[7-14] The methods of calculation were significantly different. Lipari and Kunz made progress in obtaining *ab initio* energy bands for a variety of alkali halides by means of the mixed-bases method.[15] Despite a great deal of effort, agreement among the results of different calculations for the same material is not generally obtained because of the different assumptions made in forming the crystal potential. Moreover, the electron-hole interaction should be considered in the theory.

As regards the interpretation of the optical spectra, the first, most pronounced reflectivity peaks are well assigned[2] to excitonic transitions from the upper valence band to the lowest conduction band at the Γ point in the Brillouin zone (BZ). However, it is more difficult to take into account the excitonic interaction effects on the optical spectra for the higher-energy transitions. No reliable assignment beyond the first excitonic peaks has yet been done. Different band calculations[11,14,19] give different values for the s- and d-like conduction-band energies, at the X and L points of the BZ.

The aim of this work is to gain new information on the assignment of the lower energy Γ, L, and X transitions using thermoreflectivity (TR) measurements of different alkali halides. In fact, it has been shown[16] that, through an examination of the TR line shapes and the transition-temperature coefficients, it is possible to discriminate between the L and X transitions. The spin-orbit (SO) splitting problem of the Γ exciton will also be considered.

EXPERIMENTAL APPARATUS AND GENERAL SYSTEMATICS

Thermoreflectivity (TR) measurements have been performed with the usual technique of phase-sensitive detection. Experimental details were previously described.[16,17] All spectra have been measured at near normal incidence with unpolarized light. A thermal modulation of no more than 0.5 K was observed. Generally, the modulation intensity $\Delta R/R$ in the first exciton peak was of the order of 5×10^{-3}.

TR spectra of insulators consist[16,17] of a combination of the derivative of the reflectivity with respect to the energy transition (thermal shift) and its derivative with respect to the broadening parameter (thermal broadening). In the approximation where peaks in reflectivity are taken as the position of a transition, the following procedure has been employed to determine the transition energies from the TR curves. When the broadening term is small compared to the one of the shift (thermal and wavelength-modulation spectra should be equivalent), reflectivity peaks correspond to the zero crossing points, from positive to negative, in TR spectrum (absorption-like TR line shape). Besides, inflection points in reflectivity are indicated by nonzero, positive or negative minima in the derivative spectrum. On the other hand, when the broadening term is dominant and the structure is well resolved in the modulated spectrum, the zero crossing from negative to positive is assumed to give the transition energy (dispersion-like TR line shape).

BAND STRUCTURES

At the present level of understanding, a quick look at any calculated band structure reveals that the optical spectra of the alkali halides in the 5–9 eV energy range must be explained by interband and excitonic transitions from the *p*-valence bands to *s*- and *d*-conduction bands. All the theoretical results agree on a very flat valence band having a maximum at Γ in the center of the BZ. This band is split by SO interaction, since it is derived from the outer *p* orbitals of the halogen ion. The magnitude of this splitting in the center of the BZ ranges from about 1 to 0.1 eV going from iodide to chloride crystals. The upper valence band is further split away from the center of the BZ because of symmetry conditions.

If we now try to find a clear cut, general interpretation of the optical spectra for different crystal families based on the conduction bands calculated by various authors, a number of difficulties arise. In fact we find that in the case of Rb and K halides[11,14,20]:

(a) There is always a lowest conduction-band minimum at Γ derived from the *s*-states of the alkali ion.

(b) One of the *d*-like conduction bands, which is above the *s*-like band at Γ, dips down to an absolute minimum at X, overlapping the *s*-like conduction band through the Δ line.

(c) The features of the band models given by different authors do not agree on the energy position of the X and L points for the *s*- and *d*-like conduction bands. In fact, referring to the valence band, the X and L state energies of the conduction bands are different in different calculations.

In the case of Na (and Li) halides,[8,18,19] the band structures suggest a higher X_7^+ point in the conduction band and do not show an inversion between the X_7^+ and X_6^+.

To illustrate the discussion, Fig. 1 shows the conduction-band structures for the three kinds of calculation which summarize the present understanding.[11,14,20,21] We have considered the KI crystal because in recent years the properties of KI have been the subject of many theoretical and experimental studies. Moreover, the other alkali halides may be thought, at least in principle, to present similar band features with different SO splittings and energy gaps. On this subject we note that:

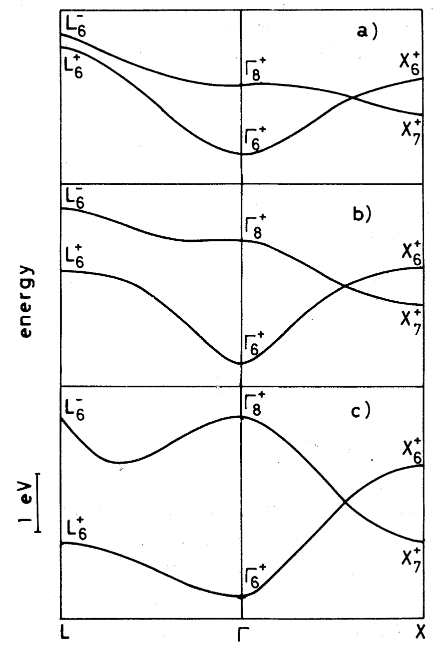

FIG. 1. Conduction-band structures of KI: (a) replot from Ref. 11, (b) from Ref. 14, (c) from Ref. 21.

(i) The X_7^+ level, related to the *d* states of the cation, is expected to move slightly downward, toward the Γ_6^+ level, when the Rb$^+$ ion is substituted for K$^+$, and upward when Na$^+$ takes the place of K$^+$, since the lowest *d* states of the alkali metals show this behavior relative to the lowest *s* level of the valence electron.

(ii) Unlike K and Rb halides, *d*- and *s*-like levels may change their order in Na halides at the X point.[11,18,19]

For a more detailed comparison among the different theoretical approaches (summarized in Fig. 1) we refer to the original papers.[11,14,20,21]

EXPERIMENTAL RESULTS

Figures 2–4 show the TR spectra of chloride, bromide, and iodide (of Na, K, and Rb), respectively, at different temperatures. The same capital letter is used to indicate transitions arising from symmetry or SO split valence bands at the same point in the BZ. Subindexed letters indicate structures of the same excitonic series.

In Fig. 5, the TR spectrum of the first exciton of KI is reported together with the wavelength logarithmic derivative spectrum at about the same temperature. This was calculated by graphical differentiation of the reflectivity curve. The two line shapes are very similar, depending on the fact that the thermal-shift modulation is predominant on the broadening one for the first exciton.

For all crystals and temperatures, A structures

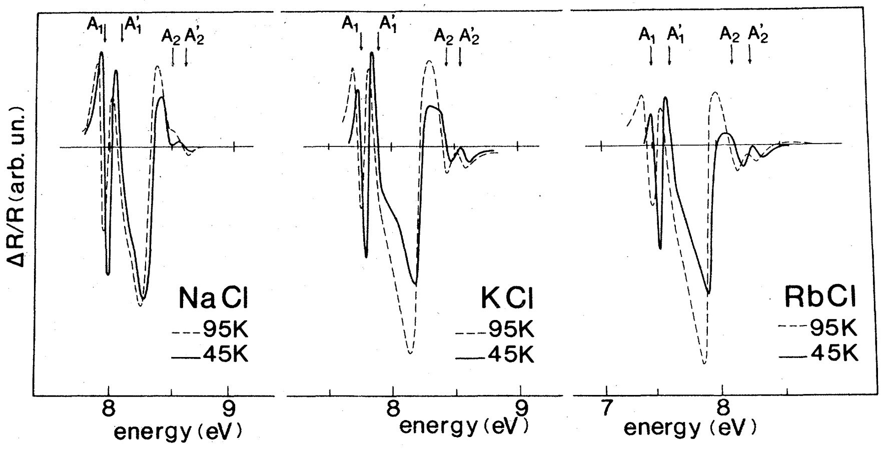

FIG. 2. Thermoreflectivity spectra of NaCl, KCl, and RbCl at 45 K (solid line) and 95 K (dashed line).

present an “absorption-like” line shape and a thermal coefficient which range from -5×10^{-4} to -2×10^{-3} eV/K. *C* structures show a “dispersion-like” line shape. The zero-crossing point, from negative to positive, has a temperature coefficient smaller, in absolute value, than 10^{-5} eV/K. *B* structures, even if they are not well resolved, appear to depend upon the temperature as the *A* structures.

We note that *C* structures are not present in the

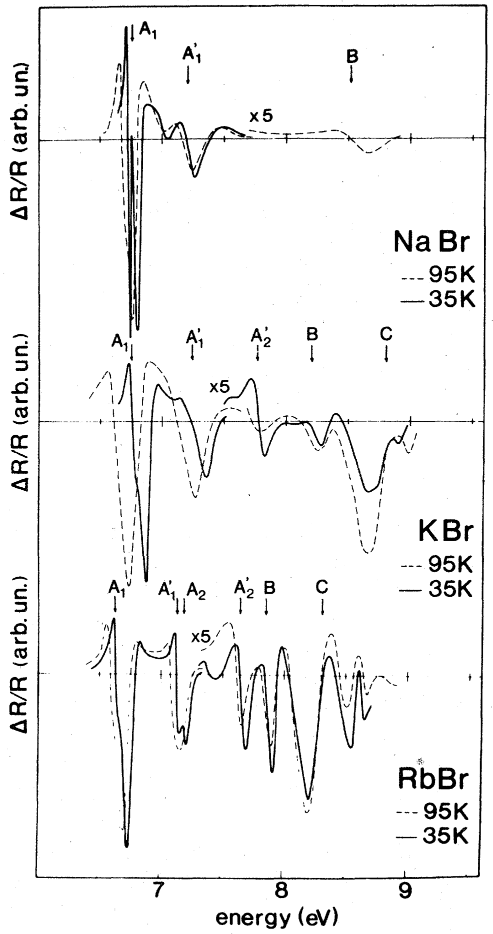

FIG. 3. Thermoreflectivity spectra of NaBr, KBr, and RbBr at 35 K (solid line) and 95 K (dashed line).

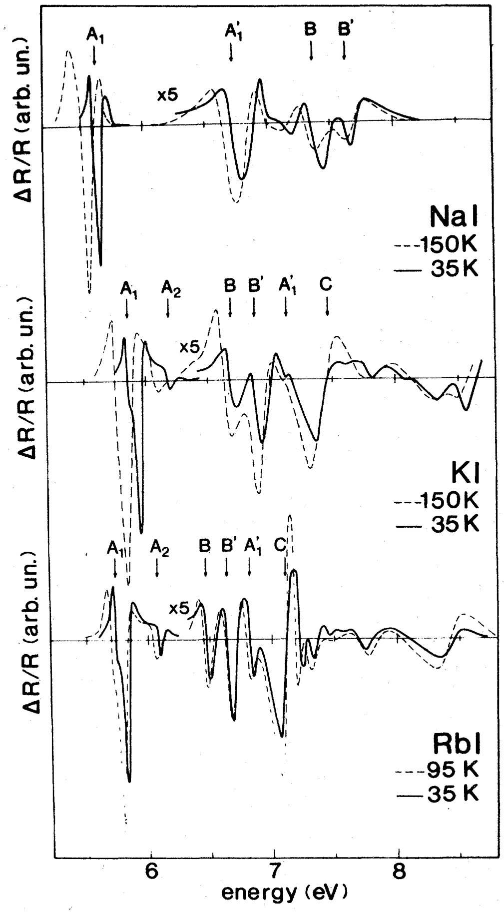

FIG. 4. Thermoreflectivity spectra of NaI and KI at 35 K (solid line) and 150 K (dashed line) and of RbI at 35 K (solid line) and 95 K (dashed line).

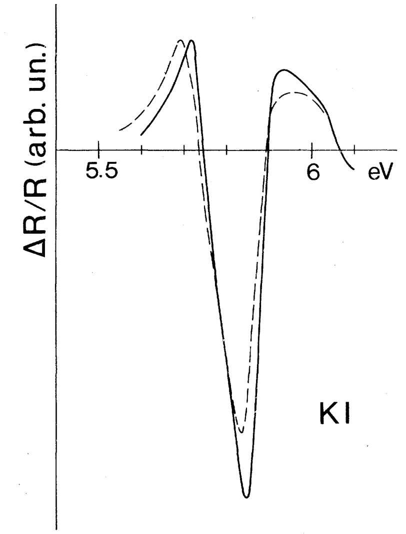

FIG. 5. Thermoreflectivity spectrum (solid line) at 150 K and wavelength logarithmic derivative spectrum (dashed line) at 165 K of the KI first exciton.

Na halides, at least in an investigated energy interval as large as the one in the NaI case. C structures are not even present in chloride TR spectra: probably the associated electronic transitions take place at energies higher than our experimental limit. B and B' structures are well defined in the iodide. In the bromide B' structures are perhaps overimposed on C structures which are broader than in iodide.

We remark that the Γ exciton splits at low temperature because of the exciton-phonon interaction.[22] However, this problem is beyond the interest of our paper. In the case of NaBr, we have performed TR measurements with very high resolution to verify the efficiency of the measurements. With lower resolution this effect generally reduces to a shoulder on the low-energy side of the A structure. In the figures, $n=2$, Γ excitons are also indicated (A_2 and A_2' structures) according to reflectivity measurements from Ref. 1.

In Table I, the energies of the structures at 35 K, deduced with our general systematics, are reported together with temperature coefficients. In Table II we report the energy differences of the A and A' structures. These values do not show temperature dependence in the range of measurement. Theoretical SO splittings of the valence band at Γ and an SO parameter ξ for the halide ion are also reported from Ref. 12.

DISCUSSION

In comparing the TR structure energies with the calculated interband energies, it must be considered that the former should be smaller than the latter by an amount equal to the exciton binding energy. While an estimate for the Γ exciton (A) is easily made, it is more difficult to take into account the excitonic interaction effects on the optical spectra for higher-energy transitions (B and C). Our first purpose is only to assign the structures to transitions at specific points in the BZ. From the experimental results, we see that:

(a) A and C structures must not be related to the same symmetry point transitions; otherwise, one should expect that both of them would behave in the same way with temperature.

(b) B and B' structures present similar line shapes but temperature coefficients distinguishably different from those for A_1 and A_1'.

(c) The energy differences of the A and A' structures do not depend on the temperature. This result is quite evident for chloride and bromide.

Now, if one takes into account the band calcula-

TABLE I. Structure energies are given from 35 K thermoreflectivity data obtained in agreement to the general systematics exposed in Sec. II. All energies are in eV. Temperature coefficients of the structures are also reported in eV/K.

TR structure energies (eV) and temp. coeff. (eV/K)	Materials NaCl	KCl	RbCl	NaBr	KBr	RbBr	NaI	KI	RbI
$A_1(\Gamma_8^- \rightarrow \Gamma_6^+)$	7.96	7.77	7.51	6.72	6.75	7.63	5.60	5.85	5.74
$-dE/dT$	6×10^{-4}	6×10^{-4}	1×10^{-3}	8×10^{-4}	2.5×10^{-3}	7×10^{-4}	8.5×10^{-4}	8.5×10^{-4}	5×10^{-4}
$A_1'(\Gamma_6^- \rightarrow \Gamma_6^+)$	8.07	7.9	7.65	7.2	7.24	7.13	6.72	~7.1	6.82
$-dE/dT$	6×10^{-4}	6×10^{-4}	1×10^{-3}	7×10^{-4}	2.5×10^{-3}	8×10^{-4}	8×10^{-4}		5×10^{-4}
$B(L_4^- \rightarrow L_6^+)$				8.51	8.2	7.85	7.35	6.68	6.47
$-dE/dT$					4×10^{-3}	5.5×10^{-4}	4.5×10^{-4}	5.5×10^{-4}	3.5×10^{-4}
$B'(L_6^- \rightarrow L_6^+)$							7.60	6.87	6.64
$-dE/dT$							4.5×10^{-4}	6×10^{-4}	3.5×10^{-4}
$C(X_7^- \rightarrow X_7^+)$					8.8	8.31		7.47	7.12
$-dE/dT$					$<10^{-5}$	$<10^{-5}$		$<10^{-5}$	$<10^{-5}$

TABLE II. Energy differences of the SO split Γ excitons (*A* and *A′* structures in figures) for different crystals at 35 K. Theoretical values of the valence-band SO splitting and a SO parameter ξ for the halide ion are also reported from Ref. 12.

Spin-orbit splittings (eV)	NaCl	KCl	RbCl	NaBr	KBr	RbBr	NaI	KI	RbI
3ξ ion	0.11	0.11	0.11	0.46	0.46	0.46	0.95	0.95	0.95
Theor. $E(\Gamma_8^-)-E(\Gamma_6^-)$	0.128	0.123	0.115	0.53	0.51	0.50	1.15	1.12	1.10
Expt. A'_1-A_1	0.11	0.13	0.14	0.48	0.49	0.50	1.12	~1.2	1.08

tions, the interpretation of the *A* structure is straightforward: it is related to a transition from the unexcited crystal to an exciton state formed by a hole in the top of valence band at Γ_8^- and by an electron in the bottom of the conduction band at Γ_6^+. The SO split structure of the Γ exciton is easily identified as the *A′* structure in the chloride and bromide [see the data reported in Table II and points (b) and (c) above].

The identification of the SO split exciton in KI and RbI is questionable. In fact, the SO splitting has been determined to be 1.4 eV (KI) and 1.24 eV (RbI) from Ref. 1 and of 0.88 eV (KI) and 0.77 eV (RbI) from Ref. 2. We will try to find the SO split exciton in the iodides from the behavior of the *A* and *A′* structures in chloride and bromide, following the procedures:

(i) In the case of chlorides and bromides, the experimental results show that there is almost no dependence of the SO splitting on the alkali metal (Table II).

(ii) In the case of NaI, *A* and *A′* structures are well resolved and present the same TR line shape. Their energy difference is temperature independent and quite close to the theoretical value predicted for the Γ exciton SO splitting (Table II).

(iii) Interpreting the *A* and *A′* structures in NaI as due to the SO split excitons, we extend the same SO value to the other iodides.

Then the *A′* structure in RbI at 6.82 eV and *A′* bump in KI at about 7.1 eV are interpreted as $\Gamma_6^- \rightarrow \Gamma_6^+$ excitons.

From the interpretation of the *A* and *A′* structures of our TR spectra, SO splittings of the Γ exciton of 0.13 ± 0.02 eV, 0.49 ± 0.02 eV, and 1.10 ± 0.02 eV are calculated for chloride, bromide, and iodide, respectively. The ±0.02-eV value results from the dependence on the alkali ion.

Now let us consider the *C* structures which presents a temperature-independent energy position. It is possible to associate these structures to transitions related to the *X* edge in agreement with the calculations of Kunz for KI and RbI crystals.[16,21] Kunz has calculated very small pressure coefficients for *X* transitions. This could mean that *X* transitions do not change their energy with temperature, assuming, of course, that the shift depends on temperature only through the change in lattice parameters. We suggest that the *C* structure is not present in the TR spectra of NaI and NaBr. This agrees with the theoretical band calculations,[8,18,19] which suggest a higher X_7^+ point in the conduction band and do not present an inversion between the X_7^+ and X_6^+ points.

Concerning the *B* and *B′* structures, we observe that they present the same temperature dependence and so they can be correlated with the SO or symmetry splitted valence band at the same point of the BZ. They could be associated with transitions from the valence band to the Γ_8^+ symmetry point of the second conduction band or to the L_6^+ point of the first conduction band. In the first case, we expect two structures, with an energy splitting equal to the SO splitting of the valence band at Γ. In the second case, the symmetry splitting of the valence band must be considered as well. In fact for KI and RbI crystals, band calculations give symmetry splitting values ranging from 0.2 to 0.6 eV,[14,20,21] while the SO splitting at *L* is close to the value at the Γ point (1.14 eV).[14,20,21] Experimentally, the energy differences of *B* and *B′* structures are of the order of 0.2 to 0.3 eV in iodide, while the SO splitting at Γ is of the order of 1.1 eV. Therefore, it seems that the *B* and *B′* structures could be associated to transitions from L_6^- and L_4^- points of the symmetry-split valence band to the L_6^+ conduction-band point. This interpretation does not conflict with all theoretical results which present the *d*-type conduction band more than 1 eV higher than the first *s*-type conduction band at Γ. However, in order to completely rule out the possibility that *B* and *B′* structures are due to transitions to *d*-type conduction bands, more reliable theoretical calculations could be useful as well as a knowledge of the binding energy of the excitons involving d-type conduction bands.

As regards NaI, we suggest that, unlike the other iodides, the B and B' structures take place at a higher energy than the A' structure. In KBr and RbBr crystals the B structure is well separated and the B' structure may be superimposed on the C structure which is broader in these crystals than in KI and RbI.

Beyond the C structure, in KI and RbI crystals other structures are observed which are associated with higher transitions. In order to obtain a general interpretation of these structures for all these crystal families, TR measurements at higher energies than 9 eV could be useful (particularly for bromide and chloride).

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