

# ELASTO- AND ELECTRO-OPTICAL DIPOLE PROPERTIES OF OFF-CENTER Ag<sup>+</sup> DEFECTS IN RbI

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Electric dipole properties of off-center Ag<sup>+</sup> defects, introduced by a diffusion technique, are investigated in RbI. After rapid quenching and cooling the absorption spectrum consists of 4 UV bands at 4.82, 4.92, 5.12 and 5.47 eV. Their oscillator strength slightly decreases then rises with increasing temperature. Weak zero moment changes in all bands are observed when high electric field is applied along the  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions only. No effect occurs along  $\langle 100 \rangle$ . The sign of the effect allows the determination of the main state of polarization of the bands: perpendicular to the dipole axis for the 4.82 and 5.12 eV, parallel to it for the 4.92 and 5.47 eV. Two models which fit equally well the results are discussed: a  $\langle 111 \rangle$  dipole model and a restrictive  $\langle 110 \rangle$  model with 90° reorientation only. They lead to a dipole moment of 1.16 eÅ, respectively 1.34 eÅ if we assume full polarization of the bands. Several arguments favor the  $\langle 111 \rangle$  model with deep off-center wells for Ag<sup>+</sup> in RbI.

## INTRODUCTION

Substitutional Ag<sup>+</sup>-center in alkali halides have been intensively studied in recent years.<sup>1,2</sup> The UV absorption spectrum is characteristic of 4d-5s parity forbidden transitions due to inversion symmetry but which become partly allowed through coupling to odd-parity phonons or static off-center distortion. Recent studies of the rubidium halides, using various techniques such as ITC,<sup>5,6</sup> ITC under uniaxial pressure,<sup>6</sup> elasto-<sup>7</sup> and electro-optics,<sup>8,9</sup> NMR<sup>10</sup> have confirmed the off-center nature of Ag<sup>+</sup> with dipoles orientations along the  $\langle 110 \rangle$  direction in RbCl and RbBr and most probably along the  $\langle 111 \rangle$  direction in RbI.

We report here on the oscillator strength, the polarization of the absorption bands and the temperature dependence of the electro-optical behavior of Ag<sup>+</sup> in RbI. Other results appear elsewhere.<sup>9</sup>

## EXPERIMENTAL TECHNIQUES

The crystals were grown under pure argon atmosphere in our laboratory by the Kyropoulos technique using ultrapure RbI (Merck). The doping of Ag was done by diffusion under argon atmosphere in a pyrex cell at ~600°C. This technique allows to have rapidly (~40 min) very homogeneous samples free from other unwanted impurities. Before optical measurements the crystals (typically 20×20×0.5-1 mm), previously cut along the  $\langle 111 \rangle$ ,  $\langle 110 \rangle$  or  $\langle 100 \rangle$  direction and optically polished were

rapidly quenched and cooled to helium temperature within one hour in order to prevent  $\text{Ag}^+$  aggregation. Dc electro-optical measurements under high electric field ( $V_{\text{max}}=12$  kV) have been performed with a Cary 17 spectrophotometer working in single beam mode, which allows measurements of change of absorbance with a sensibility of  $\Delta K \simeq 10^{-3}$  using its zero suppression facility. Some ac measurements have been done using a standard lock-in technique. In all electro optical measurements, the direction of the light was always parallel to the applied field. Linear polarization of the light was achieved with a Glan-Thompson quartz polarizer. Temperature was monitored and controlled at both sides of the sample using a calibrated Lake Shore Carbon-Glass resistor.

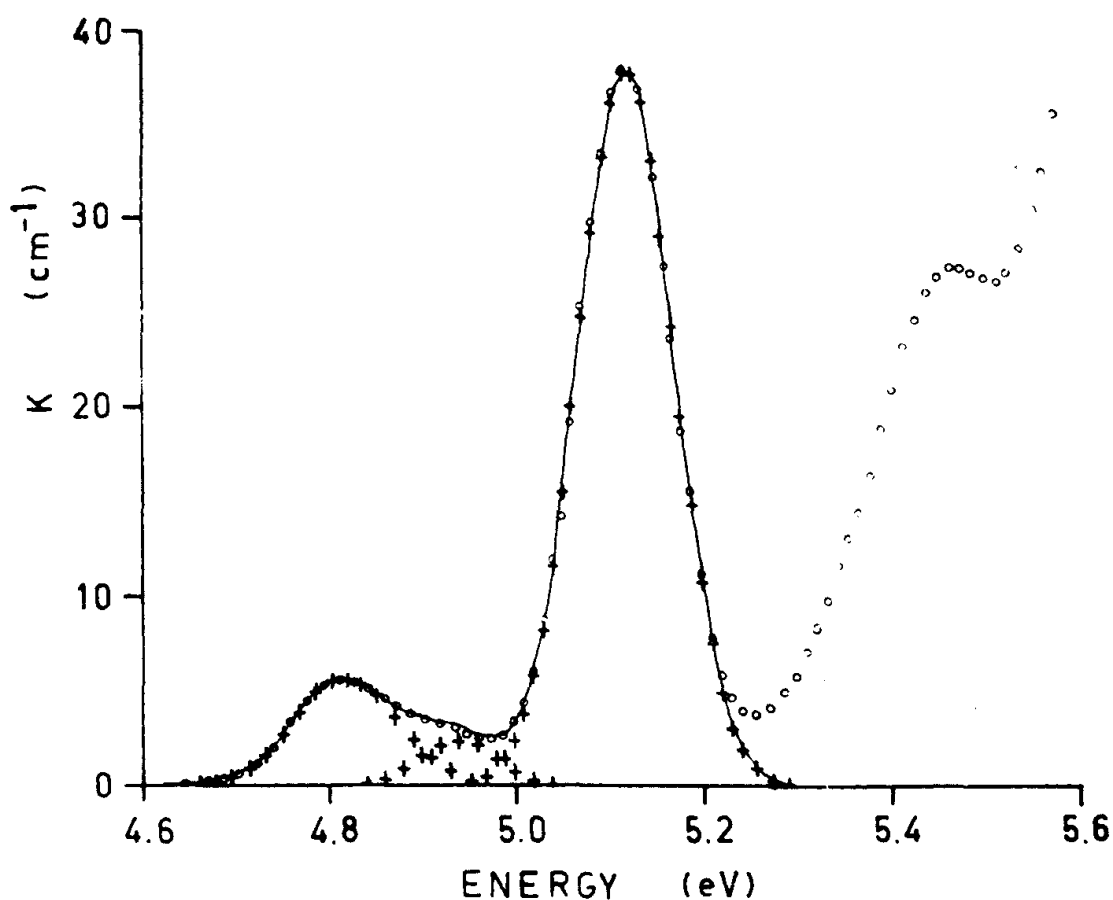


FIGURE 1 Absorption spectrum and decompositions in various gaussian shape bands of RbI:Ag measured at  $T=22.2$  K.  $\circ$ , experimental results,  $+$ , decomposition of the first three bands,  $-$ , theoretical sum of the first three bands distribution.

## EXPERIMENTAL RESULTS AND DISCUSSION

The absorption spectrum of rapidly quenched and cooled RbI:Ag is shown in Figure 1 at  $T=22.2$  K. Four bands at 4.82, 4.92, 5.12 and 5.47 eV can be identified in agreement with Jimenez *et al.*<sup>5</sup> The shape of the spectrum appears quite different

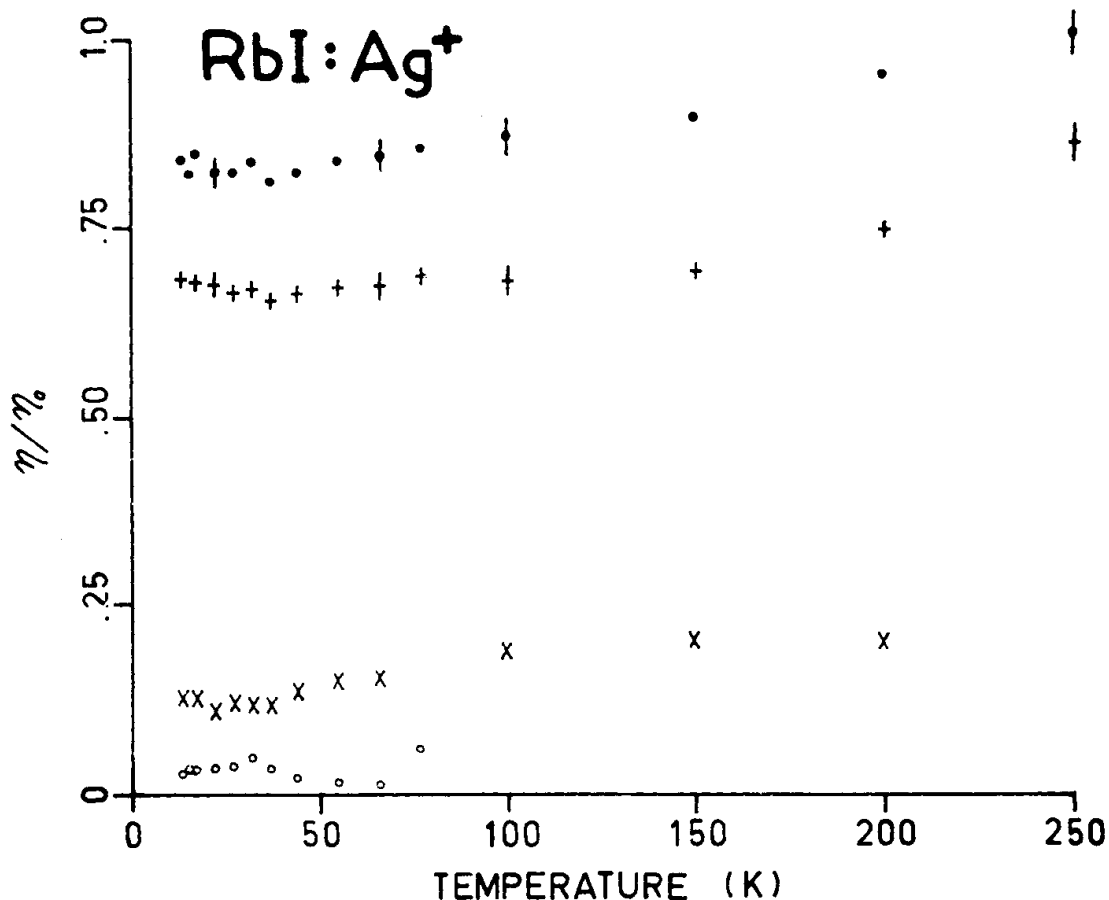


FIGURE 2 Temperature behavior of the relative oscillator strength  $\eta$  of the first three absorption bands in  $\text{RbI}:\text{Ag}^+$ . The results are normalized such that the sum gives  $\eta/\eta_0=1$  at  $T=250$  K.  $\times$ , band at 4.82 eV,  $\circ$ , band at 4.92 eV,  $+$ , band at 5.12 eV,  $\bullet$ , sum of the oscillator strength.

from those obtained for  $\text{Ag}^+$  in  $\text{RbCl}$  and  $\text{RbBr}$  and the position of the bands cannot be extrapolated with an Ivey-type law as a function of the lattice constant as was previously noted.<sup>5</sup> These results already indicate that  $\text{Ag}^+$  in  $\text{RbI}$  has probably a local symmetry different of that of  $\text{RbCl}$  and  $\text{RbBr}$ . For all temperatures, the spectrum has been decomposed in gaussian shape bands with the aid of a computer. Figure 1 shows a typical result with excellent agreement. The relative oscillator strength, proportional to the area of each band, is shown as a function of temperature in Figure 2. A very shallow minimum is observed around 40 K with a small rise as the temperature increases. According to Sittig,<sup>11</sup> this indicates a temperature dependent off-center shift of the  $\text{Ag}^+$ -ion with relatively deep potential wells. The unpolarized spectral dependence of the electric field-induced dichroism is shown in Figure 3 for an uncorrected field of  $1.32 \cdot 10^5 \text{ V cm}^{-1}$  applied along the  $\langle 111 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 100 \rangle$  directions at  $T=22.2$  K and for light propagation parallel of it. Moreover, for field applied along the  $\langle 110 \rangle$  direction,  $\Delta K/K$  was found twice the values shown in the figure when the light is polarized along the  $[1\bar{1}0]$  direction and strictly zero for light polarized along the  $[001]$  for each band. The temperature of 22.2 K is the temperature which gives the maximum  $\Delta K/K$  values. For lower temperatures,  $\Delta K/K$  diminish rapidly and it requires a longer period of time to reach the final values. This shows

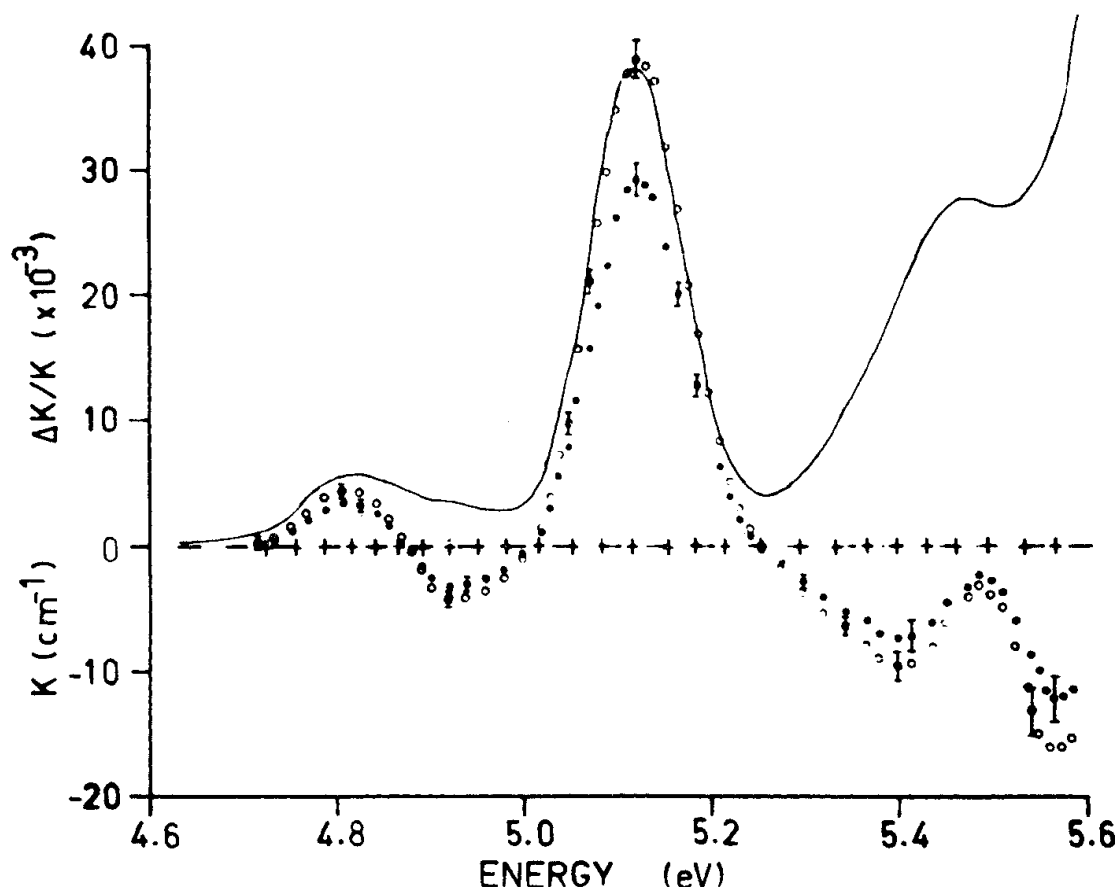


FIGURE 3 Spectral dependence of the electric field-induced dichroism  $\Delta K/K$  measured at  $T=22.2$  K with unpolarized light propagating parallel to the electric field  $E=1.32 \cdot 10^5 \text{ V cm}^{-1}$  applied along the  $\langle 111 \rangle$  direction ( $\circ$ ),  $\langle 110 \rangle$  direction ( $\bullet$ ) and  $\langle 110 \rangle$  direction (+). The full curve is the measurement of the absorption constant  $K$  ( $\text{cm}^{-1}$ ).

that the  $\text{Ag}^+$  electric dipole freeze-in in a way quite similar to that found for elastic dipoles.<sup>5</sup> The sign of the effect can be used to assign a dominant polarization of each band. The ones at 4.82 and 5.12 eV appear to be polarized perpendicular to the dipole axis while those at 4.92 and 5.47 eV are mainly polarized parallel to it. As it is physically impossible to obtain a complete alignment in the temperature and field ranges in which we observe a signal, we cannot know the real degree of polarization of the bands. In analogy with  $\text{Ag}^+$  in  $\text{RbCl}$  and  $\text{RbBr}$  and other systems and to calculate an effective dipole moment value we shall assume in the following that the bands are completely polarized as stated above. Figures 4 and 5 show the  $\Delta K/K$  values of the  $\sigma$ -polarized 4.92 eV band and the  $\pi$ -polarized 5.12 eV band, plotted against  $(E/T)^2$  for various field directions and temperature values. Similar results have been obtained for the two other bands. Several models have been already calculated and their  $\Delta K/K$  predicted;<sup>9,12,13</sup> we shall not repeat the results here. As no effect appear with field applied along the  $\langle 100 \rangle$  direction, only two of them may enter in consideration:

- 1) A normal model in which the dipoles lie along the  $\langle 111 \rangle$  direction.
- 2) A restrictive model in which the dipoles lie along the  $\langle 110 \rangle$  direction but where the reorientation can only occur in a (100) plane between the four  $\langle 110 \rangle$  direction by

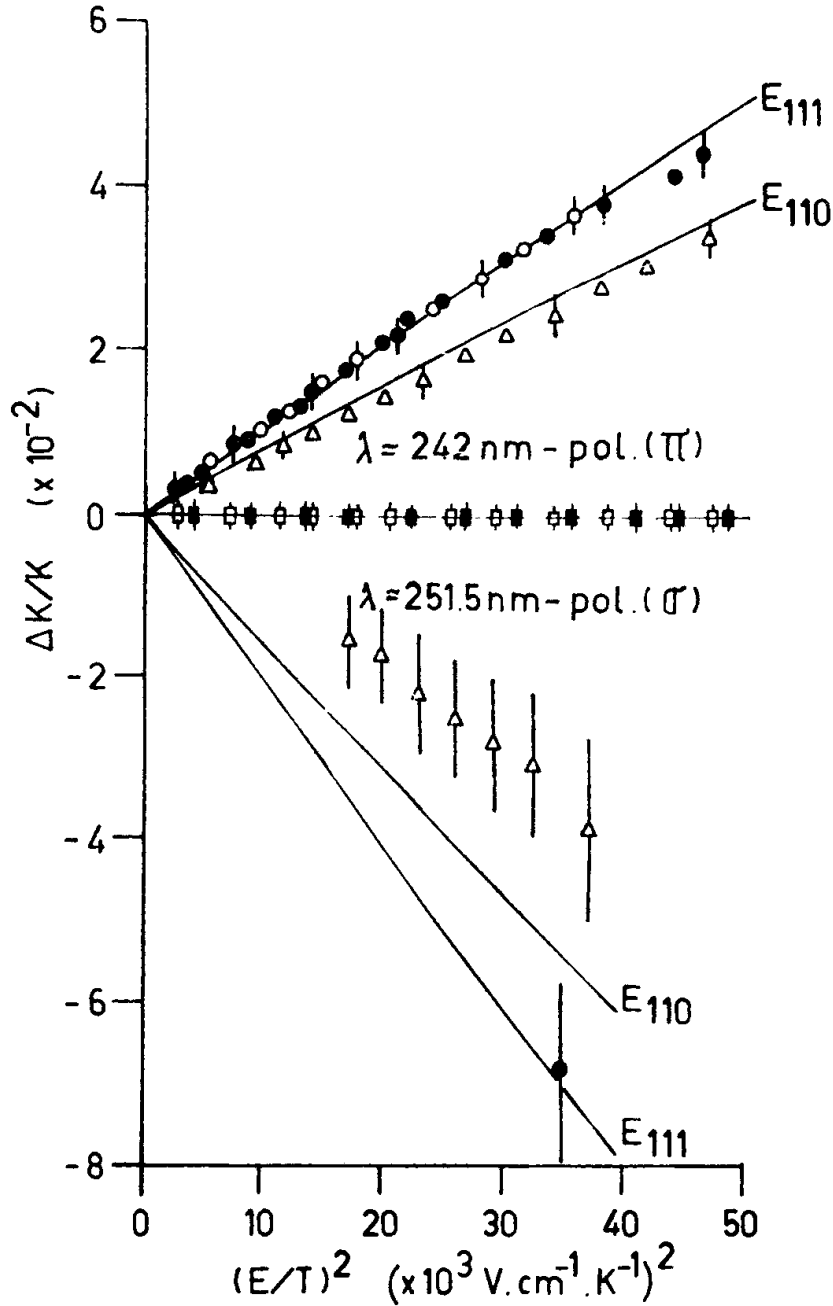


FIGURE 4 Plot of  $\Delta K/K$  as a function of  $(E/T)^2$  for the 4.92 eV  $\sigma$  polarized band and the 5.12 eV  $\pi$  polarized band measured with unpolarized light under the following experimental conditions: ●,  $E=1.32 \times 10^5 \text{ V cm}^{-1}$  and  $\parallel\langle 111 \rangle$ , ○,  $E\parallel\langle 111 \rangle$  and  $T=22.2 \text{ K}$ ; △,  $E\parallel\langle 110 \rangle$  and  $T=22.2 \text{ K}$ ; □,  $E\parallel\langle 100 \rangle$ ,  $T=22.2 \text{ K}$ ,  $\lambda=242 \text{ nm}$ ; ■,  $E\parallel\langle 100 \rangle$ ,  $T=22.2 \text{ K}$ ,  $\lambda=251.5 \text{ nm}$ . The lines are calculated with the  $\langle 111 \rangle$  model assuming complete polarization of the bands and a dipole moment  $p=1.16 \pm 0.1 \text{ eÅ}$ .

90° jumps.<sup>8,14</sup> In such a case the perpendicular transition (in  $[1\bar{1}0]$  and  $[001]$ ) are not equivalent. This particular behavior is due to a dressing effect in which a large  $E_g$  and a small  $T_{2g}$  elastic distortion characterize the surroundings of the defect.

Although the theoretical predictions are slightly different for each model, Figures 4 and 5 show, within the error bars of the experiments, that both models can be used

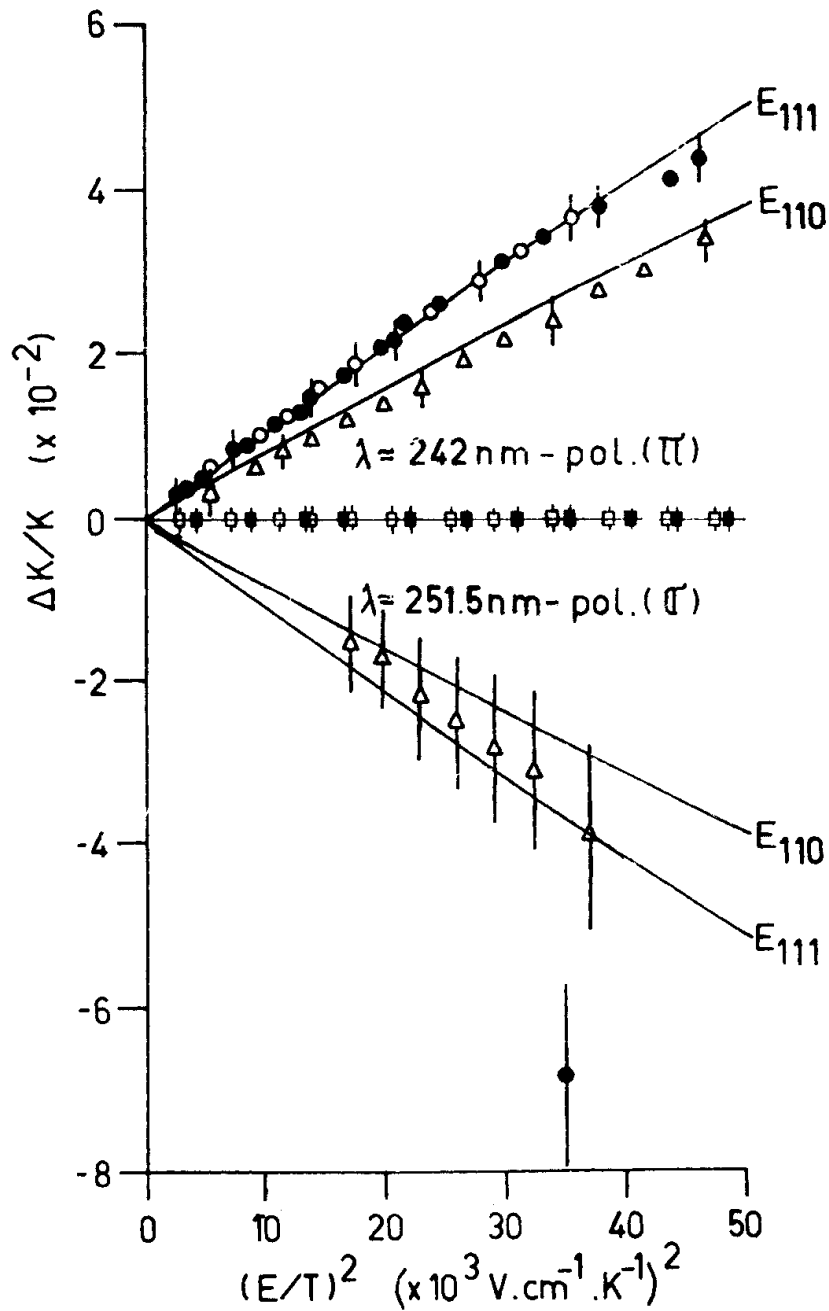


FIGURE 5 Same plot as Figure 4. The lines are calculated using the restricted  $\langle 110 \rangle$  model with  $90^\circ$  reorientation only, assuming complete polarization of the bands and a dipole moment  $p = 1.34 \pm 0.1$  eÅ.

satisfactorily to describe our results. The dipole moment value which was found to best fit the data was:

$$\langle 111 \rangle \text{ dipole model} \quad p = 1.16 \pm 0.1 \text{ eÅ}$$

$$\langle 110 \rangle \text{ restrictive dipole model} \quad p = 1.34 \pm 0.1 \text{ eÅ}$$

The impossibility to discriminate between the two models is due to the fact that the field induced absorbance variation is extremely small and that it is not possible to

reach  $E/T$  values close enough of the saturation behavior (complete alignment). Moreover the  $\sigma$  polarized bands have a very small absorption coefficient and are superimposed either to other bands or to the background absorption of the pure host material. This renders extremely difficult and uncertain the determination of  $K(0)$  and  $\Delta K(E)$ . It is also worthwhile to note that in the rubidium halides sequence, the dipole moment has a clear trend to increase indicating that the off-center position increases with the anion size ( $p=0.8\pm 0.1$  eÅ (RbCl),  $p=0.95\pm 0.1$  eÅ (RbBr),  $p=1.34\pm 0.1$  or  $1.16\pm 0.1$  eÅ (RbI)). This behavior has been predicted for Ag<sup>+</sup> and Cu<sup>+</sup> by Li *et al.*<sup>15</sup>

#### ACKNOWLEDGEMENT

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