

Magnetic circular dichroism of off-centered Cu^+ and on-centered Cu^+ in alkali halides

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Optical-absorption and magnetic-circular-dichroism (MCD) spectra of off-centered Cu^+ in KI, KBr, and KCl crystals and of on-centered Cu^+ in NaCl crystals are investigated at temperatures from 80 to 300 K. In $\text{KI}:\text{Cu}^+$ an absorption band due to the $d^{10} \rightarrow d^9p$ allowed transition is observed in addition to six absorption bands due to the $d^{10} \rightarrow d^9s$ forbidden transition. Different MCD line shape and temperature dependence are observed between the off-centered Cu^+ and on-centered Cu^+ . A discussion is given on the level assignment for the Cu^+ absorption bands observed in KI.

I. INTRODUCTION

Substitutional Cu^+ ion was previously suggested, by determination of the large and temperature-independent oscillator strength of the absorption band due to the $d^{10} \rightarrow d^9s$ forbidden transition, to occupy an off-center position in KCl, KBr, and KI.¹ Recently, by the extensive ionic thermocurrent and dielectric studies and by optical study under hydrostatic pressure by Lüty's group,^{2,3} it was established that the Cu^+ ion occupies either on-center or off-center positions in various alkali halides. The same has been concluded from the extensive optical study (including lifetime measurements) of Cu^+ -doped alkali iodides by Van Sciver's group.^{4,5} So far, many investigators, in addition to Lüty and Van Sciver, have studied the optical properties of Cu^+ in alkali halides. Several investigators have performed the experiments under an external field such as uniaxial stress,⁶ hydrostatic pressure,^{3,7} and electric field.⁸ However, an experiment using external magnetic field has not yet been made on Cu^+ -doped crystals. It is interesting to see whether or not the magnetic field effect is observed in the Cu^+ absorption bands and to see what kind of difference is induced by magnetic field between the on-centered Cu^+ and off-centered Cu^+ .

In this paper we investigate the magnetic-circular-dichroism (MCD) spectra of various alkali halides doped with Cu^+ ions to obtain evidence to justify the existence of the on- and off-centered Cu^+ ions. $\text{KI}:\text{Cu}^+$, $\text{KBr}:\text{Cu}^+$, and $\text{KCl}:\text{Cu}^+$ were chosen for the investigation of off-centered Cu^+ , whereas $\text{NaCl}:\text{Cu}^+$ for on-centered Cu^+ . Of the four crystals, we studied the absorption spectra of $\text{KI}:\text{Cu}^+$ in detail, only one band having been observed unlike other alkali halides.⁹⁻¹² A discussion is given on the level assignment of the Cu^+ absorption bands observed.

II. EXPERIMENTAL PROCEDURE

Single crystals of KI containing 0.001–0.05 mole % CuI in the melt were grown in our laboratory by the Kyropoulos method. Other crystals ($\text{KBr}:\text{Cu}^+$, $\text{KCl}:\text{Cu}^+$, and $\text{NaCl}:\text{Cu}^+$) were also grown by the same method. A block of "pure" KI crystals was obtained from the Harshaw Chemical Company, USA. Absorption spectra were measured using a Shimadzu MPS-50L spectrophotometer. The crystals were annealed for 15 min at 400 °C and quenched to room temperature prior to absorption measurement.

MCD spectra were measured using a JASCO J-40A automatic recording spectropolarimeter. The slit width of the spectropolarimeter was set to be 0.5 nm. The MCD shown in Figs. 2–4 is given by the difference between the optical densities for the left- and right-circularly polarized components of light. The polarized light travels through the crystal parallel to the magnetic field direction. A JASCO electric magnet was used to produce the magnetic field. The magnetic field could be varied from 0 to 15 kG and the crystal temperature from 95 to 300 K. The field was applied along the $\langle 001 \rangle$ direction. A 450-W xenon lamp was used as the light source. Monochromatic light passed through two prism polarizers was focused onto the crystal after passing a piezo-optical birefringence modulator of 50 kHz. The transmitted light was detected by an HTV 377 photomultiplier tube.

III. EXPERIMENTAL RESULTS

The absorption spectra of $\text{KI}:\text{Cu}^+$ and undoped KI crystals are shown in Fig. 1. A well-known Cu^+ band is observed at 4.66 eV (266.0 nm) at 295 K and at 4.72 eV (262.5 nm) at 83 K. As temperature is lowered, two new bands are found

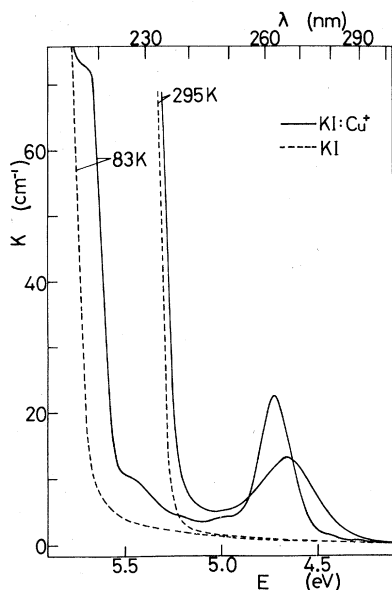


FIG. 1. Absorption spectra, taken at 83 and 295 K, of a KI:Cu⁺ crystal with a thickness of 0.79 mm and of a pure KI crystal with a 0.81-mm thickness. K , E , and λ mean absorption coefficient, photon energy, and wavelength, respectively.

at 5.46 eV (227 nm) and 5.69 eV (218 nm). The intensity ratio among the 4.72-, 5.46-, and 5.69-eV bands is about 1:0.1:3.0. In addition to the three bands, four weak bands are observed at about 4.28 eV (290 nm), 4.40 eV (282 nm), 4.98 eV (249 nm), and 5.23 eV (237 nm). The intensities of all the observed bands are almost temperature independent just as the case of the 4.72-eV band. It is suggested from the Cu⁺-concentration dependence of these bands that all of the 4.72-, 4.28-, 4.40-, 4.98-, and 5.23-eV bands arise from the same Cu⁺ ion. Regarding the 5.69-eV band, it is difficult to obtain accurate data because of overlap with the stronger exciton band; however, it appears to grow linearly with the Cu⁺ concentration. Thus it is concluded that Cu⁺ gives rise to six absorption bands in KI besides the previously observed 4.72-eV band.

Figure 2 shows the MCD spectra of the 4.72-eV band at various temperatures. A derivativelike MCD line shape is observed at a low temperature. The close examination, however, indicates that the area of the positive part in the MCD line shape is larger than that of the negative part. As temperature is raised, the negative area decreases. At all the temperatures measured, the center of the MCD is not located at the peak position of the corresponding absorption band but shifted to low energy slightly. The g value of the 4.72-eV band can be calculated from the MCD spectrum using

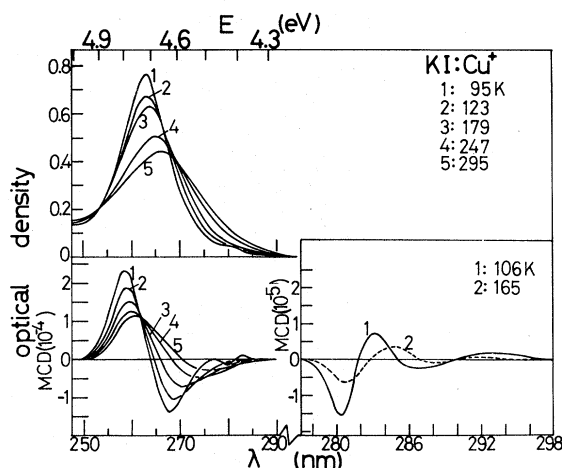


FIG. 2. Absorption (upper part) and MCD (lower part) spectra of a KI:Cu⁺ crystal (with a 0.79-mm thickness) measured at various temperatures. On the right-hand side are shown the enlarged MCD spectra for the two weak Cu⁺ bands. The applied magnetic field is 13.1 kG.

the moment method.¹³ The estimated g value is $g=0.20$ at 140 K.

The MCD signal is obtained not only for the 4.72-eV band but for the weak 4.28- and 4.40-eV bands (see Fig. 2). The 4.40-eV-band MCD has the same sign as the 4.28-eV-band MCD, but their signs are different from that of the 4.72-eV-band MCD, that is, the 4.72-eV-band MCD has a negative sign at the low-energy side in the band, whereas the MCD of the weak bands has a positive sign at their low-energy sides. Similar MCD spectra are also obtained for the Cu⁺ bands in KBr and KCl. In Fig. 3 are shown the MCD spectra of the 4.70-eV (264 nm) band in KBr:Cu⁺ and of the 4.75-eV (261 nm) band in KCl:Cu⁺, together with their absorption spectra taken at various temperatures. Their MCD line shapes and temperature dependences are quite similar to those of the 4.72-eV band in KI:Cu⁺.

Figure 4 shows the absorption and MCD spectra of NaCl:Cu⁺ at 95 and 210 K. A relatively strong band is observed at 4.88 eV (254 nm) and a weak band at about 4.51 eV (275 nm). From the absorption spectrum at a low temperature, the weak band appears to consist of two components which are close to each other. This is confirmed from the MCD spectrum in the vicinity of 4.51 eV, which consists of two negative MCD peaks at 4.59 eV (270 nm) and 4.30 eV (288 nm) at 95 K. The two negative MCD bands become broad with increasing temperature and result in a single MCD band with a negative peak above about 150 K. On the other hand, the strong 4.88-eV band has an almost positive MCD component.

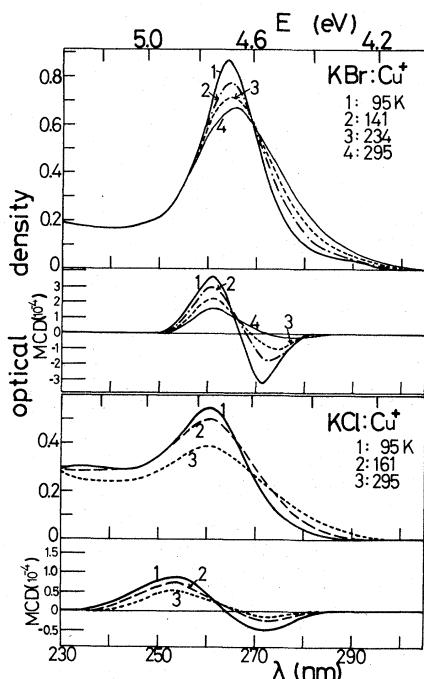


FIG. 3. Absorption (upper part) and MCD (lower part) spectra of $\text{KBr}:\text{Cu}^+$ crystal with a 2.77-mm thickness and of a $\text{KCl}:\text{Cu}^+$ crystal with a 1.68-mm thickness at various temperatures. The applied magnetic field is 14.3 kG.

IV. DISCUSSION

The relatively strong 4.72-eV band of $\text{KI}:\text{Cu}^+$ has been attributed to the $d^{10} - d^9s$ parity-forbidden transition.⁹⁻¹² The corresponding absorption band has been observed at 4.70, 4.75, and 4.88 eV in $\text{KBr}:\text{Cu}^+$, $\text{KCl}:\text{Cu}^+$, and $\text{NaCl}:\text{Cu}^+$, respectively.

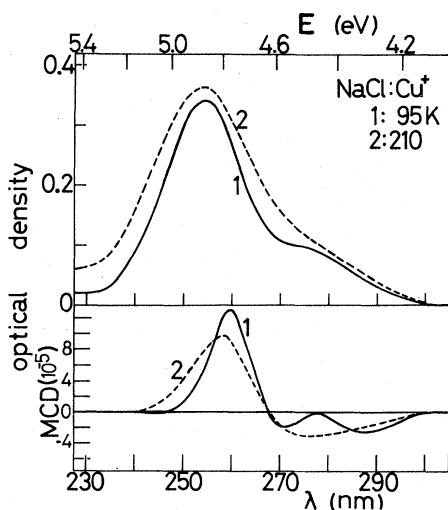


FIG. 4. Absorption (upper part) and MCD (lower part) spectra of an $\text{NaCl}:\text{Cu}^+$ crystal with a 2.96-mm thickness. The applied magnetic field is 13.1 kG.

As shown in Figs. 2, 3, and 4, the MCD line shapes of these main bands and their temperature dependences are quite similar to each other except the 4.88-eV band of $\text{NaCl}:\text{Cu}^+$. For example, at 95 K, a derivativelike MCD line shape is observed in KI, KBr, and KCl, whereas an absorption-band-like MCD line shape is found in NaCl. This seems to be associated with the fact that the Cu^+ ion in potassium halides occupies an off-center position whereas the Cu^+ ion in NaCl is in an on-center position. In the off-centered Cu^+ , a static mixing of allowed states with the d^9s state, which is induced by distortion of the surrounding lattice accompanied with a reduction of the symmetry around Cu^+ and a destruction of the parity selection rule for the on-centered Cu^+ , makes the $d^{10} - d^9s$ forbidden transition allowed in the crystal, whereas in the on-centered Cu^+ a dynamic mixing of these states, which is induced by odd-parity lattice vibration through an electron-phonon interaction, makes the forbidden transition allowed vibronically. From this, it is expected that the difference of MCD line shape is observed more prominently at a low temperature, where the lattice vibration is less effective, than at a high temperature. This is consistent with our observation at 95 K.

At high temperatures, not only the static mixing due to the lattice distortion but the dynamic mixing due to the electron-phonon interaction are effective even in the off-centered Cu^+ . (The effect of the dynamic mixing becomes strong with temperature.) This suggests that as the temperature is raised an MCD line shape similar to that of on-centered Cu^+ is observed in the off-centered Cu^+ . Certainly, it is observed that the MCD of KI, KBr, and KCl changes into an absorption-band-like line shape with increasing temperature, whose line shape is similar to that of NaCl. Therefore, it is suggested that the MCD spectra support the suggested conclusion so far, that Cu^+ in potassium halides is off center, whereas Cu^+ in NaCl is on center.

A detailed semiempirical molecular orbital (MO) calculation has been made to compute the energy levels of on-centered $\text{NaCl}:\text{Cu}^+$ and $\text{LiCl}:\text{Cu}^+$ by Pedrini.¹⁴ He assigned the main band of NaCl (i.e., the 4.88-eV band) to the ${}^1A_{1g} - d^1T_{2g}$ transition, and the satellite band with two components, which is located at about 4.51 eV, to the ${}^1A_{1g} - b^3T_{2g}$ transition (see Fig. 2 of Ref. 14). The agreement of calculation with experiment is satisfactory for the band position and relative band intensity. Such an energy-level calculation has not yet been made for the off-centered Cu^+ . The energy-level diagram of the low-symmetry off-centered Cu^+ (e.g., $\text{KI}:\text{Cu}^+$) is, strictly speaking,

different from that of the high-symmetry on-centered Cu^+ . However, although the temperature dependence of oscillator strength of the main band is different for NaCl and KI, the main band is located at almost the same position in NaCl and KI, and the main band has a similar composite satellite band at the low-energy tail in both crystals.¹⁵ Moreover, in both NaCl and KI, the MCD sign is different for the main and satellite bands as seen in Figs. 2 and 4. From such a similarity, it is suggested that the energy-level diagram of $\text{KI}:\text{Cu}^+$ is similar to that of $\text{NaCl}:\text{Cu}^+$. Therefore, we will be allowed to use tentatively the theoretically derived MO energy-level diagram of $\text{NaCl}:\text{Cu}^+$ to explain the absorption spectrum of $\text{KI}:\text{Cu}^+$. As mentioned above, the estimated g value is about 0.2. Such a small g value suggests that the main band has a strong ligand character, that is, the Cu^+ ion has a strong covalency with ligand ions. This is in agreement with the earlier suggestion⁶ which was obtained from the measurement of uniaxial stress dichroism. This indicates that the MO energy levels are certainly suitable to describe the electronic states responsible for the Cu^+ bands in alkali halides.

From the similarity of the low-energy spectrum between KI and NaCl, it is believed that the excited states of the main 4.72-eV band and satellite band (composed of the 4.28- and 4.40-eV bands) in KI are attributable to the d^1T_{2g} and b^3T_{2g} MO levels, respectively. The resolution in the composite satellite band is somewhat better in KI than in NaCl. This may be explained as follows: The splitting of the b^3T_{2g} level by the crystal-field or Jahn-Teller effect is expected to be larger in the low-symmetry off-centered Cu^+ than

in the high-symmetry on-centered Cu^+ .

According to Pedrini,¹⁴ two levels, c^1E_g and a^3T_{2g} , are located above the d^1T_{2g} level, which give rise to high-energy absorption. The c^1E_g is located at higher energy than the a^3T_{2g} , and the transition intensity to the c^1E_g is somewhat larger than that to the a^3T_{2g} . Therefore, we suggest that the c^1E_g level is responsible for the relatively strong 5.46-eV band in KI, whereas the a^3T_{2g} level for the two weak bands observed at 4.98 and 5.23 eV. Here, we took into account that, as in the case of the d^3T_{2g} , the c^3T_{2g} level splits into two levels in the low-symmetry off-center ion. (Pedrini has suggested that an absorption band due to the $^1A_{1g} - c^1E_g$ transition is hidden by the much stronger band due to the $d^{10} - d^9p$ allowed transition in NaCl.¹⁴ Taking into account his suggestion, we propose that an unknown absorption band due to the $^1A_{1g} - c^3T_{2g}$ transition in NaCl is attributable to a very weak band which appeared at about 5.8 eV.¹¹) The remaining high-energy band observed at 5.69 eV in $\text{KI}:\text{Cu}^+$ is attributable to the $d^{10} - d^9p$ allowed transition since the band has a remarkably strong intensity, just as in the cases of $\text{NaCl}:\text{Cu}^+$ and $\text{LiCl}:\text{Cu}^+$ crystals.^{16,17}

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