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Optical properties of off-centred Cu^+ ions in KMgF_3 crystals

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Abstract. Optical absorption and magnetic circular dichroism (MCD) spectra of KMgF_3 crystals with different concentrations of Cu^+ ions have been studied in the temperature range 15–296 K. Absorption bands due to isolated Cu^+ are observed at 27 000, 28 593, 31 250, 32 010 and 47 600 cm^{-1} , and their intensities are almost constant for variation of temperature. A vibronic fine structure is observed with a sharp line at 27 460 cm^{-1} on the low energy tail of the 28 593 cm^{-1} band. From the temperature behaviour of the absorptions and MCD spectra of the intense 28 593 and 32 010 cm^{-1} bands, it is concluded that the first four bands arise from the $(3d)^{10} \rightarrow (3d)^9(4s)$ transition of Cu^+ occupying an off-centred position at the K^+ site. By comparison with the $d^{10} \rightarrow d^9s$ Cu^+ absorption bands in CaF_2 and NaF , it is suggested that the 28 593 and 32 010 cm^{-1} bands are caused by the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$ transitions, respectively, while the weak 27 000 and 31 250 cm^{-1} bands are related to the triplet states ${}^3T_{2g}$ and 3E_g . The high-energy 47 600 cm^{-1} band is proposed to be attributable to the $(3d)^{10} \rightarrow (3d)^9(4p)$ transition.

1. Introduction

The spectroscopic properties of Cu^+ ions in crystals of alkali halides are well established by the large amount of experimental and theoretical investigations devoted to these systems [1, 2]. However, the assignment of all bands in the optical spectra is still under question, mostly due to the possible coexistence of copper ions bearing different electric charges in the same host material. From this point of view, some useful information can be obtained from studies on the optical properties of Cu^+ impurities in crystals of ternary compounds, which have not received so much attention up to now. Among them, fluoroperovskites (typical formula ABF_3 , where A and B stand for an alkali metal and an alkaline earth metal, respectively) offer the advantages of a cubic lattice (which allows for the identification of analogies or differences with respect to alkali halides) and of different non-equivalent substitutional locations for the dopant ions.

KMgF_3 crystals have been already doped with Cu^+ ions in order to produce a new system for laser operation [3]. However, the optical absorption has not been investigated in detail. Moreover, although photoluminescence of $\text{KMgF}_3:\text{Cu}^+$ was recently measured and compared with the results known for alkali halides [4], a systematic and detailed study of the optical absorption of this system as a function of doping and temperature is still lacking.

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It is also interesting to investigate the position of Cu^+ ions in the KMgF_3 lattice. Two possibilities are conceivable for the location of Cu^+ . One is at the K^+ lattice site, while the other is at the Mg^{2+} site. The ionic radii of K^+ and Mg^{2+} are 1.33 and 0.66 Å, respectively. Therefore, taking into account that the radius of Cu^+ is 0.96 Å, it is expected that Cu^+ is in the off-centre position if it is located at the K^+ site, while it is in the on-centre position if it is located at the Mg^{2+} site.

The low-energy absorption bands of Cu^+ are expected to be due to the parity-forbidden $(3d)^{10} \rightarrow (3d)^9(4s)$ electronic transition as observed in various ionic crystals (see e.g. [1, 2, 5]). In this paper, from the optical absorption and magnetic circular dichroism (MCD) measurements, we try to clarify the position of Cu^+ in KMgF_3 .

2. Experimental procedures

Single crystals of $\text{KMgF}_3:\text{Cu}^+$ were grown by the Kyropoulos technique. Copper ions were added as CuF_2 in the crystal growth from the melt. Due to the instability of CuF_2 at high temperatures [2], only Cu^+ ions are expected to be incorporated at high temperature during the crystal growth of KMgF_3 crystals. The crystal growth was carried out at about 1050 °C, so that no Cu^{2+} ions are likely to be found in the samples. This is a completely different situation with respect to that of LiF crystals whose relatively low melting point allows only for Cu^{2+} doping [6]. Three crystals (typical dimensions of the boules 2.5 cm of diameter and 3 cm of length) were obtained, containing different Cu^+ concentrations 1.7, 4.3 and 8.6 mol% in the melt. All samples (typical size is $4 \times 4 \times 1 \text{ mm}^3$) were sawed from the boules and polished before optical measurements.

Absorption spectra in 51 000–4000 cm^{-1} and 4000–400 cm^{-1} spectral regions were measured using Cary-5E and Shimadzu FTIR-4200 spectrophotometers, respectively. MCD spectra were measured using a JASCO J-40A spectropolarimeter. The slit widths of the Cary and JASCO spectrometers were set to be 0.1 and 0.5 nm, respectively, while the slit width of the FTIR (Fourier transform infrared) spectrometer was set to be 10 cm^{-1} . The UV-visible absorption and MCD spectra were measured at various temperatures between 294 and 16 K, while the FTIR spectra were measured only at room temperature.

The MCD signal shown in figure 6 is given by the difference between the optical densities for the right- and left-circularly-polarized components of light. The polarized light travels through the crystals parallel to the magnetic field direction. A JASCO electric magnet was used to produce the magnetic field, which could be varied from 0 to 15 kG and applied along the $\langle 001 \rangle$ direction. A 450 W xenon lamp was used as the light source.

3. Experimental results

The absorption spectra of $\text{KMgF}_3:\text{Cu}^+$ (8.6 mol% in the melt) measured at various temperatures are shown in figure 1. Several absorption bands appear in the CuF_2 -doped crystals in the photon energy region above 22 200 cm^{-1} (the corresponding wavelength is about 450 nm). The most intense Cu^+ band is observed to have a peak at 32 010 cm^{-1} (312.4 nm) with a halfwidth of 1911 cm^{-1} at 16 K. This band, labelled the A band, has a shoulder around 31 250 cm^{-1} (320 nm), whose position seems to be unchanged for variation of temperature. Since the A band shifts to the low-energy side and appreciably broadens with increasing temperature as mentioned below, the shoulder, labelled the A' band, is not observed above about 100 K. A weaker band with a halfwidth of 1130 cm^{-1} at 16 K, labelled the B band, is observed at 28 593 cm^{-1} (349.7 nm). The A and B bands are

coincident with those previously identified in the absorption spectrum of $\text{KMgF}_3:\text{Cu}$ [3] and in the excitation spectrum for the Cu^+ luminescence peaking at 415 nm [4].

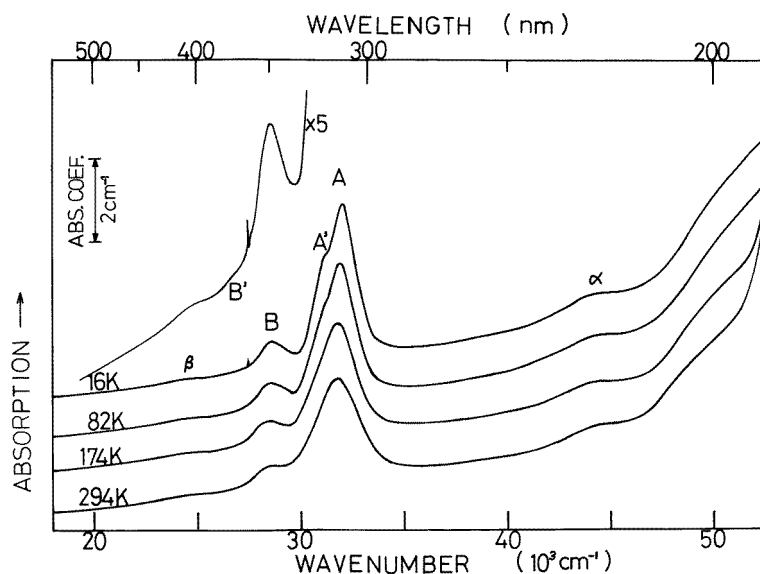


Figure 1. Absorption spectra of a $\text{KMgF}_3:\text{Cu}^+$ (8.6 mol% in the melt) crystal at various temperatures, together with the enlarged spectrum in the low-energy region at 16 K. ABS. COEF. means absorption coefficient.

Other weak bands are observed at about $44\,800\text{ cm}^{-1}$ (223 nm), labelled the α band, at about $27\,000\text{ cm}^{-1}$ (370 nm), labelled the B' band and at about $25\,000\text{ cm}^{-1}$ (400 nm), labelled the β band. The α band appears between about $45\,200\text{ cm}^{-1}$ (221.1 nm) and $40\,900\text{ cm}^{-1}$ (244.5 nm), the B' band appears between about $27\,300\text{ cm}^{-1}$ (366.3 nm) and $26\,100\text{ cm}^{-1}$ (383.1 nm) and the β band appears between about $25\,600\text{ cm}^{-1}$ (429.8 nm) and $23\,200\text{ cm}^{-1}$ (431.0 nm). The ratios of the integrated absorption areas of the B, α and β bands to the doublet-structured A band are estimated to be 0.12, 0.14 and 0.008 at 16 K, respectively.

The peak of the A band shifts to low energy with increasing temperature (the amount of the shift is 210 cm^{-1} between 16 and 294 K), while the B band peak does not show any thermal shift, as shown in figure 2. However, both bands show the same behaviour in the band width and peak height: they broaden and their peak heights decrease with increasing temperature. The B band is so strongly overlapped with the A band as temperature is increased that it is hard to estimate precisely their intensities. In figure 3 is shown the temperature dependence of the integrated absorption area of the combined A and B bands. It is observed that the A–B band area decreases slightly with increasing temperature from 16 K to about 70 K and then it is almost constant. A decrement of about 12% is obtained at 70 K. Similarly the peak height of the α band does not show any change with increasing temperature. Although it is difficult to estimate its intensity exactly because of the overlapping with an intense band appearing at high energy above $47\,600\text{ cm}^{-1}$ (210 nm), it seems that the α band area remains constant for variation of temperature.

A sharp line (called the zero-phonon line) is observed at $27\,460\text{ cm}^{-1}$ (364.7 nm) at 16 K on the low-energy tail of the B band, as seen in figure 1. Its halfwidth is 25 cm^{-1} at 16 K. The line is accompanied as shown in figure 4 with several weak sidebands at the

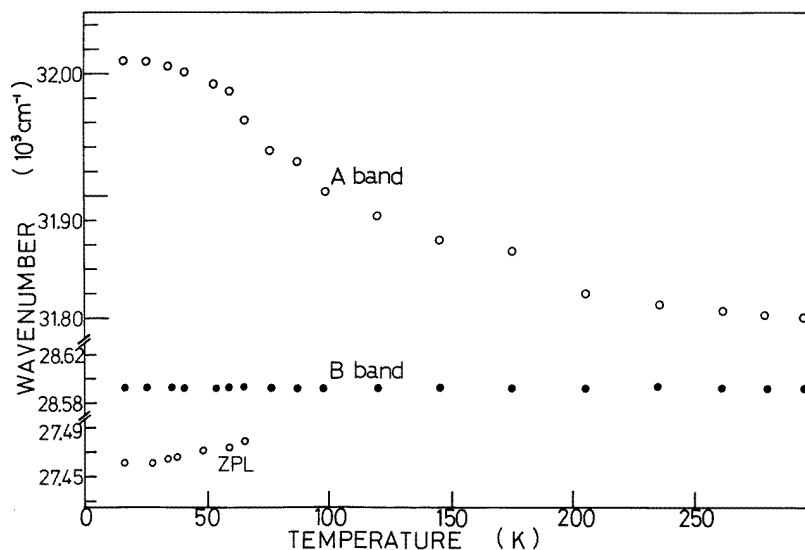


Figure 2. Temperature dependence of the peak positions of the A and B bands and of the zero-phonon line observed at the low-energy tail of the B band.

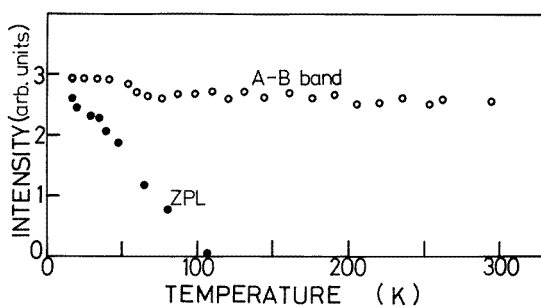


Figure 3. Temperature dependence of the intensity (i.e. integrated absorption area) of combined A and B bands and of the zero-phonon line. Note that the zero-phonon line intensity at 16 K is smaller than the A-B band intensity by about four orders.

high-energy side, which are named a, b, c and d in order of increasing energy. The energy separations between the zero-phonon line and the a, b, c and d bands are 88, 162, 221 and 283 cm^{-1} , respectively, at 16 K. The temperature dependence of the spectra (figure 4) shows that the intensity (i.e. integrated absorption area) of the zero-phonon line decreases with increasing temperature as plotted in figure 3, and the structure is not observed above 100 K together with the sidebands. Unlike the peaks of the A and B bands, its peak shifts slightly to high energy with increasing temperature (figure 2).

Figure 5 shows the transmission IR spectrum at 294 K of a $\text{KMgF}_3:\text{Cu}^+$ (8.6 mol%) crystal with a thickness of 2.08 mm. The crystal is transparent in the spectral range 22 200–1500 cm^{-1} since the spectrum remains flat at approximately 93% transmission in this region. The transmission decreases with decreasing photon energy below 1500 cm^{-1} . A very weak absorption peak is observed at 1264 cm^{-1} . Like the case of a thick KNiF_3 crystal with a thickness of 2.23 mm [7], the crystal transmission becomes negligible between about

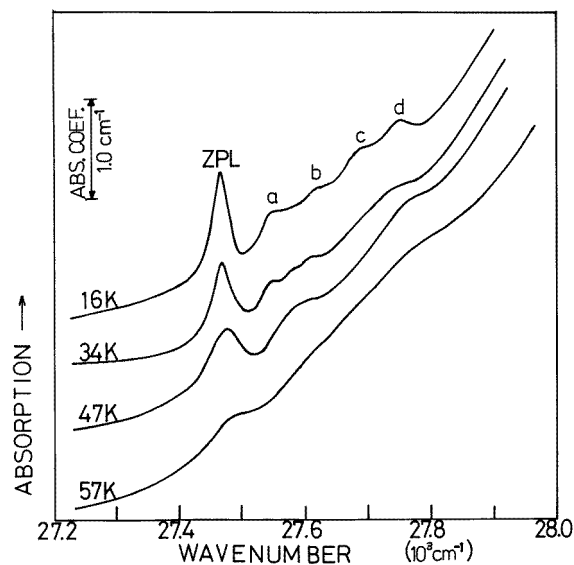


Figure 4. Absorption spectra of the zero-phonon line (ZPL) and its sidebands observed in a $\text{KMgF}_3:\text{Cu}^+$ (8.6 mol% in the melt) crystal at various temperatures. ABS. COEF. means absorption coefficient.

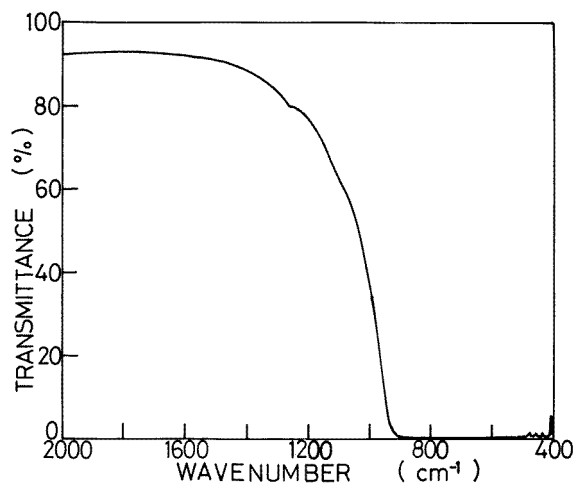


Figure 5. Transmission IR spectrum of a $\text{KMgF}_3:\text{Cu}^+$ (8.6 mol% in the melt) crystal with a thickness of 2.08 mm at 294 K.

900 cm^{-1} and about 450 cm^{-1} , as shown in figure 5. Such a decrease of transmission is due to the absorption by the fundamental IR active KMgF_3 lattice vibrations [7]. Similar spectra were obtained in the other crystals with lower Cu^+ concentrations, and no absorption due to lattice vibrations related with Cu^+ ions was observed in the $2000\text{--}400\text{ cm}^{-1}$ region.

Figure 6 shows the MCD spectra of a $\text{KMgF}_3:\text{Cu}^+$ (8.6 mol%) crystal measured at 294 and 16 K, together with the corresponding absorption spectra. A derivative-like MCD line shape is observed for each of the A and B bands at both temperatures. This indicates

that the MCD mainly comes from a diamagnetic term arising from the Zeeman shift of the absorption bands [8]. The MCD signal is larger at 16 K than at 294 K, which is consistent with the fact that both A and B absorption bands become narrower and sharper at 16 K than at 294 K, to maintain the integrated area constant. In spite of such an absorption-derivative line shape of the MCD signal, the centre of the MCD spectrum is not located at the peak position of the corresponding absorption band but slightly shifted to low energy in the A and B bands as seen in figure 6. The g -value can be calculated from the MCD spectrum using the moment method [9, 10]. The estimated g value is 2.580 and 2.004 for the A and B bands at 16 K, respectively. The MCD signal is too weak in the α and β bands to obtain the precise line shape and therefore to estimate their g values.

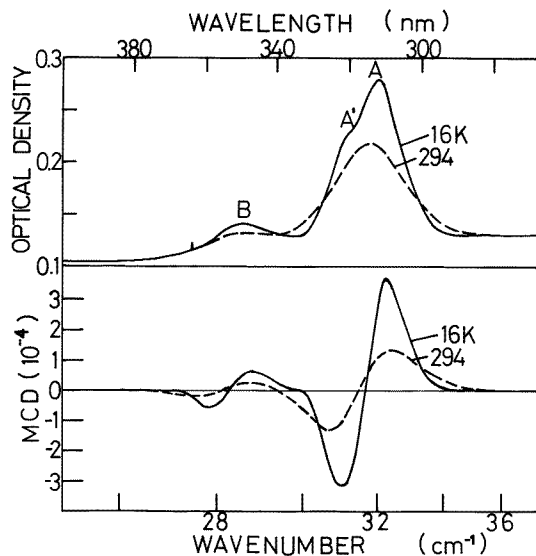


Figure 6. MCD (lower part) and absorption (upper part) spectra of a $\text{KMgF}_3:\text{Cu}^+$ (8.6 mol% in the melt) crystal with a thickness of 1.74 mm at 294 and 16 K. The applied magnetic field is 11.5 kG.

Similar MCD spectra were obtained in the other lightly doped crystals. In figure 7 the intensity of the MCD signal and the absorption coefficient at the peak of the A band are plotted against the Cu^+ concentration. A quite good proportionality to the concentration in the melt is obtained for each of the MCD and absorption band. This indicates that the Cu^+ impurity is almost uniformly incorporated in all KMgF_3 doped crystals, although an impurity segregation was expected in the $\text{KMgF}_3:\text{Cu}^+$ system on the basis of the very different melting points of the impurity and the host material.

4. Discussion

In figure 8 the peak height of the B band is plotted against that of the A band for the three crystals of KMgF_3 with different Cu^+ concentrations. There is an evident proportionality between the intensities of the A and B bands, which confirms that the A and B bands have a common origin. A similar relationship was obtained between the A and α bands, although the proportionality is not perfect because of the uncertainty in the evaluation of the peak height for the broad and weak α band. As far as the β band is concerned, such a relationship

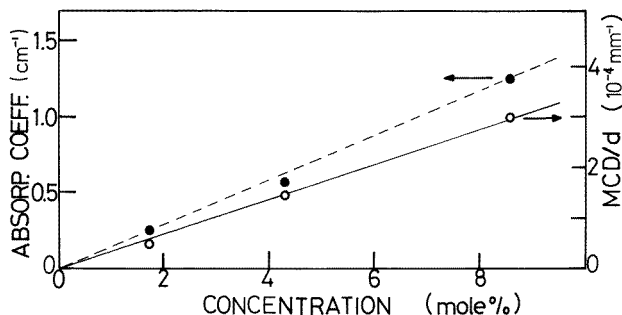


Figure 7. MCD signal (i.e. difference between the maximum and minimum MCD values, shown by open circles) and peak height (closed circles) of the A band at 294 K plotted against Cu^+ concentration in the melt. MCD/d means the MCD divided by the crystal thickness d , and ABSORP. COEFF. means absorption coefficient.

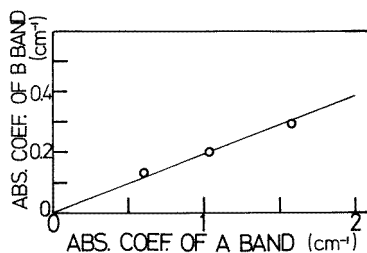


Figure 8. Peak height of the B band plotted against that of the A band measured in KMgF_3 crystals with different Cu^+ concentrations at 16 K. ABS. COEFF. means absorption coefficient.

cannot be reliably demonstrated because it is too weak and broad to estimate the height. Therefore it can be concluded that the A, B and α bands arise all from the same centre, but it cannot be explicitly suggested that the β band as well arises from the same defect.

In the absorption bands of Ag^+ ions in CsBr crystals, the oscillator strength has been observed to decrease with increasing temperature from 10 K and to remain constant at high temperatures [11]. Such a behaviour suggests a stable off-centre position of Ag^+ ions [11, 12]. This result is quite similar to that shown in figure 3, although the decrement of 20% estimated in CsBr: Ag^+ is somewhat larger than the present decrement of 12%. Additionally, the temperature independent behaviour observed above 70 K is consistent with that which is expected for deep off-centred Ag^+ and Cu^+ ions [12].

The Cu^+ absorption bands in KI crystals have been observed at 44 050, 38 095 and 35 460 cm^{-1} (227, 262.5 and 282 nm, respectively) [5]. Among these bands, the 262.5 nm band is the most intense. It is reasonable to propose, by comparing the observed Cu^+ spectra in KI and KMgF_3 , that the 262.5, 282 and 227 nm bands correspond to the A, B and α bands of KMgF_3 , respectively. Additionally the MCD line shape (including the polarity) of the 262.5 and 282 nm bands [5] is quite similar to that of the A and B bands, respectively. However the MCD line shapes of Cu^+ bands observed at 254 and 275 nm in NaCl crystals [5], which correspond to the 262.5 and 282 nm bands in KI, respectively, are not similar to those of the corresponding Cu^+ bands in KI and KMgF_3 . It is known that Cu^+ ions are located at off-centred positions in KI but at on-centred positions in NaCl [5, 12, 13]. Therefore, from the temperature dependence of the intensities of the Cu^+ bands

and from the comparison with the MCD line shapes of Cu^+ bands in KI and NaCl, it is suggested that Cu^+ ions in KMgF_3 are located at off-centred positions.

Fine structure at the low-energy tail of the B band has been observed in the excitation spectrum of the Cu^+ luminescence in KMgF_3 at 4.2 K by Lizzo *et al* [4]. Such a structure is similar to that observed in the absorption spectra in this study, but the present data allow for determining a more fine structure. The frequencies of the transverse optical (TO) phonon branch at the edge of the KMgF_3 Brillouin zone are 162, 291 and 471 cm^{-1} at 85 K, and are named TO_1 , TO_2 and TO_3 , respectively [7]. The energy separations of the b and d sidebands from the zero-phonon line are 162 and 283 cm^{-1} , respectively, at 16 K (figure 4). Since they are close to the TO_1 and TO_2 frequencies, respectively, the observed fine structure can be reliably ascribed to the lattice vibration of the bulk KMgF_3 crystal.

In $\text{NaF}:\text{Cu}^+$ crystals, the absorption bands due to $d^{10} \rightarrow d^9s$ transitions of Cu^+ have been observed at about $32\,200$, $34\,600$ and $36\,400 \text{ cm}^{-1}$ (310, 289 and 274 nm, respectively) at 2 K [14]. The first and third bands correspond to the B and A bands of $\text{KMgF}_3:\text{Cu}^+$, respectively, while the second band seems to correspond to the A' band. As in the case of the B band, a fine structure has been observed on the low-energy tail of the first band and is similar to that observed in $\text{KMgF}_3:\text{Cu}^+$. The separation between the lowest-energy sharp line (named the (0–1) line [2]) and the first sideband (named the (0–3) line) is 95 cm^{-1} . This frequency is interpreted to be associated with localized vibration of Cu^+ surrounded by F^- ions [2]. Its value is close to 88 cm^{-1} , which is the separation between the corresponding zero-phonon line and sideband a in KMgF_3 . Therefore it is suggested that such a sideband observed in $\text{KMgF}_3:\text{Cu}^+$ is caused by the localized vibration of the Cu^+ centre in the fluoroperovskite lattice.

Three absorption bands due to off-centred Cu^+ ions were observed in Cu doped CaF_2 crystals at $33\,170$, $30\,450$ and $28\,000 \text{ cm}^{-1}$ [15], namely in spectral positions which are very close to those of the A, B and B' bands of $\text{KMgF}_3:\text{Cu}^+$, respectively. Since the first band is the most intense while the last one is the weakest, the whole spectrum is very similar to that of $\text{KMgF}_3:\text{Cu}^+$. From the polarization dependence of the two-photon absorption, the high-energy $33\,170 \text{ cm}^{-1}$ band and the low-energy $30\,450 \text{ cm}^{-1}$ band have been deduced to arise from transitions to E_g and T_{2g} states, respectively [15]. In contrast, in the cases of $\text{NaF}:\text{Cu}^+$ and $\text{NaCl}:\text{Cu}^+$, the high-energy band (e.g. $36\,400 \text{ cm}^{-1}$ in NaF) has a T_{2g} character while the low-energy one ($32\,200 \text{ cm}^{-1}$ band in NaF) has an E_g character.

This is consistent with the expectation that a d orbital is split into a high-energy e_g orbital and a low-energy t_{2g} orbital in the cubic crystal field of CaF_2 , while the situation is reversed in an octahedral field like that of NaF [15]. This means that for the Cu^+ centre in CaF_2 the E_g state is higher than the T_{2g} state, and therefore the intense $33\,170 \text{ cm}^{-1}$ band and the weak $30\,450 \text{ cm}^{-1}$ band were assigned to transitions from the $^1A_{1g}$ ground state to the singlet 1E_g and $^1T_{2g}$ states, respectively, while the weakest $28\,000 \text{ cm}^{-1}$ band was related to the triplet $^3T_{2g}$ state.

An order of the energy levels similar to that of off-centred Cu^+ in CaF_2 is expected for off-centred Cu^+ in KMgF_3 although Cu^+ in KMgF_3 has a twelfold cubic coordination which is slightly different from the eightfold coordination of Cu^+ in CaF_2 . As a consequence the energy levels for the A, A', B and B' absorption bands in $\text{KMgF}_3:\text{Cu}^+$ are assigned by analogy with $\text{CaF}_2:\text{Cu}^+$ as shown in figure 9. The weak A' band and the very weak B' band are attributed to the triplet states, as in the cases of $\text{NaF}:\text{Cu}^+$ and $\text{CaF}_2:\text{Cu}^+$. Another possible assignment is conceivable for the A' band, namely a Jahn–Teller splitting of the band due to the $^1A_{1g} \rightarrow ^1E_g$ transition. However, this interpretation seems to be ruled out because the A band shifts to the low-energy side with increasing temperature, while the A' band keeps its spectral position unchanged.

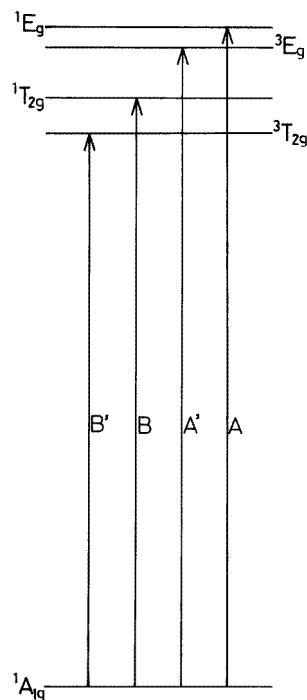


Figure 9. Schematic energy level diagram of Cu^+ in KMgF_3 and the assignment of the observed absorption bands.

According to a theoretical calculation [16], the absorption band due to the $1A_{1g} \rightarrow 1E_g$ transition is more intense in off-centred Cu^+ than that due to the $1A_{1g} \rightarrow 1T_{2g}$ transition, and the reverse for on-centred Cu^+ . This is consistent with the present assignment for Cu^+ bands in KMgF_3 , because the high-energy A band due to the $1A_{1g} \rightarrow 1E_g$ transition is observed to be more intense than the low-energy B band due to the $1A_{1g} \rightarrow 1T_{2g}$ transition. Thus the present assignment is not unreasonable.

The very weak β band, not clearly observed in all samples of crystals containing different dopant concentrations, does not seem to arise from isolated Cu^+ ions. It is impossible to obtain evidence for its positive attribution, but two reasonable hypotheses about its nature can be put forward: (i) Cu^{2+} ions, since some of the dopant Cu^{2+} ions could not be reduced to Cu^+ during the crystal growth and since absorption bands due to Cu^{2+} are expected to be located at lower energy than the Cu^+ bands, or (ii) vacancy (or impurity) perturbed Cu^+ ions. As far as the α band is concerned, the most reliable assignment is related to $(3d)^{10} \rightarrow (3d)^9(4p)$ transitions of Cu^+ which give rise to absorption bands at higher energy than the $(3d)^{10} \rightarrow (3d)^9(4s)$ bands.

5. Conclusions

Accurate and systematic measurements of absorption and MCD spectra of $\text{KMgF}_3:\text{Cu}^+$ crystals supply new information on the Cu^+ optical behaviour in ionic crystals, besides confirming previous partial results. First of all, the most intense A band and the weaker B and α bands are unquestionably due to different transitions of Cu^+ . The fine structure found

on the low-energy tail of the B band has been analysed in detail, and the attribution of at least two sidebands to transverse optical phonons allows us to ascribe the whole structure to lattice vibrations of KMgF_3 crystals. From the temperature dependence of the absorption spectra and from MCD measurements a clear indication of the off-centre configuration of Cu^+ ion replacing a K^+ ion in the cubic lattice is obtained. Localized vibrations of the Cu^+ ion surrounded by F^- anions have been also identified by analogy with $\text{NaF}:\text{Cu}^+$.

Acknowledgments

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