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Observation of absorption bands due to the $4f^7 \rightarrow 4f^7$ parity-forbidden transitions of Eu^{2+} ions in KMgF_3 crystals

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Abstract. Optical absorption and magnetic circular dichroism spectra of Eu^{2+} ions in KMgF_3 crystals have been measured. The fine structure of the absorption bands due to the $^8S_{7/2} \rightarrow ^6P_{7/2}$ and $^8S_{7/2} \rightarrow ^6P_{5/2}$ transitions in the spin- and parity-forbidden $4f^7 \rightarrow 4f^7$ intraconfigurational electronic transition has been studied at different temperatures. By comparison with the one-photon and two-photon excitation spectra for the luminescence due to the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition, it is shown that the fine structure consists of the absorption peaks due to three kinds of Eu^{2+} ion which substitutes K^+ ions but have different site symmetries, i.e. the cubic, tetragonal and trigonal symmetries.

1. Introduction

Eu^{2+} ion has the electronic configuration $4f^7 5s^2 5p^6$ (denoted f^7 hereafter) in the outer shell in the ground state and $4f^6 5s^2 5p^6 5d$ (denoted f^6d) in the first excited state. The interconfigurational electronic $f^7 \rightarrow f^6d$ transition is parity allowed, while the intraconfigurational $f^7 \rightarrow f^7$ transition is parity forbidden and the electric dipole transition is not allowed [1]. The optical absorption bands due to the latter transition of Eu^{2+} appear to lie quite close to the very intense bands due to the former transition. Therefore it is difficult to obtain clear evidence of the $f^7 \rightarrow f^7$ absorption bands because of their considerably weak intensity. So far, the $f^7(^8S_{7/2}) \rightarrow f^7$ absorption bands have been reported only in crystals of $\text{CaF}_2:\text{Eu}^{2+}$ [2] and $\text{SrAlF}_3:\text{Eu}^{2+}$ [3], without detailed description and analysis.

Unlike the case of the absorption spectrum, the $f^7 \rightarrow f^7$ transition has been observed clearly in the one-photon excitation and two-photon excitation spectra for the luminescence due to the transition from the excited f^7 state (e.g. $^6P_{7/2}$ state) or f^6d state to the ground $f^7(^8S_{7/2})$ state. Indeed in the case of the two-photon excitation process, in which the Eu^{2+} ion is raised from the ground state to the excited f^7 state by simultaneous absorption of two photons of light, such an intraconfigurational transition is electric dipole allowed, giving rise to a large transition probability. The one- and two-photon excitation spectra, however, give indirect information about the $f^7(^8S_{7/2}) \rightarrow f^7$ transition because they are obtained through the luminescence process where the excited electron is relaxed to the lowest excited state $f^7(^6P_{7/2})$ after the excitation and then it is returned to the ground state. In order to obtain

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direct information about the $f^7(^8S_{7/2}) \rightarrow f^7$ transition, the optical absorption (i.e. one-photon absorption) itself should be investigated.

In KMgF_3 the excited f^7 states of the Eu^{2+} ion lie at much lower energy with respect to the f^6d states than in other ionic crystals such as CaF_2 and alkali halides [1]. Therefore, unlike the cases of other crystals, it should be possible to observe the $f^7 \rightarrow f^7$ absorption spectrum separated from the intense $f^7 \rightarrow f^6d$ absorption spectrum clearly in KMgF_3 . So far such a spectrum has not been reported. In this paper we study the $f^7 \rightarrow f^7$ absorption spectrum in $\text{KMgF}_3:\text{Eu}^{2+}$ crystals and compare it with the one- and two-photon excitation spectra previously observed [4–6].

2. Experimental procedures

Single crystals of KMgF_3 containing various concentrations of Eu^{2+} ions were grown by the Kyropoulos method. Europium ions were added as EuCl_3 in the stoichiometric mixtures of KF and MgF_2 dehydrated powders. Previous experiments showed that doping with Eu^{3+} ions of KMgF_3 is extremely difficult if the crystal growth is not carried out in an oxidizing atmosphere [7]. This is evidently caused by a quantitative reduction process to Eu^{2+} ions during the incorporation in the perovskite lattice, which therefore contains practically only divalent ions of the dopant. In the present study, we used a crystal, grown from a melt containing 1.1 mol% of Eu^{2+} ions, which is sufficiently doped to observe the weak $f^7 \rightarrow f^7$ absorption bands.

Absorption spectra were measured using a Cary-5E spectrophotometer at various temperatures in the range 15–300 K. MCD (magnetic circular dichroism) spectra were measured using a JASCO J-40A spectropolarimeter. The slit widths of the Cary and JASCO spectrometers were normally set to be 0.05 and 0.3 nm, respectively. In the high-resolution measurement (shown by curve a of figures 3 and 4) the slit width of the Cary spectrometer was set to be 0.02 nm.

3. Experimental results

The absorption spectrum of $\text{KMgF}_3:\text{Eu}^{2+}$ (1.1 mol% in the melt) at room temperature is shown in figure 1. An intense absorption band due to the $f^7 \rightarrow f^6d$ dipole-allowed transition is observed in the region 30 000–45 000 cm^{-1} . Additionally two very weak absorption bands are observed at the low energy side of the intense band. Their peaks are at 27 830 and 28 251 cm^{-1} (the corresponding wavelengths are about 359.3 and 353.9 nm, respectively) at 296 K. The 27 830 cm^{-1} band is more intense than the 28 251 cm^{-1} band. From comparison with the previous studies of luminescence [5, 6], the weak bands are attributed to the $f^7 \rightarrow f^7$ absorption: the lower-energy band is attributed to the $^8S_{7/2} \rightarrow ^6P_{7/2}$ transition, while the higher-energy one to the $^8S_{7/2} \rightarrow ^6P_{5/2}$ transition.

Figure 2 shows the absorption spectrum of these weak bands at 16 K. Their positions are shifted towards higher energies when temperature is decreased from room temperature, e.g. the 27 830 cm^{-1} peak is shifted to 27 846 cm^{-1} at 16 K as shown in the inset of figure 2. The absorption intensities (i.e. integrated absorption areas) of these bands are little changed by the decrease of temperature, but it is observed that the bands become narrower with decreasing temperature (see the inset of figure 2). At 16 K the $^8S_{7/2} \rightarrow ^6P_{7/2}$ band consists of three bands at 27 827, 27 837 and 27 846 cm^{-1} , while the $^8S_{7/2} \rightarrow ^6P_{5/2}$ band consists of two bands at 28 262 and 28 270 cm^{-1} . Their enlarged spectra are shown in curve a of figures 3 and 4. The one-photon absorption spectrum due to the $^8S_{7/2} \rightarrow ^6P_{7/2}$ transition

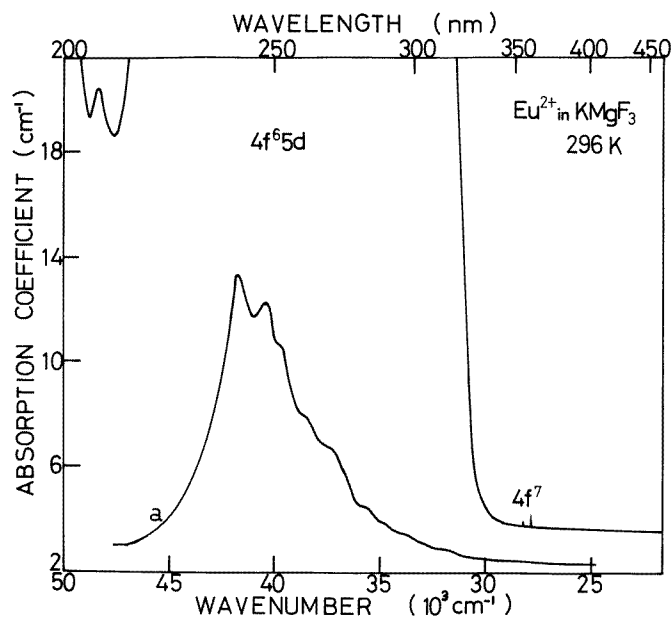


Figure 1. Absorption spectra of a $\text{KMgF}_3:\text{Eu}^{2+}$ (1.1 mol% in the melt) crystal at 296 K. The crystal thickness is 1.98 mm. The absorption band due to the $4f^7 \rightarrow 4f^6 5d$ transition (curve a) is shown in a reduced scale.

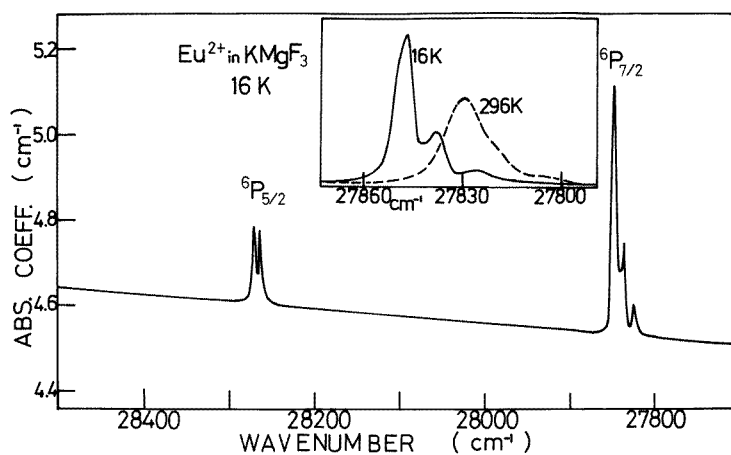


Figure 2. Absorption bands due to the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ and ${}^6P_{5/2}$ transitions in $4f^7 \rightarrow 4f^7$ parity-forbidden transitions of Eu^{2+} ions in KMgF_3 crystal at 16 K. Inset shows the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ band at 16 and 296 K. ABS. COEFF. means absorption coefficient.

is quite similar to the observed corresponding one- and two-photon excitation spectra [5, 6] for the luminescence due to ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition in the lineshape and peak positions as shown in figure 3.

Regarding the spectrum due to the ${}^8S_{7/2} \rightarrow {}^6P_{5/2}$ transition, we observed an absorption band at 28253 cm^{-1} , while it is not seen in the two-photon excitation spectrum [5] because the measurement was made in a limited range of $28259\text{--}28274 \text{ cm}^{-1}$. The observation

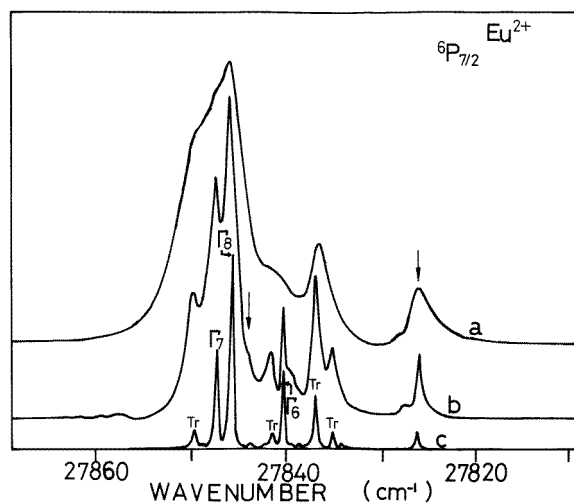


Figure 3. Fine structure of the absorption band (curve a) due to the $^8S_{7/2} \rightarrow ^6P_{7/2}$ transition of Eu^{2+} ions in KMgF_3 at 16 K, compared with the one-photon excitation spectrum in the $^8S_{7/2} \rightarrow ^6P_{7/2}$ spectral range (curve b, obtained by Ellens *et al* [6]) for the luminescence due to $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition at 4.2 K and compared with the two-photon excitation spectrum (curve c, obtained by Francini *et al* [5]) for the luminescence at 15 K. Γ_6 means the Γ_6 symmetry absorption band due to Eu^{2+} at the cubic lattice site. Tr means the absorption bands due to the trigonal Eu^{2+} ion.

of the $28\,253\text{ cm}^{-1}$ band is in agreement with the result of one-photon excitation spectra measured by Altshuler *et al* [4] and Ellens *et al* [6]. Our one-photon absorption lineshape in the range of $28\,258\text{--}28\,280\text{ cm}^{-1}$ is different from the spectrum of Altshuler *et al* regarding the peak-height ratio among the observed bands, as seen in figure 4. Our lineshape, however, is quite similar to the spectrum of Ellens *et al*.

Since the resolution of the MCD spectrometer is 0.3 nm (poorer than the case of the Cary-5E absorption spectrophotometer), it is difficult to observe the correspondence of the MCD lineshape with the absorption spectra of figures 3 and 4. The MCD lineshape is observed to be similar to the absorption lineshape which is obtained using the same MCD spectrometer. Like the case of the absorption spectra, the other $f^7 \rightarrow f^7$ absorption bands such as $^8S_{7/2} \rightarrow ^6P_{3/2}$ and $^8S_{7/2} \rightarrow ^6I$ bands were not observed in the MCD spectra.

4. Discussion

The Eu^{2+} ion has an ionic radius of 1.12 \AA , while K^+ and Mg^{2+} have radii of 1.33 and 0.65 \AA , respectively. Therefore it is assumed that the Eu^{2+} substitutes for the singly-charged K^+ with a 12-fold F^- coordination in the KMgF_3 lattice as shown in figure 5. In this case the charge-compensating positive ion vacancy is necessary and it is expected to be located at one of the K^+ sites around the Eu^{2+} ion, giving rise to Eu^{2+} complexes with axial symmetry. If the vacancy is present at one of the nearest-neighbour K^+ sites in the $\langle 100 \rangle$ axis (e.g. the site A of figure 5), the site symmetry of Eu^{2+} is tetragonal C_{4v} , and if the vacancy is located at one of the third- or second-nearest-neighbour K^+ sites in the $\langle 111 \rangle$ or $\langle 110 \rangle$ axis (e.g. the site C or B), respectively, the site symmetry is trigonal C_{3v} or C_{2v} . Francini *et al* including one (AS) of the present authors have attributed three

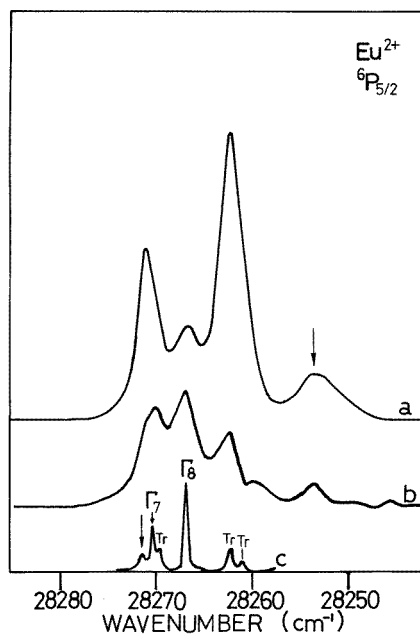


Figure 4. Fine structure of the absorption band (curve a) due to the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ transition of Eu^{2+} ions in KMgF_3 at 16 K, compared with the one-photon excitation spectrum in the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ spectral range (curve b, obtained by Altshuler *et al* [4]) at 77 K and compared with the two-photon excitation spectrum (curve c, obtained by Francini *et al* [5]) for the luminescence at 359 nm which is due to $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition at 15 K. Γ_6 means the Γ_6 symmetry absorption band due to Eu^{2+} at the cubic lattice site. Tr means the absorption bands due to the trigonal Eu^{2+} ion.

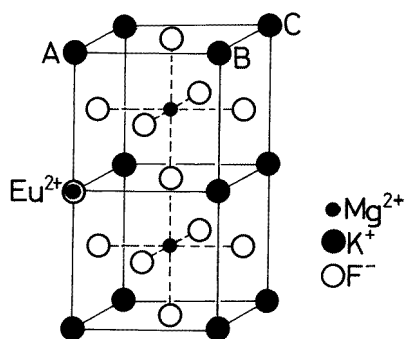


Figure 5. Crystal structure of KMgF_3 with Eu^{2+} ion. The lattice site A, B or C indicates a possible position of the charge-compensating positive ion vacancy.

lines (at 27 840.3, 27 845.8 and 27 847.3 cm^{-1}) observed in the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ two-photon spectrum to the Eu^{2+} ion at cubic site and four lines (at 27 835.0, 27 836.8, 27 841.5 and 27 849.8 cm^{-1}) to the Eu^{2+} at trigonal site from the crystal-field calculation, while two lines (at 28 267.0 and 28 270.5 cm^{-1}) observed in the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ two-photon spectrum to the cubic Eu^{2+} and three lines (at 28 261.0, 28 262.3 and 28 269.7 cm^{-1}) to the trigonal Eu^{2+} [5]. Their assignment is shown in figures 3 and 4.

Besides these lines, there are several intense lines (at 27 827, 27 843, 28 253 and 28 271 cm^{-1} lines), which have not been assigned yet: these are shown by arrows in figures 3 and 4. In the electron spin resonance experiment, Eu^{2+} ion at a tetragonal site has been observed in addition to the cubic Eu^{2+} [8]. Therefore it is suggested that these unassigned lines are due to the tetragonal Eu^{2+} . The tetragonal Eu^{2+} gives rise to four and three absorption lines in the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ and $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ transitions, respectively. Not all of these lines are observed in figures 3 and 4 clearly since it seems that some lines are overlapped with the lines due to the cubic and trigonal Eu^{2+} ions.

These assignments are consistent with the observation of four $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ luminescence lines (named A, B, C and D) by Ellens *et al.*, from which they proposed that there are at least four types of Eu^{2+} ion with different site symmetries in KMgF_3 [6]. They observed three relatively intense A, B and D luminescence lines and one considerably weak C line (see figure 3 of [6]). Therefore it is suggested that the a-, b- and d-site Eu^{2+} ions are more populated than the c-site Eu^{2+} (here we call Eu^{2+} ions which give rise to the A, B, C and D lines a-, b-, c- and d-site Eu^{2+} ions, respectively) and the A, B and D lines are caused by the cubic, trigonal and tetragonal symmetry Eu^{2+} ions although at this moment we cannot determine which luminescence line belongs to which symmetry Eu^{2+} . Besides the above-mentioned 27 835.0, 27 836.8, 27 840.3, 27 841.5, 27 845.8, 27 847.3, 27 849.8, 28 261.0, 28 262.3, 28 267.0, 28 269.7, 28 270.5 cm^{-1} and 27 827, 27 843, 28 253, 28 271 cm^{-1} excitation lines, there are very weak lines in figures 3 and 4 (e.g. a line at 27 829 cm^{-1}), which have not been assigned yet. These weak lines are probably due to the remaining minor c-site Eu^{2+} .

Eu^{2+} ion is present in alkali halide crystals with NaCl structure [1]. The Eu^{2+} ion enters the lattice substitutionally at the alkali ion site which possesses octahedral symmetry. Like the case of $\text{KMgF}_3:\text{Eu}^{2+}$, the substitutional Eu^{2+} is accompanied by a charge-compensating cation vacancy in one of the nearby alkali ion sites in alkali halides. If the vacancy is at one of the next-nearest-neighbour sites along the $\langle 110 \rangle$ directions (i.e. one of the nearest-neighbour alkali ion sites), the symmetry of the Eu^{2+} environment is C_{2v} . This is consistent with the observation of four lines in the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ transition by two-photon excitation spectroscopy [9–11]. That is to say, four absorption lines due to C_{2v} -symmetry Eu^{2+} have been observed, but absorption lines due not only to octahedral Eu^{2+} (where vacancy is located far from the Eu^{2+} site) but also to other low-symmetry Eu^{2+} accompanied by a vacancy at the second- or third-nearest-neighbour cation site are not observed. This indicates that, unlike the case of KMgF_3 , only the C_{2v} symmetry Eu^{2+} ion with a vacancy at the nearest-neighbour cation site is present in alkali halides, and the other symmetry Eu^{2+} ions are not present. This is reasonable, since the C_{2v} site-symmetry Eu^{2+} has a stronger coupling with the vacancy than that of Eu^{2+} with the other site symmetries because of the shortened distance between the vacancy and Eu^{2+} . In the case of KMgF_3 both Eu^{2+} ions with and without vacancy are present simultaneously and additionally different types of vacancy-accompanied Eu^{2+} ion (with trigonal and tetragonal site symmetries) coexist in the crystal. Why does such a difference occur in KMgF_3 ?

A possible explanation is that the location of the vacancy is not critical in KMgF_3 . The vacancy is not necessarily located at the nearest-neighbour site, and therefore Eu^{2+} ions with various kinds of local site symmetry can be present. If the vacancy is far from the Eu^{2+} site, the site symmetry can be assumed to be cubic although it is not exactly so. It seems that in monovalent crystals, such as alkali halides, the charge compensating vacancy is required to be located considerably close to the impurity to form a stable Eu^{2+} -vacancy dipole, while the formation of such an Eu^{2+} -vacancy dipole is not necessary in the KMgF_3 crystal, leading to the coexistence of various Eu^{2+} ions with different site symmetries. The

reason why, unlike the case of alkali halides, the vacancy is allowed to locate at various K^+ sites in KMgF_3 is suggested as follows. In KMgF_3 , besides the dopant Eu^{2+} , Mg^{2+} is also present in the crystal, and as a consequence the positive ion vacancy is expected to be attracted by these two divalent ions with almost the same force. Therefore it should be deduced that the result of this competition is that the vacancy is not necessarily located at the nearest-neighbour K^+ site, which produces the strongest vacancy– Eu^{2+} coupling, and a mixture of vacancies at different locations around Eu^{2+} is easily generated.

The $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{3/2}$ band is not observed but the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ and $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ bands are observed, suggesting that the selection rule $\Delta J = 0, 1$ (J : quantum number of total angular momentum) strictly holds for these $f^7 \rightarrow f^7$ transitions. This seems to indicate that these parity- and spin-forbidden $f^7 \rightarrow f^7$ bands are caused by magnetic dipole transitions. However, taking into account that Eu^{2+} with a vacancy has a non-inversion trigonal or tetragonal symmetry, the electric dipole transition is made allowed by a symmetry breaking phonon which gives rise to mixing of the $4f^7$ state with the odd-parity $4f^65d$ state. Since it is observed that the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ and $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{5/2}$ bands become broader as temperature is increased, it is suggested that the broadening is due to the line-width of the symmetry breaking phonon.

An absorption-like MCD lineshape is observed for each of the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ and $^6\text{P}_{5/2}$ bands although the resolution is poor when compared with the absorption spectra of figures 3 and 4. This indicates that the MCD mainly comes from a paramagnetic term, arising from impurity which has an unpaired electron [12]. This is consistent with the fact that Eu^{2+} ion has f^7 electron configuration in the ground state.

5. Conclusion

The one-photon absorption spectra due to parity- and spin-forbidden $f^7 \rightarrow f^7$ transition have been observed in $\text{KMgF}_3:\text{Eu}^{2+}$ crystal clearly. In CaF_2 and LiBaF_3 crystals where Eu^{2+} substitutes for cubic-symmetry Ca^{2+} and Ba^{2+} ions, respectively, no charge compensating vacancy is necessary, and three and two Eu^{2+} lines have been observed in the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ and $^6\text{P}_{5/2}$ band spectra [13–15]. Unlike the cases of CaF_2 and LiBaF_3 , at least 11 and seven lines are observed in the $^8\text{S}_{7/2} \rightarrow ^6\text{P}_{7/2}$ and $^6\text{P}_{5/2}$ band spectra in KMgF_3 doped with Eu^{2+} which substitutes for the cubic-symmetry K^+ ion, respectively. It is suggested that the Eu^{2+} spectra observed in KMgF_3 consist of absorption lines due to Eu^{2+} ions with different site symmetries, i.e. cubic, trigonal and tetragonal ones. From the line broadening and its temperature dependence, it is shown that the $f^7 \rightarrow f^7$ absorption is caused by the electric-dipole transition which is made allowed by mixing of $4f^7$ state with $4f^65d$ state due to the symmetry breaking phonon.

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