Four –Level Decay Model of $^6P_{7/2}$ Excited State of Eu^{2+} Ion in $KMgF_3$

Hai Quan SU, Xian Ming ZHANG, ChunYu ZANG, Chun Shan SHI*

Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022

Abstract: A four-level decay model of $^6P_{7/2}$ excited state of Eu^{2+} ion in $KMgF_3$: Eu^{2+} has been proposed. The decay profiles of the $^6P_{7/2}$ excited state of Eu^{2+} are two exponential and the physical implication of each term in the fit equation responsible for the model is interpreted. The data obtained spectroscopically are in good agreement with the fit results.

Keywords: Four-level decay model, divalent europium, $^6P_{7/2}$ excited state, $KMgF_3$.

Optical transitions of divalent Europium ($4f^7$) ions in $KMgF_3$ have been investigated extensively due to the potential applications for phosphors or lasers. In $KMgF_3$: Eu^{2+}, the $^6P_{7/2}$ state is at lower energy than the lowest $4f^65d$ state. However, the reported energy differences between the two states vary from author to author. Sardar *et al*.[1] estimated the value of 1250 cm^{-1} from a semilog plot of the $^6P_{7/2} \rightarrow ^8S_{7/2}$ and $4f^65d \rightarrow ^8S_{7/2}$ emission intensities *versus* T^{-1}. Altshuler *et al*.[2] found the value of 120 cm^{-1} from a fit to the temperature dependence of the $^6P_{7/2}$ decay time. Ellens and co-workers[3] obtained the value of 3300 cm^{-1} from spectrum data and a three-level model fit to the $^6I_{7/2}$ level. They also suggested that the main reason for the erroneous result for ΔE ($4f^65d$-$^6P_{7/2}$) for Eu^{2+} in the first two cases is that the results are fitted to a three-level model including the $^6P_{7/2}$, $4f^65d$ and the $^8S_{7/2}$ levels. In reality more levels ($^6P_{5/2}$, $^6P_{3/2}$, and different $4f^65d$ levels) are involved. In the simple three-level model, the temperature dependence of the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition probability (w_f in equation (2), *vide infra*), due to a change in the vibronic transition probability with temperature, is not taken into account. Hence, the values for ΔE from fits to the three-level model are inaccurate. The spectroscopically determined values for ΔE ($4f^65d$-$^6P_{7/2}$) are more accurate.

Recently we have started to study the reason for this erroneous value of ΔE. Single crystal of $KMgF_3$: Eu^{2+} has been grown in our laboratory and various optical measurements have been made. On the basis of temperature dependence of lifetime, we propose a four-level decay model and a two exponential decay equation. Good agreements are found between the fit and the spectroscopic results.

Results and discussion

The proposed four-level decay pattern is shown in **Figure1**.

According to the three level model, the decay time (τ) of the Eu^{2+} luminescence consisting of 4f-4f line emission and 5d-4f band emission, can be described by[2] following equation:

$$1/\tau = w_f + w_d \exp(-\Delta E/KT) \qquad (1)$$

Where w_d, w_f are the radiative probabilities of the lowest $4f^65d$ level and of the lowest excited 4f level, respectively. For the four-level system, another exponential term is needed and equation (1) can be rewrite as

$$1/\tau = w_f + w_{fl}exp(-\Delta E_{ff}/KT) + w_d exp(-\Delta E_{fd}/KT) \qquad (2)$$

Deactivation of the $^6P_{7/2}$ emitting states can take place via radiative decay and nonradiative decay. For Eu^{2+} ion, the probability of nonradiative decay between any of these excited states and the ground state is negligibly small and is neglected, due to the large energy difference (about $28000cm^{-1}$) between the $^8S_{7/2}$ and the excited states[4].

Figure 1   Four-level decay pattern of $^6P_{7/2}$ excited state in $KMgF_3$: Eu^{2+}
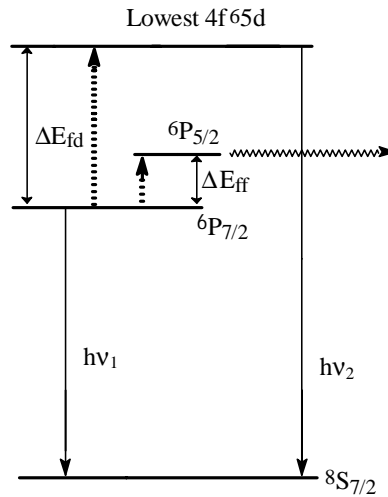
As can be seen from **Figure 1**, thermal activation of the $^6P_{5/2}$ state and the lowest $4f^65d$ states lead to opening of two additional energy dissipation tunnels. In equation (2), the deactivation rate constant of the thermally populated $4f^65d$ states is designated w_d and equals the radiative probabilities of the lowest $4f^65d$ level. ΔE_{fd} is the energy gap between the lowest $4f^65d$ states and the $^6P_{7/2}$ emitting states. The deactivation rate constant, w_{fl} is associated with low lying $^6P_{5/2}$ state, and ΔE_{ff} is the energy gap between $^6P_{5/2}$ and $^6P_{7/2}$ level. Our detailed study shows that $^6P_{5/2}$ level is a special energy dissipation tunnel and the preexponential factor w_{fl} represents the dissipation coefficient. At about 400 K, the energy loss *via* $^6P_{5/2}$ tunnel reaches its maximum. The lost energy is most possibly related to the energy transfer to the F color centers in the crystal by inter-system crossing.

W_f represents the rate constants for direct radiative decay of $^6P_{7/2}$ state. In our experiments, lifetime measurement of $^6P_{7/2}$ emission is designated with a low resolution monochromator of some 3 nm spectral resolution. Thus, the observed lifetime contains contributions from the transition probability of the vibronics (Stokes and anti-Stokes), and w_f in equation (2) consists of two terms:

$$w_f = A_{vib} + A_{zp} \qquad (3)$$

A_{vib} gives the contribution of the vibronic transitions to the total radiative transition probability (w_f) of the excited state $^6P_{7/2}$. A_{zp} represents the radiative transition probability of zero-phonon line (360 nm).

Table1 presents the lifetime data at the temperature regime 80-450 K.   Fitting the data with equation (2), we obtained the related parameters as $w_f = 281$ s^{-1}, $w_{fl} = 499$ s^{-1}, $w_{fd} = 2.8 \times 10^5$ s^{-1}, $\Delta E_{ff} = 324$ cm^{-1}, $\Delta E_{fd} = 2282$ cm^{-1}.

Table 1   Lifetime of $^6P_{7/2}$ luminescence of Eu^{2+} in KMgF$_3$ crystal

T(K)	87.0	100.1	155.0	203.9	253.0	300.2	367.1	461.0
τ(ms)	3.49	3.50	3.37	2.99	2.75	2.63	2.22	1.52

Figure 2 shows that the experimental decay data can be fitted quite well to equation (2). w_d is in good agreement with the reported data 6×10^5 s^{-1} for Eu^{2+} 5d-4f transitions[5].

Figure 2   Fitting Curve of KMgF$_3$: Eu^{2+}(1% mol)
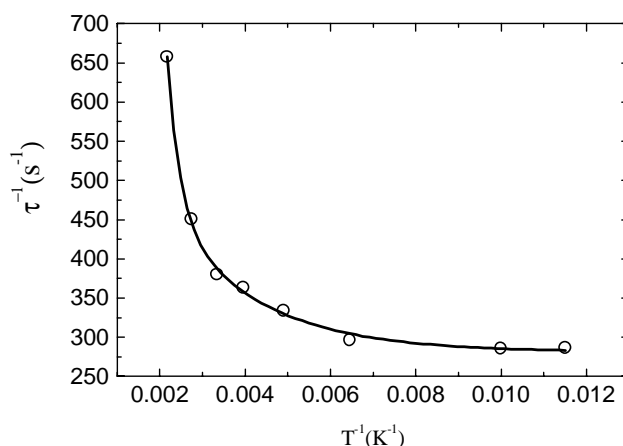
*The open circle represents the experimental data. The drawn line is a fit based on eq.(2)

In the absorption spectrum at 77 K, the absorption due to the $^8S_{7/2} \to {}^6P_{5/2}$, $^8S_{7/2} \to {}^6P_{7/2}$ at 354 and 360 nm respectively are observed, as reported by Tsuboi et al[6].   From the onset of 4f^{6}5d, $^6P_{7/2}$, $^6P_{5/2}$ absorption bands, ΔE_{ff} and ΔE_{fd} can be estimated for KMgF$_3$: Eu^{2+}.   The value is 324 and 2233 cm^{-1} respectively.   Again, these data are well agreement with the fit results.

As can be seen from the above results, there is some difference between our data and the reported ones for ΔE_{fd}.   Our results show that the calculation method is one factor, another important factor to affect the 4f^{6}5d level position is the oxygen contents in the crystals used.   Since fluoride possesses the pyrohydrolysis property (interaction with water vapour in crystal growth process) one can suppose that oxygen containing impurities in KMgF$_3$ play a very important role[5].   As literature reported[7,8,9],   the position of the 4f^{6}5d state depends on the covalency and crystal field strength at the Eu^{2+} site. Introducing oxygen into the crystal will increase the covalency and crystal field strength at the Eu^{2+} site.   As a result, the splitting (10 Dq) between e_g and t_{2g} is increased and also the centre of gravity of the 4f^{6}5d states is shifted to lower energy.   The traces

of oxygen impurities existing in our crystals is clearly shown in the absorption spectra at 204 and 224 nm as reported[10,11].

Based on equation (2), at room temperature, the dominant contribution for the total transition probability is from $^6P_{7/2}$ emission, 27% energy is lost *via* $^6P_{5/2}$ decay path and $4f^65d$ emission can be neglected in this case.   With the increase of temperature, $4f^65d$ emission gradually dominate the spectra, and at 650K 76% contributions come from this level, the line emission intensity become negligible.   This result agrees well with the reported one[1].

When temperature keeps at 77 K, there are almost no contributions from $^6P_{5/2}$ and $4f^65d$ thermally populated decay. Energy of 99.7% emits radiatively *via* $^6P_{7/2}$ excited state. Then, the two exponential terms in equation (2) can be neglected and equation (2) becomes:

$$1/\tau = w_f = A_{vib} + A_{zp} \qquad\qquad (4)$$

In equation (4), A_{vib} gives the contribution of the vibronic transitions to the total radiative transition probability (w_f) of the $^6P_{7/2}$ excited state.   The ratio of the total vibronic intensity and the total zero-phonon line intensity is given by

$$R = I_{vib}/I_{zp} = A_{vib}/A_{zp} \qquad\qquad (5)$$

From the R value and the decay time, the vibronic and zero-phonon transition probability A_{vib} and A_{zp} can be obtained by the equation (4) and (5)[3,4,12].   Using the data from emission spectrum and lifetime at 77 K, *i.e.* τ = 3.49ms and R = 2.2 (Integral intensity ratio), we get A_{zp} = 89 s^{-1} and A_{vib}=198 s^{-1}.   Thus, $w_f = A_{vib}+A_{zp}$ = 287 s^{-1}. This value well consists with that obtained from the fit result 281s^{-1}.

Acknowledgments

References

1.   D. K. Sardar, W. A. Sibley, R. Alcala, *J. Lumin.*, **1982**, *27*, 401.
2.   N. S. Altshuler, S. L. Korableva, L. D. Livanova, A. L. Stolov, *Sov. Phys. Solid State*, **1974**, *15*, 2155.
3.   A. Ellens, A. Meijerink, G. Blasse, *J. Lumin.*, **1994**, *59*, 293.
4.   A. Meijerink, *J. Lumin.*, **1993**, *55*, 125.
5.   R. Francini, U. M. Grassano, M. Tomini, S. Boiko, G. G. Tarasov, A. Scacco, *Phys. Rev. B*, **1997**, *55*, 7579.
6.   T. Tsuboi, A. Scacco, *J. Phys.Condens. Matter*, **1998**, *10*, 7259.
7.   J. Garcia, W. A. Sibley, C. A. Hunt, J. M. Spaeth, *J. Lumin.*, **1988**, *42*, 35.
8.   N. S. Altshuler, S. L. Korableva, A. L. Stolov, *Sov. Phys. Solid State*, **1976**, *18*, 679.
9.   G. Blasse, *Phys. Stat. Sol. (b),* **1973**, *55*, K131.
10. A. V. Gektin, V. K. Komar, N. V. Shiran, V. V. Shlykhturov, N. P. Nesterenko, I. M. Krasovitskaya,   V. V. Kornienko, *IEEE Trans. Nucl. Sci.*, **1995**, *42*, 311.
11. A. V. Gektin, I. M. Krasovitskaya, N. V. Shiran, *Radiat. Meas.*, **1998**, *29*, 337.
12. J. Sytsma, G. F. Imbusch, G. Blasse, *J. Chem. Phys.*, **1989**, *91*, 1456.