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Local field in glass probed by laser-induced fluorescence-line narrowing in $Ca(PO_3)_2$:Eu^{3+}

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Detailed studies have been made of the luminescence properties of Eu^{3+} ions in $Ca(PO_3)_2$ glass excited into the $^5D_1$ manifold by a tunable dye laser at 77 K. The observed excitation-wavelength dependence of the intensities and energies of the fluorescence lines is explained quite well by local-field-induced Stark splitting and J mixing. The dominant mechanism of the $^5D_0$-$^7F_0$ transition is identified as due to the mixing of the $M_J=0$ component of the $^7F_2$ manifold into $^7F_0$.

The optical spectra due to the f-f transitions of rare-earth ions, which are usually very narrow in crystals at low temperatures, have rather broad widths in glass because of site-to-site variation in the local field acting on the ions. These widths can often be narrowed by optical site-selection methods such as the laser-induced fluorescence-line narrowing,[1] which are useful in obtaining detailed information on the local field and ion-ion and ion-lattice interactions in disordered systems.[2-8] Brecher and Riseberg[6] analyzed laser-induced fluorescence spectra of Eu^{3+} in oxide and fluoride glasses and discussed a model for the behavior of the first coordination shell of a rare-earth ion in the glassy matrix. In this analysis, the local-field-induced level mixing was not taken into account. However, this effect on the luminescence properties of Eu^{3+} ions is considered to be very important.[8]

In this paper, we report the fluorescence properties of Eu^{3+} ions in $Ca(PO_3)_2$ glass studied at 77 K under monochromatic light excitation into the $^7F_1$-$^5D_1$ absorption band. It is shown that various luminescence properties of Eu^{3+}, such as the origin of the inhomogeneous broadening and the mechanism of the $^5D_0$-$^7F_0$ transition, can be well explained by the J mixing. The point symmetry at the Eu site and the values of local-field parameters are also determined.

A glass sample containing 70 mol % of Eu was excited with a cw coumarin 535 dye laser pumped by an Ar^+-ion laser. A Lyot filter was inserted in the dye laser cavity and the tunable output of the spectral width of about 2 cm^{-1} was obtained in the 523–537-nm wavelength range. Fluorescence spectra were measured using a triple-grating polychromator (Spex model 1877) equipped with an intensified silicon photodiode array detector (Princeton Applied Research model 1420) cooled at −20 °C.

Figure 1 shows the $^5D_0$-$^7F_{0,1}$ fluorescence spectra for the excitation from the lowest Stark level of the $^7F_1$ manifold into the $^5D_1$ manifold. We call the Stark levels of the $^7F_1$ and $^5D_1$ manifolds ε_+, ε_-, ε_0 and δ_+, δ_-, δ_0 in order of energy, respectively (cf. Fig. 2). The three narrow lines observed in the spectral region of the $^5D_0$-ε_0 transition are explained as follows. Because of the variation in the local-field strength acting on the Eu^{3+} ions in glass, the spread of the energy separation between the $^5D_1$ and ε_0 states is so large that for a given laser frequency, three kinds of ions are excited simultaneously, in which the exciting photon energy matches the energy separations between the ε_0 level and the three Stark levels of $^5D_1$.[7] In the region of the $^5D_0$-$^7F_0$ transition, only two lines are observed because the two low-energy fluorescence lines overlap with each other. The fluorescence line narrowing is not effective for the $^5D_0$-$\varepsilon_\pm$ lines. A broad hump around 588 nm is due to the energy transfer between the Eu^{3+} ions,[8] which will not be discussed here.

The energy separations between various levels of Eu^{3+} were determined from the analysis of the laser-induced fluorescence spectra. The energies of several levels relative to that of the $^5D_0$ state are shown by open circles in Fig. 2 as a function of the peak energy of the site-selected $^5D_0$-$^7F_0$ line. We notice that there exists a similarity be-

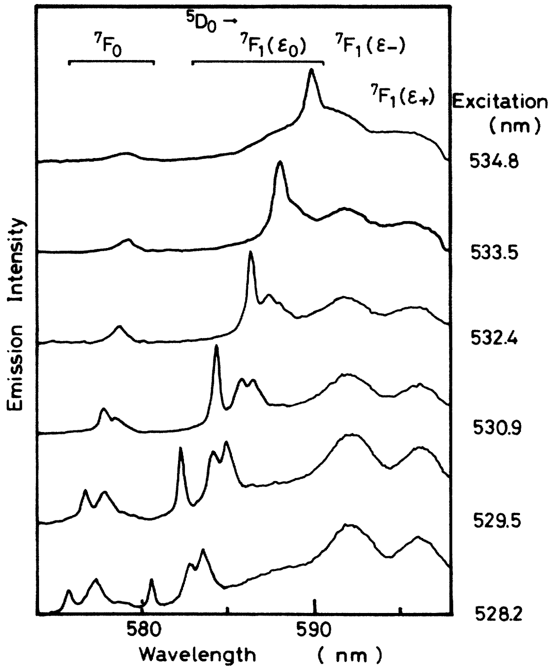

FIG. 1. Luminescence spectra of $Ca(PO_3)_2$:Eu^{3+} at 77 K for various excitation wavelengths in the $^7F_1(\varepsilon_0)$-$^5D_1$ absorption band.

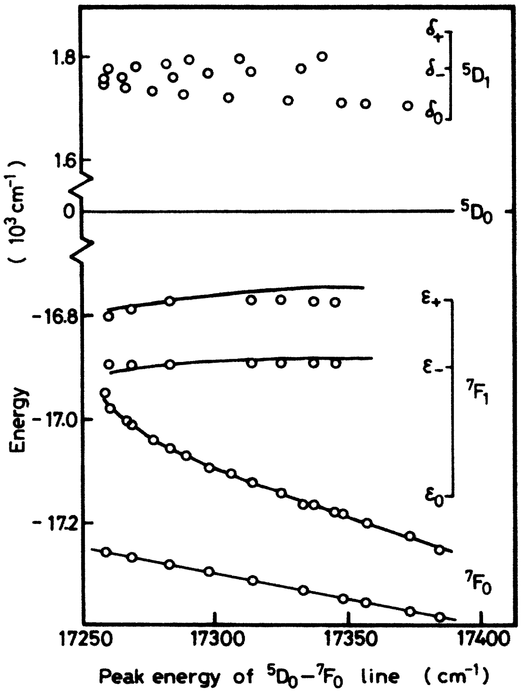

FIG. 2. The energies of several levels of Eu^{3+} in $Ca(PO_3)_2$ relative to that of $^5D_0$ as a function of the $^5D_0$-$^7F_0$ energy separation.

tween the splitting patterns of $^5D_1$ and $^7F_1$ in this material. From the fact that the $^7F_1$ and $^5D_1$ manifolds are split into three levels, besides the presence of relatively intense electric dipole transitions of $^5D_0$-$^7F_2$ and $^5D_0$-$^7F_0$,[5] the point symmetry of the Eu site in $Ca(PO_3)_2$ is restricted to D_2, C_{2v}, C_2, and C_s. The possibility of C_1 symmetry is excluded because of the clear difference in the polarization characteristics between the $^5D_0$-ε_0 and $^5D_0$-$\varepsilon_\pm$ transitions for the $^7F_0$-$^5D_0$ excitation.[5]

The intensity ratio of the $^5D_0$-$^7F_0$ to the $^5D_0$-ε_0 fluorescence for the excitation into the δ_0 level is plotted in Fig. 3 as a function of the peak energy of the $^5D_0$-$^7F_0$ line. As shown by a solid line, the intensity ratio is linearly correlated with the energy position. Since the $^5D_0$-$^7F_1$ line is due to the magnetic dipole transition,[5] the intensity of this line is considered to be almost independent of the local-field strength. Therefore this result indicates that the $^5D_0$-$^7F_0$ transition probability increases linearly with the energy separation between the $^5D_0$ and $^7F_0$ states. This is explained by the mixing of other states into $^7F_0$ and $^5D_0$ due to the local-field perturbation, because both the energy shift and the probability of the optical transition induced by the level mixing are proportional to the square of the mixing coefficient of the wave function.

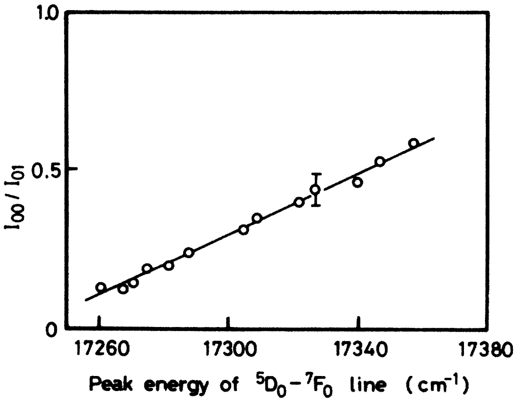

FIG. 3. The intensity ratio of the $^5D_0$-$^7F_0$ to the $^5D_0$-$^7F_1(\varepsilon_0)$ fluorescence vs the energy position of the $^5D_0$-$^7F_0$ luminescence line under the $^7F_1(\varepsilon_0)$-$^5D_1(\delta_0)$ excitation.

The $^5D_0$-$^7F_0$ line of Eu^{3+} cannot be explained by the Judd-Ofelt theory, in which the closure approximation is employed for the higher configurations of opposite parity that are admixed into the $4f^N$ states.[9,10] There exist two probable mechanisms of this transition. One is due to the mixing of a high-lying odd-parity state, for which the closure approximation is not applicable, by the linear term of the local-field potential,[11] and the other is to borrow intensity from other lines through the J mixing within the $4f^6$ configuration by the even-parity local-field potential.[12] Since the energy shift of the $^5D_0$-$^7F_0$ line is correlated with the Stark splitting of the $^7F_1$ manifold, the main cause of the spreads of the energy and optical transition probability in Fig. 3 is considered to be the site-to-site variation of the even-parity local-field strength. If the energy spreads were due to the variation of an odd-parity term, the peak energy of the $^5D_0$-ε_0 line would depend linearly on that of the $^5D_0$-$^7F_0$ line. Therefore, hereafter we consider the effect of the variation of the even-parity terms of the local-field potential.

Let us express the local-field Hamiltonian V_c by the tensor operator series as

$$V_c=\sum_{k,q}\sum_{j} B_{kq} C_q^{(k)}(\theta_j,\phi_j) , \tag{1}$$

with

$$C_q^{(k)}(\theta_j,\phi_j)=[4\pi/(2k+1)]^{1/2} Y_q^{(k)}(\theta_j,\phi_j) ,$$

where $Y_q^{(k)}(\theta_j,\phi_j)$ is the q component of the kth-order spherical harmonics and (r_j,θ_j,ϕ_j) is the position of the jth electron of the Eu^{3+} ion. In $Ca(PO_3)_2$ glass, the $^7F_1$ manifold splits into three Stark levels on account of the local-field perturbation. Further, the $^7F_2$, $^7F_4$, and $^7F_6$ states admix into the $^7F_0$ state, which may allow the $^5D_0$-$^7F_0$ transition. However, the effects of the mixing of the $^7F_4$ and $^7F_6$ states on this transition are much smaller than that of $^7F_2$, because the energy denominators are much larger and the fluorescence intensities of the $^5D_0$-$^7F_4$ and $^7F_6$ lines are much weaker than that of the $^5D_0$-$^7F_2$ lines. Further, as discussed later, J mixing in the ^5D manifolds is considered to be much smaller than that of ^7F manifolds. Therefore, if the $^5D_0$-$^7F_0$ transition is allowed by J mixing, the most important contribution will come from the mixing of $^7F_2$ into $^7F_0$ through the second-order terms of the local-field potential. Then, from the result of Fig. 3, the energy variation of the $^5D_0$-$^7F_0$ line is also ascribed to the level mixing due to the second-order terms. Therefore we shall calculate the energy shifts of the $^7F_0$ and $^7F_1$ states by the local-field potential $V_c^{(2)} = \sum_q \sum_j B_{2q} C_q^{(2)}(\theta_j, \phi_j)$. We put $B_{2\pm1} = 0$ because they are absent in the case of the point symmetries of D_2, C_{2v}, C_2, and C_s. Then, with the Russel-Saunders approximation, the Stark splitting of $^7F_1$ due to the local-field perturbation is calculated as

$$E(\varepsilon_0) - E^0(^7F_1) = B_{20}/5\ , \tag{2}$$

$$E(\varepsilon_\pm) - E^0(^7F_1) = -B_{20}/10 \pm \sqrt{6}\,|B_{2+2}|/10\ , \tag{3}$$

where E^0 is the energy in the case of $V_c^{(2)} = 0$.

Next, we take into account the mixing of other states using a simple perturbation calculation. Then, considering only the effects of the second-order terms of the local-field potential, we obtain

$$E(^7F_0) = E^0(^7F_0) - \alpha X^2 - 2\alpha Y^2\ , \tag{4}$$

$$E(\varepsilon_0) = E^0(^7F_1) + X/5 - 9\beta X^2 - 2(5\beta + 4\gamma)Y^2\ , \tag{5}$$

$$\begin{aligned} E(\varepsilon_\pm) = {} & E^0(^7F_1) - X/10 \pm \sqrt{6}Y/10 - 3(2\beta + \gamma)X^2 \\ & -2(8\beta + \gamma)Y^2 \pm 2\sqrt{6}(\beta - \gamma)XY\ , \end{aligned} \tag{6}$$

where $X \equiv B_{20}$, $Y \equiv |B_{2+2}| = |B_{2-2}|$, $\alpha = 4/75\Delta_{20}$, $\beta = 2/525\Delta_{31}$, $\gamma = 1/300\Delta_{21}$, and $\Delta_{JJ'} = E^0(^7F_J) - E^0(^7F_{J'})$. Similar results will be obtained for the $^5D_0$ and $^5D_1$ manifolds, though the calculation is complicated because the Russel-Saunders approximation is not applicable to these states.[13] However, the local-field-induced energy variations are expected to be small for the ^5D states, because the energy separations between the ^5D_J states are large and also because the reduced matrix element $\langle f^6\,{}^5D \| U^{(2)} \| f^6\,{}^5D \rangle$ is smaller than $\langle f^6\,{}^7F \| U^{(2)} \| f^6\,{}^7F \rangle$. In fact, the Stark splitting is much smaller for $^5D_1$ compared with $^7F_1$, as seen in Fig. 2. Therefore it is a good approximation to assume that the energy of the $^5D_0$ state is independent of $V_c^{(2)}$.

Since the energy variation of the $^5D_0$-$^7F_0$ line is dependent almost quadratically on that of the $^5D_0$-ε_0 line, we assume that the energies $E(^7F_0)$ and $E(\varepsilon_0)$ are determined mainly by the parameter X. Then, regarding Y as a constant, we obtain the following relation between the energy of the site-selected $^5D_0$-ε_0 line E_{01} and that of the $^5D_0$-$^7F_0$ line E_{00}:

$$E_{01} = E_{01}^* + a(E_{00} - E_{00}^*)^{1/2} + b(E_{00} - E_{00}^*)\ , \tag{7}$$

where $a = (3\Delta_{20})^{1/2}/2$, $b = 9\Delta_{20}/14\Delta_{31}$, and E^* is the energy in the case of $X = 0$. As shown by the solid line in Fig. 2, the experimental data can be fitted quite well with Eq. (7). The coefficients a and b were determined using the peak energies of the $^5D_0$-$^7F_2$ (16 327 cm^{-1}) and $^5D_0$-$^7F_3$ (15 267 cm^{-1}) fluorescence lines, while E_{01}^* and E_{00}^* were treated as adjustable parameters. From the best fit, these values were determined to be 16 889 and 17 248 cm^{-1}, respectively. The energies of the $^5D_0$-$\varepsilon_\pm$ lines calculated through Eq. (6) with the same parameter values are also shown by solid lines in Fig. 2. The agreement between the experiment and calculation is fairly good.

From the above fittings, the value of X is found to change between 0 and -1600 cm^{-1}, when the energy of the $^5D_0$-$^7F_0$ line changes between 17 248 and 17 400 cm^{-1}. The mean value of Y is also determined to be 250 cm^{-1}. It has been further found that the widths of the laser-induced fluorescence lines can be explained by taking into account the site-to-site variation of the parameter Y. Especially, the broad widths of the $^5D_0$-$\varepsilon_\pm$ lines are attributable to the presence of the linear term of Y in the energies of the $\varepsilon_\pm$ levels. From the widths of the $^5D_0$-$\varepsilon_\pm$ fluorescence lines (half-width at half maximum $\sim$70 cm^{-1}), the value of Y is estimated to range between 0 and 540 cm^{-1}. It is also suggested that the values of X and Y are not correlated with each other. We have found that the $^5D_0$-ε_0 fluorescence line at 77 K is much narrower under the ε_0-δ_0 excitation compared with the $^7F_0$-$^5D_0$ and $^7F_0$-δ_0 excitations. This fact, as well as the asymmetric spectral shape of the $^5D_0$-ε_0 fluorescence line, can also be explained by taking into account the site-to-site variation of the value of Y. The details will be reported elsewhere.

From the above results, we conclude that the spreads of the local-field parameters X and Y contribute mainly to the energy variations and the widths of the laser-induced fluorescence lines, respectively. Further, from the correlation in Fig. 3, the $^5D_0$-$^7F_0$ transition is concluded to be allowed by the mixing of the $M_J = 0$ component of the $^7F_2$ manifold into $^7F_0$ through the second-order term $B_{20}C_0^{(2)}$ of the local-field potential. The $^5D_0$-$^7F_2(M_J = 0)$ transition is allowed when the B_{10}, $B_{1\pm1}$, B_{30}, or $B_{3\pm1}$ terms are present in the local-field potential. Since they are all absent in the case of D_2 symmetry, this possibility for the Eu site is excluded.

From the polarization-correlation experiment, it is known that the $^5D_0$-$^7F_0$ line is due to the electric dipole transition.[5] This is consistent with the above interpretation that this line borrows its intensity from the electric dipole transition of $^5D_0$-$^7F_2$. The degree of polarization of the $^5D_0$-$^7F_0$ fluorescence in the direction of the exciting beam was 0.5, when the excitation by linearly polarized light was made into the $^7F_0$-$^5D_0$ absorption band.[5] This can also be explained by the above mechanism, if we assume the point symmetry of the Eu site in Ca(PO$_3$)$_2$ glass as C_{2v} or C_2. For the C_s symmetry, in which case $B_{10} = B_{30} = 0$, the degree of polarization is expected to be much smaller.

Since the X dependence of the energy and the transition probability of the $^5D_0$-$^7F_0$ line have been obtained, it is possible to calculate the spectral profile of the inhomogeneously broadened fluorescence due to this transition, provided the distribution of X is known. We have found that the asymmetric shape of this fluorescence line observed under uv-light excitation by a deuterium lamp is reproduced fairly well by assuming Gaussian distribution of the value of X.[14]

In conclusion, it has been demonstrated that the laser-induced fluorescence-line-narrowing experiment on doped Eu^{3+} ions gives detailed information on the local field in glass.

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[1] M. J. Weber, in *Laser Spectroscopy of Solids,* edited by W. M. Yen and P. M. Selzer (Springer-Verlag, Berlin, 1981), p. 189.

[2] L. A. Riseberg, Phys. Rev. Lett. **28**, 786 (1972); Solid State Commun. **11**, 469 (1972); Phys. Rev. A **7**, 671 (1973).

[3] N. Motegi and S. Shionoya, J. Lumin. **8**, 1 (1973).

[4] T. Kushida and E. Takushi, Phys. Rev. B **12**, 824 (1975).

[5] T. Kushida, E. Takushi, and Y. Oka, J. Lumin. **12/13**, 723 (1976).

[6] C. Brecher and L. A. Riseberg, Phys. Rev. B **13**, 81 (1976); **21**, 2607 (1980).

[7] J. Hegarty, W. M. Yen, and M. J. Weber, Phys. Rev. B **18**, 5816 (1978).

[8] E. Takushi and T. Kushida, J. Lumin. **18/19**, 661 (1979).

[9] B. R. Judd, Phys. Rev. **127**, 750 (1962).

[10] G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).

[11] W. C. Nieupoort and G. Blasse, Solid State Commun. **4**, 227 (1966).

[12] B. G. Wybourne, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience, New York, 1967), p. 35.

[13] G. S. Ofelt, J. Chem. Phys. **38**, 2171 (1963).

[14] T. Kushida and G. Nishimura, in *Proceedings of the 1987 International Conference on Luminescence, Beijing, China, 1987,* edited by Xu Xurong (North-Holland, Amsterdam, in press).