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Applicability of the shell model for energy transfer

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Abstract

In the cubic hexachloroelpasolite crystals $Cs_2NaSm_xEu_yGd_{1-x-y}Cl_6$ the emission from the $^4G_{5/2}$ state of Sm^{3+} is strongly quenched by cross-relaxation and energy-transfer processes. At temperatures above 100 K the energy-transfer rate consists of non-resonant contributions due to electric dipole vibronic–electric dipole vibronic interaction and a near-resonant contribution where both the donor and acceptor transitions are magnetic-dipole allowed. The near-resonant energy-transfer rate is calculated and the small discrepancy between the theoretical and experimental values shows the applicability of the shell model for highly symmetric crystals. © 1998 Elsevier Science S.A.

Keywords: Energy-transfer rate; Hexachloroelpasolite crystals; Shell model

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1. Introduction

In a previous paper we applied a shell model for the simultaneous treatment of cross-relaxation and energy-transfer processes to understand the decay kinetics of the $^4G_{5/2}$ state of Sm^{3+} in the cubic hexachloroelpasolite crystals $Cs_2NaSm_xEu_yGd_{1-x-y}Cl_6$ [1]. In this system the emission from the $^4G_{5/2}$ state of Sm^{3+} is strongly quenched by both cross-relaxation to nearby Sm^{3+} ions and energy transfer to the $^5D_0$ state of Eu^{3+} acceptors. The temperature dependence of the intrinsic decay rate k_0 of an isolated Sm^{3+} ion and the cross-relaxation rate k^{CR} to a single nearest-neighbour Sm^{3+} acceptor can be described by the coth law for vibronic transitions whereas the energy-transfer rate k^{ET} from the Sm^{3+} donor ion to a single Eu^{3+} acceptor in the first shell shows a rapid increase at temperatures above 100 K [2]. The stronger temperature dependence of this rate indicates that two different energy-transfer processes are present. At low temperatures the increase of k^{ET} is consistent with a squared coth law for electric dipole vibronic–electric dipole vibronic interaction whereas near-resonant transfer involving the Sm^{3+} $(^4G_{5/2})\Gamma_7 \rightarrow (^6H_{7/2})\Gamma_8$ donor transition and the Eu^{3+} $(^7F_1)\Gamma_4 \rightarrow (^5D_0)\Gamma_1$ acceptor transition shown in Fig. 1 as a pair of transitions BB′ becomes dominant as the temperature is raised where both transitions are of magnetic-dipole allowed electronic origin. The total energy-transfer rate to a single Eu^{3+} acceptor in the first shell shows an almost linear increase in the temperature range 200 to 300 K which is well understood in terms of the thermal population of the initial Sm^{3+} $(^4G_{5/2})\Gamma_7$ donor and Eu^{3+} $(^7F_1)\Gamma_4$ acceptor states [2]. The energy gaps between the Γ_8 and Γ_7 levels of the $^4G_{5/2}$ state of Sm^{3+} as well as between the $^7F_0$ and $^7F_1$ states of Eu^{3+} are about 350 cm^{-1}, such that the near-resonant process involving these initial states contributes to the total energy-transfer rate at temperatures >100 K.

In this paper we calculate the near-resonant contribution to the energy-transfer rate between a Sm^{3+} donor ion and a Eu^{3+} acceptor at a distance $R_1 = 7.65$ Å assuming magnetic dipole–magnetic dipole interaction among donor and acceptor ions. Within the theoretical uncertainty and the experimental error the order of magnitude of the calculated energy-transfer rate is in agreement with the near-resonant contribution to the experimental rate which is related to the exponential decay rate of luminescence from the $^4G_{5/2}$ state of Sm^{3+} in $Cs_2NaSm_{0.01}Eu_{0.99}Cl_6$ [1].

2. Theory

2.1. The shell model for energy transfer

Within our shell model assuming electric dipole (vib-

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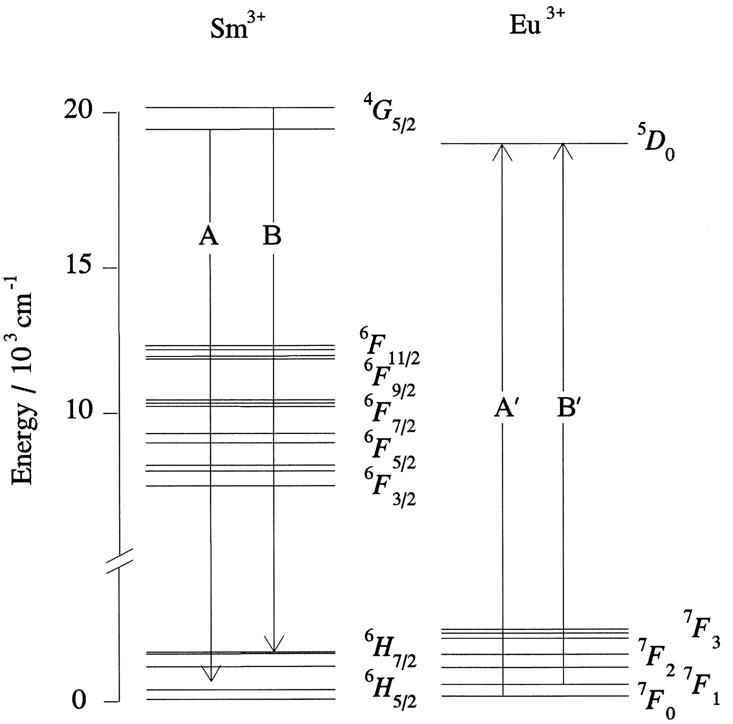

Fig. 1. Energy levels and transitions involved in the cross-relaxation and energy-transfer processes in $Cs_2NaSm_xEu_yGd_{1-x-y}Cl_6$. The letters indicate pairs of near-resonant transitions.

ronic)–electric dipole (vibronic) and/or magnetic dipole–magnetic dipole interaction among donor and acceptor ions the donor emission decay following a δ-function excitation pulse takes the form [1]

$$I(t) = I(0)\exp(-k_0 t) \prod_{n=1}^{\text{shells}} \sum_{r_n=0}^{N_n} \sum_{q_n=0}^{N_n-r_n} O^{N_n}_{r_n,q_n}(x,y) \exp\left[-\frac{2}{3}(r_n k^{\mathrm{CR}} + q_n k^{\mathrm{ET}})\left(\frac{R_1}{R_n}\right)^6 t\right] \qquad (1)$$

In the present system, k_0 is the intrinsic decay rate of an isolated Sm^{3+} ion including radiative and non-radiative relaxation processes, k^{CR} is the cross-relaxation rate from the donor ion to a chemically identical acceptor in the first shell, and k^{ET} is the rate of energy transfer to a $n=1$ acceptor chemically different from the donor. The occupancy factor $O^{N_n}_{r_n,q_n}(x,y)$ is the probability of finding r_n acceptor ions chemically identical to the donor and q_n chemically different acceptors in the nth shell at a distance R_n which has a capacity to contain N_n acceptors [1]. Since the rates k_0, k^{CR}, and k^{ET} are determined from exponential decay of the Sm^{3+} ($^4G_{5/2}$) emission in $Cs_2NaSm_{0.001}Gd_{0.999}Cl_6$, $Cs_2NaSmCl_6$, and $Cs_2NaSm_{0.01}Eu_{0.99}Cl_6$, respectively, the donor decay curves for all other concentrations of donor and acceptor ions may be calculated by Eq. (1) without any adjustable parameters.

2.2. Resonant energy transfer

For energy transfer between rare-earth ions we consider transitions from the initially excited crystal-field component $|[\alpha'_D J'_D]\Gamma'_D\gamma'_D\rangle$ of multiplet $|[\alpha'_D J'_D]\Gamma'_D\rangle$ to the lower lying crystal-field component $\langle[\alpha_D J_D]\Gamma_D\gamma_D|$ of multiplet $\langle[\alpha_D J_D]\Gamma_D|$ of the donor ion with a similar notation for the acceptor. α represents any other quantum number necessary to specify the state. The total crystal-field splitting is typically a few cm^{-1} and the population of the component levels is given by a Boltzmann distribution as

$$p_{d'} = g_{d'}\exp(-E_{d'}/k_{\mathrm{B}}T)\left[\sum_{d''} g_{d''}\exp(-E_{d''}/k_{\mathrm{B}}T)\right]^{-1} \qquad (2)$$

where the energy $E_{d'}$ is related to the position of the lowest level of the multiplet taken as $E_{d''}=0$, and $g_{d'}$ is the degeneracy of the d'th level. The resonant energy-transfer rate from a donor ion to an acceptor then becomes [3,4]

$$k^{\mathrm{ET}} = \frac{2\pi}{\hbar}\sum_{d',a} p_{d'}\,p_a |\langle da'|\hat{H}_{\mathrm{DA}}|d'a\rangle|^2 \int f_{d'd}(E) f_{aa'}(E)\,\mathrm{d}E \qquad (3)$$

For magnetic dipole–magnetic dipole interaction the Hamiltonian in Eq. (3) takes the form

$$\hat{H}^{\mathrm{MD}}_{\mathrm{DA}} = \frac{\mu_0}{4\pi}\sum_{i,j}\left[\frac{\mu^i_{d'd}\mu^j_{aa'}}{R^3} - \frac{3(\mu^i_{d'd}R)(\mu^j_{aa'}R)}{R^5}\right] \qquad (4)$$

where $\mu^i_{d'd}$ is the ith component of the magnetic-dipole moment of the donor transition and i and j running over x, y, and z. Rewriting Eq. (4) the transition matrix element is given by

$$|\langle da'|\hat{H}_{\mathrm{DA}}^{\mathrm{MD}}|d'a\rangle|^2 = \left(\frac{\mu_0}{4\pi R^3}\right)^2 \sum_{i,j} (\mu_{d'd}^{i})^2 (C_{ij})^2 (\mu_{aa'}^{j})^2 \tag{5}$$

In a face-centred cubic lattice, the components of the magnetic-dipole moment are independent of orientation such that $(\mu_{d'd}^{i})^2 = \frac{1}{3}(\mu_{d'd})^2$, etc. Introducing a geometric factor which includes the angular dependence of the interacting magnetic dipoles as

$$G_{d'd;aa'}^{\mathrm{MD}} = \tfrac{1}{9}\sum_{i,j}(C_{ij})^2 \tag{6}$$

Eq. (5) becomes

$$|\langle da'|\hat{H}_{\mathrm{DA}}^{\mathrm{MD}}|d'a\rangle|^2 = \left(\frac{\mu_0}{4\pi R^3}\right)^2 G_{d'd;aa'}^{\mathrm{MD}} (\mu_{d'd})^2 (\mu_{aa'})^2 \tag{7}$$

Writing the crystal-field states as

$$|f^N[\alpha SLJ]\Gamma\gamma\rangle = \sum_M c(JM|J\Gamma\gamma)|f^N[\alpha SL]JM\rangle \tag{8}$$

etc., the γ_0th component of the magnetic-dipole transition moment transforming as the representation Γ_4 of the octahedral double group ${}^2O$ is given by

$$\mu_{d'd}^{\Gamma_4\gamma_0} = \sum_{\gamma,\gamma'} \langle f^N[\alpha SLJ]\Gamma\gamma|\hat{m}_{\gamma_0}^{(1\Gamma_4)}|f^N[\alpha'S'L'J']\Gamma'\gamma'\rangle \tag{9}$$

where $\hat{m}^{(1\Gamma_4)} = \mu_{\mathrm{B}}(\hat{L} + 2\hat{S})$ is the magnetic moment tensor operator and μ_{B} is the Bohr magneton. Application of the Wigner–Eckart theorem to the matrix element in Eq. (9) gives [5]

$$\langle f^N[\alpha SLJ]\Gamma\gamma|\hat{m}_{\gamma_0}^{(1\Gamma_4)}|f^N[\alpha'S'L'J']\Gamma'\gamma'\rangle = \begin{pmatrix} J\Gamma & 1\Gamma_4 & J'\Gamma' \\ \gamma & \gamma_0 & \gamma' \end{pmatrix} \langle f^N[\alpha SL]J\|\hat{m}^{(1)}\|f^N[\alpha'S'L']J'\rangle \tag{10}$$

within the $\{J,\Gamma\}$ scheme. The symmetry coupling coefficients

$$\begin{pmatrix} J\Gamma & 1\Gamma_4 & J'\Gamma' \\ \gamma & \gamma_0 & \gamma' \end{pmatrix} = \sum_{M,M',q} (-1)^{J'-M'} \begin{pmatrix} J' & 1 & J \\ -M' & q & M \end{pmatrix} c(1q|1\Gamma_4\gamma_0)c(JM|J\Gamma\gamma)c(J'M'|J'\Gamma'\gamma')^{*} \tag{11}$$

are readily calculated for the various $J\Gamma \rightarrow J'\Gamma'$ electronic transitions involved in the energy-transfer process considered in this paper. The reduced matrix elements in Eq. (10) are calculated using Eqs. (10)–(13) of Ref. [6].

3. Results

3.1. Experimental decay curves

At 300 K the luminescence decay curves from the ${}^4G_{5/2}$ state of Sm^{3+} in both $Cs_2NaSm_{0.01}Gd_{0.99}Cl_6$ and $Cs_2NaSm_{0.01}Eu_{0.99}Cl_6$ show a fast non-exponential initial decay due to cross-relaxation to nearest-neighbour Sm^{3+} acceptor ions with a rate of $k^{\mathrm{CR}} = 2120\ \mathrm{s}^{-1}$. At times $> 2.5 \times 10^{-3}$ s both decay curves are essentially exponential with the lifetime of the ${}^4G_{5/2}$ state of Sm^{3+} decreasing by a factor of 6.6 for replacing Gd^{3+} by Eu^{3+}. Both decay curves are exactly described by Eq. (1) and the stronger quenching of luminescence from the ${}^4G_{5/2}$ state in $Cs_2NaSm_{0.01}Eu_{0.99}Cl_6$ is assigned to additional energy transfer between Sm^{3+} donor ions and Eu^{3+} acceptors at a rate $k^{\mathrm{ET}} = 49.9\ \mathrm{s}^{-1}$.

3.2. Numerical calculation

In the following we calculate the near-resonant magnetic dipole–magnetic dipole contribution to the energy-transfer rate from a Sm^{3+} donor ion to a single Eu^{3+} acceptor ion in the first shell. The calculation of resonant energy-transfer rates using the Förster–Dexter equation for magnetic dipole–magnetic dipole interaction [3,4] involves the determination of crystal-field eigenstates for both donor and acceptor ions and the magnetic dipolar coupling strength associated with the transitions considered in the energy-transfer process. The energy mismatch between donor emission and acceptor absorption transitions is introduced in the overlap integral of normalized lineshape functions for these transitions.

The compositions of the free-ion energy levels of Sm^{3+} and Eu^{3+} involved in the $({}^4G_{5/2})\Gamma_7 \rightarrow ({}^6H_{7/2})\Gamma_8$ donor transition and the $({}^7F_1)\Gamma_4 \rightarrow ({}^5D_0)\Gamma_1$ acceptor transition shown in Fig. 1 as a pair of transitions BB′ are taken from Refs. [7–9], respectively. The basis functions used in the calculation of magnetic-dipole transition moments are taken from Griffith [10]. We note that beside these resonant transitions a non-resonant pathway involving the ground states of both the initial donor and acceptor multiplets is present and indicated as a pair of transitions AA′ in Fig. 1.

The magnetic dipolar coupling strength for the donor transition is given by

$$\langle({}^6\mathrm{H}_{7/2})\Gamma_8|\hat{m}^{(1\Gamma_4)}|({}^4\mathrm{G}_{5/2})\Gamma_7\rangle = \sum_{\substack{S,S'\\L,L'}}\sum_{J,J'} \langle[SL]J\|\hat{m}^{(1)}\|[S'L']J'\rangle \delta_{SS'}\delta_{LL'}\Delta(JJ'1) \sum_{\gamma,\gamma',\gamma_0} c(J\Gamma_8\gamma)c(1\Gamma_4\gamma_0)c(J'\Gamma_7\gamma') \begin{pmatrix} J\Gamma_8 & 1\Gamma_4 & J'\Gamma_7 \\ \gamma & \gamma_0 & \gamma' \end{pmatrix} \tag{12}$$

The magnetic-dipole moments for the $({}^4G_{5/2})\Gamma_7 \rightarrow ({}^6H_{7/2})\Gamma_8$ donor transition and the $({}^7F_1)\Gamma_4 \rightarrow ({}^5D_0)\Gamma_1$ acceptor transition are $(1.830 \pm 0.497)\ \mu_B$ and $-(0.463 \pm 0.126)\ \mu_B$, respectively. Substitution of these values in Eq. (7) and utilizing the geometric factor for magnetic dipole–magnetic dipole interaction, $G_n^6 = \frac{2}{3}$ [11], the square of the interaction energy representing the coupling of the magnetic dipoles

$\mu_{d'd}$ and $\mu_{aa'}$ is $E^2_{\mathrm{int}} = (1.963 \pm 1.066) \times 10^{-53}\ \mathrm{J}^2$. The resonant energy-transfer rate k^{ET} between the Sm^{3+} donor ion and a nearest-neighbour Eu^{3+} acceptor is related to this interaction energy by

$$k^{\mathrm{ET}}(\mathrm{MD}) = \frac{2\pi}{\hbar} p(^4\mathrm{G}_{5/2})\Gamma_7\, p(^7\mathrm{F}_1)\Gamma_4 E^2_{\mathrm{int}} \int f_{d'd}(E) f_{aa'}(E)\mathrm{d}E \tag{13}$$

where the overlap integral is calculated using normalized Lorentzian line-shape functions for the donor emission and acceptor absorption transitions. The full width at half maximum, ΔE, is taken as 9.932×10^{-23} J for both donor and acceptor transitions, and the transition maxima are measured as $(3.352 \pm 0.001) \times 10^{-19}$ J and $(3.349 \pm 0.002) \times 10^{-19}$ J for donor and acceptor transitions, respectively, corresponding to (16872 ± 8) and $(16858 \pm 5)\ \mathrm{cm}^{-1}$. Considering these values and the integral of product Lorentzian functions which is evaluated as

$$\int f_{d'd}(E) f_{aa'}(E)\mathrm{d}E = \frac{2}{\pi} \frac{\Delta E_{d'd} + \Delta E_{aa'}}{4(E_{d'd} - E_{aa'})^2 + (\Delta E_{d'd} + \Delta E_{aa'})^2} \tag{14}$$

the value of the overlap integral is $3.625 \times 10^{-20}\ \mathrm{J}^{-1}$. At 300 K the thermal population of the Sm^{3+} $(^4\mathrm{G}_{5/2})\Gamma_7$ state and the Eu^{3+} $(^7\mathrm{F}_1)\Gamma_4$ level are about 8 and 32%, respectively. Substitution in Eq. (13) gives $k^{\mathrm{ET}} = (12.0 \pm 6.5)\ \mathrm{s}^{-1}$ for the rate of near-resonant energy transfer between a Sm^{3+} donor ion and a single nearest-neighbour Eu^{3+} acceptor ion at 300 K.

4. Conclusions

We have calculated the near-resonant contribution, $k^{\mathrm{ET}} = (12.0 \pm 6.5)\ \mathrm{s}^{-1}$, to the rate of energy transfer from a Sm^{3+} donor ion to a nearest-neighbour Eu^{3+} acceptor in the hexachloroelpasolite crystals $\mathrm{Cs_2NaSm_xEu_yGd_{1-x-y}Cl_6}$ assuming magnetic dipole–magnetic dipole interaction among donor and acceptor ions. Comparison of this rate with the total energy-transfer rate, $k^{\mathrm{ET}} = 49.9\ \mathrm{s}^{-1}$, determined experimentally from the luminescence decay curve of the $^4\mathrm{G}_{5/2}$ state of Sm^{3+} in $\mathrm{Cs_2NaSm_{0.01}Eu_{0.99}Cl_6}$ by using the shell model for energy transfer shows a discrepancy by a factor of 4. Beside the near-resonant magnetic dipole–magnetic dipole contribution the experimental rate consists of additional non-resonant electric dipole vibronic–electric dipole vibronic contributions which are not included in our calculation.

Within the uncertainty involved in the theoretical calculation the order of magnitude of the near-resonant contribution to the total energy-transfer rate is comparable with the experimental value estimated from its temperature dependence as $(30 \pm 5)\ \mathrm{s}^{-1}$. This agreement shows the applicability of the shell model to determine energy-transfer rates in crystalline solids of high symmetry.

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