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Fluorescence line narrowing Zeeman spectroscopy of Cr³⁺-doped Gd₃Sc₂Al₃O₁₂ garnet crystals: II. Calculation of the lineshape

M Yamaga†, Y Gao‡§, K P O'Donnell‡ and B Henderson‡

† Department of Physics, Faculty of General Education, Gifu University, Gifu, 501-11, Japan

‡ Department of Physics and Applied Physics, University of Strathclyde, Glasgow, G4 0NG, UK

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Abstract. The R₁ line of Cr³⁺ in an antiferromagnetic garnet crystal Gd₃Sc₂Al₃O₁₂ (GSAG) is broadened inhomogeneously and homogeneously. Site-selective techniques, such as fluorescence line narrowing (FLN), can remove the inhomogeneous broadening created by strain and compositional disorder. The FLN spectrum then reflects the broadening due to processes including spin–spin exchange interaction between Cr³⁺ ions in octahedral positions and Gd³⁺ ions in dodecahedral positions in the GSAG unit cell. A magnetic field can remove the homogeneous broadening due to antiferromagnetic exchange.

The R₁ line is associated with the spin-forbidden ²E → ⁴A₂ transition. In general, the selection rule on the R₁ line breaks down through spin–orbit interaction on the Cr³⁺ ion. Simulations of the FLN spectra of Cr³⁺:GSAG as a function of both temperature and magnetic field have been used to estimate the magnitude of the spin–spin exchange coupling constant, $J \simeq 0.25\text{--}0.33\text{ cm}^{-1}$. Such simulations also show that for the ²E → ⁴A₂ transition to antiferromagnetic GSAG the Gd³⁺ spin in the Cr³⁺–Gd³⁺ spin exchange system is present in the presence of a magnetic field ($B > 2\text{ T}$), whereas the selection rule breaks down in the absence of a magnetic field.

1. Introduction

There has been much interest in Cr³⁺-doped oxide garnets in view of their potential as tunable laser media [1]. In oxide garnets with unit cell structure corresponding to the chemical formula C₃A₂D₃O₁₂, the large rare-earth ions (Y³⁺, Gd³⁺, La³⁺) occupy the dodecahedral C sites, and the smaller metal ions (Al³⁺, Ga³⁺, Sc³⁺) occupy the octahedral A and tetrahedral D sites. Laser-active Cr³⁺ ions preferentially occupy the octahedral A sites. The pure Gd-based garnets Gd₃Ga₅O₁₂ (GGG), Gd₃Sc₂Al₃O₁₂ (GSAG), and Gd₃Sc₂Ga₃O₁₂ (GSGG) are antiferromagnetic materials and suitable for laser host crystals because they are transparent in the visible and near infrared regions.

The homogeneous broadening of the R₁ line of Cr³⁺ in antiferromagnetic GdAlO₃ crystals by spin–spin exchange interaction was reported by Murphy and Ohlmann [2]. Recently, Monteil and co-workers have discussed the homogeneous broadening of the R₁ line of Cr³⁺ in GGG [3, 4]. We have reported experimental studies of

§ Present address: Research School of Chemistry, Australian University, GPO Box 4, Canberra ACT 2601, Australia.

inhomogeneous and homogeneous line broadenings of R_1 lines by compositional disorder and by spin-spin exchange interaction between Cr^{3+} and Gd^{3+} ions, respectively, in GSAG, probed using fluorescence line narrowing (FLN) in the absence and in the presence of a magnetic field [5]. The experimental results have shown that the linewidths associated with the inhomogeneous and homogeneous broadenings of the R_1 line are approximately equal and about $13\text{--}19\text{ cm}^{-1}$. Furthermore the homogeneous broadening is reduced by a magnetic field, giving rise to resolvable splitting into three sharp Zeeman lines at $B = 3.5\text{ T}$. The energy separation (8.7 cm^{-1}) between the three Zeeman components, being larger than the Zeeman energy (3.2 cm^{-1}) at $B = 3.5\text{ T}$, was used to estimate the spin-spin exchange coupling constant 0.25 cm^{-1} .

This paper reports calculations of the FLN lineshapes of $\text{Cr}^{3+}:\text{GSAG}$ as functions of both temperature and magnetic field, taking account of the selection rule of the transition from the lowest excited ${}^2\text{E}$ state of Cr^{3+} ions to the ${}^4\text{A}_2$ ground state, in the presence of exchange coupling between the electronic spin of the central Cr^{3+} ion and the neighbouring Gd^{3+} ions. The calculated lineshapes agree fairly well with the FLN spectra observed in the ranges of $B = 0\text{--}3.5\text{ T}$ and $T = 1.6\text{--}12\text{ K}$.

2. Theory

2.1. The spin Hamiltonian of Cr^{3+}

The spin Hamiltonian of Cr^{3+} in antiferromagnetic crystals in the absence of a magnetic field is given by

$$H = H_{so} + H_{ex} \quad (1)$$

$$H_{so} = \lambda L_{\text{Cr}} \cdot S_{\text{Cr}} \quad (2)$$

where H_{so} is the spin-orbit interaction, L_{Cr} and S_{Cr} are fictitious angular and spin momenta of Cr^{3+} , λ is the effective spin-orbit coupling, and H_{ex} is the spin-spin exchange interaction between Cr^{3+} and the nearest neighbour Gd^{3+} ions. The spin-orbit interaction mixes the ${}^4\text{T}_2$ second excited state into the ${}^2\text{E}$ lowest excited state and allows the spin-forbidden transition to the ground state, ${}^2\text{E} \rightarrow {}^4\text{A}_2$. The effective spin-orbit coupling, λ , is about 100 cm^{-1} and much larger than the spin-spin exchange coupling ($\approx 0.3\text{ cm}^{-1}$) [5]. The spin state of the lowest excited state of Cr^{3+} including the spin-orbit interaction is written

$$|S_{\text{Cr}}(\Gamma_8)\rangle = |S_{\text{Cr}}({}^2\text{E})\rangle + \{ \langle S_{\text{Cr}}({}^2\text{E}) | H_{so} | S_{\text{Cr}}({}^4\text{T}_2) \rangle / [E({}^2\text{E}) - E({}^4\text{T}_2)] \} |S_{\text{Cr}}({}^4\text{T}_2)\rangle \quad (3)$$

where Γ_8 is the irreducible representation of the lowest excited state mixed with ${}^2\text{E}$ and ${}^4\text{T}_2$, and $E({}^2\text{E})$ and $E({}^4\text{T}_2)$ are energy levels without the spin-orbit interaction.

Murphy and Ohlmann [2] proposed an isotropic spin-spin exchange interaction between Cr^{3+} and Gd^{3+} ions in GdAlO_3 in order to account for the observed R_1 lineshape, which was composed of four quasi-continuous bands at low temperatures. This paper extends their phenomenological model to the $\text{Cr}^{3+}:\text{GSAG}$ system. The isotropic spin-spin exchange interaction is given by

$$H_{ex} = -JS_{\text{Cr}} \cdot S \quad (4)$$

where $S_{\text{Cr}} = \frac{3}{2}$ in the ${}^4\text{A}_2$ ground state and $S_{\text{Cr}} = \frac{1}{2}, \frac{3}{2}$ in the ${}^2\text{E}, {}^4\text{T}_2$ excited states, respectively. The total spin of the six interacting Gd^{3+} ions, $S = \sum_{i=1}^6 S_i$ where $S_i = \frac{7}{2}$, takes integral total spin values ranging from zero to 21. If the exchange constant J is small, each of the $M_S = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ levels of the $S_{\text{Cr}} = \frac{3}{2}$ ground state is split into a quasi-continuous band of exchange-coupled sub-levels having total spin quantum numbers \bar{S} given by $\bar{S} = S + \frac{3}{2}, \bar{S} = S + \frac{1}{2}, \bar{S} = |S - \frac{1}{2}|, \bar{S} = |S - \frac{3}{2}|$. In the garnets the ${}^2\text{E}$ state is split by the spin-orbit coupling and trigonal distortion into $2\bar{\text{A}}$ and $\bar{\text{E}}$ levels, of which $\bar{\text{E}}$ is the lowest. In this ${}^2\text{E}(\bar{\text{E}})$ level there are two sub-bands, one corresponding to $\bar{S} = S + \frac{1}{2}$ and the other to $\bar{S} = |S - \frac{1}{2}|$. The spin-spin exchange interaction Hamiltonian is diagonal in $\bar{S}, M_{\bar{S}}, S$ and S_{Cr} . The expectation value of equation (4) for states defined by the quantum numbers $\bar{S}, M_{\bar{S}}, S$ and S_{Cr} is given by

$$\langle \bar{S}, M_{\bar{S}}, S, S_{\text{Cr}} | H_{\text{ex}} | \bar{S}, M_{\bar{S}}, S, S_{\text{Cr}} \rangle = -(J/2)[\bar{S}(\bar{S} + 1) - S(S + 1) - S_{\text{Cr}}(S_{\text{Cr}} + 1)] \quad (5)$$

and is independent of $M_{\bar{S}}$. Figure 1 shows the electron spin density of the $S_{\text{Cr}} = \frac{3}{2}$ ground state as a function of energy, split by the spin-spin exchange interaction (equation (4)) assuming that the exchange coupling constant is positive. The bars in figure 1(a) indicate the degeneracy of the spin states with total spins \bar{S} and S , defined as $(2\bar{S} + 1)N_S$. The total number, N_S , of ways of forming a state of total spin S of Gd^{3+} is calculated in the same way as by Murphy and Ohlmann [2] and is listed in table 1. We assume that each line is represented by a Gaussian, $\exp[-(E - E_{\bar{S}})^2/2\gamma^2]$ where $E_{\bar{S}}$ is equal to the expectation value of equation (4) and γ is the width. Figure 1(b) shows the spin densities with a parameter J and $\gamma = 1.5 \text{ cm}^{-1}$. The shape with the value of $J < 0.3 \text{ cm}^{-1}$ is nearly a Gaussian, whereas those with the value of $J \geq 0.4 \text{ cm}^{-1}$ are resolved into four bands. The spin-density spectrum is associated with homogeneous broadening, resulting in the broad FLN spectrum.

Table 1. Total number N_S of vectors of length S formed by adding together six vectors of length $\frac{7}{2}$.

S	N_S	S	N_S
0	260	11	911
1	756	12	685
2	1190	13	489
3	1534	14	330
4	1770	15	210
5	1890	16	126
6	1896	17	70
7	1800	18	35
8	1624	19	15
9	1400	20	5
10	1155	21	1

When a magnetic field is applied to the $\text{Cr}^{3+}:\text{GSAG}$ system, the Zeeman interaction term is added to the spin Hamiltonian, equation (1). The isotropic Zeeman interactions of Cr^{3+} and Gd^{3+} ions are

$$H_z = g_{\text{Cr}}\mu_B S_{\text{Cr}} \cdot B + g_{\text{Gd}}\mu_B S \cdot B \simeq g_0\mu_B \bar{S} \cdot B \quad (6)$$

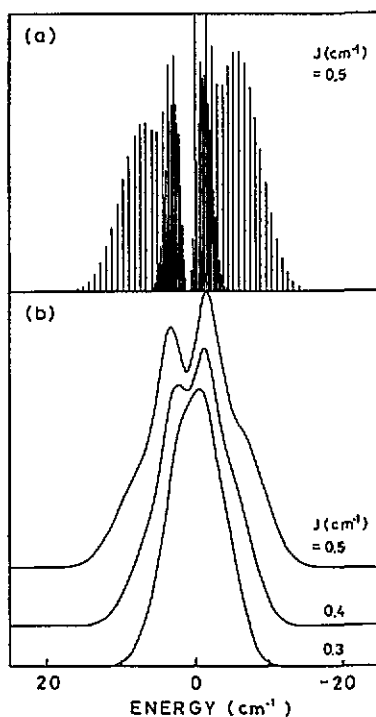


Figure 1. Spin degeneracy of the ground state as a function of energy, split by spin-spin exchange interaction (equations (4) and (5)). The lines have (a) no width, (b) a width of 1.5 cm^{-1} .

where $g_{\text{Cr}} \simeq g_{\text{Gd}} \simeq g_0 = 2.00$, μ_B is the Bohr magneton, B is an external magnetic field and \tilde{S} is a good quantum number represented by $\tilde{S} = S + S_{\text{Cr}}$. In the presence of an applied magnetic field, the spin degenerate $|\tilde{S}, M_{\tilde{S}}, S_{\text{Cr}}, S\rangle$ state splits into $2\tilde{S} + 1$ magnetic sub-levels. The lowest 4A_2 ground state is $|\tilde{S} = 21 + \frac{3}{2}, M_{\tilde{S}} = -(21 + \frac{3}{2}), S = 21, S_{\text{Cr}} = \frac{3}{2}\rangle$.

2.2. Optical transition between the ground and lowest excited states of Cr^{3+} in the exchange system

The ground and excited states, respectively, consist of four and two quasi-continuous bands created by spin-spin exchange between Cr^{3+} and Gd^{3+} ions. The ground states, denoted as $gr_0, gr_1, gr_2, gr_3, \dots$, have degeneracy $d_0, d_1, d_2, d_3, \dots$, corresponding to states with different values of \tilde{S} for $|S, M_{\tilde{S}}, S, S_{\text{Cr}}\rangle$ with degeneracy $(2\tilde{S} + 1)N_{\tilde{S}}$, and the excited states $ex_0, ex_1, ex_2, ex_3, \dots$ have degeneracy $f_0, f_1, f_2, f_3, \dots$. The spontaneous transition probability, $A_{ex_n \rightarrow gr_m}$, from the excited state ex_n to the ground state gr_m is defined as [6]

$$A_{ex_n \rightarrow gr_m} \propto d_m |\langle gr_m | \mu | ex_n \rangle|^2 \quad (7)$$

where μ is the electric or magnetic dipole operator. The absorption and emission transition probabilities are

$$W_{gr_m \rightarrow ex_n} = (f_n / d_m) A_{ex_n \rightarrow gr_m} n_\omega \quad (8)$$

$$W_{ex_n \rightarrow gr_m} = A_{ex_n \rightarrow gr_m} (1 + n_\omega) \quad (9)$$

where n_ω is the photon occupancy in the mode at transition frequency ω . The absorption coefficient for the photon energy $\hbar\omega$ corresponding to $W_{gr_m \rightarrow ex_n}$ is

$$\alpha_{gr_m \rightarrow ex_n}(\omega) \propto N_{gr_m} W_{gr_m \rightarrow ex_n} \propto N_{gr_m} f_n |\langle gr_m | \mu | ex_n \rangle|^2 \quad (10)$$

where N_{gr_m} , the number density of Cr³⁺ centres in the ground state gr_m , is determined by the Boltzmann factor. Assuming that the thermal population of the excited state is negligibly small, the number N_{gr_m} is given by

$$N_{gr_m} = N_0 (d_m / d_{total}) \exp[-(E_{gr_m} - E_{gr_0}) / k_B T] \quad (11)$$

$$d_{total} = \sum_{k=0} d_k \exp[-(E_{gr_k} - E_{gr_0}) / k_B T] \quad (12)$$

in terms of the total number of Cr³⁺ ions in the crystal, N_0 , and the energy, E_{gr_m} , of the ground state gr_m .

Next consider the luminescence intensity $I_{em}(\omega)$ emitted in the $ex_n \rightarrow gr_m$ transition at the photon energy $\hbar\omega$:

$$I_{em}(\omega) = A_{ex_n \rightarrow gr_m} N_{ex_n} \hbar\omega \propto N_{ex_n} d_m |\langle gr_m | \mu | ex_n \rangle|^2 \quad (13)$$

where N_{ex_n} is the number density of Cr³⁺ centres in the excited state ex_n , defined in the same way as the ground state occupancy, assuming that the electron excited in the optical absorption transition relaxes and is thermalized in the relaxed excited state before the radiative de-excitation to the ground state.

2.3. Selection rule of the transition between the ground and excited states in the exchange system

The selection rules of optical transitions between the ground and excited states of Cr³⁺ in GSAG include the effect of spin-spin exchange between Cr³⁺ and the six nearest-neighbour Gd³⁺ ions. Because the electric and magnetic dipole operators, μ , do not include spin operators (see equation (7)), the total spin \tilde{S} , the total spin S of Gd³⁺, and the Cr³⁺ spin S_{Cr} , should all be conserved. The spin wave function of the ²E(Γ_8) excited state used in the spin Hamiltonian, equation (1), including the effects of spin-orbit and spin-spin exchange interactions, is modified using equation (3) and (5) to

$$|\tilde{S}, M_{\tilde{S}}, S, S_{Cr}(\Gamma_8)\rangle = |\tilde{S}, M_{\tilde{S}}, S, S_{Cr}(^2E)\rangle + \alpha |\tilde{S}', M'_{\tilde{S}'}, S, S_{Cr}(^4T_2)\rangle \quad (14)$$

where α is the mixing coefficient of the ⁴T₂ second excited state with the same Gd³⁺ spin S as ²E. As a consequence, the selection rule for the total spin, \tilde{S} , and the Cr³⁺ spin, S_{Cr} , breaks down, although that of the Gd³⁺ total spin, S , is conserved. At low temperatures, only the lowest level with $S = 21$ of the quasi-continuous band of the ²E excited state is populated. Transitions to the lower $S = 21$ levels of three ⁴A₂ quasi-continuous bands then occur in accordance with the selection rule that the total spin of the Gd³⁺ ions is conserved. In consequence, three sharp lines are expected. The selection rule on the total spin of the coupled Gd³⁺ ions may be removed by [2]:

- (i) Gd-Gd interaction;
- (ii) anisotropic exchange interactions.

As a consequence transitions between the different total spin states of Gd³⁺ may occur, thereby giving rise to homogeneous broadening of R lines. Thus, the selection rule for the Gd³⁺ total spin S is very important in calculating the FLN lineshape.

2.4. Calculating the FLN lineshape

The linewidths of the R_1 lines of Cr^{3+} -doped Gd-based garnets are broadened inhomogeneously by the random local electrostatic crystal field of several different Cr^{3+} sites and homogeneously by the spin-spin exchange interaction between Cr^{3+} ions and the six nearest-neighbour Gd^{3+} ions. High-resolution site-selective spectroscopy, such as FLN, is sufficiently powerful to resolve the line structure. If the linewidth of a laser beam resonant with the transition is less than the homogeneous linewidth, the FLN line reflects the homogeneous linewidth. For the quasi-continuous bands in a magnetic field, the Zeeman energy is much larger than the exchange energy, and the FLN line is split into Zeeman components with linewidths comparable with the laser linewidth. The FLN lineshapes are separately calculated in the absence and the presence of a magnetic field.

The resonant excitation produces transitions into the quasi-continuous band of the 2E excited state. The number of Cr^{3+} sites excited by the resonant excitation $\hbar\omega$, corresponding to the transition $g_{r_m} \rightarrow ex_n$, is proportional to an absorption coefficient $\alpha_{g_{r_m} \rightarrow ex_n}(\omega)$ (equation (10)) assuming that the absorption coefficient is fairly small. The excited electron on the Cr^{3+} site relaxes to the lowest excited level at $T = 0$ without energy transfer to other Cr^{3+} sites. The lowest excited energy, $E_{m \rightarrow n}^0$ is

$$E_{m \rightarrow n}^0 = \hbar\omega + (E_{g_{r_m}} - E_{g_{r_0}}) - (E_{ex_n} - E_{ex_0}) \quad (15)$$

where $\hbar\omega$ is the resonant excitation energy. The distribution of excited Cr^{3+} sites with the lowest excited energy, $E_{m \rightarrow n}^0$, is given by

$$P_{\text{abs}}(E) \propto \sum_m \sum_n \alpha_{g_{r_m} \rightarrow ex_n}(\omega) \delta(E - E_{m \rightarrow n}^0). \quad (16)$$

The luminescence intensity of the transition $ex_n \rightarrow g_{r_m}$ is given in equation (13). The lineshape of an intrinsic luminescence from a single Cr^{3+} site is defined as

$$P_{\text{em}}(E) \propto \sum_m \sum_n I_{\text{em}}(\omega) \delta(E - E_{ex_n} + E_{g_{r_m}}) \quad (17)$$

where

$$\omega = (E_{ex_n} - E_{g_{r_m}})/\hbar. \quad (18)$$

The calculated FLN lineshape including the excitation and emission processes is the convolution of the distribution of the excited states and the intrinsic luminescence lineshape:

$$S(E) = \int_0^\infty P_{\text{abs}}(E') P_{\text{em}}(E - E') dE'. \quad (19)$$

When a magnetic field is applied, the spin-degenerate states, $|\bar{S}, M_{\bar{S}}, S, S_{\text{Cr}}\rangle$, split further into $(2\bar{S} + 1)$ magnetic sub-levels, the Zeeman energy being $g_0 \mu_B M_{\bar{S}} B_z$. The optical transitions occur between these magnetic sub-levels.

3. Comparison of the theory with the experimental results

Details of our experimental studies of FLN in the R_1 lines of the Cr^{3+} ion in GSAG at temperatures in the range 1.4–15 K and at magnetic fields up to 3.5 T have been reported [5]. Figure 2(a) shows the FLN spectra measured with excitation wavelength 692.48 nm at $T = 1.6$ K, 4.2 K and 8 K in the absence of a magnetic field. At $T = 1.6$ K the FLN peak is shifted to 692.7 nm and the lineshape is asymmetric, having a pronounced long-wavelength tail. As the temperature is increased, the FLN peak and the tail are shifted to shorter wavelengths. Above 8 K, the peak is resonant with the excitation wavelength. The spectra are enhanced on the shorter-wavelength side due to thermal population, thereby becoming more symmetric.

When a magnetic field is applied at 1.6 K, the asymmetric FLN spectrum is split into three Zeeman components as shown in figure 3(a). The applied field also causes a narrowing of each Zeeman component. When with the field at 3.46 T the temperature is increased above 1.6 K there is a gradual broadening of each Zeeman line, two non-resonant Zeeman lines are shifted to shorter wavelength, and components appear at higher energy than the excitation energy as a consequence of thermal population of excited states (figure 4(a)).

In order to explain these results, we have calculated the lineshapes of the FLN spectra of Cr^{3+} in the exchange-coupled system as a function of temperature and of magnetic field. The g -value of the ${}^2\text{E}$ excited state affects the Zeeman pattern and the linewidth of each Zeeman component. Optically detected magnetic resonance (ODMR) studies have been used to measure the ${}^2\text{E}$ excited g -values of $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ ($g_{\parallel} = 2.44$ and $g_{\perp} = 0.06$) [7]. The g -value of $\text{Cr}^{3+}:\text{GSAG}$ is assumed to be equal to 2.

3.1. In the presence of a magnetic field

As discussed in section 2.3, if the total spin of the Gd^{3+} ion, S , and the magnetic quantum number, M_S , are not conserved in a transition between the magnetic sublevels of the ${}^4\text{A}_2$ ground and ${}^2\text{E}$ excited states, many Zeeman lines should be observed at low temperatures and at high field. However, the FLN spectrum observed at $T = 1.6$ K and at $B = 3.46$ T in figure 3(a) consists of only three sharp lines. This result indicates that the Gd^{3+} total spin S and magnetic quantum numbers M_S are conserved in the presence of the applied field. The three sharp lines are due to the transitions ${}^2\text{E}(\Gamma_8) \rightarrow {}^4\text{A}_2$:

$$\begin{aligned}
 |\tilde{S} = (21 + \frac{1}{2}), M_{\tilde{S}} = -(21 + \frac{1}{2}), S = 21, S_{\text{Cr}}({}^2\text{E}) = \frac{1}{2}) \\
 \rightarrow |\tilde{S} = (21 + \frac{3}{2}), M_{\tilde{S}} = -(21 + \frac{3}{2}), S = 21, S_{\text{Cr}}({}^4\text{A}_2) = \frac{3}{2}) : P_{\frac{1}{2} \rightarrow \frac{3}{2}} = R_1 \\
 \rightarrow |\tilde{S} = (21 + \frac{1}{2}), M_{\tilde{S}} = -(21 + \frac{1}{2}), S = 21, S_{\text{Cr}}({}^4\text{A}_2) = \frac{3}{2}) : P_{\frac{1}{2} \rightarrow \frac{1}{2}} = R_2 \\
 \rightarrow |\tilde{S} = (21 - \frac{1}{2}), M_{\tilde{S}} = -(21 - \frac{1}{2}), S = 21, S_{\text{Cr}}({}^4\text{A}_2) = \frac{3}{2}) : P_{\frac{1}{2} \rightarrow -\frac{1}{2}} = R_3 \\
 \rightarrow |\tilde{S} = (21 - \frac{3}{2}), M_{\tilde{S}} = -(21 - \frac{3}{2}), S = 21, S_{\text{Cr}}({}^4\text{A}_2) = \frac{3}{2}) : P_{\frac{1}{2} \rightarrow -\frac{3}{2}} = 0.
 \end{aligned}
 \tag{20}$$

The relative integrated intensities of the three Zeeman component lines can be used to estimate $R_1:R_2:R_3 = 1:0.5:0.3$. The energy separations between the three

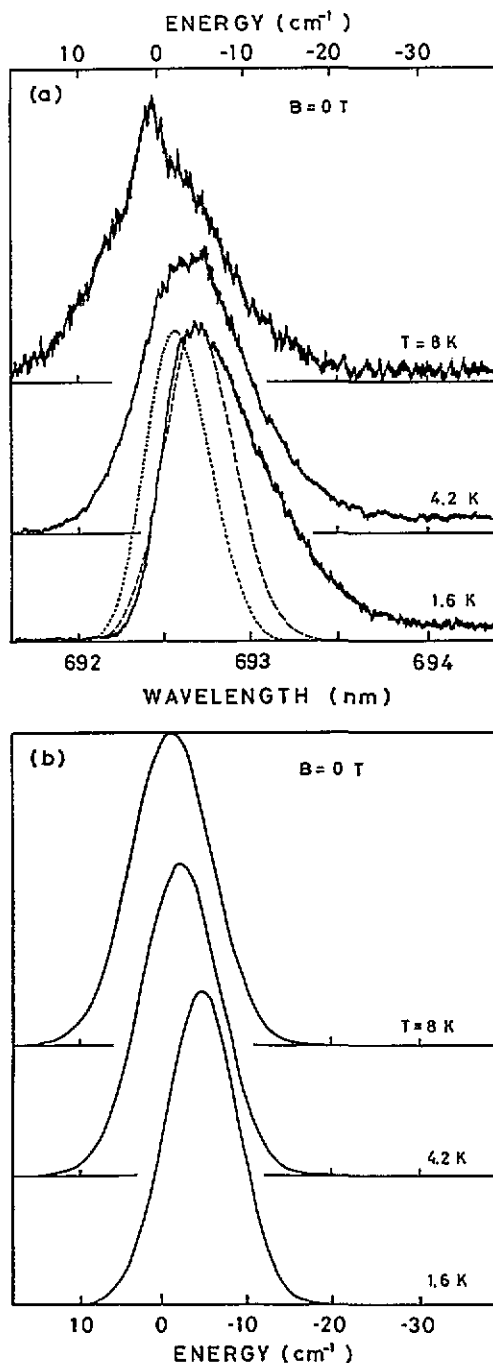


Figure 2. (a) Temperature dependence of the FLN spectra in the absence of a magnetic field: the origin of energy is equal to the resonant excitation of 692.48 nm. The dotted and dashed curves are calculated using equation (19) with the intensity ratio $R_1:R_2:R_3 = 1:0.5:0.3$, the exchange coupling constant $J = 0.33$ cm^{-1} , and the width $\gamma = 2.5$ cm^{-1} assuming that the Gd^{3+} total spin S is conserved or not, respectively. (b) Lineshapes of the FLN spectra calculated using equation (19) with $R_1:R_2:R_3 = 1:0.5:0.3$, $J = 0.33$ cm^{-1} , and $\gamma = 2.5$ cm^{-1} assuming that the Gd total spin S is not conserved through the transition.

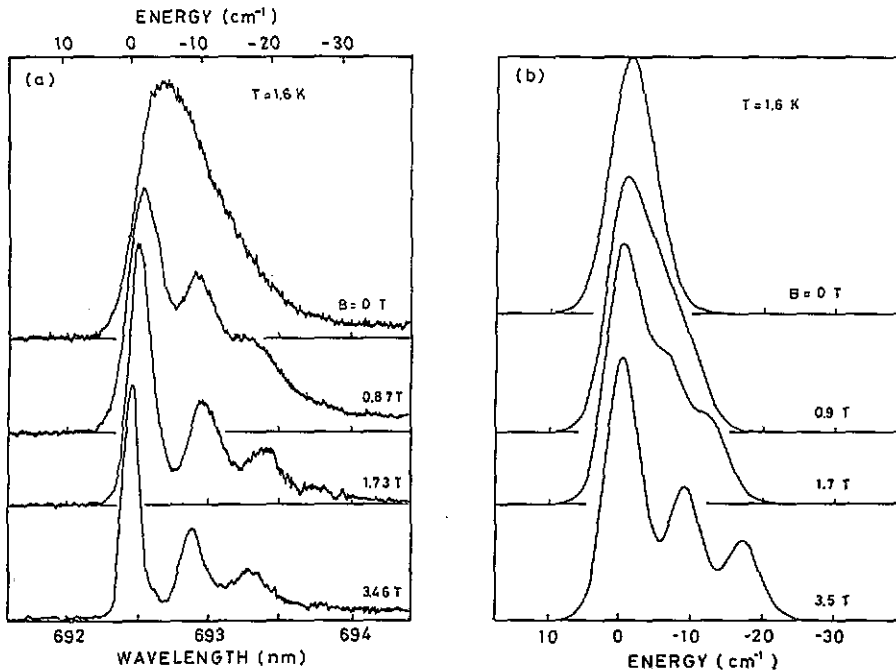


Figure 3. (a) Magnetic field dependence of the FLN spectra at $T = 1.6$ K: the origin of energy is equal to the resonant excitation of 692.48 nm. (b) Lineshapes of the FLN spectra calculated using equation (19) with the intensity ratio $R_1:R_2:R_3 = 1:0.5:0.3$, the exchange coupling constant $J = 0.25$ cm^{-1} , and the width $\gamma = 2.5$ cm^{-1} assuming that the Gd^{3+} total spin S and magnetic quantum number M_S are conserved through the transition.

Zeeman components are both equal to 8.7 cm^{-1} . Taking into account that the Zeeman energy at $B = 3.5$ T is 3.2 cm^{-1} , and that zero-field splitting is less than 1 cm^{-1} , the large energy separation, 8.7 cm^{-1} , may be the sum of the Zeeman and exchange energies [5]. The energy separations between transitions, equation (20), are then represented by

$$\begin{aligned} E\left(\frac{1}{2} \rightarrow \frac{3}{2}\right) - E\left(\frac{1}{2} \rightarrow \frac{1}{2}\right) &= 2\mu_B B + 22.5J \\ E\left(\frac{1}{2} \rightarrow \frac{1}{2}\right) - E\left(\frac{1}{2} \rightarrow -\frac{1}{2}\right) &= 2\mu_B B + 21.5J. \end{aligned} \quad (21)$$

The measured energy separation 8.7 cm^{-1} can be used to estimate the exchange coupling constant, i.e. $J = 0.25$ cm^{-1} .

First, we calculate the FLN lineshapes as a function of temperature at high magnetic field $B = 3.5$ T using equation (19), with $R_1:R_2:R_3 = 1:0.5:0.3$, $J = 0.25$ cm^{-1} , and the width $\gamma = 2.5$ cm^{-1} and assuming that the Gd^{3+} total spin S and magnetic quantum numbers M_S are conserved. As the temperature is increased, the higher-energy spin states of the quasi-continuous bands of the ground and excited states are thermally populated. The higher levels have large degeneracies as table 1 shows. The transitions from the higher-energy levels of the ground state produce line broadening of each Zeeman line, and shift the peak to shorter wavelength. Above 8 K, the components higher than the excitation energy are enhanced remarkably. The

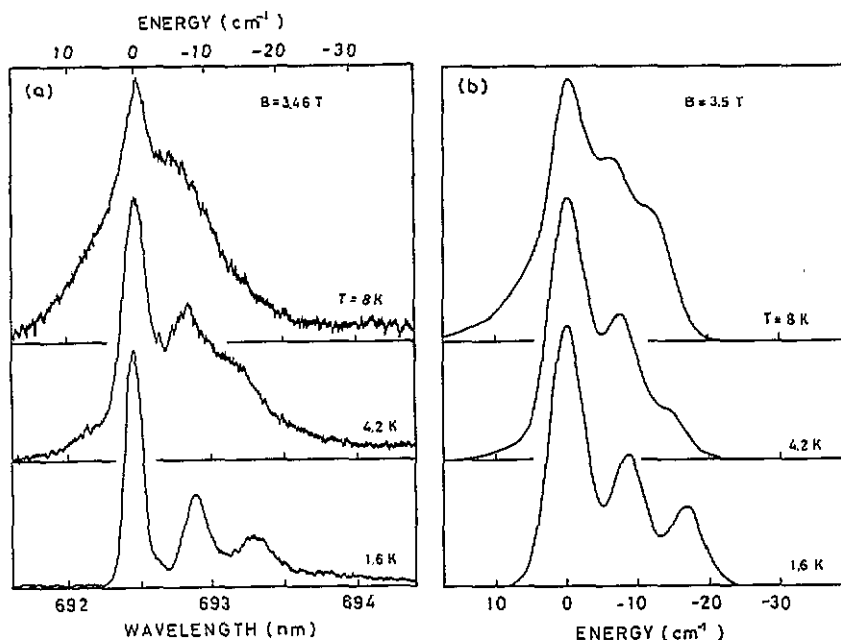


Figure 4. (a) Temperature dependence of the FLN spectra at $B = 3.46$ T: the origin of energy is equal to the resonant excitation of 692.43 nm. (b) Lineshapes of the FLN spectra calculated using equation (19) with the intensity ratio $R_1:R_2:R_3 = 1:0.5:0.3$, the exchange coupling constant $J = 0.25$ cm^{-1} , and the width $\gamma = 2.5$ cm^{-1} assuming that the Gd^{3+} total spin S and magnetic quantum number M_S are conserved through the transition.

FLN lineshapes calculated in figure 4(b) agree fairly well with the experimental data in figure 4(a).

Next, we calculate the magnetic field dependence of the FLN lines at fixed temperature $T = 1.6$ K using the same values of the parameters as those in figure 4(b). The FLN lineshapes calculated at magnetic fields below about 2 T in figure 3(b) disagree with the experimental data in figure 3(a). The calculated FLN lineshape at $B = 0$ is nearly symmetric and the resonant component is strong. The experimental FLN spectrum at $B = 0$ T is asymmetric with a large linewidth. The discrepancy suggests that the selection rule on the total Gd^{3+} spin breaks down. This effect is caused by Gd–Gd interaction and anisotropic exchange interaction as discussed in section 2.3. The former is associated with the Néel temperature T_N of the antiferromagnetic material. For GSAG T_N is not expected to be very different from that for GGG ($T_N = 0.5$ K). The former interaction may be negligible in Cr^{3+} :GSAG in the ranges of $T = 1.4$ – 12 K and $B = 0$ – 3.5 T, and the Gd^{3+} ion may be regarded as a paramagnetic ion at temperatures above 1.6 K. In consequence, the latter interaction may be dominant because the octahedron surrounding Cr^{3+} ion is distorted trigonally.

3.2. In the absence of a magnetic field

The dotted and dashed curves in figure 2(a) are calculated using equation (19) with $R_1:R_2:R_3 = 1:0.5:0.3$, $J = 0.33$ cm^{-1} , and $\gamma = 2.5$ cm^{-1} and assuming that the Gd^{3+} total spin S is conserved or not, respectively. The former is symmetric and the

peak is nearly equal to the resonant excitation, whereas the peak of the latter curve is shifted from the resonant excitation to lower energy. When the exchange coupling constant J is increased, the peak energy is shifted towards lower energy and the linewidth is much broader as shown in figure 1(b). The curve with $J = 0.45 \text{ cm}^{-1}$ fits the observed FLN spectrum at $T = 1.6 \text{ K}$ except that the peak is located at lower energy than the resonant excitation. We prefer the exchange coupling constant $J = 0.33 \text{ cm}^{-1}$ because it is close to that ($J = 0.25 \text{ cm}^{-1}$) estimated from the FLN spectrum at $B = 3.46 \text{ T}$. Figure 2(b) shows the FLN lineshapes calculated using equation (19) with $R_1:R_2:R_3 = 1:0.5:0.3$, $J = 0.33 \text{ cm}^{-1}$, and $\gamma = 2.5 \text{ cm}^{-1}$. As the temperature is increased, the peaks of the FLN lineshapes are shifted towards the resonant excitation and the linewidth is broadened. The calculation can explain the behaviour of the temperature dependence of the FLN observed in figure 2(a).

4. Conclusions

The R_1 line of Cr^{3+} in an antiferromagnetic garnet crystal $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$ (GSAG) undergoes both inhomogeneous and homogeneous broadenings. Site-selective techniques, such as fluorescence line narrowing (FLN), can remove the inhomogeneous broadening created by strain and compositional disorder. The FLN spectrum then reflects broadening processes including spin-spin exchange interaction between the Cr^{3+} and Gd^{3+} ions in GSAG. A magnetic field can remove this source of homogeneous broadening. The broad line is split into three sharp Zeeman lines at $B = 3.5 \text{ T}$. Simulation of the FLN spectra of $\text{Cr}^{3+}:\text{GSAG}$ as a function of both temperature and magnetic field may be used to estimate the spin-spin exchange coupling $J \approx 0.25\text{--}0.33 \text{ cm}^{-1}$. The selection rule for the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition is that the Cr^{3+} and Gd^{3+} spins in the $\text{Cr}^{3+}\text{--Gd}^{3+}$ spin-spin exchange system should be conserved. The selection rule on the Cr^{3+} spin is broken by the spin-orbit interaction of the Cr^{3+} ion. Simulation of the FLN lineshapes indicates that the selection rule on the Gd^{3+} spin is conserved in the presence of a magnetic field ($B > 2 \text{ T}$), whereas it is broken in the absence of a magnetic field. The latter effect may be produced by anisotropic spin-spin exchange interaction in low-symmetry crystals.

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