Magnetic-field and temperature dependence of the fluorescence lifetime of Cr^{3+} in $GdAlO_3$

J. S. Helman and A. O. Caride

Centro Brasileiro de Pesquisas Físicas (CBPF), Rua Dr. Xavier Siguad 150, Urca, Rio de Janeiro, RJ 22290, Brasil

H. C. Basso, M. C. Terrile, and R. A. Carvalho

Instituto de Físcia e Química de São Carlos, Universidade de São Paulo, 13 560 São Carlos, Brasil

(Received 4 December 1990)

The fluorescence lifetime of Cr^{3+} in $GdAlO_3$ was measured in the range 1.8–4.2 K in magnetic fields up to 6 T. The results show a remarkable dependence of the transition probabilities on magnetic order. A model based on the exchange interaction between Cr^{3+} in highly excited states and the Gd^{3+} ions is proposed.

INTRODUCTION

The optical and magnetic properties of the antiferromagnet $GdAlO_3$ with Cr^{3+} impurities substituting for Al^{3+} have been extensively studied both theoretically and experimentally.[1–13] In particular the fluorescence lifetime was measured by Ohlman et al.[1] for some temperatures above and below the Néel point and systematically by Aegerter et al.[8] throughout the antiferromagnetic phase. A sharp shortening of the lifetime with the onset of antiferromagnetic order was observed. The origin of this strong dependence on magnetic order remained, however, unexplained and motivated the present additional measurements of fluorescence lifetime with applied magnetic field. The measurements were performed at low temperatures (1.8–4.2 K) in the presence of external fields up to 6 T.

Electric dipole transitions between the $^4A_{2g}$ ground state and the first excited state ^2E_g of Cr^{3+} are spin and parity forbidden. We show here that the combined action of the spin-orbit interaction and the exchange coupling of Cr^{3+} in highly excited states with the neighboring Gd^{3+} ions provides a mechanism that makes possible those transitions and accounts for their dependence on the magnetic order of the matrix.

EXPERIMENTAL

A $GdAlO_3$ single crystal,[14,15] having a nominal Cr^{3+} concentration of 0.1%, was placed in a He bath inside a Nb-Ti superconducting split coil from IGC. The crystal was oriented with the [100] (easy axis) or [001] directions along the magnetic field. Fluorescence was excited using a Spectra-Physics cw argon laser in multiline emission. The laser light, propagating along the magnetic field, was chopped at 3 Hz by an Ealing electromagnetic shutter. The fluorescence was measured in the direction perpendicular to the magnetic field with a 0.5 m Jarrel-Ash monochromator, followed by an RCA 4832 photomultiplier and an EGG model 113 preamplifier.

Two different setups were used to measure the fluorescence lifetime. In the first, a PAR Signal Averager, connected to a microcomputer and synchronized to the shutter, recorded the time evolution of the fluorescence signal (measured at the peak of each line). The signal intensity versus time could be adjusted by a single exponential decay in every case independent of the fluorescence line, the temperature, and the magnetic field. It was verified that the four fluorescence lines had the same decay time. Taking advantage of this fact, and that the wave number of the fluorescence line at 13 754 cm^{-1} is practically independent of the magnetic field,[11] a second setup was devised in which a boxcar integrator replaced the signal averager. It sampled the intensity of this line at two different times, $I(t)$ and $I(t+T)$, with constant delay time $T=10$ ms, while the magnetic field was being swept continuously. The decay rate is given by $W=\ln[I(t)/I(t+T)]/T$. Measurements were performed at temperatures between 1.8 and 4.2 K and magnetic fields in the range 0– 6 T. The results are shown in Figs. 2– 4. W decreases with increasing magnetic field and tends to a constant value $W_0 \cong 40$ s^{-1} as the magnetization of the sample saturates. The nature of the magnetic order independent background decay W_0 was not identified.

MODEL

The fluorescence lifetime τ is related to the oscillator strength for electric dipole transitions f by[16]

$$f\tau=1.5\times 10^4 \frac{\lambda_0^2}{[(n^2+2)/3]^2 n} , \tag{1}$$

in SI units, where λ_0 is the wavelength in vacuum and n the refractive index. In the case of Cr^{3+} in $GdAlO_3$, $\lambda_0 \cong 7260$ Å and $n \cong 2.05$ yielding $f\tau=9.0\times 10^{-10}$ s. For Cr^{3+} into Al_2O_3 (ruby), the product $f\tau$ is roughly the same and, since its fluorescence lifetime is 4 ms, we get $f_{ruby}=2.5\times 10^{-7}$. Theoretically, the oscillator strength is given by

$$f=\sum_{^4A_{2g}} \frac{2m\omega_0}{3\hbar} \left| \left[{}^4A_{2g} \left| \sum_{i=1}^{3} r_i \right| {}^2E_g \right] \right|^2 , \tag{2}$$

where r_i are the coordinates of the three d electrons of

Cr^{3+} and the sum is over the $^4A_{2g}$ multiplet. $|^4A_{2g}\rangle$ and $|^2E_g\rangle$ indicate the perturbed ground and first excited state of Cr^{3+} in the cubic crystal field. m is the electron mass, $\hbar$ Planck's constant, and ω_0 the light frequency. Transitions between the unperturbed states are both spin and parity forbidden. In the case of ruby, for instance, the prohibition is lifted by the combined action of the spin-orbit interaction and the hemihedral part of the trigonal field.[17]

In $GdAlO_3$ the Cr^{3+} impurities occupy sites with *spatial* inversion symmetry. Inversion symmetry, however, is broken by the Gd spins and thus the oscillator strength depends strongly on the magnetic order of the neighboring Gd ions. We propose that the combined action of the spin-orbit interaction and the exchange coupling of Cr with the neighboring Gd ions are responsible for the lifting of the spin and parity prohibitions, respectively.

We will consider in detail the dependence of the oscillator strength on the magnetic order, while the values of the matrix elements involved will only be estimated in order of magnitude.

The exchange interaction between Cr and its neighboring Gd ions can be phenomenologically written in the form

$$V_{ex} = \sum_{i,j} J(|\mathbf{r}_i - \mathbf{R}_j|)\mathbf{s}_i \cdot \mathbf{S}_j , \tag{3}$$

where the exchange coupling J is assumed to be only a function of the distance between a Cr d electron at position $\mathbf{r}_i$ and the Gd nucleus at $\mathbf{R}_j$. $\mathbf{s}_i$ is the spin operator of the electron at $\mathbf{r}_i$ and $\mathbf{S}_j$ is the total spin operator of the Gd ion in its ground state $(S = \frac{7}{2})$. The sum over i runs over the three d electrons and the sum over j runs over the eight nearest-neighbor Gd ions.

The lowest-order term in a Taylor-series development of V_{ex} that gives a contribution to the decay rate is

$$V'_{ex} = \frac{1}{6} \sum_i \left[\frac{\partial^3 V_{ex}}{\partial x_i \partial y_i \partial z_i}\right]_0 x_i y_i z_i . \tag{4}$$

This has A_{2u} symmetry in the cubic group and lifts the parity prohibition. Using (3)

$$V'_{ex} = C \sum_\alpha \sum_j R_j^x R_j^y R_j^z S_j^\alpha \sum_i x_i y_i z_i s_i^\alpha \tag{5}$$

with

$$C = -\frac{1}{6R^3}\left[\frac{\partial^3 J}{\partial R^3} - \frac{3}{R}\frac{\partial^2 J}{\partial R^2} + \frac{3}{R^2}\frac{\partial J}{\partial R}\right] \quad at \ R = R_0 , \tag{6}$$

where $R_0 = 3.23$ Å is the Cr-Gd distance. Cubic symmetry ensures that the sum over the modulus square of the matrix elements of s_i^α between the intervening states [which below we generically call $|M|^2$, Eq. (27)] will be independent of α. Thus, in calculating the transition rate we will be concerned with the thermodynamic average

$$D = \left\langle \left|\sum_\alpha \sum_j R_j^x R_j^y R_j^z S_j^\alpha\right|^2 \right\rangle , \tag{7}$$

namely,

$$D = \sum_j \sum_{j'} \sum_\alpha \sum_{\alpha'} R_j^x R_j^y R_j^z R_{j'}^x R_{j'}^y R_{j'}^z \langle S_j^\alpha S_{j'}^{\alpha'}\rangle . \tag{8}$$

Neglecting correlations between different components of the Gd spins

$$D = \sum_j \sum_{j'} R_j^x R_j^y R_j^z R_{j'}^x R_{j'}^y R_{j'}^z \langle S_j \cdot S_{j'}\rangle . \tag{9}$$

We shall write

$$\mathbf{S}_j = \langle \mathbf{S}_j\rangle + \mathbf{Y}_j , \tag{10}$$

where $\langle \mathbf{S}_j\rangle$ is the thermodynamic average of the spin operator $\mathbf{S}_j$ and $\mathbf{Y}_j = \mathbf{S}_j - \langle \mathbf{S}_j\rangle$ the spin fluctuation operator. Note that $\langle \mathbf{Y}_j\rangle = 0$ and $\langle \mathbf{Y}_j^2\rangle = S(S+1) - \langle \mathbf{S}_j\rangle^2$. Replacing (10) into (9) we have

$$D = I_0 + I_1 + I_2 , \tag{11}$$

where

$$I_0 = \left[\sum_j R_j^x R_j^y R_j^z \langle S_j\rangle\right]^2 , \tag{12}$$

$$I_1 = \sum_j (R_j^X R_j^Y R_j^Z)^2 [S(S+1) - \langle S_j\rangle^2] , \tag{13}$$

$$I_2 = \sum_j \sum_{j'\neq j} R_j^x R_j^y R_j^z R_{j'}^x R_{j'}^y R_{j'}^z \langle Y_j \cdot Y_{j'}\rangle . \tag{14}$$

We note that I_0 vanishes for a ferromagnetic alignment while it is maximum for saturated two-sublattice antiferromagnetic order. Since $(R_j^x R_j^y R_j^z)^2 = q$, with $q = R_0^6/27$, the term I_1 gives an important contribution even for fully disordered Gd spins. In the following we will neglect the correlation between the fluctuations of next-nearest-neighbor Gd spins. The correlation between the fluctuations of nearest-neighbor Gd spins will be described by the parameter p defined by

$$\langle Y_j \cdot Y_{j'}\rangle = [S(S+1) - \langle S_j\rangle^2]^{1/2}[S(S+1) - \langle S_{j'}\rangle^2]^{1/2}p . \tag{15}$$

p varies in the range $-1 < p < 1$. $p > 0$ ($p < 0$) means ferromagnetic (antiferromagnetic) correlation. We note that $R_j^x R_j^y R_j^z R_{j'}^x R_{j'}^y R_{j'}^z = -q$ for nearest-neighbor j, j'. Next, we write explicit expressions for D corresponding to particular magnetic configurations. We obtain, from Eqs. (11)–(15), $D = 64qS^2F$ where

$$F = \sigma^2 + (1 + 1/S - \sigma^2)(1 - 3p)/8 \tag{16}$$

for antiferromagnetic order (AF) with reduced sublattice magnetization $\sigma(T) = \langle S_j\rangle_T/S$;

$$F = (1 + 1/S - m^2)(1 - 3p)/8 \tag{17}$$

in the paramagnetic region (PM) where $m(T,H) = \langle S_j\rangle_{T,H}/S$ is the reduced magnetization;

$$F = (\sigma_A + \sigma_B)^2/4 + [1 + 1/S - (\sigma_A^2 + \sigma_B^2)/2]/8$$
$$- (3p/8)[(1 + 1/S - \sigma_A^2)(1 + 1/S - \sigma_B^2)]^{1/2} \tag{18}$$

for an antiferromagnet in an external field applied along the easy direction. $\sigma_{A,B}(T,H)$ are the reduced sublattice

magnetizations;

$$F = (\sigma \sin\varphi)^2 + (1 + 1/S - \sigma^2)(1 - 3p)/8 , \quad (19)$$

$$F = (\sigma \cos\varphi)^2 + (1 + 1/S - \sigma^2)(1 - 3p)/8 , \quad (19')$$

for an antiferromagnet in the spin-flop (FL) region, $\sigma(T)$ is the reduced sublattice magnetization and φ its angle with respect to the easy direction. Equations (19) and (19') apply for H parallel and perpendicular to the easy direction, respectively.

The order of magnitude of the parameter C given by (6) can be estimated by assuming a form for the function $J(R)$. A tractable and reasonable form is[13]

$$J(R) = J_0 e^{-R/\rho} , \quad (20)$$

where ρ is of the order of the radius of the Cr ion. Thus

$$C = \frac{J_0 e^{-R_0/\rho}}{6R_0^3 \rho^3} \left[1 + \frac{3\rho}{R_0} + \frac{3\rho^2}{R_0^2} \right] . \quad (21)$$

There are only two possibilities of fluorescent decay mediated by V'_{ex}; they are denoted by I and II in Fig. 1. Their amplitudes R_I and R_{II} are proportional to the products of the transition matrix elements involved, divided by the corresponding energy denominators:

FIG. 1. Energy level scheme for Cr^{3+} showing the intervening mechanisms in the fluorescence of ruby and Cr doped $GdAlO_3$.

$$R_I \propto \frac{\langle ^4A_{2g}|\zeta_{s.o.}(T_{1g})|^2T_{2g}\rangle \langle ^2T_{2g}|V'_{ex}(A_{2u})|\Gamma_u(^2T_{1u})\rangle \langle \Gamma_u(^2T_{1u})|P(T_{1u})|^2E_g\rangle}{[E(^2T_{2g}) - E(^4A_{2g})][E(\Gamma_u) - E(^2T_{2g})]} , \quad (22)$$

$$R_{II} \propto \frac{\langle ^2E_g|\zeta_{s.o.}(T_{1g})|^4T_{1g}\rangle \langle ^4T_{1g}|V'_{ex}(A_{2u})|\Gamma_u(^4T_{2u})\rangle \langle \Gamma_u(^4T_{2u})|P(T_{1u})|^4A_{2g}\rangle}{[E(^4T_{1g}) - E(^2E_g)][E(\Gamma_u) - E(^4T_{1g})]} , \quad (23)$$

where $\zeta_{s.o.}(T_{1g})$ is the spin-orbit operator and $P(T_{1u})$ stands for the electric dipole operator. The symmetry of each operator is indicated in parentheses. The value of the spin-orbit matrix elements is $\zeta \simeq 200$ cm^{-1}. As it is shown below the exchange operator $V'_{ex}(A_{2u})$ is of the order of $K\sqrt{F} \simeq 450$ cm^{-1}. The energy denominators have the approximate values: $E(^2T_{2g}) - E(^4A_{2g}) \simeq 21\,000$ cm^{-1}, $E(\Gamma_u) - E(^2T_{2g}) \simeq 97\,000$ cm^{-1}, $E(^4T_{1g}) - E(^2E_g) \simeq 10\,000$ cm^{-1}, and $E(\Gamma_u) - E(^4T_{1g}) \simeq 93\,000$ cm^{-1}.

For the amplitude R_{ruby} of the dominant decay process of ruby (Fig. 1), which we give for comparative purposes, we have[17]

$$R_{ruby} \propto \frac{\langle ^2E_g|\zeta_{s.o.}(T_{1g})|^4T_{2g}\rangle \langle ^4T_{2g}|V_{he}(T_{2u})|\Gamma_u(^4T_{2u})\rangle \langle \Gamma_u(^4T_{2u})|P(T_{1u})|^4A_{2g}\rangle}{[E(^4T_{2g}) - E(^2E_g)][E(\Gamma_u) - E(^4T_{2g})]} , \quad (24)$$

where $V_{he} \simeq 350$ cm^{-1} is the hemiedral part of the trigonal field in ruby and the energy denominators have the approximate values $E(^4T_{2g}) - E(^2E_g) \simeq 4000$ cm^{-1} and $E(\Gamma_u) - E(^4T_{2g}) \simeq 100\,000$ cm^{-1}.

In view of the smaller denominators the second process (23) dominates and we will restrict ourselves to it. We can write

$$|\langle ^4T_{1g}|V'_{ex}|\Gamma_u(^4T_{2u})\rangle|^2 = K^2F , \quad (25)$$

where

$$K = 0.9J_0 e^{-R_0/\rho} \left[1 + \frac{3\rho}{R_0} + \frac{3\rho^2}{R_0^2} \right] |M| \quad (26)$$

with

$$M = \langle ^4T_{1g}|\sum_i x_i y_i z_i s_i^\alpha|\Gamma_u(^4T_{2u})\rangle/\rho^3 . \quad (27)$$

For instance, if we put $\rho = 1$ Å and $M = 1$ then $K = 0.08J_0$.

It follows from Eqs. (2) and (24) that in order of magnitude the oscillator strength of ruby is proportional to the factors $G_{so} = |\zeta/[E(^4T_{2g}) - E(^2E_g)]|^2$ and $G_{he} = |V_{he}/[E(\Gamma_u) - E(^4T_{2g})]|^2$ responsible for the lifting of the spin and parity prohibitions; thus, we write $f_{ruby} = GG_{so}G_{he}$, where $G = 8.16$ is adjusted to reproduce the value of the oscillator strength of ruby. We shall as-

sume that the same constant G applies to Cr into GdAlO$_3$. This is justified because the parameter G depends only on electric dipole matrix elements which are common to the fluorescence of Cr^{3+} in ruby and in GdAlO$_3$. Thus, with values corresponding to process II above, we have

$$f = G \left[\frac{200}{10\,000} \right]^2 \left[\frac{K}{93\,000} \right]^2 F \qquad (28)$$

and from (1), the decay rate induced by the spin disorder is

$$1/\tau = 4.19 \times 10^{-4} K^2 F . \qquad (29)$$

We shall denote by W_0 the decay rate induced by other mechanisms independent of the magnetic configuration of the matrix. Thus, to compare with experiment, we add to $1/\tau$ a constant background decay rate W_0, namely,

$$W = W_0 + 1/\tau . \qquad (30)$$

It is noteworthy that in the case of cubic symmetry considered here, the exchange interaction alone[18] cannot lift both the spin and parity prohibitions. The lowest nonvanishing order in the development of the exchange interaction has A_{2u} symmetry. Thus, when acting on the ground state $^4A_{2g}$ or the excited state ^2E_g, it does not lead to any intermediary state of adequate symmetry to be connected to the other by a dipole transition (T_{1u}). Hence, the spin-orbit interaction is necessary as well.

COMPARISON WITH EXPERIMENT

Figure 2 shows the decay rate as a function of temperature in the absence of magnetic field. The experimental values were taken from Ref. 8. The theoretical result (solid line) was obtained from Eq. (30) using the expression for F given by (16) with values of $\sigma(T)$ calculated within the molecular field approximation.[5] The fitting yields $p = -0.2$, $K = 463$ cm^{-1}, and $W_0 = 40$ s^{-1}. If we

FIG. 3. Fluorescence decay rate vs magnetic field perpendicular to the easy axis. Experiment ($\triangle$) at 2 K, ($\bigcirc$) at 4.2 K; theory: solid lines.

assume $\rho = 1$ Å and $|M| = 1$, this yields $J_o = 5.8 \times 10^3$ cm$^{-1} = 0.7$ eV. This value of J_0 is compatible with that previously found (0.85 eV) for the lower states of Cr in GdAlO$_3$.[13]

Figure 3 shows the decay rate as a function of the magnetic field (perpendicular to the easy axis) for $T = 4.2$ K (paramagnetic region) and $T = 2$ K (below the Néel temperature). The theoretical results for $T = 4$ K were obtained from Eq. (30) with F given by Eq. (17). Those for $T = 2$ K were calculated using F given by Eq. (19') in the AF region ($H < 3$ T) and by Eq. (17) in the PM region ($H > 3$ T). A smooth interpolation was made in the transition region. The same values for p, K, and W_0 found above were used. The values of σ, φ, and m were calculated within the molecular field approximation.[5]

Figure 4 shows the decay rate as a function of the mag-

FIG. 2. Temperature dependence of the decay rate in the absence of magnetic field. Experimental data taken from Fig. 6 of Ref. 8 ($\bigcirc$). Theory: solid line.
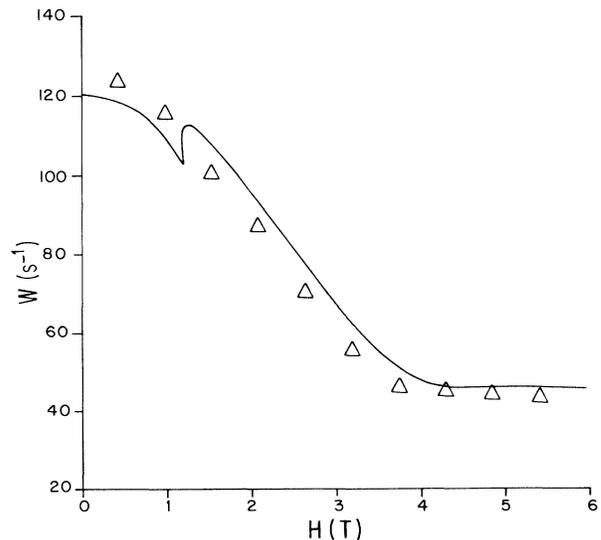
FIG. 4. Fluorescence decay rate vs magnetic field (parallel to easy axis) at 1.8 K. Experiment ($\triangle$). Theory: solid line.

netic field (parallel to the easy axis) for $T=1.8$ K. The theoretical results were obtained form Eq. (30) with F given by Eq. (18) in the AF region ($H<1.2$ T), Eq. (19) in the SF region ($1.2<H<3$ T), and Eq. (17) in the PM region ($H>3$ T). Smooth interpolations were made in the transition regions. Again the same values for p, K, and W_0 found above were used here. The values of σ_A, σ_B, σ, φ, and m were calculated within the molecular field theory.[5] The theory predicts a discontinuity in the decay rate at the AM-FL transition. This was not shown, however, by our experimental results possibly because the noise level was not low enough or a small misalignment of the crystal easy axis broadened the AM-FL discontinuity.

The changes of the oscillator strength of the fluorescent lines with temperature and magnetic field are also apparent in the corresponding absorption.[1,8,19] The correlation[20] is not immediate, however, as it involves the magnetic Franck-Condon effect.[11]

SUMMARY AND DISCUSSION

We propose a model which accounts for the strong dependence on magnetic order of the luminescence decay rate of Cr^{3+} in the two-sublattice antiferromagnet $GdAlO_3$. The luminescent transition is in principle spin and parity forbidden. The spin orbit interaction lifts the spin prohibition. The different orientations of the spins of the eight neighboring Gd ions break the inversion symmetry of the crystal field potential via the exchange coupling between the 3d electrons of Cr and the 4f electrons of the Gd ions, thus lifting the parity prohibition.

The model yields the dependence of the decay rate in terms of the parameters which describe the magnetic order of the matrix in its different phases. Cr in its excited state ^2E does not influence the magnetic order of the neighboring Gd spins[9,11] which may thus be accurately

described within the molecular field approximation with coupling constants appropriate to the pure matrix.[5] The magnitude of the electric dipole transition matrix elements involved are borrowed from the similar case of ruby. The theory still involves three adjustable parameters which were determined form the experimental data Figs. 2–4

(1) The background constant decay rate $W_0=40$ s^{-1}, which is most probably induced by the presence of other impurities or defects.

(2) The correlation between fluctuations of the Gd spins $p=-0.2$, whose evaluation is beyond the molecular field approximation. Although this parameter should be temperature dependent it was considered to be constant within the limited temperature range of the experiments. An independant value of this correlation, obtained from the splitting of the luminescence lines at $T=1.5$ K in the spin-flop phase, yielded $p=-0.3$.[12]

(3) The parameter $K=463$ cm^{-1} is basically connected to the derivatives of the exchange intergrals between the 3d electrons of Cr in the highly excited states $^4T_{1g}$ and the f electrons of Gd. We modeled this interaction in the most simple possible way (following Ref. 13). This permits analytical calculations and, in order of magnitude, we arrive at a value for the preexponential factor of Eq. (20) of $J_0=0.7$ eV which is consistent with the 0.85 eV obtained for that of the direct exchange of Cr in the lower states ^2E_g and $^4A_{2g}$.[13]

[1]R. C. Ohlman, R. Mazelski, and J. Murphy, Technical Summary Report, ARPA Order No. 305, Code 4730, 1967, available from National Technical Information Service, Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161 (unpublished).

[2]K. W. Blazey and G. Burns, Proc. Phys. Soc. London 91, 640 (1967).

[3]K. W. Blazey and H. Rohrer, Phys. Rev. 173, 574 (1968).

[4]J. Murphy and R. C. Ohlman, Optical Properties of Ions in Crystals, edited by H. M. Crosswhite and H. W. Moos (Interscience, New York, 1969), p.239.

[5]K. W. Blazey, H. Rohrer, and R. Webster, Phys. B 4, 2287 (1971).

[6]J. S. Helman, J. Phys. Chem. Solids 32, 251 (1971).

[7]J. S. Helman, R. A. Carvalho, H. Panepucci, M. C. Terrile, M. A. Aegerter, and E. Soarez, Soild State Commun. 31, 1015 (1979).

[8]M. A. Aegerter, H. C. Basso, and H. J. Scheel, in Proceedings of the International Conference on Lasers, New Orleans, 1980 (S.T.S. Press, McLean, Va., 1981), p. 383.

[9]J. S. Helman and W. Baltensperger, Phys. Rev. B 25, 6847 (1982).

[10]J. Mustre de Leon, J. S. Helman, and G. Cisneros, Solid State Commun. 46, 841 (1983).

[11]M. Matsuoka, M. A. Aegerter, H. Panepucci, M. C. Terrile, J. S. Helman, and H. J. Scheel, Phys. Rev. Lett. 50, 204 (1983).

[12]J. S. Helman, Phys. Rev. B 39, 3389 (1989).

[13]M. del Castillo-Mussot, D. Guenzburger, and J. S. Helman, J. Magn. Magn. Mater. 95, 154 (1991).

[14]H. J. Scheel and E. O. Schulz-Dubois, J. Cryst. Growth 8, 304 (1971).

[15]H. J. Scheel, J. Cryst. Growth 13/14, 560 (1972).

[16]G. F. Imbusch, in Luminescence Spectroscopy, edited by M. D. Lumb (Academic, New York, 1978), p. 27.

[17]S. Sugano and Y. Tanabe, J. Phys. Soc. Jpn. 13, 880 (1958).

[18]Y. Tanabe, T. Moriya, and S. Sugano, Phys. Rev. Lett. 15, 1023 (1965).

[19]H. C. Basso, M. C. Terrile, and R. A. Carvalho (unpublished).

[20]W. Beall Fowler and D. L. Dexter, Phys. Rev. 128, 2154 (1962).