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BRIEF REPORTS

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Parity- and spin-forbidden optical transitions of Cr^{+3} in $GdAlO_3$

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In this paper, the electric-dipole transition induced by exchange is used to explain the strong dependence of spin- and parity-forbidden transitions of Cr^{+3} on the sublattice magnetization of an antiferromagnet host. [S0163-1829(97)03840-X]

I. INTRODUCTION

The $GdAlO_3$ is an antiferromagnetic crystal and the dopant Cr^{+3} ion replaces an Al^{+3} in the center of an almost perfect cube with eight Gd^{+3} in vertices.[1] This system has been studied over the past thirty years[2–5] and in previous papers the strong dependence of spin- and parity-forbidden $^4A_2-^2E$ transitions with temperature[6] and applied magnetic field[7] was reported. Empirically, the dependence was fit to the sublattice magnetization square. Recent results have shown that this behavior can be applied only to parity-spin-forbidden transitions. Since the intensity of the electric-dipole transition due to crystal-field distortion and spin-orbit coupling[9] is independent of temperature or magnetic field, another mechanism should be responsible for this behavior.

A mechanism involving electric-dipole transitions induced by exchange is used to explain this experimental behavior. Such a mechanism was proposed by Tanabe *et al.*[8] to explain magnon side bands in transition-metal fluorides without inversion symmetry and will be referred in this paper as TSM.

Some considerations about how to apply this mechanism to a high-symmetric system are made. A simple model is developed which fits the experimental data.

II. THEORY

Let (a) be a magnetic atom placed at the vertices of a simple cubic lattice with an antiferromagnetic phase transition. Let (b) be also a magnetic doping atom, which replaces a nonmagnetic one located in the cube center. This arrangement yelds a site with spatial inversion symmetry, although without magnetic inversion symmetry, for (b).

For an electric-dipole transition between two states Γ^g_α, Γ^g_β of (b) with the same parity and different spins, TSM is expressed as

$$\langle \Gamma^g_\alpha\downarrow|\vec{P}_{\rm ex}|\Gamma^g_\beta\uparrow\rangle=\sum_{\Gamma^u_i\downarrow}\langle\Gamma^g_\alpha\downarrow|\vec{P}|\Gamma^u_i\downarrow\rangle\frac{\langle\Gamma^u_i\downarrow|V_{\rm ex}|\Gamma^g_\beta\uparrow\rangle}{(E_{\Gamma^u_i\downarrow}-E_{\Gamma^g_\beta\uparrow})}+\sum_{\Gamma^u_j\uparrow}(\vec{P}\leftrightarrows V_{\rm ex}),\tag{1}$$

where $\Gamma^u_i\downarrow$, $\Gamma^u_j\uparrow$ are odd-parity excited states in (b), $V_{\rm ex}$ is the exchange term between (a) and (b), $\vec{P}$ is the electric-dipole operator, and $(\vec{P}\leftrightarrows V_{\rm ex})$ is the converse expression.

As a tridimensional array is considered, $V_{\rm ex}$ should be added for all (a) neighbors of (b) resulting in

$$\langle\Gamma^u_i\downarrow|V_{\rm ex}|\Gamma^g_\beta\uparrow\rangle=\sum_k\langle\Gamma^u_i\downarrow,\varphi(a)_k\uparrow|V_{ee}|\Gamma^g_\beta\uparrow,\varphi(a)_k\downarrow\rangle\tag{2}$$

for the flip of both spins, where $\varphi(a)_k$ is ground state of the k-(a) neighbor and V_{ee} is the two-electron Coulomb operator. Here no excitation to another level for (a) will be considered. The same applies to $\langle\Gamma^g_\alpha\downarrow|V_{\rm ex}|\Gamma^u_i\uparrow\rangle$.

Now one must consider the (b)-site point symmetry properties. Since (b) has a spatial inversion symmetry, the k terms of Eq. (2) can be arranged in pairs of opposite atoms, for instance, k and $k+1$:

$$\langle \Gamma_i^u\downarrow|V_{\rm ex}|\Gamma_\beta^g\uparrow\rangle=\sum_{k\text{-odd}}\left(\langle \Gamma_i^u\downarrow,\varphi(a)_k\uparrow|V_{ee}|\Gamma_\beta^g\uparrow,\varphi(a)_k\downarrow\rangle + \langle \Gamma_i^u\downarrow,\varphi(a)_{k+1}\uparrow|V_{ee}|\Gamma_\beta^g\uparrow,\varphi(a)_{k+1}\downarrow\rangle\right). \tag{3}$$

As $\varphi(a)_k$ and $\varphi(a)_{k+1}$ differ just by a translation and $\Gamma_i^u\downarrow$ is an odd function,

$$\langle \Gamma_i^u\downarrow,\varphi(a)_k\uparrow|V_{ee}|\Gamma_\beta^g\uparrow,\varphi(a)_k\downarrow\rangle = -\langle \Gamma_i^u\downarrow,\varphi(a)_{k+1}\uparrow|V_{ee}|\Gamma_\beta^g\uparrow,\varphi(a)_{k+1}\downarrow\rangle, \tag{4}$$

so Eq. (3) should be zero. However, if (b) has no magnetic inversion symmetry, the number of $(a)_k$-neighbors with, e.g., spin down *will not be* equal to the number of $(a)_{k+1}$ in the same configuration and Eq. (3) will not be zero. This happens, e.g., by antiferromagnetic ordering in the lattice.

To discuss this point, two different situations will be considered.

(1) The exchange interaction between (a)-(b) is weaker than (a)-(a): Supposing there is a strong magnetic field applied to the crystal, and the spins are all aligned up, Eq. (3) will be zero (regardless of the symmetry breaking induced by thermal fluctuations). Decreasing the applied field to the spin-flip phase will mean that some (a) atoms in the lattice will present spin-down electrons. Since a Γ^u magnetic symmetry should be present, the spin-down will be more likely, e.g., in $(a)_k$ than $(a)_{k+1}$ resulting in

$$\langle \Gamma_i^u\downarrow|V_{\rm ex}|\Gamma_\beta^g\uparrow\rangle=\sum_{k\text{-odd}}\langle \Gamma_i^u\downarrow,\varphi(a)_k\uparrow|V_{ee}|\Gamma_\beta^g\uparrow,\varphi(a)_k\downarrow\rangle - (\simeq 0)$$

and as the number of spin-down sites is proportional to sublattice magnetization

$$\langle \Gamma_i^u\downarrow|V_{\rm ex}|\Gamma_\beta^g\uparrow\rangle=\varepsilon M(H,T), \tag{5}$$

where $0\leqslant M\leqslant 1$ is related to the spin-down occupation. Applying Eq. (5) to Eq. (1) results in

$$\langle \Gamma_\alpha^g\downarrow|\vec{P}_{\rm ex}|\Gamma_\beta^g\uparrow\rangle=\sum_{\Gamma_i^u\downarrow}\langle \Gamma_\alpha^g\downarrow|\vec{P}|\Gamma_i^u\downarrow\rangle\frac{\varepsilon M(H,T)}{(E_{\Gamma_i^u\downarrow}-E_{\Gamma_\beta^g\uparrow})} + \sum_{\Gamma_j^u\uparrow}(\text{converse}) \tag{6}$$

and for the transition probability,

$$w_{\beta\to\alpha}\propto|\langle \Gamma_\alpha^g\downarrow|\vec{P}_{\rm ex}|\Gamma_\beta^g\uparrow\rangle|^2\propto|\varepsilon|^2(M(H,T))^2.$$

2. The exchange interaction between (a)-(b) is stronger than (a)-(a): Now, for the same situation described previously, the spins of $(a)_k$ and $(a)_{k+1}$ will remain parallel. However their neighborhood, consisting of (a) atoms outside the cube considered until now, will keep the antiferromagnetic ordering, thus perturbing the $(a)_k$ and $(a)_{k+1}$ spin state but with different intensities: if one remains more likely spin up, the other will remain spin down. Thus, one can write for the last

$$|\varphi(a)\uparrow\rangle_k^p-|\varphi(a)\uparrow\rangle_k^0=\sum_l\frac{\langle\varphi(a)_k\downarrow,\varphi(a)_l\uparrow|V_{\text{ex}(a-a)}|\varphi(a)_k\uparrow,\varphi(a)_l\downarrow\rangle}{\Delta E}|\varphi(a)\downarrow\rangle_k^0, \tag{7}$$

where $|\varphi(a)\uparrow\rangle_k^p$ is the a_k-atom perturbed state, ΔE is the energy difference between $|\varphi(a)\downarrow\rangle_k^0$ and $|\varphi(a)\uparrow\rangle_k^0$, and the sum involves all the l first neighbors. Again, the number of spin-down sites is proportional to the sublattice magnetization.

Applying Eq. (7) to Eq. (3) and assuming that all l terms are equal, we have

$$\langle \Gamma_i^u\downarrow|V_{\rm ex}|\Gamma_\beta^g\uparrow\rangle=\sum_{k\text{-odd},l}\langle \Gamma_i^u\downarrow,\varphi(a)_k\uparrow|V_{ee}|\Gamma_\beta^g\uparrow,\varphi(a)_k\downarrow\rangle\frac{\langle\varphi(a)_k\downarrow,\varphi(a)_l\uparrow|V_{\text{ex}(a-a)}|\varphi(a)_k\uparrow,\varphi(a)_l\downarrow\rangle}{\Delta E}M(H,T) \tag{8}$$

or

$$\langle \Gamma_i^u\downarrow|V_{\rm ex}|\Gamma_\beta^g\uparrow\rangle=\gamma M(H,T), \tag{9}$$

where

$$\gamma=\varepsilon\sum_l\frac{\langle\varphi(a)_k\downarrow,\varphi(a)_l\uparrow|V_{\text{ex}(a-a)}|\varphi(a)_k\uparrow,\varphi(a)_l\downarrow\rangle}{\Delta E}.$$

Applying Eq. (9) to Eq. (1) results in

$$\langle \Gamma_\alpha^g\downarrow|\vec{P}_{\rm ex}|\Gamma_\beta^g\uparrow\rangle=\sum_{\Gamma_i^u\downarrow}\langle \Gamma_\alpha^g\downarrow|\vec{P}|\Gamma_i^u\downarrow\rangle\frac{\gamma M(H,T)}{(E_{\Gamma_i^u\downarrow}-E_{\Gamma_\beta^g\uparrow})} + \sum_{\Gamma_j^u\uparrow}(\text{converse}) \tag{10}$$

and finally,

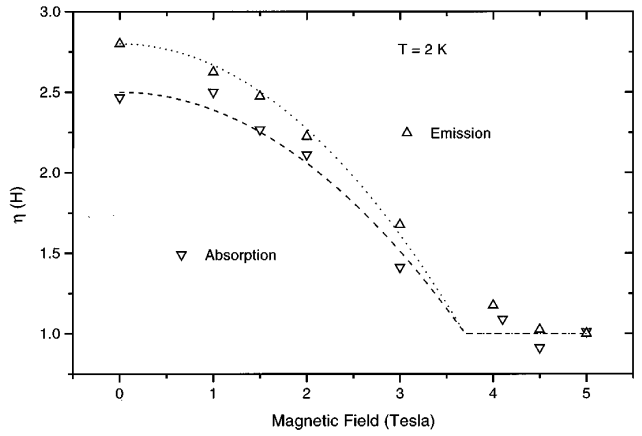

FIG. 1. The transition probability for $^4A_2 \rightarrow {}^2E$ calculated from absorption measurements done under magnetic field and at 2 K (down triangles). The same, but for $^2E \rightarrow {}^4A_2$ and from luminescence decay (up triangles). Dashed and dotted lines are from Eq. (13).

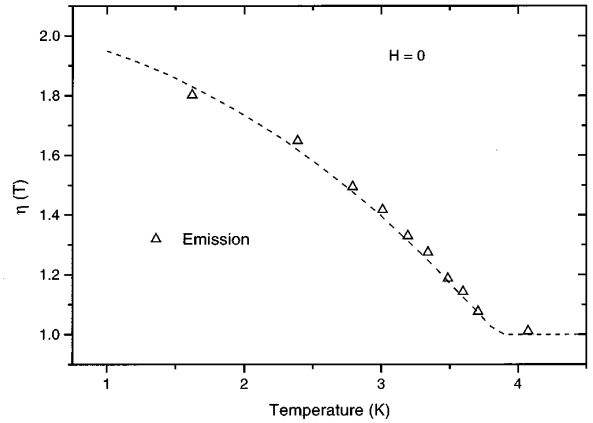

FIG. 2. The transition probability for $^2E \rightarrow {}^4A_2$ from luminescence decay (up triangles). The dashed line is from Eq. (13).

$$w_{\beta\rightarrow\alpha} \propto \left|\langle \Gamma_\alpha^g \downarrow | \vec{P}_{\mathrm{ex}} | \Gamma_\beta^g \uparrow \rangle\right|^2 \propto |\gamma|^2 (M(H,T))^2,$$

where $|\gamma|^2$ can be approximated to

$$|\gamma|^2 = |\varepsilon|^2 \left| \sum_l \frac{\langle \varphi(a)_k \downarrow, \varphi(a)_l \uparrow | V_{\mathrm{ex}(a-a)} | \varphi(a)_k \uparrow, \varphi(a)_l \downarrow \rangle}{\Delta E} \right|^2$$
$$\approx |\varepsilon|^2 l \upsilon^2 \qquad (11)$$

with υ as an average value for the perturbation term.

Thus, an ion in a spatial inversion-symmetric position without magnetic inversion symmetry will always have an electric-dipole matrix element between states with the same parity but with different spins, which is proportional to magnetization.

III. APPLICATION

In Fig. 1 the transition probability results for $^4A_2 - {}^2E$ at 2 K and under magnetic field are presented. The measurements have been done for absorption (down triangles) and emission (up triangles) and normalized to 1 for $H \geqslant 4$ T. The difference between them comes from the relation between Gd-Gd and Cr-Gd exchange: for emission, Gd-Gd exchange is bigger than Cr-Gd; for absorption, the opposite prevails.[2]

Figure 2 shows emission results for $H=0$ and $1.7\ \mathrm{K} \leqslant T \leqslant 4\ \mathrm{K}$.

The electric-dipole matrix element, due to crystal-field distortion and spin-orbit coupling[9] is expressed by

$$\langle \Gamma_\alpha^g \downarrow | \vec{P}_{\text{odd-so}} | \Gamma_\beta^g \uparrow \rangle = \sum_{\Gamma_i^u \downarrow, \Gamma_\gamma^g \downarrow} \langle \Gamma_\alpha^g \downarrow | \vec{P} | \Gamma_i^u \downarrow \rangle \frac{\langle \Gamma_i^u \downarrow | V_{\mathrm{odd}} | \Gamma_\gamma^g \downarrow \rangle}{(E_{\Gamma_i^u \downarrow} - E_{\Gamma_\gamma^g \downarrow})} \frac{\langle \Gamma_\gamma^g \downarrow | V_{S-O} | \Gamma_\beta^g \uparrow \rangle}{(E_{\Gamma_\gamma^g \downarrow} - E_{\Gamma_\beta^g \uparrow})} + \sum_{\Gamma_i^u \uparrow, \Gamma_\gamma^g \uparrow} (\vec{P} \leftrightarrows V_{S-O}), \qquad (12)$$

which will be assumed as the dominant one for $H \geqslant 4$ T (at 2 K), or $T \geqslant T_N$ (3.9 K, $H=0$ T). The V_{odd} can be a static or a phonon-induced (dynamic) crystal-field operator and V_{S-O} is the spin-orbit operator. Thus

$$\eta(H,T) = \frac{\left|\langle \Gamma_\alpha^g \downarrow | \vec{P}_{\mathrm{ex}} | \Gamma_\beta^g \uparrow \rangle\right|^2}{\left|\langle \Gamma_\alpha^g \downarrow | \vec{P}_{\text{odd-so}} | \Gamma_\beta^g \uparrow \rangle\right|^2} + 1 \qquad (13)$$

is the expression which should fit the experimental data.

In transition-metal ions, Γ_i^u states come from p-d hybridization and have high energy. Consequently, the sum that involves $\Gamma_i^u \downarrow, \Gamma_\gamma^g \downarrow$ in Eq. (6), Eq. (10), and Eq. (12) can be simplified by closure, resulting in

$$\frac{\langle \Gamma_\alpha^g \downarrow | \vec{P}_{\mathrm{ex}} | \Gamma_\beta^g \uparrow \rangle}{\langle \Gamma_\alpha^g \downarrow | \vec{P}_{\text{odd-so}} | \Gamma_\beta^g \uparrow \rangle} = \frac{(\varepsilon \text{ or } \gamma) M(H,T)}{\langle \Gamma_i^u \downarrow | V_{\mathrm{odd}} | \Gamma_\gamma^g \downarrow \rangle} \frac{(E_{\Gamma_\gamma^g \downarrow} - E_{\Gamma_\beta^g \uparrow})}{\langle \Gamma_\gamma^g \downarrow | V_{S-O} | \Gamma_\beta^g \uparrow \rangle}. \qquad (14)$$

For the $^4A_2 - {}^2E$ transition in $GdAlO_3$:Cr^{+3} we have $\langle \Gamma_i^u \downarrow | V_{\mathrm{odd}} | \Gamma_\gamma^g \downarrow \rangle (\text{dynamic}) \approx 100\ \mathrm{cm}^{-1}$; $\langle \Gamma_\gamma^g \downarrow | V_{S-O} | \Gamma_\beta^g \uparrow \rangle \approx 180\ \mathrm{cm}^{-1}$; $E_{\Gamma_\gamma^g \downarrow} - E_{\Gamma_\beta^g \uparrow} \approx 4000\ \mathrm{cm}^{-1}$.

As $M(H,T)$ is related to the sublattices antiparallelism, we have

$$M(H,T) = \sqrt{\sigma^2 - \sigma^2 \cos^2(\varphi)} = \sigma \sin(\varphi),$$

where φ is the angle between mean-field sublattice magnetization and applied field and $\sigma=\langle S\rangle/S$, given by[10]

$$\sigma(T)=B[(S^2/T)(J_1-J_2+\Delta K)\sigma(T)],$$

$$\cos(\varphi)=(g\mu_B H/S)/[(2J_1+\Delta K)\sigma].$$

To fit the experimental data, the following values were assumed: $l=3$; $\upsilon=0.54$; $\varepsilon=\Sigma_{k-\mathrm{odd}}\langle\Gamma_i^u\downarrow,\varphi(a)_k\uparrow|V_{ee}|\Gamma_\beta^g\uparrow,\varphi(a)_k\downarrow\rangle=7\ \mathrm{cm}^{-1}$; $J_1=0.67$ K; $J_2=-0.09$ K with ΔK equal to Ref. 10, and the dashed (γ) and dotted (ε) lines drawn in Fig. 1, for $\eta(H)$ resulting from Eq. (13). The same values are applied in Fig. 2 for $\eta(T)$.

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