

MAGNETIC FRANCK-CONDON EFFECT IN A SYSTEM CONSTITUTED BY A MAGNETIC IMPURITY IN A MAGNETIC MATRIX: Cr^{3+} in GdAlO_3

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*Presented at the Fourth Europhysical Topical Conference on "Lattice Defects in Ionic Crystals",
Dublin, Ireland, 1982*

Absorption and emission measurements of the ${}^4\text{A}_2\text{-}{}^2\text{E}$ transitions of Cr^{3+} in GdAlO_3 at $T \leq 4.2$ K, in magnetic fields up to 6 T parallel to the easy axis, are consistent with a magnetic Franck-Condon principle for which the energy difference between the absorption and emission lines arises mainly from the spin relaxation, rather than the neighboring ion space coordinates around the impurity. The Cr-Gd exchange-coupling constant changes with the applied magnetic field from $J=2.1$ cm^{-1} at $H=0$ to $J_{\text{sat}}=1.46$ cm^{-1} at high field.

INTRODUCTION

GdAlO_3 is a uniaxial antiferromagnet.¹ Its magnetic phase diagram showing the paramagnetic-antiferromagnetic-spin flop-saturated paramagnetic transitions have been determined as a function of temperature and magnetic field.^{2,3} The antiferromagnetic phase transition occurs at a Néel temperature $T_N=3.89$ K. Cr^{3+} ions (spin 3/2 in the ${}^4\text{A}_2$ ground state and 1/2 in the ${}^2\text{E}$ excited state) replace Al^{3+} ions at the center of a slightly distorted cube formed by eight nearest Gd^{3+} ions (spin 7/2). This configuration is called hereafter the Gd-cluster.

The ${}^4\text{A}_2\text{-}{}^2\text{E}$ absorption spectrum is rather complex and still not yet well understood; for $T > T_N$ the 2 main peaks located at $\sim 13,825$ cm^{-1} are separated by ~ 28 cm^{-1} . This splitting is independent of temperature⁷ which indicates that its origin is due to crystal field interaction and not due to an exchange interaction in the ${}^2\text{E}$ excited state of the Cr^{3+} ions as it was thought earlier.²⁻⁶ The ${}^2\text{E}\text{-}{}^4\text{A}_2$ emission spectrum consists of 4 lines located at $\sim 13,750$ cm^{-1} and separated by ~ 12 cm^{-1} . This splitting has been shown to originate from a strong Cr-Gd exchange interaction ($J=2.1$ cm^{-1}) in the ${}^4\text{A}_2$ ground state of Cr^{3+} . The most remarkable observation is the fact that the absorption and emission transition which connect the lowest energy state of the ${}^4\text{A}_2$ ground state and that of the ${}^2\text{E}$ excited state do not coincide and present an unusual Stokes shift of ~ 28 cm^{-1} . Moreover³ since the Cr-Gd exchange interaction is more than one order of magnitude larger than the antiferromagnetic Gd-Gd exchange $I=0.1$ cm^{-1} it is expected that below T_N the Gd spins of the cluster align themselves in the Cr-spin direction inducing a larger splitting between the four fluorescence lines. Surprisingly the separation decreases with decreasing temperatures indicating that the antiferromagnetic order prevails.

Recently a magnetic Franck–Condon principle was proposed to solve this puzzle.⁸ This contribution reports on the 4A_2 – 2E absorption and emission lines energies as a function of magnetic field which confirm the validity of the concept.

MAGNETIC FRANCK–CONDON PRINCIPLE

The magnetic Franck–Condon principle postulated for a magnetic impurity states that the magnetic order of its nearest surrounding will remain frozen during an electronic transition (absorption or emission) between its different magnetic levels.⁸ Figure 1a shows its application for Cr^{3+} impurity in GdAlO_3 .

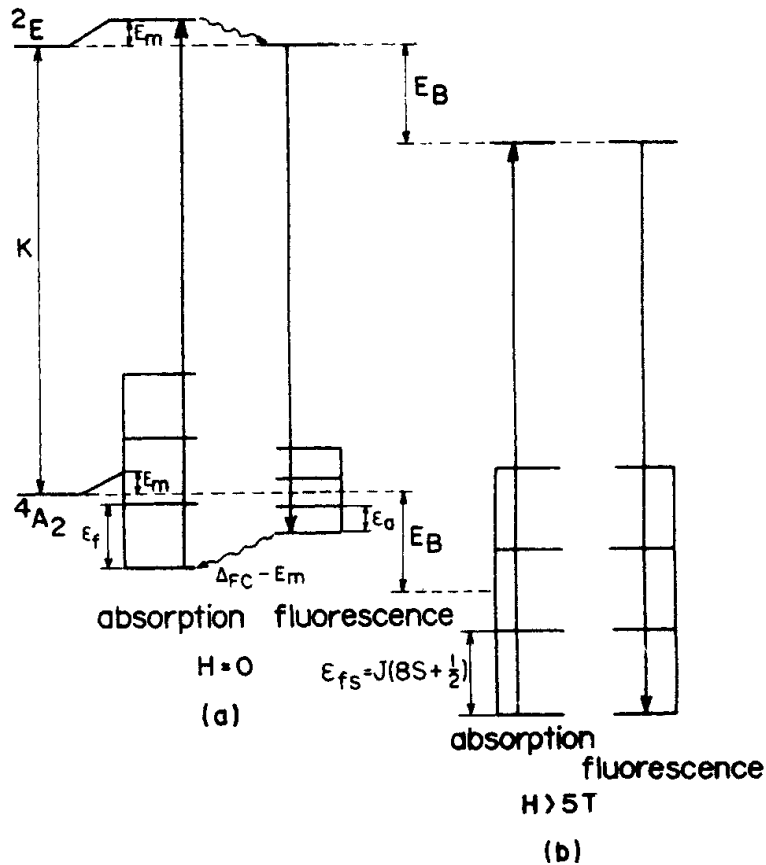


FIGURE 1 Energy levels and optical cycle describing the magnetic Franck–Condon principle (a) $H=0$ the magnetic order of the Gd^{3+} cluster remains frozen-in during vertical optical transitions; (b) relaxation of Gd^{3+} cluster spin coordinates occurs in the 2E excited states (ferromagnetic to antiferromagnetic order) and in the 4A_2 ground states (antiferromagnetic to ferromagnetic order).

For $T < T_N$ and in absence of external magnetic field the Gd^{3+} -cluster is ferromagnetically ordered in the ground state because of the strong exchange coupling between Cr^{3+} and Gd^{3+} ($J=2.1 \text{ cm}^{-1}$). Due to the presence of the Cr^{3+} ion, the cluster energy is lower in energy by an amount E_m and is stabilized by the energy

—(3/2) ε_f coming from the exchange interaction, where ε_f is the mean splitting of the four ground state levels of the Cr^{3+} . During the ${}^4\text{A}_2\text{-}{}^2\text{E}$ absorption transition, the Gd^{3+} cluster remains ferromagnetically ordered. In the excited states, as the exchange energy J' is very small,⁷ the cluster relaxes rapidly to an antiferromagnetically ordered relaxed state, releasing the excess energy E_m . It is worth noting from Figure 1a that E_m cancels out. During the fluorescence, the antiferromagnetic order of the cluster remains frozen so that the average splitting $\varepsilon_a < \varepsilon_f$, observed in the fluorescence, results from the interaction between Cr^{3+} ions and the antiferromagnetically ordered Gd^{3+} cluster. Eventually the cluster relaxes towards the more stable ferromagnetic state leading to an enhanced ground state splitting ε_f . The energy difference between the absorption and fluorescence line, called Δ_{FC} is given by

$$\Delta_{FC} = \frac{3}{2}(\varepsilon_a - \varepsilon_f), \quad \text{for } E_m < \Delta_{FC} \quad (1)$$

An external magnetic field tends to align the cluster spins along the field direction lowering the energy of the cluster by a certain amount E_B (Figure 1b). As the magnetic field is increased, the magnetic order of the cluster in the excited and ground states is mainly determined by the magnetic field rather than by the exchange interactions; when the field is high enough to saturate the cluster magnetization, spins relaxation in the Gd^{3+} cluster states no longer exists, and the Stokes shift Δ_{FC} vanishes.

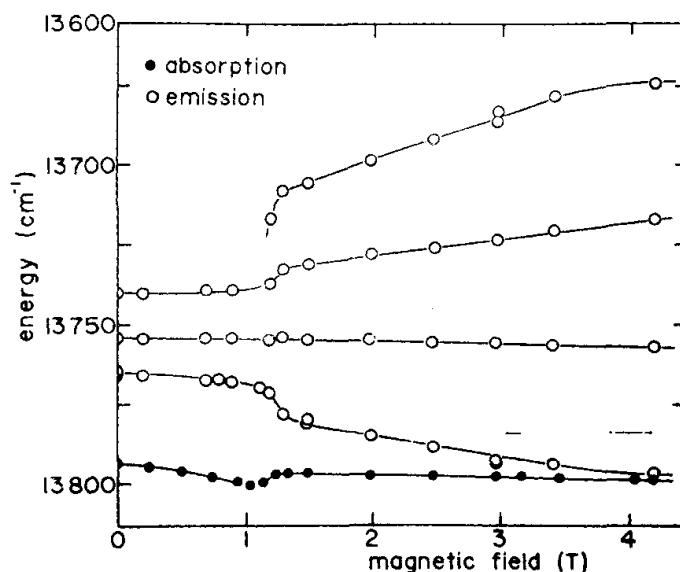


FIGURE 2 Emission and lowest absorption energies of the ${}^4\text{A}_2\text{-}{}^2\text{E}$ transition measured as a function of the applied magnetic field at $T=1.5$ K (open circles) emission, (solid circles) absorption.

EXPERIMENTAL RESULTS

Absorption and emission energies were measured at 1.5 K as a function of magnetic field applied along the easy *a*-axis using the same 50 cm Jarrel-Ash monochromator. Figure 2 shows the fluorescence and the lowest-energy absorption lines. The jumps at about 1.2 T reflect the antiferromagnetic spin-flop (AF-SF) phase transition as

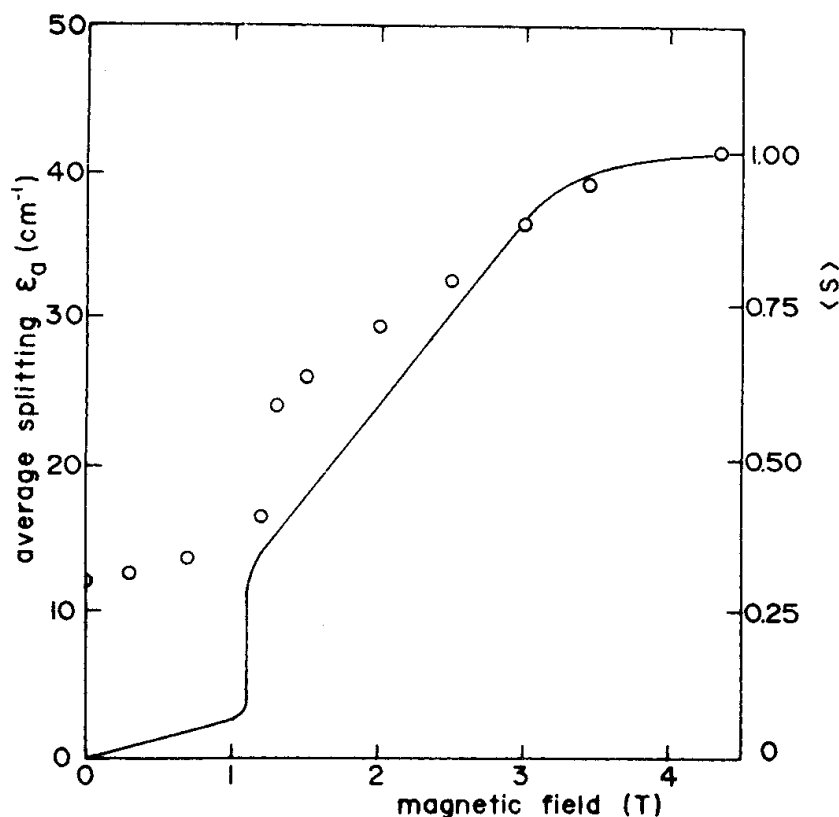


FIGURE 3 Average fluorescence splitting ϵ_a of the ${}^2E-{}^4A_2$ transitions of Cr^{3+} measured as a function of the applied magnetic field at $T=1.5$ K (open circles). The solid line is the magnetization of the pure GdAlO_3 matrix at 1.5 K, taken from Ref. 2.

predicted from the pure GdAlO_3 phase diagram.^{2,3} Above ~ 5 T, the absorption and the highest-energy fluorescence lines have the same energy, showing that lattice or spin relaxation do not contribute any more to the fluorescence shift. Absence of the usual Franck–Condon effect agrees with the Cr^{3+} results in nonmagnetic hosts such as ruby.⁹ The magnetic-field dependence of the average value ϵ_a of the three slightly different splittings observed in fluorescence and the Stokes shift Δ_{FC} are plotted in Figures 3 and 4. No data are yet available for ϵ_f to evaluate Δ_{FC} ; we can, however, estimate its value assuming that we can describe the ordering effect of the Cr^{3+} ion on the Gd^{3+} cluster by an effective Weiss field, which governs the splitting of the relaxed ground state at zero field $\epsilon_f(0)$. From the measured value $\Delta_{FC}(0)=28$ cm^{-1} and Eq. (1), we find $\epsilon_f(0)=32$ cm^{-1} . We estimate the Weiss-field size by comparing $\epsilon_f(0)$ with $\epsilon_a(H)$ measured in fluorescence under external field, since in this case the cluster polarization is mainly produced by the external magnetic field. According to Figure 3, this occurs for $H_w=2.4$ T; this value is certainly an upper limit for the effective field produced by the chromium on the Gd^{3+} cluster as part of the splitting is due to Cr–Gd spin correlations. Neglecting correlations and the AF–SF transition effect of the second neighbors on the cluster, we approximate $\epsilon_f(H)=\epsilon_a(H+2.4)$. Replacing ϵ_f in Eq. (1) we finally get Δ_{FC} as is shown by the solid line in Figure 4. Vanishing Δ_{FC} at high field is the main evidence for the proposed magnetic Franck–Condon effect governing the optical cycle. This is further corroborated by the close resemblance of the observed and the calculated Δ_{FC} at all fields.

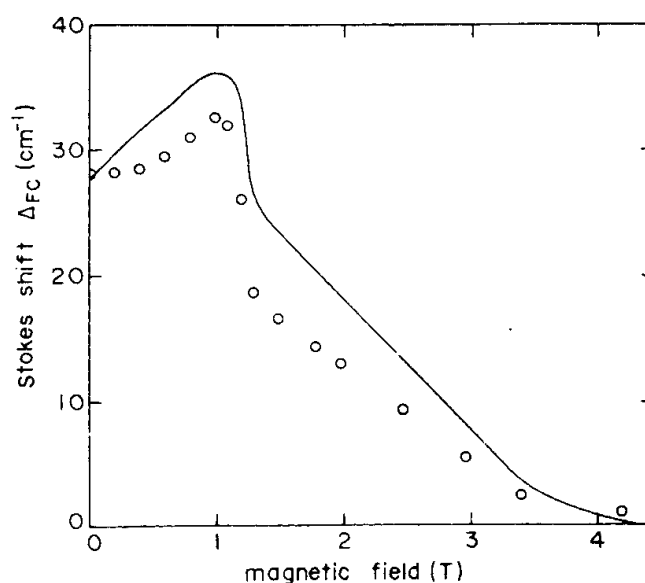


FIGURE 4 Stokes shift Δ_{FC} between the lowest-energy absorption line and the highest-energy fluorescence line measured as a function of the applied magnetic field at $T=1.5$ K; (open circles) experiment, (solid line) theory.

The Weiss field H_w can be written in terms of J as

$$H_w = \frac{3}{2} \frac{J}{g \mu_B}$$

where $g=2$ is the g factor of Gd^{3+} , μ_B the Bohr magneton and $3/2$ stands for the Cr^{3+} spin in the ground state. Using the previously reported value⁶ of $J=2.1$ cm^{-1} we find $H_w=3.37$ T, which is inconsistent with the 2.4 T obtained above. Here, J was adjusted to fit the experimental fluorescence splitting in the paramagnetic region and in absence of external magnetic field. On the other hand, at 1.5 K and for $H>4$ T, the cluster magnetization is practically saturated (solid line in Figure 3). In such a case, the splitting is given by $\varepsilon_a=J(8S+1/2)$, where $S=7/2$ stands for the Gd spin.⁸ Thus, from the observed saturated value of the splitting $\varepsilon_a=41.5$ cm^{-1} , we extract $J_{sat.}=1.46\pm 0.06$ cm^{-1} .

This indicates that the Cr-Gd coupling changes when the Gd cluster is forced into a ferromagnetic order, and implies that the value of J and the magnetization of the Gd cluster are linked. The correlation between these can be found fitting at each field the experimental splitting⁶ ε_a measured at 4.2 K to its theoretical expression.⁸ The J values obtained are plotted in Figure 5 as a function of the reduced magnetization $m(H)$ of the Gd cluster.

Further experimental evidence for the dependence of the Cr-Gd exchange coupling on magnetic order exists. From Figure 3, the reduced magnetization at 1.5 K in a field of 2.4 T is approximately 0.7. According to Figure 5, this corresponds to $J\approx 1.6$ cm^{-1} leading to a Weiss field of 2.57 T, in agreement with $H_w=2.4$ T. On the other hand, $J=2.1$ cm^{-1} leads to $H_w=3.3$ T at the nearest Gd sites, which almost completely saturates the cluster magnetization already at zero applied field: this

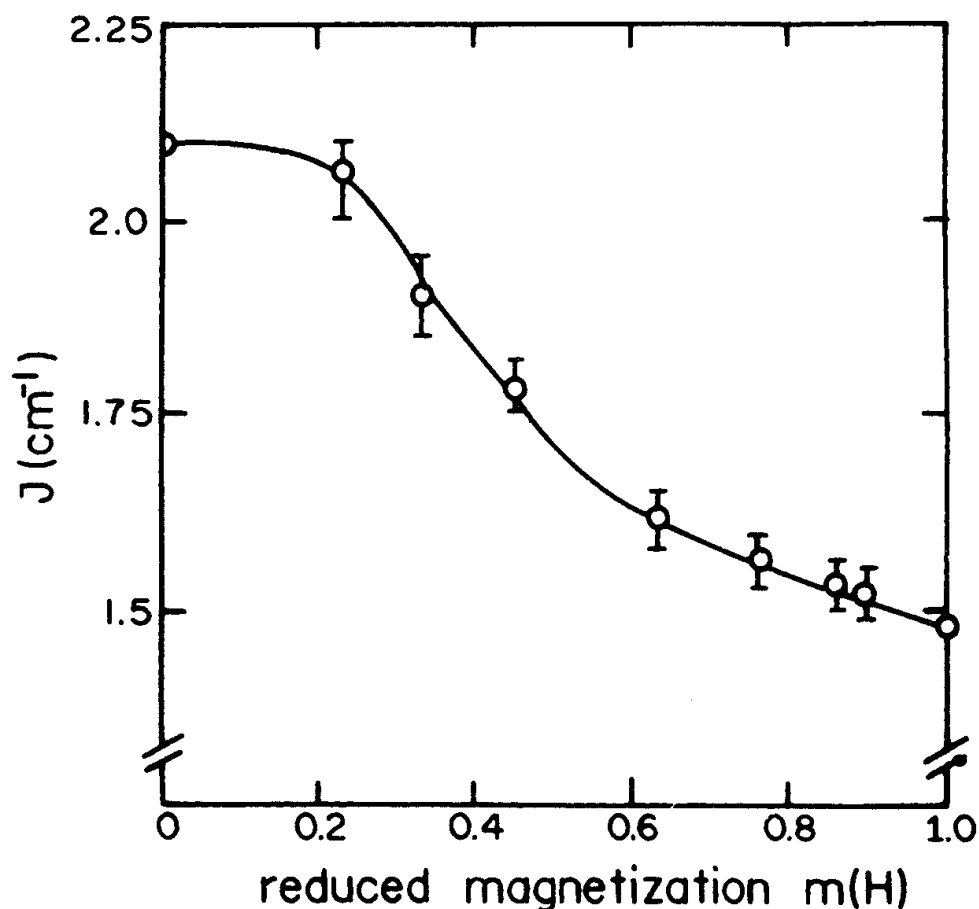


FIGURE 5 Calculated Cr-Gd exchange-coupling constant J (solid line) from experimental data of ϵ_a measured at 4.2 K (open circles) as a function of the Gd-cluster reduced magnetization $m(H)$, taken from Ref. 2.

would prevent the observation at 1.5 K of the effect of the spin-flop transition and of the initial rise of Δ_{FC} (Figure 4). Furthermore, the energy E_m necessary to promote the Gd cluster to a saturated ferromagnetic order is given approximately by $48 S^2 I = 59 \text{ cm}^{-1}$; it is larger than the Δ_{FC} observed: this would prevent any relaxation in the ground states after the fluorescence. On the other hand, the smaller J value accounts for the effects arising from non-saturating of the relaxed ground state.

The changes in the effective J may reflect the missing of higher order terms in the Hamiltonian or a change in the interatomic distances around the Cr^{3+} in the ${}^4\text{A}_2$ state as it is observed a simultaneous change of the fluorescence lifetimes and intensities related to the magnitude of the low-symmetry components of the local crystal field.

ACKNOWLEDGEMENT

This work was supported by FAPESP, CNPq, FINEP, BID (Brasil). We acknowledge fruitful discussions with Professors W. Baltensperger and J. Helman.

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