Evidence for the Magnetic Franck-Condon Effect in a System of an Interstitial Magnetic Impurity in an Antiferromagnetic Matrix: Cr^{3+} in $GdAlO_3$

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(Received 6 May 1982)

Absorption and emission measurements of the $^4A_2$-^2E 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 $J_{sat} = 1.46$ cm^{-1} at high field.

The Franck-Condon principle for magnetic states was recently introduced[1] to remove an inconsistency in interpreting the ^2E-$^4A_2$ luminescence spectra of Cr^{3+} in the antiferromagnet $GdAlO_3$ ($T_N = 3.89$ K). In this matrix, a Cr^{3+} ion replaces Al^{3+} at the center of a slightly distorted cube formed by the eight nearest Gd ions, here called the Gd^{3+} cluster. Luminescence spectra in the absence of magnetic field have been measured by Murphy and Ohlman[2] and by Blazey and Burns,[3] and by our group[4] in magnetic fields up to 6 T. The value $|J| = 2.1$ cm^{-1} of the effective exchange-coupling constant between the $\frac{3}{2}$ spin of the $^4A_2$ ground state of Cr^{3+} and the $\frac{7}{2}$ spin of a nearest-neighbor Gd^{3+} was obtained from the fluorescence-line splitting measured above T_N in absence of external magnetic field.[2-5] J decreases with increasing field down to a saturated (minimum) value 1.46 ± 0.06 cm^{-1}. As J in any case is more than one order of magnitude larger than the antiferromagnetic Gd-Gd exchange $I = 0.1$ cm^{-1},[6] below T_N the Gd spins in the cluster ought to align in the Cr-spin direction, thus inducing a larger splitting in the fluorescence.[5] Surprisingly, the splitting decreases with decreasing temperature for $T < T_N$, indicating that antiferromagnetic order prevails. A magnetic Franck-Condon effect was recently proposed[1] to solve this "puzzle." We report on absorption and emission line energies as a function of magnetic field, which confirm this concept.

Previous work[2,3] estimated a value J' for the excited Cr^{3+} ^2E level in the range 3.2–4.3 cm^{-1} from the splitting of the absorption line assumed to arise from exchange. This splitting (~ 30 cm^{-1}) does not change with temperature practically up to 77 K.[3,7] Thus we assume here that the ^2E level is split by a crystal field and that the Cr-Gd exchange-coupling constant J' in the ^2E excited Cr^{3+} ion is much smaller than that in the $^4A_2$ ground state. Thus, the Gd^{3+} cluster around an excited Cr^{3+} is antiferromagnetically ordered for $T < T_N$. A Franck-Condon principle applied to magnetic states keeps frozen the antiferromagnetic order of the Gd^{3+} cluster during the fluorescence transition,[8] so that the splitting ϵ_a observed in fluorescence results from the interaction between Cr^{3+} and the unrelaxed antiferromagnetically ordered Gd^{3+} cluster. Eventually, the cluster relaxes towards the more stable ferromagnetic state leading to an enhanced relaxed ground-state splitting ϵ_f, as illustrated in Fig. 1(a) for $J' = 0$. The Gd^{3+} cluster ferromagnetic state, higher in energy by E_m in the absence of chromium, is stabilized by the energy $-\frac{3}{2}\epsilon_f$ coming from the Cr-Gd exchange interaction. Analogously, during the absorption transition, the Gd^{3+} cluster remains ferromagnetically ordered. Afterwards, since J' is small, the cluster relaxes much faster than the luminescence lifetime, to an antiferromagnetic state, releasing the excess energy E_m. It is apparent from Fig. 1(a), that E_m cancels out and the energy dif-
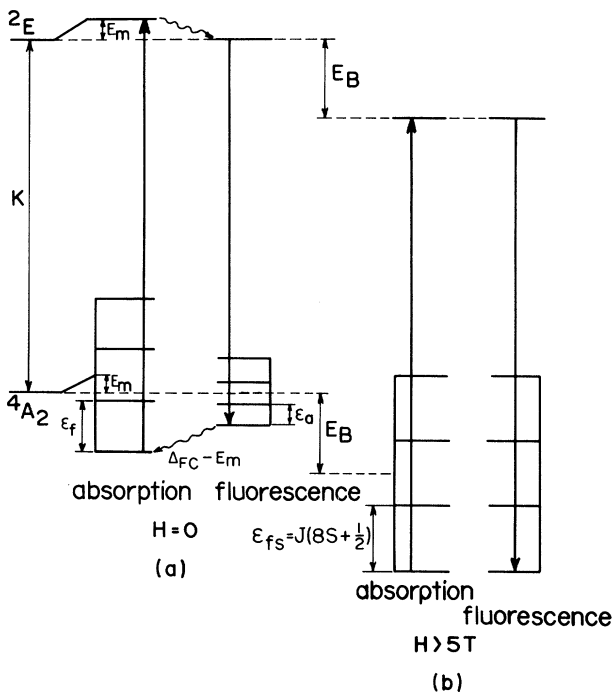

FIG. 1. Energy levels and optical cycle describing the mangetic Franck-Condon principle. (a) For $H = 0$, (b) for $H > 5$ T (saturation of the cluster magnetization). The magnetic order of the Gd^{3+} cluster remains frozen-in during vertical optical transitions; the relaxation of Gd^{3+} cluster spin coordinates occurs in the ^2E excited states (ferromagnetic to antiferromagnetic order) and in the $^4A_2$ ground states (antiferromagnetic to ferromagnetic order).

FIG. 2. Emission and lowest absorption energies of the $^4A_2$-^2E transition measured as a function of the applied magnetic field at $T = 1.5$ K. Open circles emission; solid circles, absorption.

ference between the absorption and fluorescence lines Δ_{FC}, when $E_m < \Delta_{FC}$, is given by

$$\Delta_{FC} = \tfrac{3}{2}(\epsilon_f - \epsilon_a). \tag{1}$$

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. 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, spin relaxation in the Gd^{3+} cluster states no longer exists, and the Stokes shift Δ_{FC} vanishes [Fig. 1(b)].

The $GdAlO_3$:Cr^{3+} crystal was grown from high-temperature solutions as described elsewhere.[7] Absorption and emission energies were measured at 1.5 K as a function of magnetic field applied along the easy a axis. Figure 2 shows the fluorescence and the lowest-energy absorption lines. The jumps at about 1.2 T reflect the antiferromag-
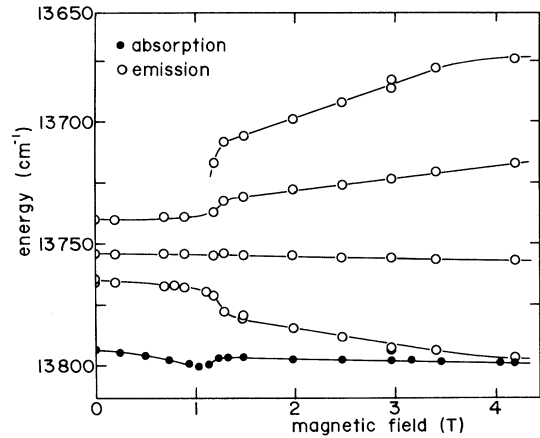
netic spin-flop (AF-SF) phase transition as predicted from the pure $GdAlO_3$ phase diagram.[6,9] Above ~ 5 T, the absorption and the highest-energy fluorescence lines have the same energy, showing that lattice or spin relaxations do not contribute to the fluorescence shift. Absence of the usual Franck-Condon effect agrees with the Cr^{3+} results in nonmagnetic hosts such as ruby.[10] The magnetic-field dependence of the average values ϵ_a of the three slightly different splittings observed in fluorescence and the shift Δ_{FC} are plotted in Figs. 3 and 4. Calculation of the Stokes shift Δ_{FC} requires knowledge of the splittings ϵ_f and ϵ_a of the relaxed and unrelaxed $^4A_2$ ground states, respectively. As no data are yet available for ϵ_f, we shall roughly estimate Δ_{FC} from the knowledge of ϵ_a alone. As the ordering effect of the Cr^{3+} ion on the Gd^{3+} cluster can be described by an effective Weiss field, the splitting of the relaxed ground state at zero field, $\epsilon_f(0)$, originates mainly from polarization of the cluster due to this Weiss field. From the measured value $\Delta_{FC} = 28$ cm^{-1} and Eq. (1), we find $\epsilon_f(0) = 32$ cm^{-1}. The Weiss-field size can now be estimated 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 Fig. 3, this occurs for $H_w = 2.4$ T, certainly an upper limit for the effective field produced by chromium on the Gd^{3+} cluster since 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 can approximate
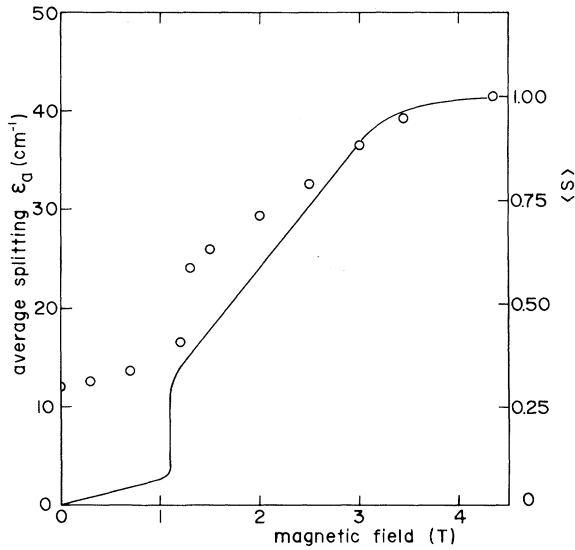
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FIG. 3. Average fluorescence splitting ϵ_a of the ^2E-$^4A_2$ transitions of Cr^{3+} measured as a function of the applied magnetic field at $T = 1.5$ K (open circles). The solid line is the magnetization of the pure $GdAlO_3$ matrix at 1.5 K. Taken from Ref. 9.

$\epsilon_f(H) = \epsilon_a(H + 2.4)$. Replacing ϵ_f in Eq. (1), we find the result for Δ_{FC} shown by the solid line in Fig. 4. Vanishing Δ_{FC} at high fields 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 calculated Δ_{FC} at all fields.

The Weiss field H_w can be written in terms of J as $H = \frac{3}{2}J/g\mu_B$, where $g = 2$ is the g factor of Gd^{3+}, μ_B the Bohr magneton, and $\frac{3}{2}$ stands for the Cr^{3+} spin in the ground state. Using the previously reported value[4] of $J = 2.1$ cm^{-1} gives a Weiss field $H_w = 3.37$ T, 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 Fig. 3). In such a case, the splitting is given by $\epsilon_a = J(8S + \frac{1}{2})$, where $S = \frac{7}{2}$ stands for the Gd spin.[1] Thus, from the observed saturated value of the splitting $\epsilon_a = 41.5$ cm^{-1}, $J_{sat} = 1.46 \pm 0.06$ cm^{-1} can be extracted.

This clearly shows that the Cr-Gd coupling changes when the Gd cluster is forced into a ferromagnetic order, implying that the value of J and the magnetization of the Gd cluster are somehow linked. The correlation between these can be found by fitting at each field the experimental
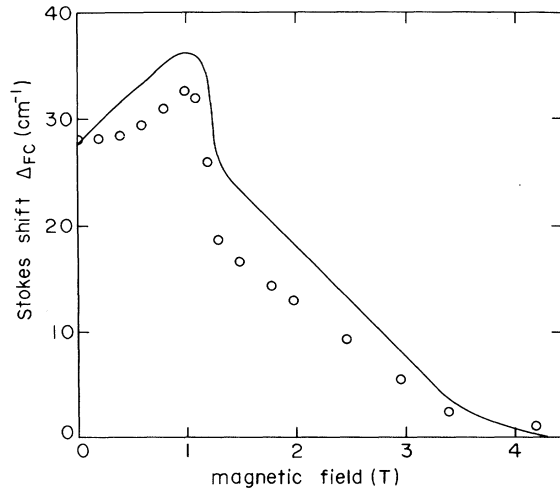

FIG. 4. Stokes shift Δ_{FC} between the lowest-energy absorption line and the highest-energy fluorescence line measured as a function of the applied magnetic field at $T = 1.5$ K: open circles, experiment; solid line, theory.

splitting[4] ϵ_a measured at 4.2 K by its theoretical expression.[1] The J values obtained are plotted in Fig. 5 as a function of the reduced magnetization $m(H)$ of the Gd cluster. In a previous report[4] a good fit was obtained for ϵ_a at 4.2 K by use of a phenomenological theory with a constant $J = 2.1$ cm^{-1}. The agreement was, however, fortuitous for two compensating reasons as explained in Ref. 1.

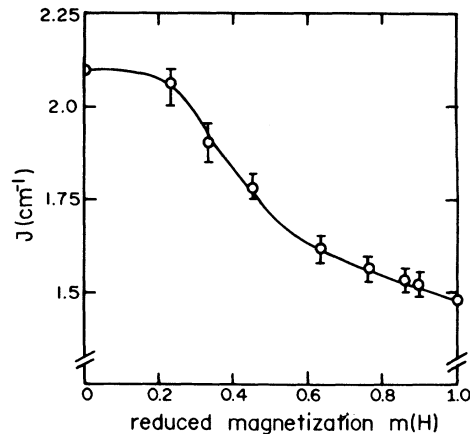Further experimental evidences for the dependence of the Cr-Gd exchange coupling on magnetic

FIG. 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. 9.

order exist. From Fig. 3, the reduced magnetiza-
tion at 1.5 K in a field of 2.4 T is approximately
0.7. According to Fig. 5, this corresponds to J
≈ 1.6 cm^{-1} leading to a Weiss field of 2.57 T, con-
sistent 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,
almost completely saturating the cluster magneti-
zation at zero applied field and preventing the ob-
servation at 1.5 K of the effect of the spin-flop
transition and the initial rise of Δ_{FC} (Fig. 4).
Furthermore, the energy E_m necessary to pro-
mote the Gd cluster to a saturated ferromagnetic
order is given approximately by $48S^2J = 59$ cm^{-1};
it is larger than the Δ_{FC} observed, therefore
preventing relaxation in the ground states after
the fluorescence. On the other hand, the smaller
J value accounts for the effects arising from non-
saturation 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 $^4A_2$ state with magnetic field as
there 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.

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Systematic Trends in Short-Range Coulomb Effects among Nearly One-Dimensional Organic Conductors

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A resolution to the controversy over the magnitude of the effective short-range Cou-
lomb interaction in molecular conductors is proposed by showing that it depends very
strongly on band filling because of intermolecular correlations.

The variety of electronic properties in nearly
one-dimensional organic charge-transfer salts is
remarkably rich. Structurally similar materials,
consisting of chemically similar molecules,
range from Mott insulators[1] through organic met-
als[2,3] and superconductors.[3] Although the sys-
tematics of this behavior have not been fully de-
veloped, there is little doubt that they depend
heavily upon the effective short-range interac-
tions among conduction electrons.[4] These inter-
actions, however, remain poorly characterized.
Intense controversy persists over whether they
are large[5] or small[2,6] compared with the conduc-
tion bandwidth, and strong experimental evidence
has appeared on each side.[2,5,6]

We seek here to resolve that controversy. We
argue that the short-range interactions in these
materials are not fixed, but are self-consistently