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COMPETITION BETWEEN THE Cr^{3+} - Gd^{3+} DIRECT EXCHANGE AND
SUPEREXCHANGE IN Cr DOPED GdAlO_3

by

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Abstract

The temperature dependence of the fluorescence spectrum of Cr^{3+} diluted impurities in GdAlO_3 and the magnetic Franck-Condon effect observed in this system indicate that the exchange coupling constant J_E between Cr^{3+} in the 2E excited state and Gd^{3+} is very small, in the sense that $|J_E| \ll J_g$, where J_g is the exchange coupling constant between Cr^{3+} in the ground state 4A_2 and Gd^{3+} . Here this is interpreted as resulting from a cancellation between the ferromagnetic direct $\text{Cr}^{3+} - \text{Gd}^{3+}$ exchange interaction and the antiferromagnetic superexchange which takes place through the oxygen ions.

Key-words: Exchange and superexchange interaction; Impurity absorption in insulators; Photoluminescence.

1. Introduction

The temperature and magnetic field dependence of the optical spectrum of Cr^{3+} impurities substituting for Al^{3+} in the antiferromagnet GdAlO_3 have been extensively studied both experimentally and theoretically [1-11]. A model has been developed which accounts for the splittings and linewidths of the fluorescence spectrum [8,11], yielding the phenomenological exchange coupling constants $J_g = 2.05 \text{ cm}^{-1}$ and $J'_g = -0.25 \text{ cm}^{-1}$ between the Cr^{3+} ion in the ground state ${}^4\text{A}_2$ and its nearest neighbor (n.n) and next nearest neighbor (n.n.n) Gd^{3+} ions, respectively [11]. Here a positive exchange constant means antiferromagnetic coupling. It has also been shown that a consistent description of the temperature dependence of the fluorescence spectrum and of the magnetic Franck-Condon effect observed in this system requires that the exchange coupling constant J_E between Cr^{3+} in the excited state ${}^2\text{E}$ and the neighboring Gd^{3+} ions be much smaller than J_g (at least one order of magnitude smaller) [8,10].

The vanishingly small value of J_E is puzzling and we propose that it may result from a fortuitous cancellation between a ferromagnetic direct $\text{Cr}^{3+} - \text{Gd}^{3+}$ exchange interaction and an antiferromagnetic superexchange through the oxygen ions. The calculation of phenomenological exchange constants from first principles involves a large computational effort and even so the results may not be accurate enough to give a reliable value for a parameter which represents the sum of two contributions with opposite signs. Nevertheless, we demonstrate here

the plausibility and consistency of the cancellation mentioned above as resulting from the expansion of the Cr^{3+} wavefunctions in going from the ${}^4\text{A}_2$ to the ${}^2\text{E}$ state.

2. Model

We admit that a spin interaction between Cr^{3+} and Gd^{3+} takes place both through the direct overlapping of the Cr -3d and Gd -4f wavefunctions, and through the intermediate O -2p wavefunctions. The former is ferromagnetic, while the latter is usually antiferromagnetic. The phenomenological exchange coupling constants which describe the net interaction are therefore written as

$$J_g = J_{gd} + J_{gs}$$

$$J'_g = J'_{gd} + J'_{gs} \quad (1)$$

$$J_e = J_{ed} + J_{es}$$

$$J'_e = J'_{ed} + J'_{es}.$$

The subindices g and e stand for ground and excited state, respectively; d and s denote direct and superexchange interaction and the primes refer to next nearest neighbors.

The states ${}^4\text{A}_2$ and ${}^2\text{E}$ of Cr^{3+} are both derived from the cubic t_g^3 configuration [12] (have the same spatial shape), dif

fering only in the total spin and radial wavefunctions. The 2E state is a little bit expanded in relation to the 4A_2 state to accommodate the increased Coulomb repulsion between electrons due to its lower spin.

Since the direct exchange interaction results from the overlapping of the wavefunctions of the ions, we assume that, asymptotically, it depends exponentially on the $Cr^{3+} - Gd^{3+}$ distance:

$$J_{gd} = b \exp(-R/r_g)$$

$$J'_{gd} = b \exp(-R'/r_g)$$

(2)

$$J_{ed} = b \exp(-R/r_e)$$

$$J'_{ed} = b \exp(-R'/r_e).$$

Here, $R = (\sqrt{3}/2)a$ and $R' = (\sqrt{11}/2)a$ are the distances from Cr to the n.n and n.n.n Gd's, respectively; $a = 3.731 \text{ \AA}$ is the lattice constant, and r_g and r_e describe the range of the direct exchange interactions. Since the 2E state is expanded in relation to the 4A_2 state, we expect $r_e > r_g$. Considering that both the 4A_2 and 2E states have the same shape, a single factor b is used.

The superexchange interaction between Cr^{3+} and its n.n.n. Gd^{3+} ions will be neglected: $J'_{gs} = J'_{es} = 0$. Such interaction involving at least two intermediate oxygens, although very difficult to estimate, is certainly small in comparison with the

others. Indirect or polarization exchange should also be negligible in this insulating host [13,14]. Furthermore, we assume that the superexchange interaction does not depend on whether Cr^{3+} is in the ground or excited state, and put

$$J_{gs} = J_{es} . \quad (3)$$

The underlying idea in the model is that the overlap integrals responsible for the direct exchange are correlated to the range of the corresponding 3d orbitals of Cr^{3+} , more precisely, it seems reasonable to identify the quantity $p = (r_e - r_g)/r_g$ with the relative variation of the radii of Cr^{3+} in the states 2E and 4A_2 . With this in mind, we performed self-consistent calculations for the free ion Cr^{3+} to investigate approximately the effect of different spin states on the range of the 3d wave function.

The Cr^{3+} wavefunctions were calculated employing the self-consistent spin-polarized atomic local density method [15], with the Kohn-Sham exchange potential [16]. All radial functions are defined numerically on a one-dimensional grid. Mean values $\langle r \rangle$ are obtained by numerical integration. The 4A_2 state was simulated by prescribing an occupation of the d-orbitals of three spin up electrons. The state 2E was simulated by prescribing an occupation with total spin 1/2. The corresponding mean radii of the 3d orbitals were calculated with the result $(\langle r \rangle_{1/2} / \langle r \rangle_{3/2}) - 1 = 0.007$, which we use as an approximate value for p [17]. It is encouraging that the difference of the calculated total energies of the spin 1/2 and 3/2 con

figurations, $E_{1/2} - E_{3/2} = 2.5$ eV, comes close to the energy of the fluorescent transition $E_{2E} - E_{4A_2} = 1.73$ eV [4].

3. Results and discussion

The model contains the four adjustable parameters J_{gs} , b , r_g and r_e , which must satisfy the following equations

$$\begin{aligned} J_g &= b \exp(-R/r_g) + J_{gs} = 2.05 \text{ cm}^{-1} \\ J'_g &= b \exp(-R'/r_g) = -0.25 \text{ cm}^{-1} \\ J_E &= b \exp(-R/r_e) + 3b \exp(-R'/r_e) + J_{gs} = 0 \\ p &= (r_e - r_g)/r_g = 0.007. \end{aligned} \tag{4}$$

The factor 3 in the expression for J_E accounts for the fact that there are three n.n.n. for each n.n. Gd. The first three equations are imposed by experiment and the fourth results from the theoretical calculation. This yields $J_{gs} = 35.2 \text{ cm}^{-1}$, $b = -0.85$ eV and $r_g = 0.606 \text{ \AA}$. An error of 10% in p implies errors of 10%, 20% and 2% in J_{gs} , b and r_g , respectively. The numerical values obtained for the parameters seem reasonable. The superexchange coupling J_{gs} turns out to be of the order of $10 - 100 \text{ cm}^{-1}$, like in many magnetic insulators. Although Eqs. (2) are not intended to hold down to $R=0$, it is satisfying that the parameter b results of the order of one eV as expected for intraatomic exchange. The value obtained for r_g is comparable to the radius

of the ion Cr^{3+} (0.69 Å) [18], as derived from measured interatomic distances in solids, and to the calculated $\langle r \rangle_{3/2} = 0.59 \text{ Å}$. We remind, however, that these results rely on Eq. (3) which cannot be a priori justified without falling into the difficulties inherent to first-principles calculations of superexchange. A departure from it would influence the numerical values of the parameters.

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