Mechanism for nonuniform broadening of the NMR spectrum of orbitally degenerate centers in crystals with mixed-valence ions

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A mechanism is proposed for the nonuniform broadening of the NMR spectrum of Jahn–Teller centers formed by mixed-valence ions. The effect stems from a nonuniform distribution of the net charge and of the spin density among the various nuclei of the impurity center upon the splitting of a degenerate term in the random crystal fields. This broadening is governed by isotropic hyperfine interactions and is distinct from the conventional mechanisms, which stem from anisotropic hyperfine interactions at Jahn–Teller ions.

1. In cubic magnetic materials it is fairly common to find ions of a $3d$ element in two states, which differ in valence; one of these states may be orbitally degenerate. Charge-transfer processes strongly influence the NMR spectrum of these ions. These processes are pertinent to, for example, ions of an impurity center (a cluster) formed by the nearest neighbors of a nonisovalent impurity or a vacancy. There is particular interest in the behavior of such centers which have a degenerate ground state. Such centers have an anomalously strong influence on the magnetic-anisotropy constant, the magnetostriction constant, resonance properties, and other properties of magnetically ordered crystals.

In this letter we wish to analyze the distinctive features of the spectrum of NMR ions in which the $3d^n$ electron configuration is characterized by a nondegenerate ground state, while the $3d^{n\mp1}$ configuration is characterized by an orbital doublet (an E term). This term can arise upon a splitting of a cubic T term by a trigonal crystal field, as is typical of Co^{2+}, Fe^{2+}, Cr^{4+}, etc., ions in octahedral sites of cubic magnetic materials with the spinel or garnet structure. As the impurity center in these crystals we consider a triad of exchange-coupled $3d$ ions with an extra t_{2g} hole, which arises (for example) when there are anion vacancies (Fig. 1). A distinctive feature of Jahn–Teller states of such clusters is seen when the degeneracy is lifted: The lifting of degeneracy gives rise to a nonuniform distribution of the net charge which accompanies a characteristic deformation of the system. In random crystal fields, the NMR spectrum of the ions of the cluster spreads out into a band with a width on the order of the parameter of the isotropic hyperfine interaction. The proposed mechanism for the nonuniform broadening of the spectra of nuclear transitions is typical of a broad

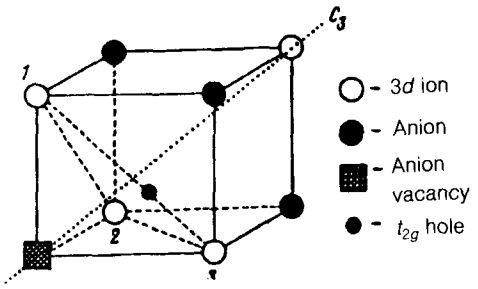

FIG. 1. Triad of exchange-coupled 3*d* ions in octahedral sites of a spinel with an excess hole.

class of coordination compounds, including high-T_c superconducting oxides and doped fullerites.

2. For simplicity, in describing the hyperfine interaction in the impurity complex we restrict the discussion to the isotropic term in the Hamiltonian $\hat{H}_{\rm hf}$ for ions with the $3d^n$ configuration,

$$\hat{H}_{\rm hf}\,(3d^n)=A_0'(\mathbf{IS}'), \tag{1}$$

and to the isotropic term and the anisotropic term which is linear in the orbital angular momentum for the $3d^{n\mp1}$ state,[1]

$$\hat{H}_{\rm hf}\,(3d^{n\mp1})=A_0(\mathbf{IS})+A_1\hat{\sigma}_\zeta I_\zeta\,,\quad \hat{\sigma}_\zeta=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}. \tag{2}$$

Here I is the nuclear spin of the 3*d* ion; $\mathbf{S}$, $\mathbf{S}'$and A_0, A_0' are the spins and the parameters of the isotropic hyperfine interaction in the $3d^n$ and $3d^{n\mp1}$ configurations; $\hat{\sigma}_\zeta$ is an orbital operator defined in the space of functions of the E term; and the subscript ζ means the projection onto the trigonal symmetry axis.

The NMR frequencies of a cluster formed by a collectivization of an excess t_{2g} electron or hole at the 3*d* ions nearest the impurity depends strongly on the structure of its ground state. The splitting of the degenerate term stems from the spin–orbit coupling and the low-symmetry crystal fields. It is described by the following effective Hamiltonian:[2,3]

$$\hat{H}_{\rm el}=-q\lambda\hat{\sigma}_\zeta S_\zeta+h_\xi\hat{\sigma}_\xi+h_\eta\hat{\sigma}_\eta\,,\quad \hat{\sigma}_\xi=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\quad \hat{\sigma}_\eta=\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}, \tag{3}$$

where h_ξ and h_η are components of the random low-symmetry crystal field at the cluster, λ is the parameter of the spin–orbit coupling, and q is a parameter of the reduction of the spin–orbit coupling in the ground state of the triad in comparison with an individual $3d^{n\mp1}$ ion.

In the wave function Ψ_0 of the lowest of the split states of the complex, with the maximum projection of the total spin, the wave functions of the individual centers can be represented with different weights:

$$\Psi_0 = \sum_{k=1}^{3} [C_{0,k}^{(+)}\varphi_k(+) + C_{0,k}^{(-)}\varphi_k(-)], \tag{4}$$

where the functions $\varphi_k(\mp)$ represent antisymmetrized products of wave functions of the ions of the triad with a t_{2g} electron or a hole in site k ($k=1-3$) in one of the states E_μ ($\mu = \mp$) (Ref. 4). This lowering of the symmetry of the triad in the random crystal fields causes a "splitting" of the NMR frequencies ω_k associated with the various ions of the triad:

$$\omega_k^2 = \{[A_0'S' + (A_0S - A_0'S')W_k]^2 + A_1^2 \Delta W_k^2$$
$$+ 2[A_0'S' + (A_0S - A_0'S')W_k]A_1 \Delta W_k(\mathbf{n}\cdot\mathbf{n}_k)\},$$
$$W_k = |C_{0,k}^{(+)}|^2 + |C_{0,k}^{(-)}|^2, \quad \Delta W_k = [|C_{0,k}^{(+)}|^2 - |C_{0,k}^{(-)}|^2]^2. \tag{5}$$

Here $\mathbf{n}_k$ is a unit vector along the local trigonal axis of ion k in the triad. The difference (ΔW_k) between the populations of the ($+$) and ($-$) states at ion k is due to the spin–orbit coupling; a difference between the values of W_k arises only when there are random crystal fields.

There is accordingly a new mechanism for an inhomogeneous broadening of NMR frequencies. This mechanism stems from charge-transfer effects and is associated with isotropic hyperfine interactions. This mechanism is important for clusters of all types with a degenerate ground state in systems with significant random fields.

In the absence of random fields, the NMR frequencies of the ions of the triad are

$$\omega_k^2 = \{\omega_0^2 + (qA_1/3)^2 + 2\omega_0 qA_1(\mathbf{n}\cdot\mathbf{n}_k)/3\}, \quad \omega_0 = |(2/3)A_0'S' + (1/3)A_0S|, \tag{6}$$

where we have used the circumstance that we have $W_k = 1/3$ for all k when there is a splitting of the degenerate E term by a spin–orbit coupling. Transfer effects lead to a renormalization of the parameters of the isotropic and anisotropic hyperfine interactions in comparison with isolated Jahn–Teller ions.

When there are substantial random fields, which dominate the splitting of the degenerate state, we have the following result from expression (5) for the NMR frequencies ω_k:

$$\omega_k = |2A_0'S' + A_0S + (A_0'S' - A_0S)\cos(\varphi - \varphi_k)|/3, \tag{7}$$
$$\cot\varphi = h_\xi/h_\eta, \quad \varphi_k = 2\pi k/3.$$

The spectrum $I(\omega)$ of NMR frequencies takes the following form after an average is taken over various angular configurations of the random fields:

$$I(\omega) = \pi^{-1}\{(A_0'S' - A_0S)^2/9 - (\omega - \omega_0)^2\}^{-1/2}. \tag{8}$$

An absorption band of width $2|A_0'S' - A_0S|/3$ thus arises, with peaks in the intensity $I(\omega)$ at the frequencies

$$\omega_\mp = \omega_0 \mp (A_0'S' - A_0S)/3, \tag{9}$$

corresponding to the edges of the spectral distribution. One of the absorption edges $\omega_{\mp}$ in (9) is equal to the NMR frequency of an ion with a nondegenerate $3d^n$ electron configuration. In this limit, the spin–orbit coupling is completely "frozen," and the nonuniform broadening is due entirely to the isotropic hyperfine interactions.

For an arbitrary relation between the parameters $q\lambda$ and the random-field dispersion Γ, spectra of both types may be seen. In this case, the role of transfer effects will consist of (on the one hand) reducing the spin–orbit coupling parameters and (on the other) renormalizing the parameters of the isotropic hyperfine interaction and the associated inhomogeneous broadening of the NMR spectrum of degenerate centers in random crystal fields. The contribution of the anisotropic hyperfine interaction to the NMR frequencies depends on the angle (ϑ) between the magnetization and the symmetry axis of the triad. It falls off as ϑ approaches $\pi/2$ (the average value of the orbital angular momentum satisfies $\langle \sigma_\xi \rangle \propto \cos\vartheta$). The effect of random fields on the shape of the spectrum increases sharply in this case.

Spectral features like those discussed here have been observed in the NMR spectra of mixed-valence chromium ions in chromium chalcogenide spinels.[5,6]

In conclusion we would like to point out that the oxide high-T_c superconductors, in which orbitally degenerate complexes with oxygen ions of intermediate valence can form,[7] look promising as a field for applying these results.

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