

Dynamic contraction of the NMR spectrum of Jahn–Teller Mn^{3+} ions in a lithium ferrite

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The high-temperature NMR spectrum of Jahn–Teller ions with a highly anisotropic interaction has been studied experimentally. A dynamic contraction of the NMR spectrum of Mn^{3+} ions has been observed in a lithium ferrite. The contraction stems from relaxation processes in the orbital subsystem. As the temperature is raised, the populations of the Jahn–Teller states, which reduce the quadrupole splitting of individual lines and which contract the overall absorption band, become equal.

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1. In this letter we are reporting an experimental study of the spectra of NMR frequencies of impurity Jahn–Teller ions in cubic magnetic materials at high temperatures. We selected for this study the Jahn–Teller ions Mn^{3+} in octasites (B) of a lithium ferrite. The hyperfine fields at the nuclei of $Mn^{3+}(B)$ ions have a substantial anisotropic component and therefore depend strongly on the state of the orbital subsystem. The splitting of the lowest-lying vibron states of the $Mn^{3+}(B)$ ion is determined primarily by the low-symmetry crystal field of the lithium sublattice of the ferrite.

At low temperatures, at which the characteristic parameter of the splitting of a degenerate term satisfies $E \gg k_B T$, and the quantum-mechanical and quantum-statistics expectation values of the orbital variables are essentially the same, the NMR spectrum is independent of the relation between the resonant frequency ω and the relaxation time τ of the Jahn–Teller subsystem. The resultant NMR spectrum is a superposition of several anisotropic spectra of Mn^{3+} ions in crystallographically different octasites.

At high temperatures, $k_B T \gg E$, the situation is radically different if $\omega \tau \ll 1$. The anisotropic components of the hyperfine fields are determined by the difference between the populations of the split states; they tend toward zero as the temperature is raised. As a result, there should be a significant contraction of the NMR absorption band of the Jahn–Teller ions. A similar effect observed in the ESR of Cu^{2+} ions has been labeled a “dynamic spectral contraction” (Ref. 1, for example). A distinctive feature of these intranuclear transitions is that not only the width of the total absorption band but also the shapes of the individual peaks depend on the temperature. The reason is that the parameters of the quadrupole interaction, which determine the widths of these peaks, also

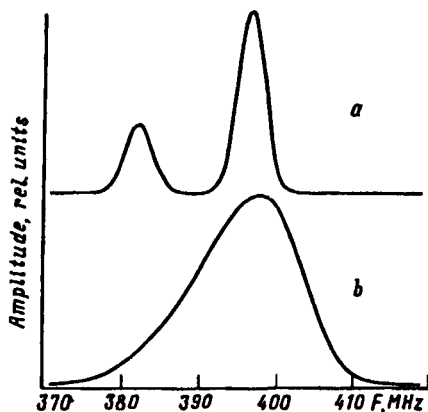


FIG. 1. NMR spectra of $Mn^{3+}(B)$ in $Li_{0.5}Fe_{2.5}O_4:Mn$ single crystals at 300 K. a— $H_0=0$; b— $H_0=1.5$ kOe.

depend on the populations of the Jahn–Teller states which are split in the low-symmetry fields.

2. The NMR spectra of $Mn^{3+}(B)$ ions were measured by a spin-echo method on single crystals of manganese-doped lithium ferrites (the doping level was 1.5% by mass) at temperatures of 77 and 300 K. The NMR spectrum of this system was studied at 4.2 K in Ref. 2. Unfortunately, the intensity of the NMR signals of $Mn^{3+}(B)$ was not sufficient for measurements of the spectra of an individual single crystal in an external magnetic field. Accordingly, the mass was increased by preparing a sample as a disordered set of single crystals fixed in paraffin. When a saturating external magnetic field was applied, the magnetization M in each single crystal had its own direction. The resultant spectrum consisted of a superposition of the NMR spectra of the $Mn^{3+}(B)$ in each single crystal. At 77 K the spectra were measured in fields up to 2.5 kOe. There was essentially no change in the spectra over the field range 1.5–2.5 kOe. At 300 K, the measurements were carried out in an external field of 1.5 kOe. The intensity of the NMR signal was insufficient for measurements in stronger fields.

Figures 1 and 2 show NMR spectra of $Mn^{3+}(B)$ ions in a zero external magnetic field (a) and in a field of 1.5 kOe (b) at temperatures of 300 and 77 K, respectively. In the absence of an external field, i.e., when the directions of M are parallel to the $[111]$ axes, the width of the lines in the NMR spectra of the $Mn^{3+}(B)$ ions decreases from 9 to 4 MHz as the temperature is raised from 77 to 300 K. This width remains constant over the temperature range from 4.2 to 77 K.

When an external magnetic field of 1.5 kOe is applied, the frequency range of the spectrum decreases with increasing temperature. The absorption peak at 300 K is more than 25 MHz lower than at 77 K.

3. Here are the Hamiltonians of the hyperfine (H_{HF}) and quadrupole (H_Q) interactions of the Mn^{3+} ion in an octasite of a spinel with a $[111]$ trigonal axis:

$$H_{HF} = H_{HF}^{cub} + H_{HF}^{trig}; \quad (1)$$

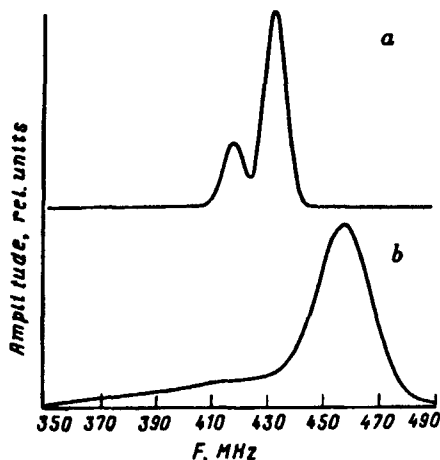


FIG. 2. NMR spectra of $Mn^{3+}(B)$ in $Li_{0.3}Fe_{2.5}O_4:Mn$ single crystals at 77 K. a— H_0 ; b— $H_0=1.5$ kOe.

$$H_{HF}^{cub} = A_1(\mathbf{IS}) + (A_2/2)\{U_{E\varphi}(3I_zS_z - (\mathbf{IS})) + \sqrt{3}U_{E\epsilon}(I_xS_x - I_yS_y)\},$$

$$H_{HF}^{trig} = A_3(3I_\zeta S_\zeta - (\mathbf{IS})) + (A_4/4)\{U_{E\vartheta}(2I_xS_y + 2I_yS_x - I_xS_z - I_zS_x - I_yS_z - I_zS_y) + \sqrt{3}U_{E\epsilon}(I_yS_z + I_zS_y - I_xS_z - I_zS_x)\},$$

$$I_\zeta = (I_x + I_y + I_z)/\sqrt{3}, \quad S_\zeta = (S_x + S_y + S_z)/\sqrt{3};$$

$$H_Q = (C/2)\{U_{E\vartheta}(3I_z^2 - I(I+1)) + \sqrt{3}U_{E\epsilon}(I_x^2 - I_y^2)\}. \quad (2)$$

Here S and I are the electron and nuclear spins of the Mn^{3+} ion; A_1 , A_2 , A_3 , and A_4 are parameters of the isotropic and anisotropic hyperfine interactions;³ C is the parameter of the quadrupole splitting; and $U_{E\vartheta}$ and $U_{E\epsilon}$ are orbital operators which act in the space of functions of the cubic E term.⁴ The quadrupole interactions due to the presence of the seed trigonal symmetry in octasites are comparatively small; we are omitting them to streamline the equations. The lowering of the symmetry of the octasites in the lithium ferrite is incorporated by the presence of a corresponding splitting of the degenerate state.

According to expressions (1) and (2), the NMR frequency of the $Mn^{3+}(B)$ ions in the position under consideration is

$$\omega = \gamma_n |\mathbf{H}|, \quad H_i = \sum_{j=x,y,z} T_{ij} M_j / |\mathbf{M}|, \quad \gamma_n T_{ij} = \begin{pmatrix} c - \Delta_- & h & d_+ \\ h & c - \Delta_+ & d_- \\ d_+ & d_- & c - \Delta \end{pmatrix}, \quad (3)$$

$$c = A_1 \langle S \rangle_T, \quad \Delta = A_2 \langle S \rangle_T \langle U_{E\vartheta} \rangle, \quad \Delta_{\pm} = A_2 \langle S \rangle_T \langle -U_{E\vartheta} \pm \sqrt{3}U_{E\epsilon} \rangle / 2,$$

$$h = (A_3 + A_4 \langle U_{E\vartheta} \rangle / 2) \langle S \rangle_T, \quad d_{\pm} = (A_3 - A_4 \langle U_{E\vartheta} \pm \sqrt{3}U_{E\epsilon} \rangle / 4) \langle S \rangle_T.$$

Here γ_n is the nuclear gyromagnetic ratio; $\langle \dots \rangle_T$ means a quantum-statistics expectation value; $\langle \dots \rangle$ is correspondingly the quantum-mechanical ($\omega\tau \gg 1$) or quantum-statistics ($\omega\tau \ll 1$) expectation value; and $\langle S \rangle_T \equiv |\langle S \rangle_T|$.

Oxygen octahedra stretched out along the z , x , or y axis correspond to split orbital states of the $Mn^{3+}(B)$ ion. The type of stretching in the ground state is determined by the symmetry of the octasite in the lithium ferrite. The eigenvalues of the operators $U_{E\theta}$ and $(-U_{E\theta} \pm \sqrt{3}U_{E\epsilon})/2$ in these states are

$$1, -1/2, -1/2(z); \quad -1/2, 1, -1/2(x); \quad -1/2, -1/2, 1(y).$$

At low temperatures ($k_B T \ll E$), only the ground state of the $Mn^{3+}(B)$ ions is filled. As a result, the parameters of Hamiltonian (1) can be determined directly from the low-temperature spectrum:

$$A_1 = c/2, \quad A_2 = \Delta/2 = -\Delta_{\pm}, \quad A_3 = (h + 2d)/6, \quad A_4 = 2(h - d)/3, \quad (4)$$

where we are considering sites with oxygen octahedron stretched out along the z axis ($d_+ = d_- = d$). According to the data of Ref. 2 we have

$$A_1 = -211.15, \quad A_2 = 52, \quad A_3 = 2.85, \quad A_4 = -0.6 \text{ MHz.}$$

Let us first consider the contraction of the absorption band in a magnetic field as the temperature is raised. For simplicity we omit small terms due to H_{HF}^{trig} and H_Q in the NMR frequencies in (3):

$$\omega_k = (A_1^2 + A_2^2 p^2 / 2 + A_2 p (A_1 + A_2 p / 4) (3n_k^2 - 1))^{1/2} \langle S \rangle_T, \quad \mathbf{n} = \mathbf{M} / |\mathbf{M}|. \quad (5)$$

Here we have $k = x, y, z$, depending on the type of elongation of the oxygen octahedron in the octasite occupied by the Mn^{3+} ion, and the parameter p characterizes the magnitude of this deformation. It is given by

$$p \equiv p(T) = (1 - \exp\{-E/(k_B T)\}) / (1 + 2 \exp\{-E/(k_B T)\}), \quad \omega\tau \ll 1. \quad (6)$$

The upper edge (ω_{\max}) and the lower edge (ω_{\min}) of the absorption band are reached at directions of the magnetization \mathbf{n} corresponding to the values $n_k = 1$ and 0. In other words, for $\mathbf{M} \parallel [001], [110], \dots$, we have

$$\omega_{\max} = |A_1 - A_2 p(T) / 2 \langle S \rangle_T|, \quad \omega_{\min} = |A_1 + A_2 p(T) \langle S \rangle_T|. \quad (7)$$

The total width of the NMR absorption, with a random distribution of the magnetizations of the various single crystals in the external field, is therefore $\sim (3/2)A_2 \langle S \rangle_T p(T)$. As the temperature is raised to 300 K, the corresponding decrease in $\langle S \rangle_T$ is on the order of 7%, so the contraction of the spectrum is determined primarily by the temperature dependence of the tetragonality parameter $p(T)$ in (6). The model proposed here gives a fairly good description of the observed effect with plausible values of the splitting of the orbital doublet, $E \sim 10^2$ K, by the low-symmetry field of the lithium sublattice.

The quadrupole interaction leads to a splitting of the frequencies [see (3)] of the transitions between different nuclear sublevels m_I :

$$\delta\omega(m_I - 1 \rightarrow m_I) = (3C/2) \langle U_{E\theta} \rangle (3\beta_z^2 - 1) (m_I - 1/2). \quad (8)$$

Here we are considering the same type of octasite as in (4); the β_i are the direction cosines of the quantization axis for the nuclear spin. The directions of the magnetization \mathbf{M} and the nuclear spin I are generally not the same, because of the substantial anisotropic hyperfine interaction:

$$\beta_z \cong n_z [A_1 + A_2 \langle U_{E\theta} \rangle] / (A_1^2 + A_2^2 \langle U_{E\theta} \rangle^2 (1 + 3n_z^2) / 4 + A_1 A_2 \langle U_{E\theta} \rangle (3n_z^2 - 1))^{1/2}.$$

As a result, we find the following expression for $\delta\omega$ in the case $\mathbf{M} \parallel [111]$:

$$\begin{aligned} \delta\omega(m_I - 1 \rightarrow m_I) &= 3C(A_2 p^2 (A_1 + A_2 p/4) / (A_1^2 + A_2^2 p^2/2)) (m_I - 1/2) \\ &\cong 3C(A_2 p^2 / A_1) (m_I - 1/2). \end{aligned} \quad (9)$$

We see that the quadrupole component of the width of the peaks in the NMR spectrum should decrease with increasing temperature in accordance with $p^2(T)$ when the magnetization is directed along the trigonal axes (in the absence of an external magnetic field). This conclusion explains the observed decrease in the width of the peaks in the NMR spectrum of the $\text{Mn}^{3+}(B)$ ions.

We note in conclusion that the effect discussed here may also occur in a long list of systems with Jahn–Teller ion, whose orbital degeneracy is lifted by random crystal fields. The difference from the situation discussed here may be substantial for the intensity of the spectrum at the center of the absorption band. In the case of the present paper, centers with a splitting energy E on the order of T may play a significant role even at low temperatures.

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