Electron-nucleus interaction of a non-Kramers ion

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The electron-nucleus interaction of the non-Kramers Tb^{3+} ion with nearest-neighbor F^- nuclei in fluorite crystals is studied experimentally for the first time.

The electron-nucleus interaction (ENI) of a paramagnetic ion with the ligands surrounding it in crystals (the so-called ligand or super-hyperfine interaction) is being intensively studied both by different experimental methods (EPR, NMR, ENDOR, RFDP) and by theoretical methods. This pertains especially to iron-group elements and, to a lesser extent, to the rare-earth elements. There are no data on the ENI of non-Kramers ions.

The purpose of this study is to observe and analyze the interaction of the ion $Tb^{3+}(4f^8, {}^7F_6)$ with the nuclei of nearest-neighbor fluorine ions in the CaF_2 crystals.

The Tb^{3+} ion in fluorite isomorphically replaces Ca^{2+} and the charge is canceled locally by the additional F^- ion, which is situated in the interstices of the first coordination sphere.[1] In a tetragonally symmetrical crystal field, the principal term ${}^7F_6$ is split into seven singlets and three doublets, where the lowest levels are two singlets Γ_{t3} and Γ_{t4}—a non-Kramers doublet.[2] Electron paramagnetic resonance can occur only in parallel fields.[1]

The experimental study was conducted using a 3-cm ENDOR spectrometer with rf modulation of the constant magnetic field $H(f_m = 100$ kHz) at $T = 6$–9 K. The Tb^{3+} concentration was ~0.005 wt.%. Since optimal conditions for observing non-Kramers ions are not known, we developed an ENDOR cavity that makes it possible

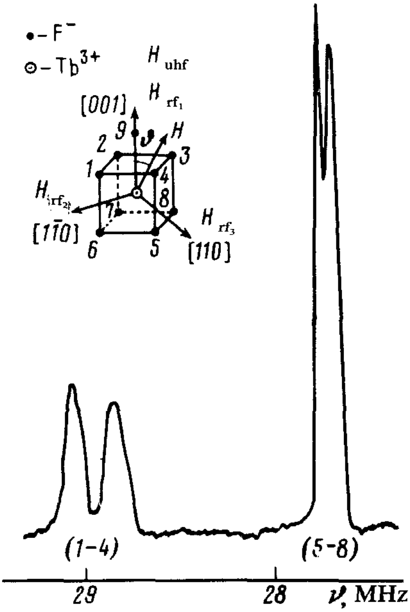

FIG. 1. Geometry of the experiment and the ENDOR spectrum of Tb^{3+} in CaF_2 with $H \parallel [001]$. $T = 8.2$ K, $m = -3/2$, $H = 65$ Oe. Inset: H_{rf_1}, H_{rf_2}, and H_{rf_3} are the orientations of the field H_{rf} which are used in the experiment.

to produce different electromagnetic-field geometries at the location of the sample.[3] It was established that the intensity of the ENDOR signal is virtually independent of the orientation of the ratio-frequency nuclear pump H_{rf} relative to H_{uhf} and H. Figure 1 shows the ENDOR spectrum of the first coordination sphere of F^-, where the numbers (1–4) and (5–8) correspond to lines belonging to specific fluorine ions.

The local symmetry of each of the eight $F^-_i (i = 1,\ldots\ldots,8)$ ions is C_s, while the symmetry of the additional F^-_9 ion is C_{4v}, so that the ENI tensors for F^-_i and F^-_9 in a system of coordinates associated with the central ion (Tb^{3+}) have the following form:

$$a_i = \begin{pmatrix} a_1 & a_2 & a_4 \\ a_2 & a_1 & a_4 \\ a_5 & a_5 & a_3 \end{pmatrix} \qquad a_9 = \begin{pmatrix} a_\perp & 0 & 0 \\ 0 & a_\perp & 0 \\ 0 & 0 & a_\parallel \end{pmatrix}.$$

For a non-Kramers ion with $g_\perp = 0$ the tensors are transformed to the form:

$$a_i = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ a_5 & a_5 & a_3 \end{pmatrix} \qquad a_9 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & a_\parallel \end{pmatrix}.$$

In determining the frequencies of ENDOR transitions due to a strong hyperfine interaction, we took into account the electron-spin quantization with respect to the effective magnetic field formed by vector addition of the external and hyperfine fields.

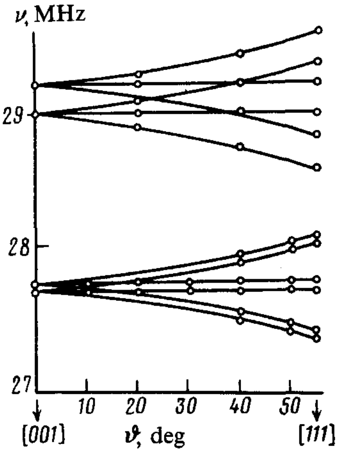

FIG. 2. Angular dependence of the ENDOR lines in the (110) plane. $m = -3/2$, $T = 7.3$ K. The light points are the measurements.

$$\nu(F_i^-) = [(a_3 < S_z > - \nu_L \cos\theta)^2 + 2a_5^2 < S_z >^2 - 2\sqrt{2}a_5 <S_z> \nu_L \sin\theta + \nu_L^2 \sin^2\theta]^{1/2},$$

$$\nu(F_9^-) = [a_{\|}^2 < S_z >^2 - 2a_{\|} < S_z > \nu_L \cos\theta + \nu_L^2]^{1/2},$$

where

$$S_{\text{eff}} = \frac{1}{2},\ I = \frac{3}{2},\ < S_z > = \frac{M(g_{\|}\beta A + Am)}{[(g_{\|}\beta H + Am)^2 + \Delta^2]^{1/2}} = M\left[1 - \left(\frac{\Delta}{h\nu}\right)^2\right]^{1/2},$$

ν_L is the Larmor frequency of the F$^-$ ion, θ is the angle between the direction of H and the z axis of the complex, $g_{\|} = 17.8$, $A = 6.27$ GHz, and $\Delta = 5.19$ GHz.[1]

In order to identify the ENDOR lines for their association with a particular F$^-$ ion, we measured the angular dependence (Fig. 2). We might note that the ENDOR signal from F$^-{}_9$ was not observed because the conditions required for its observation were absent. For this reason, we determined the quantity $a_{\|}$ from the super-hyperfine structure of the EPR lines. The experimental values of the ENI parameters are listed in Table I, where $a_{\text{dip}} = g_{\|}\beta g_n^F \beta_n / R^3$ and (1–9) correspond to the F$^-$ ions.

TABLE I.

	(1 – 4)	(5 – 8)	9
	MHz		
a_3	32,60 ± 0,15	2,52 ± 0,07	68,5 ± 10,
a_{dip}	0	0	65,4
a_5	43,60 ± 0,20	47,36 ± 0,12	–
a_{dip}	50,36	50,36	–

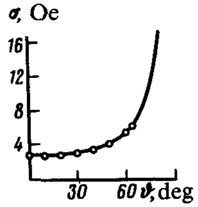

FIG. 3. Angular dependence of σ. The light points are the measurements. $T = 16$ K.

The signs of the parameters are arbitrary. As is evident from Table I, the ENI parameters for $F^-_{(1-4)}$ are different from those for $F^-_{(5-8)}$, indicating that the nearest-neighbor environment of the Tb^{3+} ion is substantially distorted.

A exact solution was obtained in weak fields for the spin-Hamiltonian with allowance for nine nearest fluorine ions. The resonant fields and the interval between the adjacent components of the super-hyperfine structure of the EPR line (σ) can be written in the form

$$H_{m,K,m_9^F} = \frac{1}{\cos\theta}\left[-(Am + a_\parallel m_9^F) + K\sqrt{a_3^2 + 2a_5^2} + \sqrt{(h\nu)^2 - \Delta^2}\right],$$

$$\sigma = \frac{1}{\cos\theta} f(a_\parallel, a_3, a_5) = \frac{1}{\cos\theta}\,\mathrm{const},$$

where $K = \Sigma_{i=1}^{8} I^F$

The super-hyperfine structure of the EPR lines of Tb^{3+} in CaF_2 was interpreted using the ENDOR data. A mechanism for broadening the EPR lines due to deflection of H from z was determined. This broadening, as is evident from the expression for σ is due only to the dependence of σ on the angle between H and the z axis of the complex. Figure 3 confirms this mechanism.

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