Indirect superhyperfine interaction in $HoVO_4$(Gd)

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Exceptionally large linewidths are observed in the EPR spectra of Gd impurities in the singlet ground-state system $HoVO_4$. A new indirect superhyperfine interaction between the Gd^{3+} electrons and the Ho^{3+} nuclei through a highly polarizable Ho^{3+} electronic state is proposed to account for this behavior. The calculated linewidths are found to be in good agreement with the observations.

Holmium vanadate has recently attracted interest as an ideal insulator with enhanced nuclear magnetism[1-4] and which therefore may be used for enhanced nuclear cooling.[1] In this paper we report the discovery of a new type of superhyperfine interaction in the EPR spectrum of $HoVO_4$(Gd), which is closely related to the above phenomena.

The interesting properties of $HoVO_4$, with tetragonal zircon structure D_{4h}^{19}, arise from the fact that, although the ground state ($4f^{10}\,{}^5I_8$) of the Ho^{3+} ion with site symmetry D_{2d} in this compound is a Γ_1 singlet (with $M_J \approx 0$), the excited states are not far away and can easily be admixed into the ground state by external or internal magnetic fields. In particular, the first excited state, a Γ_5 doublet[3] with $M_J \approx \pm 1$, is only ~ 21 cm^{-1} away and can readily be admixed into the ground state by a magnetic field perpendicular to the c axis. Thus a highly anisotropic magnetic polarization may be induced in the ground electronic state by an external magnetic field. The induced electronic moment may then act as an intermediary in the interaction of the Ho^{165} nuclei of spin $\frac{7}{2}$ with the applied magnetic field and so give rise to an enhanced effective nuclear moment.[4] In an EPR experiment, the electronic magnetic moment induced by the dipolar interaction with the impurity can similarly act as an intermediary and so produce an indirect superhyperfine interaction between the impurity electronic states and the Ho nuclei.

Our experiments were performed at ~ 9 GHz on 1%, 0.1%, and 0.01% Gd/Ho flux grown $HoVO_4$(Gd) crystals in the temperature range $1.55 < T < 10$ K. A typical spectrum of the fine structure with the external magnetic field along the c axis is shown in Fig. 1. For the lower two concentrations the seven fine structure lines are of the same width, 168 ± 5 G. For the highest concentration, the Gd-Gd interaction increases the average linewidth to ~ 200 G. At temperatures higher than ~ 10 K, the dipolar broadening from the first excited Ho^{3+} doublet rapidly increases the linewidth and the spectrum cannot be resolved. Also when the magnetic field is perpendicular to the c axis the spectrum is not resolvable due to the reduced fine structure splitting and wider lines. The line shapes are Gaussian. The spectrum shows tetragonal symmetry even at the lowest temperature. There is thus no phase transition above 1.55 K.

The Gd^{3+} ($4f^7\,{}^8S_{7/2}$) spin Hamiltonian[5] is

$$\mathcal{H}_{\mathrm{Gd}} = \mu_B g_s \vec{H}\cdot\vec{S} + \sum_{nm} B_n^m O_n^m , \tag{1}$$

where the two terms in Eq. (1) are respectively the Zeeman and the crystal-field interactions. The measureable parameters in Eq. (1) are

$$g_s = 1.997 \pm 0.005 ,$$

$$B_2^0 = [(-1.212 \pm 0.006)\times 10^{-2} - (3.2 \pm 0.4)\times 10^{-5} T(K)]\ \mathrm{cm}^{-1} ,$$

$$B_4^0 = (-4.2 \pm 0.3)\times 10^{-6}\ \mathrm{cm}^{-1} ,$$

$$B_6^0 = (3.8 \pm 0.4)\times 10^{-8}\ \mathrm{cm}^{-1} .$$

The most interesting observation is that the lines are unusually wide even with the lowest Gd^{3+} concentration and at very low temperatures where almost all Ho^{3+} ions will be in the ground singlet. The usual sources of line broadening (i.e., hyperfine interaction

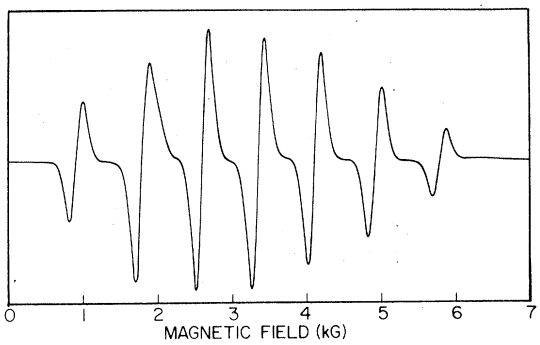

FIG. 1. EPR spectrum of $HoVO_4$ (0.1% Gd) at $T = 5$ K with the magnetic field along the c axis.

with Gd^{155} and Gd^{157} nuclei, direct superhyperfine interactions with V^{51} and Ho^{165} nuclei and the remnant Gd-Gd interaction) are all estimated to produce a combined linewidth of ~ 8 G. Furthermore, since the external magnetic field is applied along the z direction, the Ho^{3+} ground state is expected to remain almost nonmagnetic and make negligible contribution to the Gd^{3+} linewidth.

To explain the large linewidths we propose the following mechanism: With the magnetic field along the z axis (c axis of the crystal) the Gd^{3+} electronic spin $\vec{S}$ is quantized along this axis. The dipolar magnetic field produced by the Gd electrons has transverse components at the Ho positions. These components induce transverse electronic magnetic moments in the Ho^{3+} ions. The magnetic field produced by the induced moments produce large fields in the transverse direction at the Ho nuclei. As a result there will be an induced superhyperfine interaction between the Gd electrons and the Ho nuclei.

The relevant part of the Hamiltonian for a Gd-Ho pair with the Gd at the origin and the Ho at $\vec{r}$ ($x=3.56$, $y=0$, $z=1.57$ Å) is

$$\mathcal{H}_{\text{Gd-Ho}} = \mathcal{H}_{\text{Gd}} + \mathcal{H}_{\text{Ho}} + kS_zJ_x \ , \tag{2}$$

where

$$\mathcal{H}_{\text{Ho}} = \mathcal{H}_{\text{CF}} + \mu_B \vec{H}\cdot(g_J\vec{J} - g_I\vec{I}) + A_J\vec{J}\cdot\vec{I} + \mathcal{H}_Q \ . \tag{3}$$

The four terms in Eq. (3) are respectively the crystal field, Zeeman (electronic and nuclear), magnetic hyperfine and nuclear electric quadrupolar interactions. The last term in Eq. (2) with

$$k = -3g_sg_J\mu_B^2(xz/r^5) \tag{4}$$

is that part of the Gd-Ho dipolar interaction which induces a magnetic moment along the x axis in Ho^{3+} ground state when the Gd^{3+} moment is quantized along the z axis by the external magnetic field. Note that the Gd-Ho isotropic *exchange* interaction does *not* have such a term and is ignored along with the rest of the dipolar interaction.

The Hamiltonian (2) can be projected onto the Ho^{3+} singlet ground state and up to second order in perturbation the effective Hamiltonian with $\vec{H} = (0,0,H_z)$ is

$$\mathcal{H}_{\text{eff}} = H_{\text{Gd}} - \mu_B g_I H_z I_z + \mathcal{H}_Q - a_x[\tfrac{1}{2}A_J^2(I_x^2 + I_y^2) + \tfrac{1}{2}k^2S_z^2 + A_JkS_zI_x] \ , \tag{5}$$

where

$$a_x = \frac{1}{\Delta}\,|\langle g|J_\pm|e\rangle|^2 \ , \tag{6}$$

$|g\rangle$ and $|e\rangle$ being ground and excited Ho^{3+} electronic states. The last term in the brackets in Eq. (5) gives the indirect superhyperfine interaction between the Gd^{3+} electrons and the Ho nucleus

$$\mathcal{H}_{SHF} = -a_xA_JkS_zI_x \equiv -AS_zI_x \ . \tag{7}$$

From Ref. 4

$$a_x = \frac{\hbar(\gamma_x - \gamma_I)}{g_JA_J\mu_B} \ , \tag{8}$$

where $\gamma_x/2\pi$ and $\gamma_I/2\pi$ are the enhanced and the bare nuclear resonance frequencies. Equations (4), (7), and (8) combine to give the induced hyperfine parameter

$$A = 3g_s\mu_B(xz/r^5)\,\hbar(\gamma_x - \gamma_I) \ . \tag{9}$$

From the measured values, $g_s = 1.997$, $\gamma_x/2\pi \cong (1420\ \text{MHz})T^{-1}$ (Ref. 4), and $\gamma_I/2\pi \cong (9\ \text{MHz})T^{-1}$ (Ref. 6), we calculate: $A \cong 17.5$ G. The linewidth of Gd^{3+} is found by compounding all the possible resultant hyperfine fields of four equivalent Ho nearest-neighbor nuclei and is ≈ 189 G. This is in qualitative agreement with the measured width of 168 ± 5 G. The difference may be attributed to the much smaller Ho nuclear Zeeman and electric quadrupolar interactions [the second and third terms in Eq. (5)] which try to align the Ho nuclear moment away from the x axis towards the z axis and so decrease the effect of A. There could also be a partial cancellation of the dipolar term by the anisotropic exchange which has been ignored in our analysis.

The term $-\frac{1}{2}a_xk^2S_z^2$ in Eq. (5), together with a similar term coming from[7] $K(S_xJ_x + S_yJ_y)$ where K represents both dipolar and exchange parameters, makes a positive contribution to B_2^0. This term is temperature dependent, since it varies with the level population of the Ho^{3+}. It accounts for the unusual sign and magnitude of the temperature-dependent part of B_2^0.

In conclusion, we can explain the unusually large linewidth of $HoVO_4(Gd^{3+})$ in terms of a new kind of superhyperfine interaction between the Gd^{3+} electrons and the Ho^{165} nuclei, which is brought about by the large transverse magnetic polarizability of the ground singlet electronic state of Ho^{3+}. While this is the first time that such effect has been seen, it can now be predicted to occur to a less-marked degree in certain other rare-earth compounds which we hope to investigate in the future.

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