Spin excitations and new orientational transition in a holmium orthoferrite with magnetic vacancies: $HoFe_{1-x}Al_xO_3$

A. A. Mukhin, I. V. Fedorov, A. É. Egoyan, S. P. Lebedev, G. V. Kozlov, and A. S. Prokhorov
Institute of General Physics, Russian Academy of Sciences, 117942 Moscow, Russia

A. M. Balbashov and I. Yu. Parsegov
Moscow Energetics Institute, 105835 Moscow, Russia

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Dynamic properties of holmium orthoferrite are strongly influenced by low concentrations of nonmagnetic Al^{3+} dopant ions (magnetic vacancies). Anomalies are observed on the temperature dependence of two antiferromagnetic-resonance modes in the submillimeter spectra of $HoFe_{1-x}Al_xO_3$. These anomalies (a discontinuity and slope changes in the frequencies) point to a spin-flip transition at $T=60$ K from a weakly ferromagnetic Γ_4 state to an antiferromagnetic Γ_1 state, induced by magnetic vacancies. A model is offered to explain the observations. The exchange field of the magnetic vacancies is determined.

Studies[1–4] have revealed that low concentrations of nonmagnetic Al^{3+} impurity ions, i.e., magnetic vacancies, strongly affect the magnetic-anisotropy energy and spin–flip transitions in rare-earth orthoferrites $RFeO_3$, where R^{3+} is a rare-earth ion. The effect stems from the appearance of a strong additional exchange field $\mathbf{H}_{mv}=\pm H_{mv}\mathbf{G}$ ($H_{mv}\sim 10^4$ Oe) at the rare-earth ion, because of a decompensation of the antiferromagnetic neighborhood of Fe^{3+} ions ($\mathbf{G}$ is the dimensionless antiferromagnetism vector of the Fe subsystem). As a result, the magnetic-anisotropy energy acquires an additional component. Depending on the anisotropy of the magnetic susceptibility of the R subsystem, this additional component may lead to a strong increase in the temperature of the spin–flip transition in $DyFeO_3$ (Ref. 1), a suppression of this transition in $TbFeO_3$ (Ref. 4), and new spin–flip transitions in $HoFeO_3$ (Refs. 2 and 3).

Previous studies of orthoferrites with magnetic vacancies have dealt with only static properties (the magnetization and magnetostriction). The dynamic properties of the system are also expected to exhibit strong effects of magnetic vacancies. This comment applies to both the behavior of antiferromagnetic-resonance modes of the Fe subsystem and electronic excitations in the R subsystem (R modes). In the latter subsystem we could expect to find some new R modes, associated with the additional splitting of the ground multiplet of the R^{3+} ion in the field of the magnetic vacancies. In this letter we are reporting the first study of dynamic properties of an orthoferrite with magnetic vacancies, specifically, the system $HoFe_{1-x}Al_xO_3$ ($x=0.075$).

The single crystals which were the test samples were grown by float zoning with radiative heating. The samples were plane-parallel platelets cut perpendicular to the *a* and *b* axes of the orthorhombic crystal. The transverse dimensions were on the order of 1 cm, and the thickness was ~ 1.5 mm.

The experiments were carried out on an Épsilon submillimeter backward-wave-tube spectrometer[5] over the frequency range 2–25 cm^{-1} with a resolution of 0.001 cm^{-1} at temperatures from 4.2 to 300 K. We measured the frequency spectra of the transmission spectrum $T(\omega)$ of the samples as a linearly polarized plane wave was incident normally on them.

Three absorption lines were found in the $T(\omega)$ spectra. Two of them, which are fairly narrow ($\Delta\omega/\omega \sim 10^{-2}$), were identified as antiferromagnetic resonance modes [a quasiferromagnetic mode $\omega_1(\mathrm{Fe})(F)$ and a quasiantiferromagnetic mode $\omega_2(\mathrm{Fe})$ (AF)]. The third, which was extremely broad ($\Delta\omega/\omega \sim 1$), was identified as a rare-earth mode $\omega_3(\mathrm{R})$. The latter mode is determined by electron transitions within the ground quasidoublet of the Ho^{3+} ion. The F mode is excited at $T > 60$ K by a field $h \| a, b$ axes, while at $T < 60$ K it is excited only by a field $h \| a$. The antiferromagnetic mode is excited by a field $h \| c$, and the R mode by a field $h \| b$. At $T < 60$ K, there is an abrupt intensification of the antiferromagnetic-resonance modes. Analysis of the $T(\omega)$ spectra with the help of the existing formulas for the transmission of a plane-parallel slab and the harmonic-oscillator model for the dispersion of the magnetic permeability, $\mu(\omega)$ (Ref. 6, for example), made it possible to determine parameters of the modes: resonant frequencies, linewidths, and contributions of the modes to the static magnetic permeability.

Figure 1 shows the temperature dependence of the frequencies of the modes observed. The softening and jump in the frequency of the antiferromagnetic mode $\omega_2(\mathrm{Fe})$, the slope change for the frequency of the F mode $\omega_1(\mathrm{Fe})$, and the change in the excitation conditions for the antiferromagnetic-resonance modes, along with the jumps in their intensities at $T_M = 60$ K, led us to conclude that a first-order spin–flip transition occurs at this point in $HoFe_{0.925}Al_{0.075}O_3$ in the *ab* plane, from a weakly ferromagnetic $\Gamma_4(G_xF_z)$ phase to an antiferromagnetic $\Gamma_1(G_y)$ phase. This conclusion is in agreement with the data of Ref. 3, where a corresponding orientation reversal was observed in $HoFe_{1-x}Al_xO_3$ at $T \sim 60$ K, although in that other case the change in orientation occurred through a $\Gamma_{12}(G_yG_zF_x)$ angular phase.

The behavior observed for the resonant modes in $HoFe_{0.925}Al_{0.075}O_3$ is qualitatively different from that for pure $HoFeO_3$, in which the anomalies occur at three temperatures ($T_1 = 58$, $T_2 = 51$, and $T_3 = 39$ K), which correspond to the spin–flip transitions[6,7] $\Gamma_4(G_xF_z) \rightarrow \Gamma_{24}(G_xF_zF_zF_x) \rightarrow \Gamma_{12}(G_yG_zF_x) \rightarrow \Gamma_2(G_zF_x)$.

To analyze the dynamic properties and spin–flip transition in $HoFe_{1-x}Al_xO_3$, we take an approach which we used previously[6] in describing the dynamics of phase transitions in pure $HoFeO_3$. The most important point here is to take into account the subsystem of Ho^{+3} ions, which we describe in the two-level approximation by means of the spin Hamiltonian

$$\mathscr{H}_{\mathrm{eff}} = -\sum_i \left[\Delta_{cf}\hat{\sigma}^i_\zeta + \Delta^i_{\mathrm{M}}(\mathbf{H},\mathbf{F},\mathbf{G})\hat{\sigma}^i_\xi + \Delta E^i_{vv}(\mathbf{H},\mathbf{F},\mathbf{G})\right]. \quad (1)$$

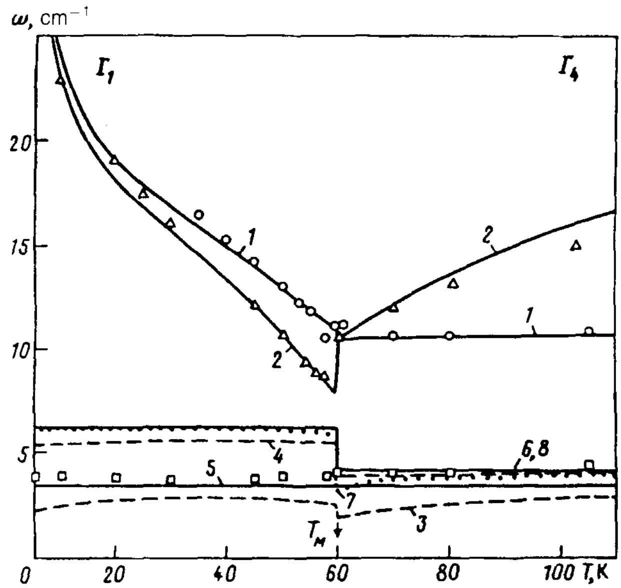

FIG. 1. Temperature dependence of the frequencies of resonant modes in $HoFe_{1-x}Al_xO_3$. Points: Experimental. Curves: Theoretical. Curve 1—ω_1(Fe); 2—ω_2(Fe); 3—ω_{1a}(R); 4—ω_{2a}(R); 5—ω_{1b}(R); 6—ω_{2b}(R); 7—ω_{2c}(R); 8—ω'_{2c}(R).

Here $\hat{\boldsymbol{\sigma}}^i=(\hat{\sigma}^i_\xi, \hat{\sigma}^i_\eta, \hat{\sigma}^i_\zeta)$ are the components of the Pauli matrices of the ground quasidoublet of the ith Ho^{3+} ion; the quantity Δ_{cf} determines the splitting of this doublet in two in the crystal field; and $\Delta^i_{\mathrm{M}}(\mathbf{H},\mathbf{F},\mathbf{G})=\boldsymbol{\mu}^i_0(\mathbf{H}+a\mathbf{F}+pH_{mv}\mathbf{G})+BG_z$ determines that in the external magnetic field $\mathbf{H}$, the isotropic ($a\mathbf{F}$) and anisotropic (BG_z) Ho–Fe exchange fields, and the field of the magnetic vacancy, $pH_{mv}\mathbf{G}(p=\pm 1$, depending on the site occupied by the vacancy); $\boldsymbol{\mu}^i_0=(\mu^x_0, \pm\mu^y_0, 0)$ is the magnetic moment of the quasidoublet for the two nonequivalent sites of the Ho^{3+} ions; $\mathbf{F}$ and $\mathbf{G}$ are the dimensionless ferromagnetism and antiferromagnetism vectors, respectively, of the Fe subsystem; and ΔE^i_{vv} is the downward Van Vleck shift of the center of gravity of the quasidoublet due to the introduction of excited states.

We characterize the nonequilibrium state of the R subsystem by the expectation values of the Pauli matrices of the ith R ion, $\langle\hat{\boldsymbol{\sigma}}^i\rangle=\boldsymbol{\sigma}^i$. For R ions near which there is no magnetic vacancy there are two nonequivalent sites. For R ions which have one magnetic vacancy in their nearest neighborhood, there are four nonequivalent sites. The relative number of the former is $(1-zx)$, and that of the latter is zx at $x\ll 1$, where $z=8$ is the number of nearest R ions in the neighborhood of a magnetic vacancy. Six sublattices must therefore be introduced in order to describe the R subsystem.

Constructing a nonequilibrium thermodynamic potential for the system, which depends on $\mathbf{F}$, $\mathbf{G}$, and $\boldsymbol{\sigma}_\alpha$ ($\alpha=1$–6) (Ref. 3), and using (by analogy with Ref. 6) Landau–Lifshitz equations for $\mathbf{F}$ and $\mathbf{G}$ and corresponding equations incorporating the longitudinal relaxation for the variables of the R subsystem as the equations of motion, we calculated resonant frequencies in the Γ_4 and Γ_1 phases, respectively. There are a total of eight resonant modes: two antiferromagnetic-resonance modes in the Fe subsystem and six R modes.

$\Gamma_4(G_xF_z)$ phase. For the modes of symmetry $\Gamma_{23}(h\|a,\ b)$ (where Γ_{ij} are irreducible representations of the space group of the orthoferrites, D_{2h}^{16}), there are five resonant modes. Three of them [the F mode $\omega_1(\mathrm{Fe})$ and the two R modes $\omega_{1a,2a}(\mathrm{R})$] are found from the equation

$$\omega^2=\omega_{10}^2-\Delta\omega_z^2\left\{(1-zx)\frac{\omega^2}{\omega_{\mathrm{R1}}^2-\omega^2}+zx\left[\frac{\omega^2}{\omega_{\mathrm{R2}}^2-\omega^2}\cos^2\chi+\frac{i\omega}{\omega_r+i\omega}\sin^2\chi\right]\right\}. \qquad (2)$$

The others are $\omega_{1\mathrm{b}}(\mathrm{R})\simeq\omega_{\mathrm{R1}}$ and $\omega_{2\mathrm{b}}(\mathrm{R})\simeq\omega_{\mathrm{R2}}$.

For the modes of symmetry Γ_{14} $(h\|c)$, there are three resonant modes. Two of them [the antiferromagnetic mode $\omega_2(\mathrm{Fe})$ and one R mode $\omega_{2c}(\mathrm{R})$] are found from the equation

$$\omega^2=\omega_{20}^2-zx\Delta\omega_y^2\left[\frac{\omega^2}{\omega_{\mathrm{R1}}^2-\omega^2}\cos^2\chi+\frac{i\omega}{\omega_r+i\omega}\sin^2\chi\right]. \qquad (3)$$

The frequency of the other R mode is $\omega_{2c}'(\mathrm{R})\simeq\omega_{2\mathrm{R}}$.

$\Gamma_1(G_y)$ phase. In this phase the corresponding mode frequencies are given by the same equations as for the Γ_4 phase, with G_x replaced by G_y, $\omega_{10,20}$ by $\omega_{10,20}'$, and $\Delta\omega_y$ by $\Delta\omega_x$.

In addition to the resonant modes, the system contains relaxation R modes, which are determined by the longitudinal relaxation frequency of the R ion. Incorporating these modes is important for reconciling the description of the static and dynamic properties of the system and for reaching an understanding of the nature of the soft mode.

In the expressions written above, the quantities $\omega_{\mathrm{R1}}=2\Delta_{\mathrm{cf}}/\hbar$ and $\omega_{\mathrm{R2}}=2(\Delta_{\mathrm{cf}}^2+\Delta_{\mathrm{ex}}^2)^{1/2}/\hbar$ are the frequencies of transitions between levels of the ground quasidoublet of the Ho^{3+} ion which respectively do not and do have one magnetic vacancy in their nearest neighborhood; ω_r is the longitudinal relaxation frequency of the Ho^{3+} ions; $\Delta_{\mathrm{ex}}^2=\Sigma(\Delta_{\mathrm{ex}}^1G_i)^2$ $(i=x,\ y,\ z)$ is the exchange splitting of the quasidoublet in two;

$$\Delta_{\mathrm{ex}}^{x,y}=\mu_0^{x,y}H_{\mathrm{mv}};\quad \Delta_{\mathrm{ex}}^z=B+\mu_0^x aH_D/2H_E;$$

H_E and H_D are the fields of respectively isotropic and antisymmetric exchange in the Fe subsystem;

$$\Delta\omega_i^2=\gamma\omega_E(\Delta_{\mathrm{ex}}^i)^2/k_BT\mu_{\mathrm{Fe}};\quad \omega_E=2\gamma H_E;$$

$\mu_{\mathrm{Fe}}=5\mu_B$; γ is the gyromagnetic ratio of the Fe^{3+} ions;

$$\tan\chi=\Delta_{\mathrm{ex}}/\Delta_{\mathrm{cf}};\quad \omega_{10,20}^2=\gamma\omega_E K_{ac,ab}^{\mathrm{eff}}/\mu_{\mathrm{Fe}};$$

$$\omega_{10}'^2=\gamma\omega_E(+K_{ac}^{\mathrm{eff}}-K_{ab}^{\mathrm{eff}}+K_2''-K_2')/\mu_{\mathrm{Fe}};\quad \omega_{20}'^2=\gamma\omega_E(-K_{ab}^{\mathrm{eff}}-K_2')/\mu_{\mathrm{Fe}}.$$

The quantities $K^{\rm eff}_{ac,ab}$, K'_2, and K''_2 are the anisotropy constants and the effective thermodynamic potential

$$\Phi(\mathbf{G}) = \frac{1}{2} K^{\rm eff}_{ac} G_z^2 + \frac{1}{2} K^{\rm eff}_{ab} G_y^2 + \frac{1}{4} K_2 G_z^4 + \frac{1}{4} K'_2 G_y^4 + \frac{1}{2} K''_2 G_y^2 G_z^2,$$

which is found by minimizing the original nonequilibrium potential with respect to $\mathbf{F}$ and σ_α. The point at which the first-order phase transition $\Gamma_4 \to \Gamma_1 (G_x \to G_y)$ occurs is determined by the condition $K^{\rm eff}_{ab}(T_M) + K'_2/2 = 0$. The effective anisotropy constants are

$$K^{\rm eff}_{ac}(T) = K^0_{ac}(T) - (\Delta^z_{\rm ex})^2/k_B T + zx(\chi^x_{\rm R} - \chi^z_{\rm R}) H^2_{mv},$$

$$K^{\rm eff}_{ab}(T) = K^0_{ab}(T) - zx(\chi^y_{\rm R} - \chi^x_{\rm R}) H^2_{mv};$$

where $K^0_{ac,ab}$ are the anisotropy constants of the Fe subsystem, renormalized by the Van Vleck contribution of the Ho subsystem,[6,7] and $\chi^i_{\rm R} = (\mu^i_0)^2/k_B T + (\chi^i_R)_{vv}$ $(i = x, y, z)$ is the magnetic susceptibility of the Ho^{3+} ions. The first term here is determined by the ground quasidoublet, and the second by the Van Vleck contribution. The $\Gamma_4 \to \Gamma_1$ phase transition occurs because of an increase in the negative contribution to $K^{\rm eff}_{ab}$ (because of the relation $\chi^y_{\rm R} > \chi^x_{\rm R}$), which is determined by the field of the magnetic vacancies.

Figure 1 shows the temperature dependence of the frequencies we calculated for resonant modes. These calculations were carried out with the values $K^0_{ac}(0) = 0.18$ K, $K^0_{ab}(0) = -0.146$ K, $K'_2 = -0.2$ K, $K''_2 = -0.1$ K, $\Delta^z_{\rm ex} = 3.5$ K, and $H_{mv} = 8$ kOe, which were found by fitting the experimental data. The other parameter values corresponded to pure $HoFeO_3$ (Ref. 6). The value of the field H_{mv} was determined directly from the size of the jump $\Delta\omega_2$ of the quasiantiferromagnetic mode at the point of the transition, for which we find the following expression from (3):

$$\Delta\omega_2^2 = \omega_2(T^+_{\rm M})^2 - \omega_2(T^-_{\rm M})^2 = \gamma\omega_E zx H^2_{mv}\,[(\mu^y_0)^2 - (\mu^x_0)^2]/k_B T_{\rm M}.$$

It can be seen from Fig. 1 that the model-based calculations give a generally good description of the experimental data. We would simply point out that since the R modes are extremely broad, it is difficult to distinguish two closely spaced modes, $\omega_{1b}({\rm R}) = \omega_{\rm R1} = 3.4$ cm^{-1} and $\omega_{2b}({\rm R}) = \omega_{\rm R2} = 4$–$6$ cm^{-1} in the transmission spectra. They are seen as a single, broad, intense mode, whose frequency $\omega_3({\rm R})$ is shown in the form of experimental points in Fig. 1. The width of this mode, $\Delta\omega_{\rm R} = 3$–4 cm^{-1}, undergoes essentially no decrease with decreasing T, in contrast with that of pure $HoFeO_3$. The apparent reason is the existence of several components of this mode, which are broadened because of fluctuations of the magnetic-vacancy field and the R–R interaction field. The other R modes $(\omega_{1a,2a}, \omega_{2c})$ are far less intense, and in the transmission spectra they are seen only faintly $(h \| a)$ or not at all $(h \| c)$.

With regard to the nature of the soft mode in this system, we would point out that the latter is a low-lying relaxation R mode, which is simple to find at $|\omega| \ll \omega_{20}$, $\omega_{\rm R1,2}$ from (3):

$$\omega = i\omega_r\omega_{20}^2 / (\omega_{20}^2 + zx\Delta\omega_y^2 \sin^2\chi).$$

That result holds for the Γ_4 phase; the corresponding result for the Γ_1 phase is found by replacing ω_{20} by ω'_{20}, $\Delta\omega_y$ by $\Delta\omega_x$, and G_x by G_y. The softening of this mode is determined by the decrease in $K_{ab}^{\rm eff}(T)$ as $T \to T_{\rm M}$. At the point $T_{\rm M}$, there is a jump for both the soft mode and the higher-lying antiferromagnetic mode ω_2(Fe), because of the difference in the strengths of the interaction of the magnetic vacancy with the Ho subsystem in the Γ_4 and Γ_1 phases. Interestingly, in $DyFeO_3$, in which the same $\Gamma_4 \to \Gamma_1$ spin–flip transition occurs, the transition differs in dynamics: There is no jump in the frequency ω_2(Fe) (Ref. 8), because of the very weak interaction with lower-lying R modes.

In summary, this study has revealed that magnetic vacancies cause several new features in not only the static but also the dynamic properties of orthoferrites. This study has made it possible, in particular, to directly determine the field of a magnetic vacancy, H_{mv}.

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