Observation in $TmFeO_3$ of direct electronic transitions inside the principal multiplet of a rare-earth ion

A. M. Balbashov, A. A. Volkov, G. V. Kozlov, S. P. Lebedev, A. A. Mukhin, A. Yu. Pronin, A. S. Prokhorov, and A. M. Prokhorov
Institute of General Physics, Academy of Sciences of the USSR

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The far-IR absorption spectra of $TmFeO_3$ measured at $T = 4.2$–300 K and $\nu = 100$–1000 GHz have revealed five magnetic-resonance lines. Two of these lines are associated with the antiferromagnetic resonance of the Fe subsystem and the other three lines are associated with the electronic transitions between the lower singlets of the principal multiplet of the Tm^{3+} ion.

In the crystals of rare-earth orthoferrites $RFeO_3$, the principal multiplet of the rare-earth R^{3+} ion splits in a crystal field either into doublets (the Kramers ions) or into singlets (the non-Kramers ions).[1] The electronic transitions inside the Kramers

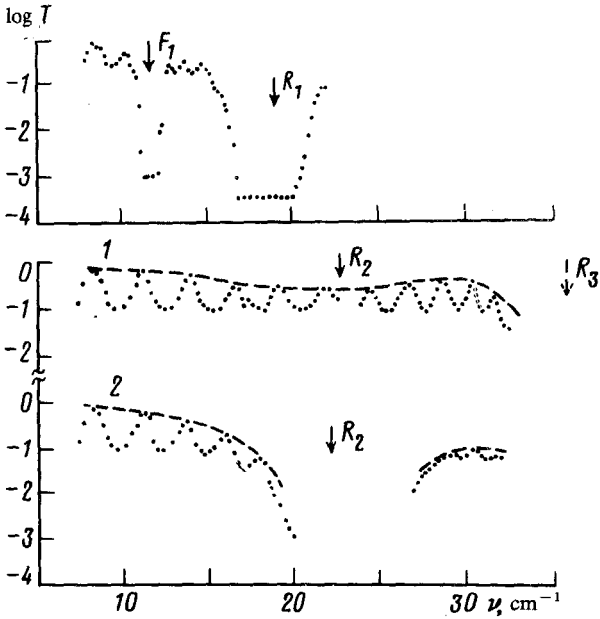

FIG. 1. Transmission spectra of a 0.279-mm-thick plane-parallel $TmFeO_3$ wafer measured for two types of polarization of an rf magnetic field: (a) **h** is parallel to the c axis, $T = 4.2$ K and (b) **h** is parallel to the b axis, $T = 4.2$ K (curve 1) and $T = 9.5$ K (curve 2).

doublets, which are split in an external (exchange) field, were studied in Refs. 2–4. Direct transitions between the singlets in the non-Kramers ions, to the best of our knowledge, have not been observed.

Using the optical data, according to which the distance between the lower singlets in the non-Kramers Tm^{3+} ion of $TmFeO_3$ corresponds to the energy of a submillimeter-range photon, we have studied the submillimeter absorption spectra of $TmFeO_3$.

Using the "Epsilon" submillimeter LOV spectrometer,[5] we carried out the measurements in the frequency range 100–1000 GHz at temperatures between 4.2 and 300 K. We have studied $TmFeO_3$ single crystals grown by the crucible-free zone-melting method with radiation heating and cut in the shape of a-cut plane-parallel wafers with a 10×10-mm cross section and thickness of ~ 1 mm.

The spectra measured after a double polarization of the rf field; (**h** is parallel to the c axis and **h** is parallel to the **b** axis) revealed five absorption lines. Of these five lines, two rather narrow lines ($\nu/\Delta\nu \sim 10^2$) are seen in the entire temperature interval studied. These are the previously reported[6–9] antiferromagnetic-resonance modes—a quasiferromagnetic F_1 mode of frequency ν_1^{Fe} and a quasiantiferromagnetic F_2 mode of frequency ν_2^{Fe} (Figs. 1 and 2). The temperature dependence of their parameters exhibits an anomaly at the points of the phase transitions, $T_{R1} \sim 90$ K and $T_{R2} \sim 80$ K, which are caused by a change in the orientation of the weak ferromagnetic moment **M** of the crystal from the c axis to the a axis.

The other three substantially broader absorption lines R_1, R_2, and R_3 (Fig. 1) are seen in the $TmFeO_3$ spectra only at low temperatures. To determine the nature of these lines, we have compared their resonance frequencies, the excitation conditions,

and the temperature dependences of the intensities of these lines with the corresponding data of Ref. 10, in which the distances between the singlets of the principal multiplet of the rare-earth ion were determined from the optical spectra of $TmFeO_3$ and the wave functions of these singlets were determined.

1. Resonance frequencies. In Figs. 1 and 2 we see that the frequency of the absorption line $R_1(\nu_{01}^R)$ corresponds to the energy of the transition from the ground-state singlet E_0 to the first excited singlet E_1, the frequency of the line $R_2(\nu_{12}^R)$ corresponds to the energy of the transition from E_1 to the second excited singlet E_2, and the frequency of the line $R_3(\nu_{02}^R)$ corresponds to the energy of the transition from E_0 to E_2.

2. Excitation conditions. The R_2 and R_3 modes become excited when **h** is parallel to the b axis, consistent with the selection rules for the matrix elements of the $E_1 - E_2$ and $E_0 - E_2$ transitions[10]:

$$\langle \psi_{A_1}^{(0,1)} | \mu_{a,b} | \psi_{A_2}^{(2)} \rangle \neq 0, \quad \langle \psi_{A_1}^{(0,1)} | \mu_c | \psi_{A_2}^{(2)} \rangle = 0,$$

where μ_i is the component of the operator of the magnetic moment of the Tm^{3+} ion ($i = a,b,c$), $\psi_{A_1}^{(n)}$ and $\psi_{A_2}^{(n)}$ are the wave functions which are related to the A_1 and A_2 representations of the point group C_S that describes the symmetry of the crystalline medium of the Tm^{3+} ion, and the superscript n specifies the singlets.

The conditions for the excitation of the R_1 mode (**h** is parallel to the c axis) are

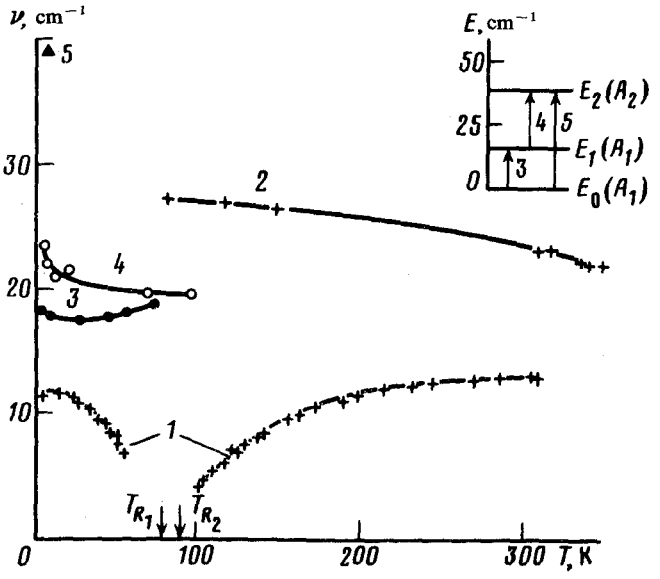

FIG. 2. Temperature dependence of the antiferromagnetic-resonance frequencies and of the rare-earth modes in $TmFeO_3$. 1—ν_1^{Fe}; 2—ν_2^{Fe}; 3—ν_{01}^R; 4—ν_{12}^R; and 5—ν_{02}^R. Inset—The splitting of low-lying levels of the Tm^{3+} ion in a crystal field[10] and the transitions between these levels which correspond to the absorption lines $R_{1,2,3}$ detected in the submillimeter spectra.

also in agreement with the selection rules for the matrix elements of the $E_0 - E_1$ transition[10]:

$$\langle \psi_{A_1}^{(0)} | \mu_{a,b} | \psi_{A_1}^{(1)} \rangle = 0, \quad \langle \psi_{A_1}^{(0)} | \mu_c | \psi_{A_1}^{(1)} \rangle \neq 0.$$

3. The temperature dependence. The R_1,R_2, and R_3 modes behave differently as the temperature is lowered: The intensity of the first two modes increases, while that of the third mode decreases (Fig. 1). This behavior is also consistent with the identification of these modes with the $E_0 - E_1$, $E_1 - E_2$, and $E_0 - E_2$ electronic transitions. As the temperature is lowered, the population of the ground-state level E_0 increases and that of the excited levels decreases, which accounts, respectively, for the increase in the intensities of the R_1 and R_3 modes and the decrease in the intensity of the R_2 mode.

We can assert, therefore, that the low-temperature lines detected in the submillimeter absorption spectra of $TmFeO_3$ are modes of the electronic resonance of the rare-earth subsystem of the crystal and are linked with the direct transitions between the three lower singlets of the principal multiplet of the non-Kramers Tm^{3+} ion.

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