Observation of magnetic dipole and electric dipole electron transitions in the ground multiplet of the rare-earth ion in $TmFeO_3$

G. V. Kozlov, A. A. Mukhin, A. Yu. Pronin, A. S. Prokhorov, V. Železny,[1)] and J. Petzelt[1)]
Institute of General Physics, Academy of Sciences of the USSR

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Magnetic dipole and electric dipole rare-earth modes observed in the submillimeter absorption spectra and the far-IR reflection spectra of the orthoferrite $TmFeO_3$ stem from electron transitions within the ground multiplet of the Tm^{3+} ion. The symmetry is determined. The observed electronic excitations are classified.

The rare-earth ions (R^{3+}) in orthoferrites ($RFeO_3$) occupy positions which are not centrally symmetric. As a result, not only magnetic dipole but also electric dipole electron transitions are allowed even within the ground electronic configuration of the rare-earth ion ($4f^{(n)}$). Among these transitions, there is particular interest in transitions between states within the ground multiplet of the rare-earth ion, which is split in the crystal field and the exchange field. Observations of rare-earth modes (R modes) due to such transitions in orthoferrites have been reported in several places (e.g., Refs. 1–3). However, the important question of the nature of the corresponding transitions (magnetic dipole? electric dipole?) remains open. We have observed, in the particular case of the orthoferrite $TmFeO_3$, that these transitions are both magnetic dipole and electric dipole transitions, so they determine not only the magnetic properties but also the dielectric properties of the orthoferrites. The test samples here were $TmFeO_3$ samples grown by float zoning and cut in the form of *a*-cut, *b*-cut, and *c*-cut plane-parallel plates. An Épsilon submillimeter backward-wave-tube spectrometer[4] was used to measure the transmission spectra over the frequency range 3–33 cm^{-1} at temperatures from 4.2 to 300 K.

Figure 1 shows some illustrative transmission spectra. Against the background of oscillations stemming from an interference in the sample, we see intense absorption

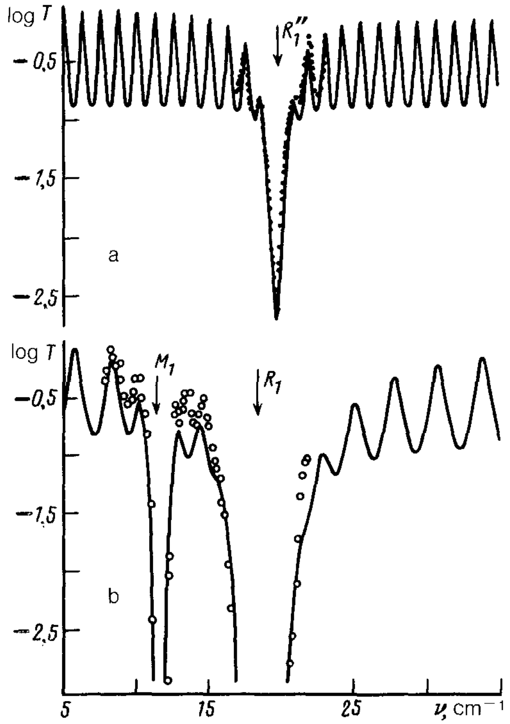

FIG. 1. Transmission spectra of plane-parallel $TmFeO_3$ samples. a—$\vec{e}\|\vec{a}$, $\vec{h}\|\vec{b}$ $T=11$ K (*c*-cut, with thickness $d=0.803$ mm); b—$\vec{e}\|\vec{b}$, $\vec{h}\|\vec{c}$, $T=4.2$ K (*a*-cut, $d=0.279$ mm). Points—Experimental; solid lines—theoretical.

lines M_1, R_1, and R_1''. We observed a total of seven absorption lines in the transmission spectra. Two of them, fairly narrow ($\Delta\nu/\nu \approx 10^{-2}$) and observable over the entire temperature range, are known antiferromagnetic-resonance modes in the Fe subsystem: M_1 and M_2. The other, broader absorption lines ($\Delta\nu/\nu \approx 1$), R_1 ($\vec{h}\|\vec{c}, \vec{e}\|\vec{b}$), R_1' ($\vec{h}\|\vec{a}, \vec{e}\|\vec{b}$), R_1''($\vec{h}\|\vec{b}, \vec{e}\|\vec{a}$), R_2 ($\vec{h}\|\vec{b}, \vec{e}\|\vec{c}$), and R_3 ($\vec{h}\|\vec{b}, \vec{e}\|\vec{c}$), are observed only at $T<100$ K. We have identified them as R modes (more on this below).

The reflection spectra were measured on a Bruker IFS 113V Fourier spectrometer at temperatures of 300, 80, and 20 K over the range $\nu = 10$–100 cm^{-1}. An important aspect of reflection spectra is that the line profile allows one to immediately draw the qualitative conclusion that the line is associated with a magnetic dipole or electric dipole electron transition. This conclusion follows directly from the expression for the reflection coefficient of a semi-infinite medium.[5] From that expression one easily sees that for a dielectric mode this coefficient increases as its resonant frequency is approached from below, while it decreases as it is approached from above. For a magnetic mode, the opposite behavior prevails.

Figure 2 shows some illustrative reflection spectra. We see several lines, varying in shape. The shape of the M_1 and R_1 ($\vec{h}\,\|\vec{c}$, $\vec{e}\|\vec{a}$) lines tells us immediately that the corresponding modes are of a magnetic nature, while the shape of the R_2, R_3, and R_4 ($\vec{h}\,\|\vec{a}$, $\vec{e}\|\vec{c}$) lines tells us that the corresponding modes are of a dielectric nature. For the c-cut sample at $T = 20$ K, at a frequency of 40 cm^{-1}, we also observed lines R_3' ($\vec{h}\,\|\vec{b}$, $\vec{e}\|\vec{a}$) and R_3'' ($\vec{h}\,\|\vec{a}$, $\vec{e}\|\vec{b}$). These lines were far weaker than R_3 and had a different shape, indicating that the corresponding R modes were of a magnetic nature. To identify the observed lines and to determine the symmetry of the modes, we classified the electronic excitations in the crystal, taking into account the selection rules for electronic transition in the Tm^{3+} ion. The $^3H_6$ ground multiplet of the non-Kramers Tm^{3+} ion splits into singlets in the low-symmetry crystal field of the orthoferrite. These singlets are characterized by two irreducible representations (A_1 and A_2) of the symmetry point group C_S, which describes the local surroundings of the rare-earth ion (see the inset in Fig. 3).

The matrix elements between these states are nonzero for the following components of the magnetic ($\vec{\mu}$) and electric ($\vec{d}$) dipole moments of the rare-earth ion:[6]

$$\mu_z,\ d_x,\ d_y \quad \text{для}\ A_1 - A_1 \quad \text{или} \quad A_2 - A_2\ ,$$

$$\mu_x,\ \mu_y,\ d_z \quad \text{для} \quad A_1 - A_2\ , \qquad (1)$$

where the x, y, z axes coincide with the crystallographic a, b, c axes of the orthorhombic crystal. In order to classify the excitations in the crystal, we need to consider the

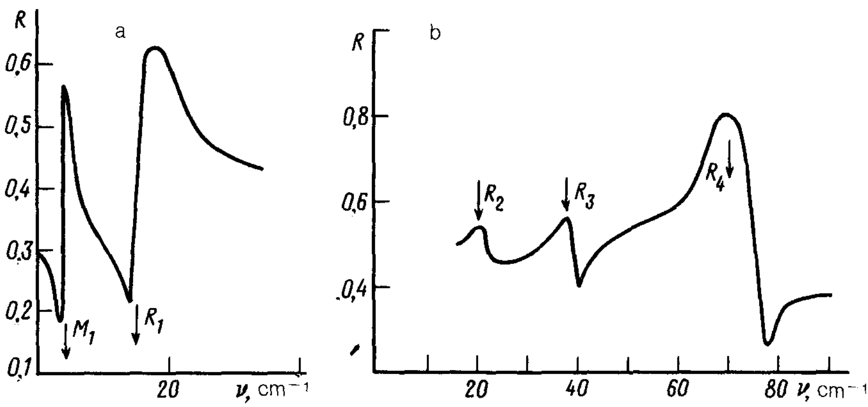

FIG. 2. Reflection spectra of a plane-parallel $TmFeO_3$ sample at $T = 20$ K (b-cut, $d = 2.152$ mm). a—$\vec{e}\|\vec{a}$, $\vec{h}\,\|\vec{c}$; b—$\vec{e}\|\vec{c}$, $\vec{h}\,\|\vec{a}$.

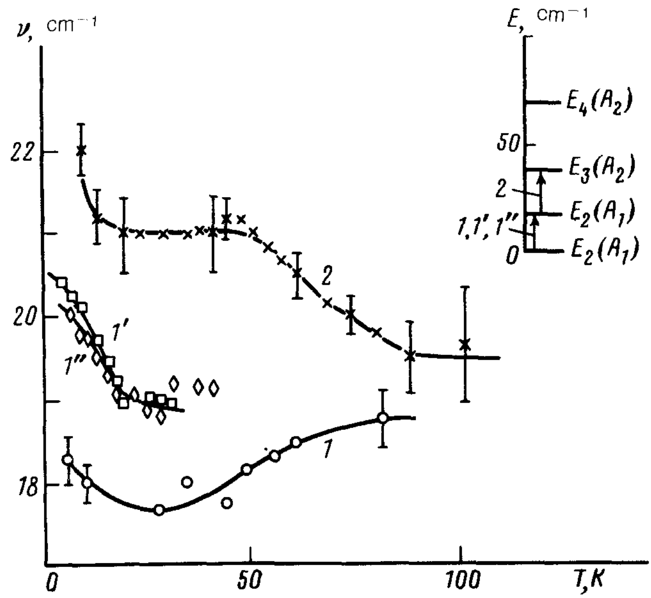

FIG. 3. Temperature dependence of the frequencies of the rare-earth modes (1) R_1, (1′) R_1', (1″) R_1'', and (2) R_2. The inset shows the lower part of the spectrum of the ground multiplet of the Tm^{3+} ion in $TmFeO_3$ (Ref. 6).

crystalline and magnetic spatial symmetry of the system. In $TmFeO_3$ at $T < 100$ K there is an $F_x G_z$ magnetic configuration, which corresponds to the irreducible representation Γ_2 of the space group D_{2h}^{16}–$Pbnm$, where $\vec{F}$ and $\vec{G}$ are the ferromagnetism and antiferromagnetism vectors of the Fe subsystem. It is convenient to use the representations of the D_{2h}^{16}–$Pbnm$ group to characterize the symmetry of the electronic excitations also (see, for example, Refs. 7 and 8). A classification of the oscillations and the conditions for their excitation are given in Table I for the Γ_2 $(F_x G_z)$ magnetic configuration. Various electron transitions between the states of the Tm^{3+} ion in the crystal field have been taken into account. There are four different types of oscillations. Two of these oscillations, which correspond to the irreducible representations Γ_{12} and Γ_{34}, have an inversion center and are excited only by a magnetic field. The two others, Γ_{56} and Γ_{78}, have no inversion center, and they are excited only by the electric field (see also Ref. 8). The components of $\vec{e}$ and $\vec{h}$ in parentheses in Table I excite the corresponding R modes only when the mixing of $|A_1\rangle$ and $|A_2\rangle$ states due to the R–Fe interaction is taken into account. As a rule, this mixing is considerably slighter than the splitting in the crystal field.

Taking the discussion above into account, and using optical data,[6] we have interpreted our experimental results in the following way. In terms of energy, the lines R_1, R_1', and R_1'' correspond to transition from the $E_1(A_1)$ ground singlet to the nearest excited level $E_2(A_1)$. The conditions for the excitation of the R_1' $(\vec{e}\|\vec{b}, \vec{h}\|\vec{a})$ and $R_1''(\vec{e}\|\vec{a}, \vec{h}\|\vec{b})$, modes, observed in the transmission spectra, agree with the selection

TABLE I.

Representation of sp. gr. D_{2h}^{16}	AFMR modes of Fe subsyst.	*R* modes			
		A_1–A_2 transition $A_1 - A_2$		A_1–A_1, A_2–A_2 transitions $A_1 - A_1$, $A_2 - A_2$	
	$\vec{h}$ [7,8]	$\vec{h}$	$\vec{e}$	$\vec{h}$	$\vec{e}$
Γ_{12}	h_x	h_x	-	(h_x)	-
Γ_{34}	h_y, h_z	$h_y(h_z)$	-	$h_z(h_y)$	-
Γ_{56}	-	-	(e_x)	-	e_x
Γ_{78}	-	-	$e_z(e_y)$	-	$e_y(e_z)$

rules for the electric dipole transition $E_1(A_1)$–$E_2(A_1)$ in (1). As a result, according to this table, the symmetry of the electric dipole mode R_1' is determined by the reducible representation Γ_{78}, while that of mode R_1'' is determined by Γ_{56}. The conditions for the excitation of the R_1 mode in the reflection spectra ($\vec{h}\|\vec{c}$, $\vec{e}\|\vec{a}$) and the transmission spectra ($\vec{h}\|\vec{c}$, $\vec{e}\|\vec{b}$) agree with the selection rules for magnetic dipole and electric dipole $E_1(A_1)$–$E_2(A_1)$ transitions simultaneously. The shape of the reflection lines of the R_1 mode (Fig. 2a) indicates directly that this line is due primarily to a magnetic dipole transition excited by a field $\vec{h}\|\vec{c}$, so it has a symmetry Γ_{34}, according to Table I. This conclusion also follows from the circumstance that the intensity of the R_1 mode observed in the transmission spectra ($\vec{e}\|\vec{b}$, $\vec{h}\|\vec{c}$) (Fig. 1b) is vastly greater than that of the purely electric dipole modes R_1'' (Fig. 1a) and R_1'.

We turn now to the other lines. The energy of the line R_2 corresponds to a transition from an excited singlet $E_2(A_1)$ to the neighboring excited singlet $E_3(A_2)$; the lines R_3, R_3', and R_3'' correspond to transitions from $E_1(A_1)$ to $E_3(A_2)$; and the line R_4 corresponds to a transition from $E_1(A_1)$ to $E_4(A_2)$. The conditions for the observation of the lines R_2, R_3, and R_4 in the reflection spectra ($\vec{e}\|\vec{c}$, $\vec{h}\|\vec{a}$) and the transmission spectra ($\vec{e}\|\vec{c}$, $\vec{h}\|\vec{b}$) agree with the selection rules for both electric dipole and magnetic dipole transitions. The shape of the reflection lines indicates directly that these lines are due primarily to electric dipole ($\vec{e}\|\vec{c}$) transitions, so they have a symmetry Γ_{78}, according to Table I. In the other experimental geometry, i.e., without the electric field component e_z, there are two weak modes R_3' ($\vec{e}\|\vec{a}$, $\vec{h}\|\vec{b}$) and R_3'' ($\vec{e}\|\vec{b}$, $\vec{h}\|\vec{a}$) in the reflection spectra. The shape of the lines and the excitation conditions of these modes correspond to purely magnetic dipole $E_1(A_1)$–$E_3(A_2)$ transitions with symmetries Γ_{34} and Γ_{12}, respectively.

This identification of the lines also agrees completely with the temperature dependence of their intensities. For the lines R_1, R_1', R_1'', R_3, R_3', R_3'', and R_4, the intensity increases with decreasing T, while for the line R_2 it first increases and then decreases.

Figure 1 shows the temperature dependence of the frequencies of the R_1, R_1', R_1'', and R_2 modes as found from the transmission spectra. As T decreases, the frequencies of the R_1, R_1', and R_1'', modes, which correspond to the same electronic transition, $E_1(A_1)$–$E_2(A_1)$, are different. The differences stem from differences in the manifestation of the R–R and R–Fe interactions for magnetic dipole and electric dipole R modes.

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[1)] Institute of Physics, Academy of Sciences of the Czechoslovakian Federal Republic, Prague.

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