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Raman scattering study of magnons at the spin-reorientation transitions of $TbFeO_3$ and $TmFeO_3$

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The temperature dependence of $\vec{q} \sim 0$ magnons in $TbFeO_3$ and $TmFeO_3$ has been investigated by Raman scattering. On approaching the spin-reorientation transition from above, the lower magnon branch (M_1) of $TbFeO_3$ shows a remarkable stiffening, while $TmFeO_3$ exhibits the familiar mode-softening behavior. It is proposed that the stiffening of M_1 in $TbFeO_3$ can be understood in terms of the stronger exchange coupling expected in this case between the iron and rare-earth moments, owing to the magnetic ordering of the Tb^{3+} spins just below the spin-reorientation transition.

Ferrimagnetic crystals of the rare-earth orthoferrite ($RFeO_3$, $R \equiv$ rare-earth ion) group exhibit several striking magnetic phenomena,[1] including canted antiferromagnetism and spin-reorientation (SR) transitions. Both of these properties have stimulated a number of experimental and theoretical studies. The SR transition involves the spontaneous rotation of the weak ferromagnetic moment from one crystallographic axis to another, within a narrow temperature interval. Recent investigations show that SR transitions can be second order[2,3] and may be associated with the softening of a low-lying magnon of the system,[4–6] in a manner analogous to displacive structural phase transitions caused by unstable phonon modes.[7] In this paper we report a Raman scattering study of magnons in $TbFeO_3$ and $TmFeO_3$ near their SR transitions. We find an unusual *stiffening of the lower magnon branch* in $TbFeO_3$, whereas in $TmFeO_3$ the corresponding magnon exhibits the familiar mode-softening behavior. In the context of the ordering of Tb^{3+} spins just below the SR transition of $TbFeO_3$, our results point to the crucial role of the exchange interactions between iron and rare-earth moments in determining the spin dyanmics of these crystals.

Single crystals of $TmFeO_3$ and $TbFeO_3$ were grown at Bell Laboratories by the flux method. The orientation of the as-grown faces were checked by the Laue method and found to be orthorhombic. The a, b, and c axes were unambiguously identified by observing on a diffractometer Bragg reflections up to the third order. The sample faces were polished with Syton before the experiments. Raman scattering experiments were performed in the backscattering (reflection) geometry with a spectral resolution of ~ 1 cm^{-1}. Spectra were excited with ~ 150 mW of 6471-Å radiation from a Kr^+ ion laser. A cylindrical lens focused the laser beam to a line image on the sample face, thus minimizing sample heating effects due to the laser beam. The scattered radiation was dispersed with a triple monochromator and detected with a photon counting system. A variable temperature cryostat was used for measurements over 5–300-K range. Other details of the experimental procedure and equipment are described elsewhere.[8]

Both $TmFeO_3$ and $TbFeO_3$ belong to the space group $D_{2h}^{16}(Pnma)$. Above the SR transition region, their net ferromagnetic moment points along the c axis, while below the transition it lies along the a axis. The respective spin configurations are denoted[1] $\Gamma_4(F_z)$ and $\Gamma_2(F_x)$. Adopting a two-sublattice model of the four Fe^{3+} spins in each unit cell, one obtains two doubly degenerate spin-wave branches,[9] M_1 and M_2. For $\vec{q} \sim 0$, the lower-frequency mode M_1 is found to exhibit considerable softening near the SR region of $RFeO_3$ crystals studied so far.[4–6] Phenomenologically, the softening has been explained[5] by the temperature dependence of the two-fold anisotropy constants, A_{xx} and A_{zz}. By considering the magnetic point group of these crystals ($m'm'm$), White *et al.*[6] deduced the following form of the Raman tensors for M_1 and M_2, which are applicable above the SR region:

$$M_1: \begin{bmatrix} 0 & 0 & iC \\ 0 & 0 & F \\ iG & H & 0 \end{bmatrix}; \quad M_2: \begin{bmatrix} A & iB & 0 \\ iD & E & 0 \\ 0 & 0 & I \end{bmatrix}. \tag{1}$$

Thus M_1 and M_2 will appear as Raman lines in mutually exclusive polarizations (configurations). Also, M_2 should be seen for diagonal components of the tensor, in contrast to the purely antisymmetric tensor which characterizes one-magnon scattering observed in several other systems.[8,10]

Figure 1 shows the spectra of M_1 and M_2 for $TbFeO_3$ at 300 K. We believe this is the first investigation of the magnon spectrum of $TbFeO_3$. The strongest signals for both magnons were obtained in backscattering from the a face. Also, as expected, M_2 does appear in the diagonal polarization. By recording both Stokes and anti-Stokes components of all the spectra, it was possible to determine the magnon frequencies to within an accuracy of ± 0.2 cm^{-1}. The frequencies of M_1 and M_2 are 11.8 and 18.5 cm^{-1}, respectively. The SR transition of $TbFeO_3$ is known to be within the 5–10-K range. The temperature variation of M_1 and M_2 is shown in Fig. 2. In constrast to the M_1 magnon of other $R\,FeO_3$ crystals,[4–6] here, far from softening, it shows a continual stiffening as the temperature approaches the SR region, its frequency remaining constant right through the transition. M_2 shows an increase in frequency for lower temperatures, in agreement with the results reported by Kozhizuka and Ushioda[5] for $ErFeO_3$.

We now contrast this with the situation in $TmFeO_3$, where our results complement the previous inelastic neutron scattering study of Shapiro *et al.*[4] The increased energy resolution of the light scattering technique also permits one to determine the magnon frequencies with a higher accuracy. Figure 3 shows the spectra of M_1 and M_2 at 300 K; their respective frequencies are 13.8 and 24.4 cm^{-1}. The SR transition of $TmFeO_3$ occurs[11] between 84–93.6 K. Figure 4 shows the variation of M_1 and M_2 with temperature.

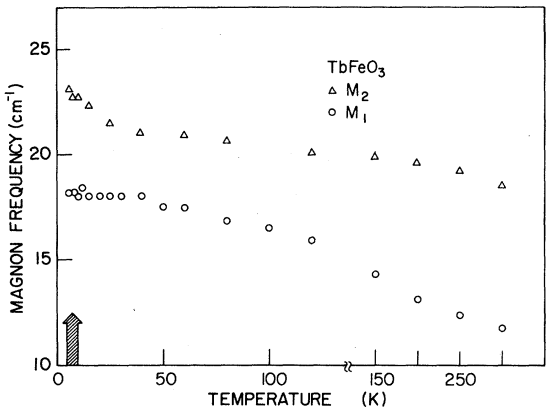

FIG. 2. Temperature dependence of the M_1 and M_2 magnon frequencies in $TbFeO_3$ over 5–300 K. The shaded arrow in the 5–10-K range corresponds to the SR transition region. Note scale change in temperature axis after 130 K.

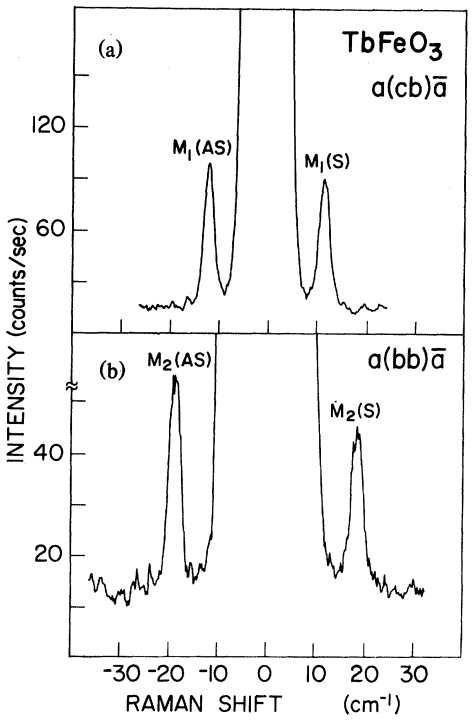

FIG. 1. Stokes (S) and anti-Stokes (AS) components of the magnons in $TbFeO_3$; $T = 300$ K. (a) M_1 magnon; (b) M_2 magnon. Their respective polarizations are indicated.

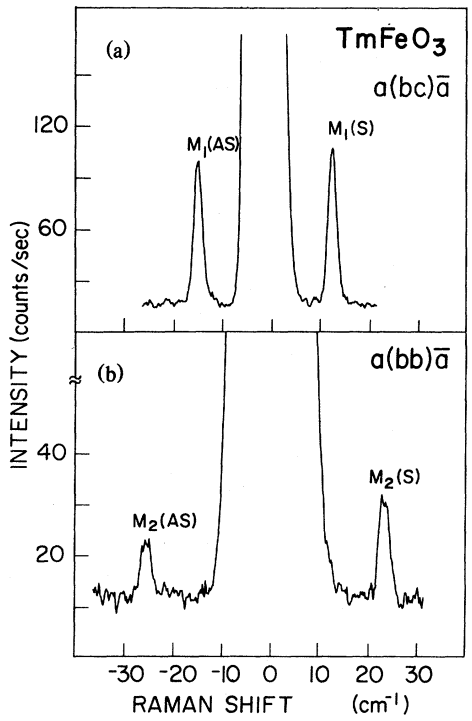

FIG. 3. Stokes (S) and anti-Stokes (AS) components of the magnons in $TmFeO_3$; $T = 300$ K. (a) M_1 magnon; (b) M_2 magnon. Their respective polarizations are indicated.

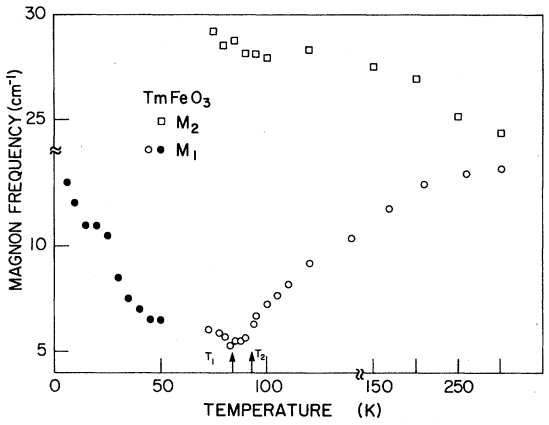

FIG. 4. Temperature dependence of the M_1 and M_2 magnons in $TmFeO_3$ over 5–300 K. Arrows at 84 and 93.6 K denote, respectively, the upper and lower SR transition temperatures, T_2 and T_1. Note scale change in temperature axis after 140 K. The open circles represent the M_1 magnon in $\Gamma_4(F_z)$ spin configuration, whereas the filled circles represent the same magnon now in $\Gamma_2(F_x)$ configuration.

We find a marked softening of M_1 on approaching the SR region. However, the softening is definitely incomplete and the frequency stays finite within the transition region. Again, M_2 shows a gradual increase in frequency as the temperature is lowered.

In both $TbFeO_3$ and $TmFeO_3$ we observe a drastic decrease in the intensity of M_1 and M_2 on approaching the SR transition from above. Below the transition region, the spin configuration changes[1] to $\Gamma_2(F_x)$ and M_1 is now observed from the c face in crossed polarization. The frequency of M_1 increases below the SR transition until it reaches again the room-temperature value. The intensity is extremely low at all temperatures below the SR transition, and our accuracy in determining the magnon frequency is correspondingly lower, now ± 0.5 cm^{-1} as compared to the ± 0.2 cm^{-1} mentioned earlier. Further, we were not able to observe the M_2 magnon below the SR transition. We are currently investigating the magnon and phonon spectra of related $R\,FeO_3$ crystals. These results will be published in due course.

We now discuss the possible origin of the unique behavior of the M_1 magnon in $TbFeO_3$. The SR transition occurs only in those $R\,FeO_3$ crystals where the rare-earth ion carries a net spin.[1] The coupling between iron and rare-earth spins is an essential feature of the theoretical analysis given by Yamaguchi[12] for this transition. $TbFeO_3$ is rather unique among $R\,FeO_3$ crystals in that its SR transition lies just above the temperature interval where the rare-earth moments themselves become ordered. The latter transition is manifested in the specific-heat data of de Combarieu *et al.*[13] which shows a peak at 3.2 K. For other $R\,FeO_3$ crystals examined hitherto,[4–6] the situation is quite different as their SR transition lies at much higher temperatures,[1] and the magnetization of the rare-earth sublattices is expected to be much less significant in that range. In $TbFeO_3$, one therefore expects a much stronger exchange coupling between Fe^{3+} and Tb^{3+} spins near the SR transition. We believe this could account for the continual stiffening of M_1.

It is known that the SR transition itself can occur in one of two ways[2,3]: (a) an abrupt jump of the spins, resulting in a first-order transition at a certain temperature, or (b) two successive second-order phase transitions at temperatures T_1 and T_2, the spins beginning to rotate in a coherent manner at one temperature and reaching their new orientation at the other. To our knowledge, the nature of the transition in $TbFeO_3$ has not been conclusively determined yet. It is tempting to speculate whether the SR transition here indeed might be first order, thanks to the strength of the coupling between Fe^{3+} and Tb^{3+} spins. If so, one would not expect M_1 to soften at this transition. However, this speculation can be confirmed only through a specific-heat study of this crystal; a similar investigation by Moldover *et al.*[14] showed the transition in $YbFeO_3$ to be definitely second order.

In summary, our experiments revealed an example of magnon stiffening, in addition to the familiar softening effect, near the SR transition of $R\,FeO_3$ crystals. The effect is clearly dependent upon the extent of the exchange coupling between the two distinct magnetic species of the system.

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