Inelastic-light-scattering study of magnon softening in $ErFeO_3$

N. Koshizuka
Electrotechnical Laboratory, Sakura-mura, Ibaraki, Japan 305

S. Ushioda
University of California, Irvine, California 92717
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The observation of Raman scattering due to one-magnon excitation is reported for the first time on canted antiferromagnetic $ErFeO_3$ which has a zero-angular-momentum ground state. The magnon softening phenomenon, associated with the spin-reorientation phase transitions of this crystal, is studied through the thermal behavior of one-magnon scattering. The temperature dependence of two antiferromagnetic magnon modes is analyzed on the basis of a simple free-energy form for this spin system. Some peculiar features such as the failure of the soft-mode frequency to vanish at the spin-reorientation temperatures are discussed briefly. It was found that the weak ferromagnetic moment in this canted antiferromagnet must be taken into account for a satisfactory explanation of the polarization properties of the one-magnon spectra. However, the theoretical detail requires further clarification. The prominent intensity enhancement of the soft magnon line near the transition temperature is interpreted to be a result of population increase due to the mode softening associated with spin reorientation.

I. INTRODUCTION

The rare-earth orthoferrites $RFeO_3$ are typical canted antiferromagnets having a number of intriguing magnetic properties such as spin-reorientation (SR) phase transitions.[1] These crystals have a weakly distorted perovskite structure with space group D_{2h}^{16}-*Pbnm*.[2] One of the orthoferrites, $ErFeO_3$ ($T_N = 633$ K), exhibits a rotational-type SR.[1] The antiferromagnetic spin axis of Fe^{3+} ions is slightly tilted ($\sim 1°$) from the a axis at room temperature; this arrangement is called $\Gamma_4(G_xF_z)$ spin configuration. With decreasing temperature the spin axis begins to rotate away from the a axis at T_2 and is directed along the c axis below T_1 with the spin configuration $\Gamma_2(G_zF_x)$.

This SR phenomenon is considered to be a typical displacive-type second-order phase transition.[3,4] Stable spin configurations for this system were investigated by Yamaguchi on the basis of detailed free-energy considerations which take into account the anisotropic exchange interaction between the rare-earth and the transition-metal ions.[5] The dynamics of the SR process was investigated by means of microwave resonance,[6] ultrasound propagation,[7,8] and inelastic neutron scattering[9] experiments. Shapiro *et al.* obtained the spin-wave dispersion relation of $TmFeO_3$ and $ErFeO_3$ by neutron scattering measurements and found the softening of the magnon frequency associated with SR.[9] Light scattering has some advantage over neutron scattering in measuring the energy spectrum of the zone center ($\vec{k} \sim 0$) magnons with high resolution. Furthermore, it can provide additional information on the spin structure through the polarization properties of one-magnon spectra.

In this paper, we report on a Raman-scattering study of magnon softening associated with SR in $ErFeO_3$. To our knowledge this is the first observation of one-magnon Raman scattering in zero orbital angular momentum systems of transition-metal ion compounds. In anisotropic systems first-order Raman scattering by magnons has been studied extensively,[10,11] and one-magnon Brillouin scattering[12] in isotropic systems has been studied using a Fabry-Perot interferometer.

II. EXPERIMENT

Single crystals of $ErFeO_3$ were grown using a floating zone furnace with a power source of 1.5-kW tungsten lamp (Nichiden Kikai). The sample surfaces were polished to a mirrorlike finish with the colloidal silica polishing agent "Syton" (Monsanto). The spectra were measured using a Raman spectrophotometer system (Jasco R750) equipped with a triple monochromator and a photon counting system. A minicomputer (YHP21MX) was used to control the wavelength drive, to store the number of photon counts in the memory, and to display the spectrum on a cathode ray tube. An incident beam of Kr 647.1-nm (Spectra Physics 164) laser light at the power level of 25 mW cw was focused onto the crystal surface. The scattered light was detected by a

cooled photomultiplier (RCA C31034A). A closed cycle Displex refrigerator (Air Products and Chemicals) was used for measuring the temperature dependence of the Raman spectra down to 15 K.

III. RESULTS

Judging from the existing data on the SR temperature of various $R\text{FeO}_3$ crystals, we must assume that the transition temperature is sample dependent. Therefore, we needed to determine the SR temperatures of ErFeO_3 crystals grown by our furnace through measurement of the temperature dependence of magnetization: We found that for our sample T_1 and T_2 are $T_1 = 90 \pm 0.5$ K and $T_2 = 103 \pm 2$ K.

All the Raman-scattering measurements were made in a backscattering configuration with linearly polarized light for both the incident and scattered beams.

Before we present the results for one-magnon Raman scattering, we illustrate the phonon spectra of ErFeO_3 in Fig. 1. These spectra were obtained at room temperature for various polarization configurations. The photon count rate of the maximum peak in the spectra is 150 counts/sec for the slit width of 500 μm. The $R\text{FeO}_3$ have four formula units per unit cell and the normal-mode decomposition in these crystals is given by[13] $\Gamma = 7A_{1g} + 8A_{1u} + 7B_{1g} + 8B_{1u} + 5B_{2g} + 10B_{2u} + 5B_{3g} + 10B_{3u}$. Among these modes, 24 modes are Raman active: $7A_{1g}(xx,yy,zz)$, $7B_{1g}(xy,yx)$, $5B_{2g}(zx,xz)$, and $5B_{3g}(yz,zy)$. All the predicted lines were observed for the totally symmetric A_{1g} modes; however, only some of the lines were found for other symmetries. The frequencies and the mode assignments are given in Table I. In addition to the phonon lines in Fig. 1, there are three lines at 645, 925, and 1300 cm^{-1} in the frequency region from 550 to 1500 cm^{-1}. The line at 645 cm^{-1} is thought to be an impurity-related phonon line, because the intensity of this line increases rapidly with addition of a small amount ($\sim 1\%$) of impurity ions such as Co^{2+} or Ti^{4+}. The broad line at 925 cm^{-1} with the width of about 150 cm^{-1} is assigned to two-magnon (magnon-pair) scattering for the following reasons: The frequency of the peak position is nearly equal to twice the zone boundary magnon energy estimated from the exchange parameters of ErFeO_3. Furthermore, the frequency shifts (~ 60 cm^{-1}) to the higher-energy side with decreasing temperature from room temperature to 40 K; this behavior is consistent with the thermal shift of the magnon-pair excitation

TABLE I. Frequencies and assignments of Raman lines in ErFeO_3 at room temperature.

Frequencies (cm^{-1})	Assignments
15 ± 1	one magnon, M_1
24 ± 1	one magnon, M_2
112 ± 1	A_{1g}, B_{1g}
140 ± 1	A_{1g}
163 ± 1	B_{1g}
264 ± 2	B_{3g}
273 ± 1	A_{1g}
322 ± 3	B_{1g}
345 ± 1	A_{1g}
365 ± 2	B_{3g}
424 ± 2	A_{1g}
434 ± 3	A_{1g}, B_{2g}, B_{3g}
481 ± 3	B_{2g}
505 ± 2	A_{1g}, B_{1g}
645 ± 5	Impurity related phonon
925 ± 10	Two magnon
1300 ± 5	Two phonon

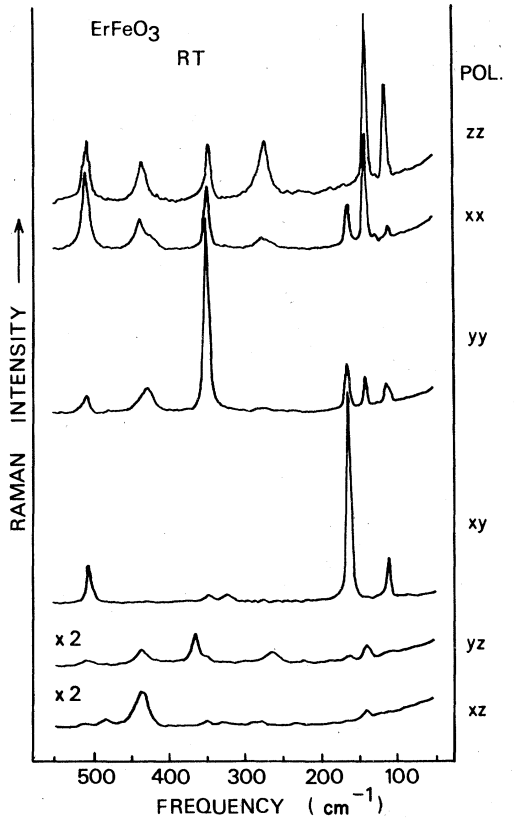

FIG. 1. Stokes Raman spectra of ErFeO_3 at room temperature for various polarization configurations. Polarization directions are denoted as xy, where x and y denote the directions of the electric vectors of the incident and scattered radiation, respectively.

energy in the ordered state.

Figure 2 shows the low-frequency Stokes spectra of $ErFeO_3$ at various temperatures for the polarization configuration $z(xy)\bar{z}$ in the conventional notation. Peak M_1 is definitely assigned to one-magnon scattering for the following reasons: (1) The frequency of peak M_1 coincides with the energy of the lower magnon mode ω_1 obtained by the neutron scattering experiment by Shapiro *et al.*[9]; (2) the polarization property of this line reflects the antisymmetric character of the Raman tensor due to magnon excitation.[10,14]

As seen in Fig. 2, the frequency of peak M_1 decreases with increasing temperature and reaches a maximum at the lower SR temperature T_1. Accompanying this softening of the frequency, the intensity of line M_1 increases up to T_1, and then decreases and disappears at the upper SR temperature T_2. The temperature dependence of the integrated intensity of this line is shown in Fig. 3. The maximum photon count rate of this line is nearly 50 counts/sec with the slit width of 300 μm. Above T_2, one-magnon scattering is found in other polarization configurations, $x(zy)\bar{x}$ and $x(yz)\bar{x}$, and furthermore, another magnon line M_2 appears in the configuration $z(yx)\bar{z}$ and $z(xy)\bar{z}$. The latter line M_2 originates from the excitation of the higher magnon mode ω_2.

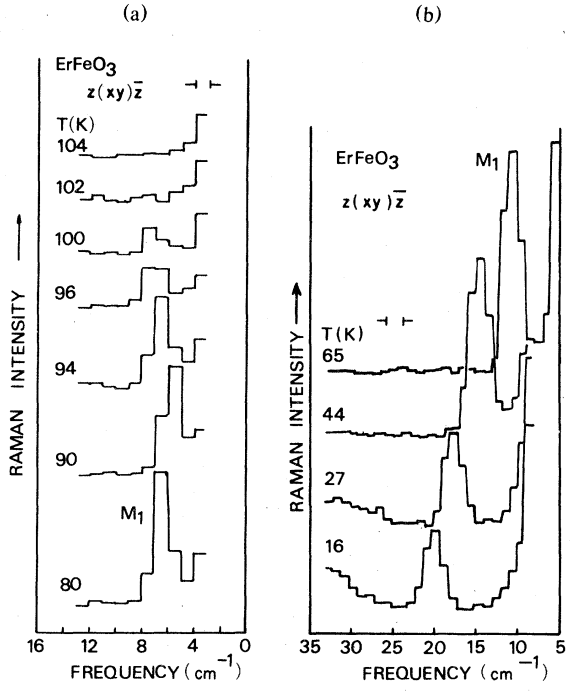

FIG. 2. Low-frequency Raman spectra of $ErFeO_3$ at various temperatures for the polarization configuration $z(xy)\bar{z}$, (a) below the SR temperatures, (b) in the vicinity of the SR temperatures. Peak M_1 is assigned to one-magnon scattering due to the excitation of the lower magnon mode ω_1.

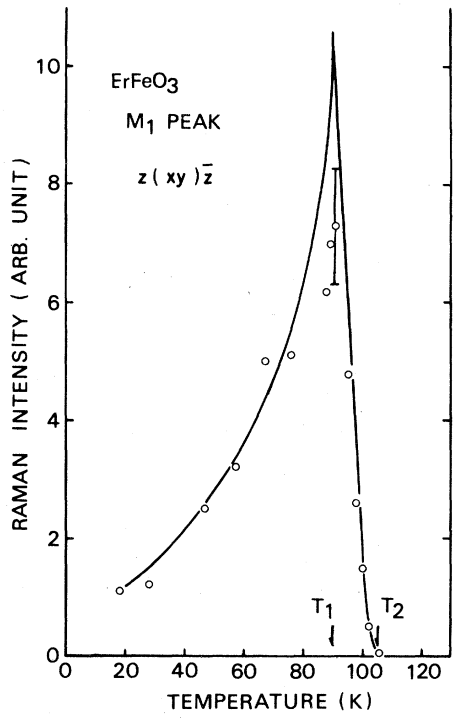

FIG. 3. Integrated intensity of line M_1 vs temperature. Solid curve exhibits the temperature dependence of scattering extinction coefficient $h \propto (n_0+1)\sin^2\theta$ for Stokes Raman line.

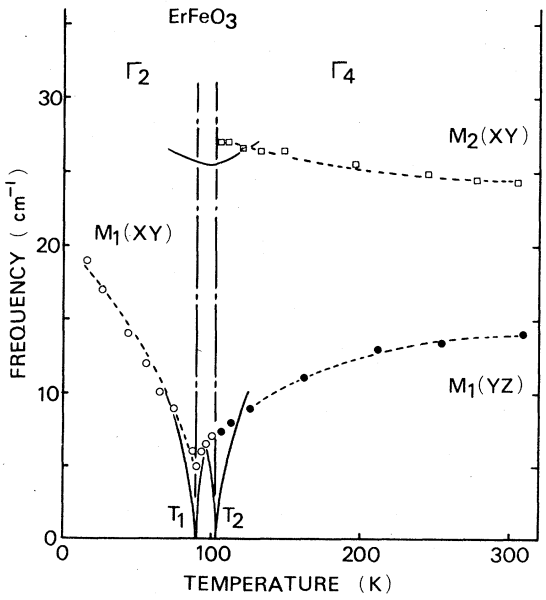

FIG. 4. Magnon frequencies vs temperature. Solid curves exhibit the temperature dependences of magnon frequencies calculated from Eq. (3) with appropriate exchange and anisotropy parameters. Note that Eq. (3) is valid only near the transition temperatures T_1 and T_2. The dashed curves simply connect the experimental points.

The frequencies of these one-magnon lines as a function of temperature are shown in Fig. 4. The frequency of the magnon mode at ω_1 has a minimum at T_1, while no dip is observed at T_2; this observation is consistent with the neutron scattering result.[9] The other mode ω_2 exhibits no softening in contrast to the lower mode. Its frequency increases slightly with decreasing temperature down to T_2; however, interestingly, this line is not observed in any polarization configuration below T_2.

IV. ANALYSIS AND DISCUSSION

In $ErFeO_3$ the SR occurs by a smooth, continuous, and coherent rotation of all the spins. This process is driven by the anisotropy terms with different temperature dependence that appear in the free energy of the form[3]:

$$F(T)=F_0+\tfrac{1}{2}K_2(T)\cos2\theta+K_4\cos4\theta \ , \qquad (1)$$

where θ is the angle between the z axis and the weak ferromagnetic moment; K_2 and K_4 are the twofold and the fourfold anisotropy coefficients. The angular dependence of the magnetization in the SR region obtained from the equilibrium condition $\partial F/\partial\theta=0$ is

$$\cos2\theta=-K_2(T)/8K_4, \quad T_1\leq T\leq T_2 \ . \qquad (2)$$

On this basis the SR is expected to show two second-order transformations at T_1 and T_2 with order parameters $\frac{1}{2}\pi-\theta$ and θ, respectively.

The occurrence of a soft mode is associated with these phase transitions; in this case $\vec{k}=0$ spin-wave mode of the acoustic branch is the one that becomes soft. The frequencies of the two low-lying $\vec{k}=0$ modes are given approximately by[7,9]

$$\begin{aligned}(\hbar\omega_1)^2&=[4E/(2S)^2](-\tfrac{1}{2}K_2\cos2\theta-4K_4\cos4\theta) \ ,\\ (\hbar\omega_2)^2&=[4E/(2S)^2](K_0-\tfrac{1}{4}K_2\cos2\theta-K_4\cos4\theta) \ ,\end{aligned} \qquad (3)$$

where $E=-6J(2S)^2$ is the effective two-sublattice exchange constant, and $K_0=\frac{1}{2}(A_{xx}+A_{zz})$ and $K_2=-2(A_{xx}-A_{zz})$ are defined by twofold anisotropy constants A_{xx} and A_{zz}. Equation (3) gives the characteristic behavior of the soft mode for zero external field. The solid curves in Fig. 4 are obtained from Eq. (3) using the following parameters: $E=3071$ cm^{-1}, $K_0=1.45$ cm^{-1}, $K_2(T)=1.97-0.020T$ cm^{-1}, and $K_4=0.022$ cm^{-1}. These parameter values are consistent with those for $TmFeO_3$ in Ref. 9. The frequency of the lower mode ω_1 goes to zero at T_1 and T_2 as shown in Fig. 2, thus giving rise to an instability in the spin system. It is clear that the linear temperature dependence for $K_2(T)$ should be assumed only near the SR temperature region. There are two peculiar discrepancies between the experimental and the calculated temperature dependences: (1) The soft-mode frequency does not reach zero at either of the SR temperatures. (2) An asymmetry is observed in the softening behavior about T_1 and T_2 of $ErFeO_3$. These features are also reported in Ref. 9 in the neutron scattering study of this crystal, and several possible explanations were discussed.

A magnetoelastic coupling effect, which was examined in detail on the elastic response by Gorodetsky and Lüthi,[7] is thought to provide an explanation for the failure of the soft-mode frequency in $ErFeO_3$ to vanish at T_1 or T_2. However, Shapiro *et al.*[9] exclude this possibility from their quantitative estimate of the effect; that is, unrealistically large magnetoelastic constants, which are larger than that suggested by Gorodetsky and Lüthi, are necessary to account for their observation. They thought that sample inhomogeneity is a more likely cause for nonvanishing of the soft-mode frequency in this system.

Concerning the asymmetry of the softening behavior about T_1 and T_2, we recall the effect of an external magnetic field found by Horner and Varma[3]; the lower transition temperature T_1 shifts to the higher side and the upper one T_2 disappears when an external field is applied perpendicular to the c axis, and vice versa with the field parallel to the c axis. The absence of a dip at T_2 for the soft mode seems to be due to such a magnetic field effect, although no external field was applied in the present experiment. The same kind of asymmetry was also observed for the curve of the spontaneous magnetization versus temperature of $ErFeO_3$. The upper T_2 is ambiguous compared with the clear transition temperature of T_1. The absence of the soft-mode dip at T_2 seems to be related to the ambiguity of the transition temperature.

Although several explanations are possible for the observed magnon-softening behavior, it would be necessary first to make clear whether they are characteristic of the SR in $ErFeO_3$ alone or more general through studies of other $RFeO_3$ crystals.

Next we will discuss the polarization properties and the temperature dependence of the one-magnon scattering spectra. The mechanisms for light scattering by one- and two-magnon excitations were studied by Fleury and Loudon[10] and by Moriya[14] in the early stage of magnon studies by light scattering. Fleury and Loudon adopted a photon-magnon interaction model based on an indirect electric dipole coupling via the spin-orbit interaction.[15] They supposed a simple two-sublattice antiferromagnetic crystal in which each magnetic unit cell contains two spins which are pointed in the positive- and negative-z directions by the uniaxial anisotropy field. In their model they consider the ground state with spin S and zero orbital angular momentum, $L=0$, and an excited P state with $L=1$ and the same spin S as the ground state. The ground state is split into $2S+1$ sublevels by the

exchange field and the excited state is split into three components by the spin-orbit interaction. The Stokes scattering extinction coefficient for the one-magnon process in such a simple antiferromagnet is[10]

$$h = [2M_s\eta_s\omega_i\omega_s^3(n_0+1)(u_0+v_0)^2\Gamma^2/g\beta\eta_i c^4] \times |\epsilon_i^z\epsilon_s^{\pm} - \epsilon_i^{\pm}\epsilon_s^z|^2 \ , \quad (4)$$

where M_s is the saturation magnetization, $\eta_i(\eta_s)$ and $\omega_i(\omega_s)$ are the refractive index and the angular frequency of the incident (scattered) radiation, respectively, n_0 is the Bose-Einstein factor for the magnons of frequency ω_0, and $\epsilon_i(\epsilon_s)$ is the polarization vector of the incident (scattered) radiation. Γ is given by Eq. (24) of Ref. 10 which contains a product of the excited state spin-orbit coupling and two electric-dipole-moment matrix elements. The expression with superscript + (−) holds for the down (up) magnon. u_0 and v_0 are the coefficients which are conventionally used to transform spin operators to magnon operators with $k=0$ in an antiferromagnet.[10]

The polarization factor in Eq. (4) means that if the incident light is polarized along z, the two magnon branches produce circularly polarized scattered light with opposite senses in the xy plane. The antiferromagnetic spin axis of $ErFeO_3$ is nearly along the z direction in the magnetic phase $\Gamma_2(G_zF_x)$ below T_1. If we neglect the spin canting and assume a simple two sublattice antiferromagnet for this crystal, the polarization property of one-magnon scattering should be the same as in the case of a simple antiferromagnet. However, the experimental result contradicts this prediction; the one-magnon scattering for the lower mode ω_1 is observed in the polarization configuration xy. In the spin configuration $\Gamma_4(G_xF_z)$ above T_2, although the polarization property for the higher mode ω_2 is consistent with the above prediction, the polarization property for the soft mode ω_1 cannot be explained by the theory. Comparing the results for line M_1 with spin configurations, it is found that the ferromagnetic component plays an important role in determining the polarization properties: If the magnon excitation for the soft mode ω_1 is caused by spin-operator components perpendicular to the weak ferromagnetic moment, the polarization property can be interpreted within the framework of Fleury and Loudon's model[10] and the spin-dependent electric polarizability theory by Moriya.[14] It is clear that the polarization property of the lines M_1 and M_2 reflects the difference between the precession motions of the modes ω_1 and ω_2.[16]

The temperature dependence of the scattering extinction coefficient is given by $h \propto (n_0+1)$(polarization factor) in first approximation. We assume $\sin^2\theta$ as the polarization factor, where θ is the same angle defined before. Thus the solid curve in Fig. 3 is given by the equation $h = A(n_0+1)\sin^2\theta$, where the proportionality factor A is determined by the experimental value at 20 K. A good agreement with the experiment means that the rapid intensity increase with approach toward T_1 arises from the enhancement of magnon population associated with the softening of its frequency together with the temperature increase. If the frequency of the soft mode goes to zero at T_1 or T_2 as predicted by Eq. (3), the intensity enhancement behavior should be more divergent. The fact that the intensity of the soft magnon line is limited to a finite value must be related to the weak degree of mode softening at the SR temperatures. Dynamically, the SR phase transition is driven by a large fluctuation of the precession motion in the xz plane[16] caused by the enhancement of the soft-magnon population near the transition temperatures.

V. CONCLUSION

Raman scattering due to one-magnon excitation was observed for the first time in erbium orthoferrite, which is a zero-angular-momentum system. The magnon-softening phenomenon was studied in the temperature range of the SR phase transitions of this crystal, and it was analyzed on the basis of a simple free-energy-density expression for this spin system. Anomalous temperature dependence of the low-frequency soft mode remains as a problem which cannot be explained by the simple free-energy model. As it is probable that this peculiar feature is characteristic of the SR only in $ErFeO_3$, we should determine whether it has an intrinsic origin due to erbium ions by studying the softening behavior of other $R\,FeO_3$ crystals.

An explanation of the polarization property of one-magnon scattering spectra was initially attempted on the basis of the simple two-sublattice antiferromagnet model in which the weak ferromagnetic moment is neglected. However, it was found that the presence of the ferromagnetic component is an important factor in explaining the polarization property especially for the soft-magnon line. Since the polarization property of one-magnon scattering reflects the spin structure, it will be very useful in determining the spin structure of $R\,FeO_3$. The intensity enhancement of the soft-magnon line near the SR temperatures was interpreted as due to the increase of the magnon population caused by the frequency softening.

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