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FAST TRACK COMMUNICATION

New magnetic phase transitions in $BiFeO_3$

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Abstract

We observed Raman scattering from magnons in the frequency range from 10 to 65 cm^{-1} in $BiFeO_3$ single crystals at cryogenic temperatures; the temperature dependence of the magnon frequency at 18.2 cm^{-1} approximates an $S = 5/2$ Brillouin function up to the temperature (∼280 K) at which the magnon becomes overdamped. The diverging cross section and the frequency shift at ∼140 and ∼200 K implies a spin-reorientation transition as in orthoferrites.

Ferroelectromagnetic materials, i.e. multiferroics, exhibit ferroelectric (or antiferroelectric) properties in combination with the ferromagnetic (or antiferromagnetic) properties [1, 2]. Additionally they exhibit the phenomenon called magnetoelectric coupling, i.e. magnetization induced by an electric field and electric polarization by a magnetic field. These phenomena also give rise to unusual dynamical effects, which can be observed in optical experiments. Magnetic excitations in multiferroic polar crystals [1, 2] are generally not pure spin waves but contain significant contributions to their Raman scattering cross sections from electric dipole matrix elements. These so-called electromagnons exhibit different dynamical characteristics from magnon scattering in centrosymmetric lattices [3–6].

Bismuth ferrite has become an extremely popular material these days because of its rare or even unique properties of having room-temperature ferroelectric and magnetic order [7]. It is a rhombohedrally distorted ferroelectric perovskite ($T_c \approx$ 1100 K) with the space group $R3c$. It shows G-type canted antiferromagnetism up to 643 K (T_N) [7], in which all neighboring magnetic spins are oriented antiparallel to each other. In addition, the axis along which the spins are aligned precesses throughout the crystal, resulting in a modulated spiral spin structure with a long periodicity of ∼620 Å. It has a rather small magnetization but it shows very large polarization of ca. 100 $\mu C\,cm^{-2}$, both in thin-film [8] and single-crystal [9] forms. Despite the abundant research on $BiFeO_3$, relatively little is known about its spin-wave excitation. In the present study we grew highly pure single crystals by the flux method and obtained the Raman spectra with a high-resolution spectrometer down to 10 cm^{-1} in frequency shift. The spectra revealed two strong one-magnon lines and four relatively weak branches in the frequency range 10–65 cm^{-1}, and we showed that the lower frequency follows the temperature dependence of an Fe^{+3} $S = 5/2$ Brillouin function up to 280 K (0.44 T_N), above which it becomes overdamped. The temperature-dependent magnon scattering studies showed anomalous behavior at 140 and 200 K, which are associated with the spin-reorientation transition temperatures in BFO single crystals.

A single crystal of $BiFeO_3$ was prepared by employing a flux method [10]. The x-ray diffraction revealed rhombohedral structure with grown surface $(001)_{\mathrm{cubic}}$ [10]. Raman scattering data were obtained using a T64000 spectrometer (Horiba Inc.) equipped with a triple-grating monochromator and a Coherent Innova 90C Ar^+-laser with the excitation wavelength at 514.5 nm. The spectral resolution was typically less than 1 cm^{-1}.

Raman scattering data for BFO single crystals were obtained by employing two distinct normal backscattering in VV and VH geometries, and the results at 80 K are presented in figure 1. In VV and VH configurations, the propagation direction of the relevant phonon wavevector **k** is parallel and perpendicular to the $[010]_c$ axis of the cubic BFO (schematically illustrated in the inset of figure 1). The spectra were from the face (010) of the single crystal that is not perpendicular to a principal axis of polarization (111), and therefore it includes modes of all symmetries. As presented in figure 1, we observed two intense peaks at 18.2 and 26.6 cm^{-1}

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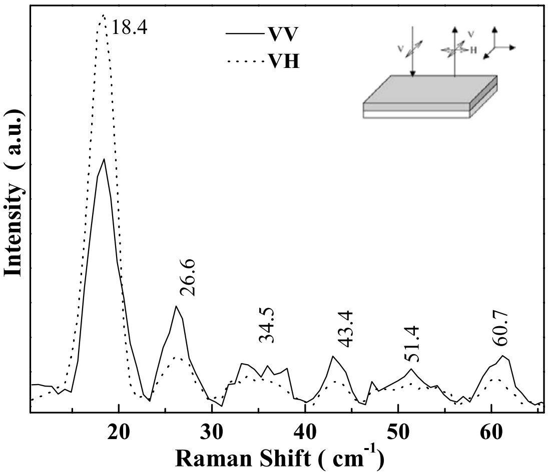

Figure 1. Raman spectra from magnon in BiFeO$_3$ single crystal at 80 K.

and weak-intensity frequency modes at 34.5, 43.4, 51.4 and 60.7 cm^{-1} in both scattering configurations. In addition, we observed 14 first-order Raman peaks at 80 K; these modes are essentially the same as in the Raman spectra of BiFeO$_3$ with the *R*3*c* symmetry [11, 12]. The two intense one-magnon branches are at 18.2 and 26.6 cm^{-1} that are considered to be 'electromagnons' with electric dipole moment and not a pure spin wave. The lower-energy line agrees[4] with the sharp infrared reflectivity feature at 20 cm^{-1}. Katsura *et al* [5] developed a theory for explaining the neutron scattering spectra in helical magnets and suggested that the two lowest modes are due to conventional magnon scattering whereas other modes arise from magnon dispersion and a folded magnetic Brillouin zone and are hence relatively weak in magnitude. This proposed model is very close to BiFeO$_3$ experimental data, in which the observed one-magnon lines are at 18.2 and 26.6 cm^{-1}. The intensity of these magnons changes abruptly as we change the configuration from VV to VH in figure 1, revealing that these two modes follow the polarization configuration similar to that observed from magnons in orthoferrites [13–15].

In order to study the origin of these two magnons in the BiFeO$_3$ single crystal we compared our result to the rare earth orthoferrites [13–15]. The classic study of Raman scattering from magnons in orthoferrites was carried out by White, Nemanich and Herring [13]. They found that in each of the five isomorphs two one-magnon branches were observed, labeled as σ and γ. The σ branch has the polarizability tensor components xz and yz, whereas the γ mode has xx, yy, zz and xy polarization components. The γ magnon mode is necessarily higher in frequency. In ErFeO$_3$ [14], they found the room-temperature frequencies of these two modes to be 14 and 23 cm^{-1}; these values are very close to our results in BiFeO$_3$. These frequencies are given by

$$\omega_\sigma = 24JS[2(K_x - K_z)S + 2JSa^2k^2]^{1/2} \qquad (1)$$

$$\omega_\gamma = 24JS[6DS\tan\beta + 2K_xS + 2JSa^2k^2]^{1/2}. \qquad (2)$$

Here J is the exchange energy between Fe ions separated by distance a, D is the antisymmetric exchange, β is the weak canting angle, $K_{i,j}$ are anisotropy constants and k is the wavevector. The orthoferrites such as ErFeO$_3$ have orthorhombic crystallographic (chemical) primitive cells and also orthorhombic magnetic cells [14]. The crystallographic chemical cell in BiFeO$_3$ is rhombohedral; however, the magnetic cell is monoclinic with space group Bb [16], with a small distortion from orthorhombic. Therefore we can use equations (1) and (2) for bismuth ferrite in its ambient phase.

Venugopalan *et al* have pointed out [15] that the σ magnon branch corresponds to the cooperative motion of the magnetization vectors of the two sublattices along the narrow elliptical orbits in the ac plane of RFeO$_3$ (R = Tb, Tm) single crystals; this magnon has the net ferromagnetic moment oscillating at the characteristic ferromagnetic resonance frequency. In contrast, the γ mode has magnetization vectors precess along elliptical orbits whose major axis is the b direction and this produces no change in ferromagnetic moment. This is then often termed the antiferromagnetic resonance mode. Whereas the σ mode is very temperature-dependent near a spin-reorientation transition temperature, the γ mode is unaffected.

To study the behavior of observed electromagnons with temperature in BFO single crystals, we performed micro-Raman scattering measurements by employing two different normal backscattering geometries (VV and VH) in the temperature range between 80 and 300 K, and their results are presented in figures 2(a) and (b). In general, we observed that the σ magnon at 18.2 cm^{-1} associated with ferromagnetic ordering is strongly temperature-dependent, whereas the γ magnon at 26.6 cm^{-1} and other magnon frequencies at 34.5, 43.4, 51.4 and 60.7 cm^{-1} disappeared above a certain temperature without showing any remarkable frequency shift.

Finally, in [10], we show that BiFeO$_3$ exhibits spin glass behavior at low temperature with T_{SG}(spin-glass) = 29.4 K. In the present context it is important that the spin glass exponent $z\upsilon = 1.4$. This is close to the value 2.0 in the original mean-field Kirkpatrick–Sherrington model [19] and very different from the values ca. 9–10 for Ising models [20]. This seems compatible with the present interpretation of spectra as electromagnons; these modes are not pure spin waves and consequently their electric dipole part is Coulombic and long range, yielding apparently mean-field exponents.

Figure 3(a) illustrates the σ magnon (18.2 cm^{-1}) scattering intensity from 80–280 K. The singular peak at 140 and 200 K is reproducible and in agreement with the frequency data in figure 3, indicating thereby some spin reorientation heretofore unpredicted. Figure 3(b) shows that the magnon linewidth remains very narrow (3.0–3.5 cm^{-1}) and it is nearly temperature-independent from 80–230 K. Figure 3(c) shows that the σ magnon frequencies vary approximately as the Brillouin function for $S = 5/2$ for up to 280 K [20]. Note that the data points near 140 and 200 K do not fall on the curve. Above 280 K the data appeared overdamped; these results agree generally with those in [13–15]. The σ magnon

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[4] An unpublished dataset attributed to Professor Z Schlesinger at UC Santa Cruz appears on the web site of J W Orenstein (Berkeley), showing a sharp infrared reflectivity feature around 20 cm^{-1}.

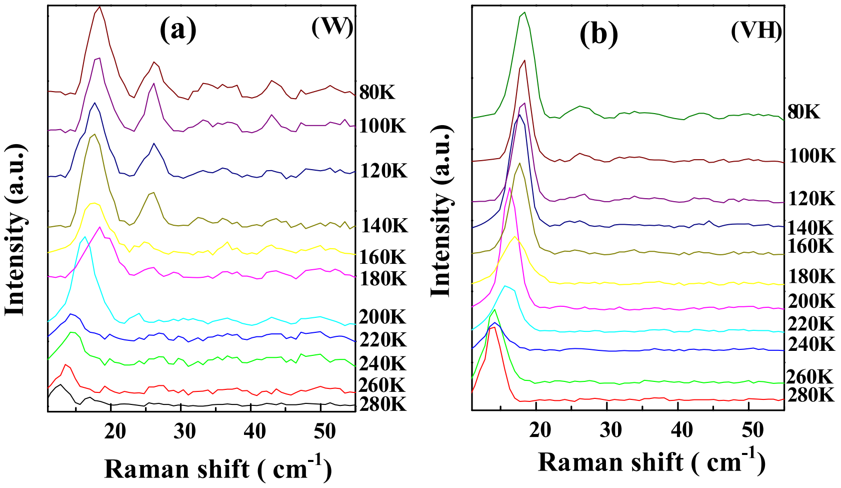

Figure 2. Temperature-dependent electromagnon spectra of a BiFeO$_3$ single crystal (a) in VV configuration and (b) in VH configuration. (This figure is in colour only in the electronic version)

at 18.2 cm^{-1} varies smoothly from 80 to 280 K, but neither its frequency nor its intensity varies monotonically with the temperature; instead there is an abrupt increase in the intensity at 140 and 200 K and a shift down in frequency by $\sim$4 cm^{-1}. The variation of the frequency shift and the intensity of the γ magnon at 26.6 cm^{-1} with temperature are presented in figure 2. This mode disappears above 140 and 200 K in VH and VV configurations, respectively, and its frequency is temperature-independent from 80 to 200 K and shifted only up to 1 cm^{-1}. These effects are reproducible on heating and cooling. Their origin is unknown, though other RFeO$_3$ materials are known to have spin-reorientation transitions at comparable temperatures (e.g. 84–94 K in TmFeO$_3$) [15]. In [10] we show that zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves in single-crystal bismuth ferrite split below ca. 250 K and that the ZFC curves exhibit a sharp cusp at 50 K. This suggests a spin glass behavior at low temperatures with competition between ferromagnetic and antiferromagnetic ordering and may relate to the unexplained anomaly near 200 K in the present work.

It is useful to try to relate our data and especially the model used to other descriptions. A rather detailed model of magnon in the spiral structure of BiFeO$_3$ has been made available recently [17] that predicts a series of approximately evenly spaced lines in the Raman effect, resembling the electron Landau levels in a semiconductor under applied magnetic fields. Recently Cazayous *et al* observed Raman data of BFO single crystal described as electromagnon [18] which seem in good agreement with that model. Here we would like to relate that model briefly to the one we use, and to the four-dimensional description of Janner and Janssen [3] for incommensurate structures. First, although the experiments and data of [3] agree well for the frequency spacing of the magnon lines, they do not explain why two lines are much more intense than all the others; this is odd because they are not the first lines in either of the two sequences. Second, the model does not explain the number of lines—that is, why the sequences stop at six or seven transitions and do not continue.

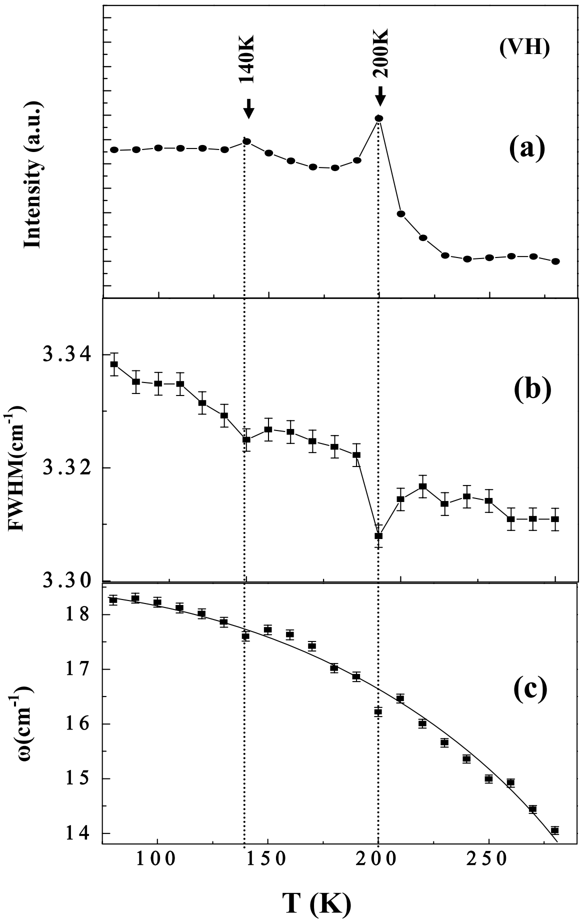

Figure 3. Temperature dependence of the magnon mode at 18.2 cm^{-1} in the temperature range between 80 and 280 K. (a) Integrated intensity, (b) FWHM, (c) experimental correlation between the electromagnon frequency softening of the one-magnon branch at 18.2 cm^{-1} and the $S = 5/2$ Brillouin function.

We suggest that there are actually three reasonable models for the data. The model of [17] gives a good description at very low temperatures, where most of the transitions have comparable intensity. However, for an incommensurate spiral structure the four-dimensional representations of Janner and Janssen [3] offer a rigorous alternative. The Janner–Janssen model predicts three modes in [4D] for maximal symmetry. These are labeled R3(00Γ), R3(00Γ)t, and Rc(00Γ). Of these three, the R3(00Γ)t is a transverse mode and the others longitudinal. Thus, using only the incommensurate character of the structure, we anticipate three Raman modes, one transverse and two longitudinal, in accord with the high-intensity modes we see in figure 1. It would appear that this description is good in the temperature region from about 140 K to above room temperature.

In summary, high-resolution Raman data are presented showing two one-magnon branches in bismuth ferrite. The lower branch near 18.4 cm^{-1} is ferromagnetic-like and varies with temperature as an $S = 5/2$ Brillouin function up to 0.44 T_N, above which it becomes overdamped or instrumentally unresolved from the elastically scattered laser light. The higher-frequency magnon near 26.6 cm^{-1} is weaker in intensity, temperature-independent, and it resembles the antiferromagnetic mode in orthoferrites. Anomalies in magnon frequency and temperature are unexpectedly found at 200 and 140 K, which may suggest a spin-reorientation transition similar to those observed in most of the rare earth orthoferrites. This is the first investigation of its kind on $\mathrm{BiFeO_3}$, and prior to our work the magnetic structure was considered to be unchanged from ambient temperatures to cryogenic temperatures, based upon the original work of Sosnowska *et al* [21], which showed a very long period (∼620 Å) incommensurate cycloid. Thus, the existence of two new magnetic phase transitions was not predicted or anticipated.

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