Spin-charge-lattice coupling through resonant multimagnon excitations in multiferroic $BiFeO_3$

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Spin-charge-lattice coupling mediated by multimagnon processes is demonstrated in multiferroic $BiFeO_3$. Experimental evidence of two- and three-magnon excitations as well as multimagnon coupling at electronic energy scales and high temperatures are reported. Temperature dependent Raman experiments show up to five resonant enhancements of the two-magnon excitation below the Néel temperature. These are shown to be collective interactions between on-site Fe *d-d* electronic resonance, phonons, and multimagnons. © *2009 American Institute of Physics*.
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Spin-charge-lattice coupling is central to the current interest in multiferroic materials. In particular, the coupling between magnetization and polarization can lead to cross-coupled phenomena such as magnetic control of polarization and electrical control of magnetism.[1,2] Multiferroic materials with both polar and magnetic order parameters usually show a relatively low-symmetry crystal structure due to the absence of both time and space inversion symmetries; hence, a strong interaction between the low-lying magnetic and lattice excitations can occur, leading to rich new physics phenomena. One widely studied mechanism for spin-charge coupling is through electromagnons, which are single-magnon spin waves that are excited by an ac electric field.[3–6] A relatively unexplored mechanism in multiferroics is through multimagnon excitations, which are known to be very sensitive to temperature effects and phase transitions.[7]

Bismuth ferrite, $BiFeO_3$, the focus of this study, has a robust ferroelectric polarization ($\sim 100\ \mu C/cm^2$) at room temperature (RT),[8] that is the largest among known ferroelectrics. At RT, $BiFeO_3$ is a rhombohedrally distorted ferroelectric perovskite with space group $R3c$ and a Curie temperature, $T_C < 1100$ K.[9] It also shows a *G*-type canted antiferromagnetic order below Néel temperature, $T_N < 640$ K, and, in the bulk, an incommensurately space-modulated spin structure along $(110)_h$.[10] During the past few years, various physical properties of $BiFeO_3$ have been reported to show anomalies across T_N.[11–14] However, with the exception of neutron diffraction, none of these properties, have cleanly distinguished the magnetism from the polar contribution in this material. This makes the study of coupled phenomena challenging. Here we show that combining Raman scattering and linear optical spectroscopy of multimagnons, phonons, and electronic energy levels can reveal spin-charge-lattice coupling in this system.

For our experiments, 4.5 μm $BiFeO_3$ film on (110) $DyScO_3$ and $BiFeO_3$ single crystal were grown according to Refs. 12 and 14. The thick films were relaxed and had $(001)_p$ pseudocube-on-pesudocube epitaxial geometry, with trigonal C_{3v} crystal structure. Raman spectra were recorded under excitation at 488 nm in a backscattering geometry by using a WITec alpha 300 S confocal Raman microscope equipped with a Linkam heating stage. Raman spectra were collected in unpolarized geometry. Optical transmittance measurements were performed using a Perkin Elmer Lambda-900 spectrometer between 4 and 730 K.

Though magnons energy are typically small ($<100\ cm^{-1}$), Raman scattering for spin wave optical branches at higher energies have been previously reported in iron oxides due to their large unit cell, their corresponding multimagnon excitations located at energies larger than $1000\ cm^{-1}$.[15] Figures 1(a) and 1(b) depict the high frequency unpolarized Raman spectra for a 4.5 μm thick epitaxial film of $BiFeO_3$ collected at different temperatures. Further details on the temperature dependent Raman spectra under $1300\ cm^{-1}$ can be found in Refs. 11, 14, and 16. Evidence for two- and three-magnon scattering at the shoulder of a previously reported two-phonon overtone can be observed, their energy values peaking at ~ 1530 and $2350\ cm^{-1}$, respectively. The two- and three-magnon excitations were identified by using the striking spectral similarity between $BiFeO_3$ and α-Fe_2O_3, the simplest case of an iron oxide containing only FeO_6 octahedra, where not only two-magnon scattering but also two-phonon overtones at very similar energies have been reported.[14,15] (Our films and crystals were

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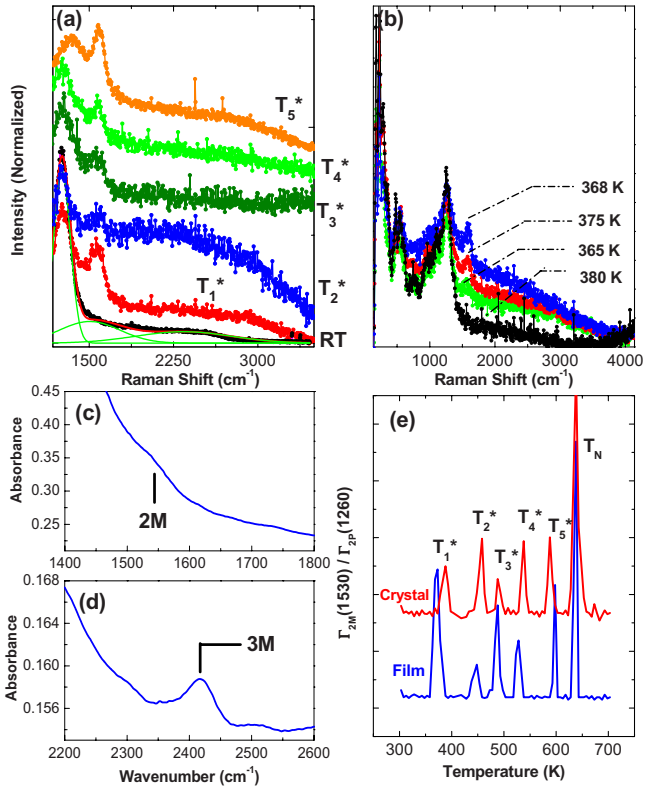

FIG. 1. (Color online) (a) Temperature-dependent Raman spectra of a 4.5 μm thick epitaxial $BiFeO_3$ film. The three Gaussian fits to RT spectra correspond to two-phonon, two-magnon, and three-magnon replica, respectively, from low-to-high wavenumber shift. For clarity, the spectra at T_1^* =365 K, T_2^*=450 K, T_3^*=490 K, T_4^*=530 K, and T_5^*=600 K, are normalized and vertically translated. (b) Evolution of the Raman spectra collected around T_1^* [(c) and (d)] RT midinfrared linear absorption measured on a $BiFeO_3$ bulk single crystal. (e) Integrated intensity ratio between the two-magnon and two-phonon Raman overtones as a function of temperature.

confirmed to be phase-pure $BiFeO_3$ by using synchrotron x-ray diffraction, transmission electron microscopy, and scanning probe microscopy). RT midinfrared absorption experiments were performed in the same spectral range [Figs. 1(c) and 1(d)]. The two-magnon absorption band can be seen around 1550 cm^{-1} [see Fig. 1(c)], though the strong contribution to the absorption spectra of the second order overtones in the 1400–1800 cm^{-1} energy range precludes resolving this peak. At higher energies [Fig. 1(d)], an absorption band centered at ~2415 cm^{-1} is well resolved, which reasonably matches the three-magnon excitation from Raman scattering. These results not only support our previous assignments but also point out strong coupling interactions between the spin system (Fe–Fe exchange interaction) and electric dipole active excitations in $BiFeO_3$.

Based on the position of the two magnon scattering observed in the Raman spectra, an estimate of the nearest neighbor exchange J, described by the Heisenberg Hamiltonian, can be made. If spin deviations are created on adjacent sites in a perovskite antiferromagnet, the excitation frequency of the system arising from two-magnon scattering is given by $J(2Sz-1)$, where S refers to the individual spin on the magnetic site and z represents the number of nearest neighbors to that site.[7] In bismuth ferrite, the spin on Fe^{3+} site is $S=\frac{5}{2}$ and the number of nearest neighbors around Fe cation is $z=6$. The frequency shift of the two magnon peak to the first approximation is given by $\omega(2M)=J(2Sz-1)=29J$. From experiments, the two magnon scattering peak is observed at 1530 cm^{-1} for $BiFeO_3$ in both film and crystal. Thus, the value of exchange interaction is obtained as $J \sim 1530/29=52.8$ $cm^{-1}=6.54$ meV. This estimated value is in agreement with first principle calculations performed on $BiFeO_3$ using LDA+U method (for $U=5$ eV), where the $|J|$ value is estimated to be 7.4 meV.[17]

As the samples were heated, a striking enhancement of the two-magnon Raman bands was observed *only* within a ~10 K window around six different temperatures of T_1^* =365 K, T_2^*=450 K, T_3^*=490 K, T_4^*=530 K, T_5^*=600 K, and T_N=645 K, as seen from Figs. 1(a) and 1(e). Similar results were observed in single crystals. Unfortunately, the weak intensity and considerable linewidth of the two- and three-magnon excitations prevented a study of their temperature dependence in terms of frequency shift, broadening, and total intensity. Nonetheless, from the ratio between two-magnon (<1550 cm^{-1}) and two-phonon (<1260 cm^{-1}) excitations as a function of temperature, a clear plot of the temperature driven multimagnon enhancement can be obtained [Fig. 1(e)]. Since anomalies in the measured resistivity and induced magnetization were observed only at T_N, and not at any of T_1^* to T_5^*, it rules out spin reorientation transitions except at T_N. Also, a lack of any anomalous lattice parameter changes at these temperatures[18] suggests that these are not structural phase transitions. We note that the two-phonon overtone—strongly enhanced due to the resonance with the intrinsic absorption edge—also couples strongly to T_N as shown previously.[14] Hence, since the excitation energy ($E_{exc}<2.54$ eV) is close to the bandedge, these anomalies appear to be (multi)magnon/phonon-assisted electronic resonances driven by temperature shifts. To further explore this possibility, we first probed the electronic structure of $BiFeO_3$ at high energies, i.e., close to the band edge.

Temperature dependent linear absorption measurements (from $T=5$ to 730 K) and parameterization analysis were performed on a $BiFeO_3$ film on $DyScO_3$ (110). For the series of temperature dependent measurements, the complex index of refraction ($N=n+ik$) were extracted by fitting the experimental ellipsometric spectra to an optical model consisting of a semi-infinite $DyScO_3$ substrate/100 nm $BiFeO_3$ film/air ambient structure. Free parameters correspond to the parameterization of the $BiFeO_3$ dielectric function[19] represented by this film by a Lorentz oscillator, three Tauc–Lorentz oscillator sharing a common Tauc gap, and a constant additive term to ε_1 represented by ε_∞.[20,21] Figure 2(a) shows an example of experimental transmittance spectra at $T=5$ K for the 100 nm $BiFeO_3/DyScO_3$ substrate stack and fit to the corresponding model. It displays an absorption onset at ~2.2 eV, a small shoulder centered at $E_{TL}\sim 2.5$ eV, deriving from onsite d-to-d excitations of the Fe^{3+} ions and two larger features near 3.2 and 4.5 eV that are assigned as charge transfer excitations.[22,23] All temperature dependent experimental spectra and fits are in good agreement. Figure 2(b) shows the position of the $E_{TL}\sim 2.5$ eV shoulder extracted from a parameterization of the absorption spectrum as a function of temperature. As observed, it shows singularities at T_1^* ~380 K, $T_5^*\sim 580$ K, and T_N, consistent with the previously reported band gap temperature dependence,[24,25] and the current Raman results. Furthermore, from the results displayed in Fig. 2(b), it can be seen that all the singularities observed in the magnetic Raman response [Fig. 1(e)] occurs within the

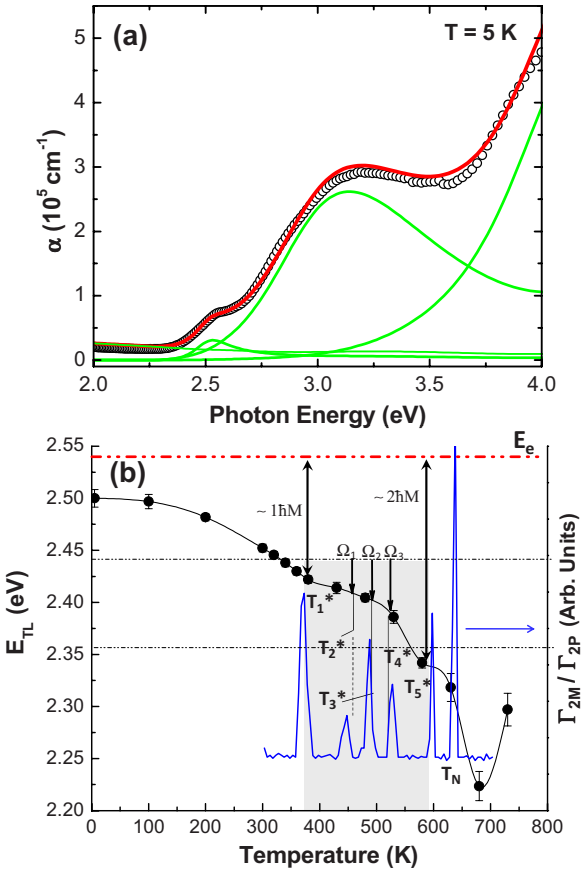

FIG. 2. (Color online) (a) Absorption spectrum obtained for a 100 nm $BiFeO_3$ film on $DyScO_3$(110). Solid lines are fits to the parameterized dielectric function at 5 K. (b) (Left axis) Energy position, E_{TL}. Also shown are resonance conditions at T_i^* ($i=1-5$) and T_N involving the Raman excitation wavelength E_{exc}, Tauc–Lorentz energy, E_{TL}, one- and two-magnon and phonons Ω_1, Ω_2, and Ω_3. (Right axis) Integrated intensity ratio between the two-magnon and two-phonon Raman overtones as a function of temperature.

energy range of $E_{TL} \sim 2.43-2.34$ eV. In terms of E_{TL}, the first magnon anomaly at $T_1^* \sim 2.43$ eV is located ~ 0.11 eV below the Raman pump energy ($E_{exc}=2.54$ eV), while the $T_5^* \sim 2.34$ eV is located ~ 0.2 eV below the Raman pump. These values are close to the expected one-magnon energy ~ 0.1 eV and the observed two-magnon energy ~ 0.19 eV in Fig. 1. Further, the energy separation between T_1^* and the other four transitions in terms of the corresponding shift in E_{TL} are on the 20–50 meV scale. We note that even when a detailed correspondence with specific phonon or magnon modes in $BiFeO_3$ is presently unwarranted, these energies are clearly on the lattice (phonon and magnon) energy scale.[16] Therefore, the above analysis suggests that the observed Raman enhancements arise from collective interactions involving (multi)magnons, phonons, and electronic states. Indeed, an additional signature for such phonon-magnon interaction at these resonances can be observed in the broad background peak that appears only at these magnon resonances [see Fig. 1(b)]. Such broad features have also been seen in the Raman signal of multiferroic $YMnO_3$ and are attributed to two-magnon-phonon interactions, where phonons act as intermediate states.[26]

In summary, we have shown experimental evidence for spin-charge-lattice coupling in multiferroic $BiFeO_3$. Using a near resonant excitation wavelength (2.54 eV), six Raman enhancements of two-magnon excitations are observed with temperature: one at T_N arising from the antiferromagnetic phase transition and five new ones below T_N, which are shown to be combined resonances involving electronic levels, phonons, and magnon states. The work highlights the sensitivity of multimagnon spectroscopy to spin-charge coupling in multiferroics that has been minimally explored so far and appears to be broadly applicable to other multiferroics and magnetoelectrics.

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