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Phonon anomalies and the ferroelectric phase transition in multiferroic BiFeO$_3$

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We report a temperature-dependent Raman scattering investigation of the multiferroic material bismuth ferrite BiFeO$_3$ (BFO). The observed loss of the Raman spectrum at the ferroelectric Curie temperature T_C should be in agreement with a cubic $Pm\bar{3}m$ structure of the high-temperature paraelectric phase. Surprisingly, the ferroelectric-to-paraelectric phase transition is not soft-mode driven, indicating a nonconventional ferroelectric. Furthermore, our results reveal pronounced phonon anomalies around the magnetic Néel temperature T_N. We tentatively attribute these anomalies to the multiferroic character of BFO.

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In past years there has been increasing interest in so-called magnetoelectric multiferroics, which show spontaneous magnetic and ferroelectric ordering, thus two ferroic properties, within the same phase. On the way towards a fundamental understanding of multiferroics, the experimental observation and understanding of the coupling mechanism between the ferroelectric and magnetic orders are of great interest. Important advances were, for instance, made through the use of second-harmonic light, dielectric and magnetic measurements, or structural investigations.[1,2] In contrast, very little is known about the behavior of phonons in magnetoelectric multiferroics, although investigations of phonons have in the past played a crucial role in the understanding of classic ferroelectrics. Phonons are also known to be influenced by spin correlation, thus offering a complementary tool.[3]

Recent investigations of HoMnO$_3$ by Raman and IR spectroscopy[4] and of LuMnO$_3$ by transmittance and reflectance measurements[3] have revealed the importance of phonon effects in multiferroics. The latter have been underpinned by both the observation of extraordinary spin-phonon interactions in YMnO$_3$ detected by thermal conductivity measurements[5] and the report of a strong spin-lattice coupling in HoMnO$_3$ derived from thermal expansion measurements.[6] A similar coupling is expected to exist in most, if not all, multiferroics but up to now the available data have been restricted to rare-earth (RE) manganites.

Motivated to determine and understand the role of phonons in multiferroics, we have undertaken a Raman scattering study of BiFeO$_3$ (BFO). Bismuth ferrite is an interesting model system because it presents a number of distinct features compared to RE manganites: BiFeO$_3$ is a very robust multiferroelectric since it presents a coexistence of ferroelectric and antiferromagnetic orders up to unusually high temperatures: In bulk single crystals, BiFeO$_3$ has an antiferromagnet (AFM) Néel temperature T_N of $\sim$370 °C and a ferroelectric Curie temperature T_C of $\sim$830 °C.[7] Furthermore, BFO presents exchange interactions only in the Fe^{3+} subsystem, whereas RE manganites present two correlated magnet subsystems (R^{3+} and Mn^{3+}). Moreover, the ferroelectricity in BFO is conditioned by the stereochemically active $6s^2$ lone pair of Bi^{3+}, while it has been proposed that the ferroelectricity in RE manganites originates in magnetic interactions.[2]

Our temperature-dependent Raman study reveals (i) the loss of the Raman spectrum at the Curie temperature T_c, indicating a cubic $Pm\bar{3}m$ structure for the paraelectric phase—interestingly, this transition is not soft-mode-driven—and (ii) strong phonon anomalies around the Néel temperature T_N for some particular phonons.

Single crystals of BiFeO$_3$ were grown using a Fe$_2$O$_3$/Bi$_2$O$_3$ flux in a platinum crucible. Translucent crystals with a shape of thin platelets ($\approx$1 mm $\times$ 0.2 mm) have been isolated, and Laue backscattering indicates a $[001]_{\text{pc}}$ orientation of the platelets (pseudocubic setting). Raman spectra were recorded in backscattering geometry with a LABRAM Jobin-Yvon spectrometer using a He-Ne laser (632.8 nm) as excitation line. Temperature measurements in the range from 25° to 850 °C have been carried out by using a commercial LINKAM heating stage placed under the Raman microscope. The Raman spectra before and after heating are identical, attesting to the reversibility of temperature-induced changes. Contrary to earlier studies[8] we observe no sample decomposition above 810 °C.

The room-temperature structure of BiFeO$_3$ crystals is a highly rhombohedrally distorted perovskite with space group $R3c$.[9,10] The crystal structure of the high-temperature paraelectric phase has not been conclusively determined, a cubic $Pm\bar{3}m$ and a rhombohedral $R\bar{3}c$ phase being currently considered.[11] With respect to the cubic $Pm\bar{3}m$ structure the rhombohedral structure is obtained by an antiphase tilt of the adjacent FeO$_6$ octahedra and a displacement of the Fe^{3+} and Bi^{3+} cations from their centrosymmetric position along $[111]_{\text{pc}}$. The 10 atoms in the unit cell of the rhombohedral $R3c$ structure give rise to 15 Raman-active modes:

$$\Gamma_{\text{Raman},R3c} = 4A_1 + 9E.$$

Figure 1 presents Raman spectra of BiFeO$_3$ from room temperature up to 820 °C. The Raman spectra are well defined and provide reference spectra for both thin-film investigations and a potential countercheck of first-principles

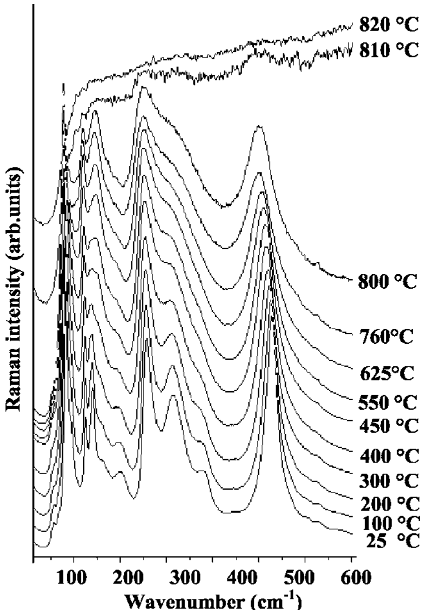

FIG. 1. Temperature-dependent Raman spectra of BiFeO$_3$.

ab initio calculations.[11,12] The overall spectral signature does not change notably in the range from 25 to 800 °C. This temperature behavior indicates that BiFeO$_3$ maintains its room-temperature structure up to 800 °C, which is in agreement with previous investigations.[8,9] With increasing temperature all bands shift to low wave number (Fig. 2) and broaden, a behavior which is explained by thermal expansion and thermal disorder, respectively.

While the Raman response is still very well defined at 800 °C, it is suddenly strongly reduced at 810 °C and, finally, totally lost at 820 °C (Fig. 1). At first sight, such a spectral evolution should be linked with a structural phase transition towards a high-temperature cubic $Pm\bar{3}m$ phase for which any first-order Raman scattering is forbidden. The latter observation is not unusual knowing that most perovskite-type oxides crystallize at high temperature in a $Pm\bar{3}m$ structure. Note that the ferroelectric- ($R3c$) to paraelectric- ($Pm\bar{3}m$) phase transition is *not* accompanied by the observation of a soft mode. At first sight, this is unexpected knowing that the ferroelectric-paraelectric phase transition of classic ferroelectrics like PbTiO$_3$ is soft-mode driven. However, the absence of a soft mode can be related to the fact that the space groups $R3c$ and $Pm\bar{3}m$ are not in a pure supergroup or subgroup relation, implying a first-order (not soft-mode-driven) transition as illustrated by the abrupt loss of the Raman signature.

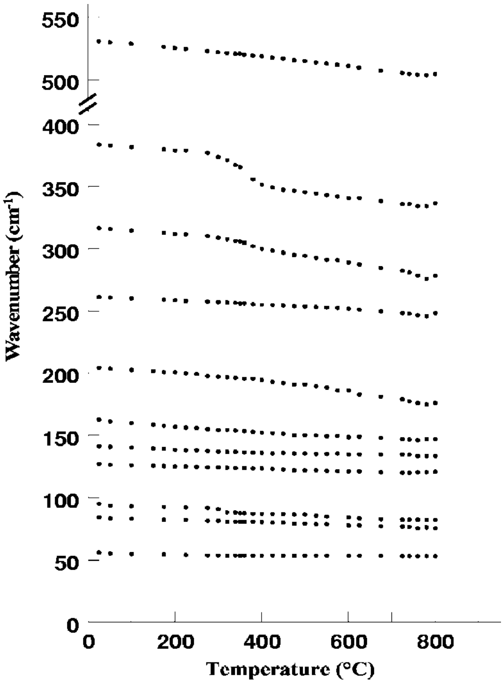

FIG. 2. Temperature-dependent evolution of the Raman band position for BiFeO$_3$.

We now discuss the evolution of the Raman signature around the antiferromagnetic-paramagnetic (AFM-PM) phase transition ($T_N \approx 370$ K).[7] Let us first recall that this magnetic transition is not accompanied by a structural phase transition,[8,9] as supported by the fact that the overall Raman spectral signature is maintained across the AFM-PM transition. Nevertheless, a closer inspection of the temperature-dependent Raman spectra reveals noticeable spectral changes in the vicinity of T_N. Upon cooling, the most remarkable observation is a marked continuous steplike anomaly in the evolution of wave number for several bands (Fig. 2). To place emphasis on these anomalies, Figs. 3(a) and 3(b) present a more detailed view for some bands, and Fig. 4 presents some representative spectral deconvolution of the region where the strongest anomaly is observed. It can be seen that the phonon anomaly is very pronounced for the band at 380 cm^{-1} [Figs. 3(b) and 3(c)] still clearly observed for the band at 315 cm^{-1}, but not observed for other bands like the high-wave-number band at 550 cm^{-1} [Fig. 3(a)]. We note that the earlier reported[3,4,6] phonon anomalies for the multiferroics HoMnO$_3$ and LuMnO$_3$ are also large and that the spin-phonon interactions in the multiferroics YMnO$_3$ are considered to be extraordinary.[5] The reported anomalies[3,4] in the phonon spectra of the multiferroics HoMnO$_3$ and LuMnO$_3$ are by a factor of $\sim 3-5$ smaller than what we observed in BFO [Fig. 3(c)], but for manganites other specific mechanism might be determinant. We also observe anomalies in the full width at half maximum (FWHM) and in intensity (not shown), again clearly pointing at two changes of regime. The occurrence of such a change of signature can be understood within the concept of hard-mode spectroscopy. This concept predicts that any change in structural and/or physical properties will, in principle, lead to variations in all phonon characteristics (frequency, intensity, and FWHM).[13]

At T_N, the anomalies in wave number are characterized by a sudden frequency hardening: e.g., the band at 380 cm^{-1} crosses upon cooling from a rate of $\Delta\omega/\Delta T \approx -0.02$ cm^{-1}/°C in the PM phase (region I) to a pronounced hardening of ≈ -0.2 cm^{-1}/°C in the AFM phase (region II). Upon further cooling, the $\Delta\omega/\Delta T$ slope reverts back to a slow rate of ≈ -0.015 cm^{-1}/°C (region III) at a temperature hereafter called $T^* \approx 275$ °C. The low-wave-number shift in regions I and III corresponds to a classic

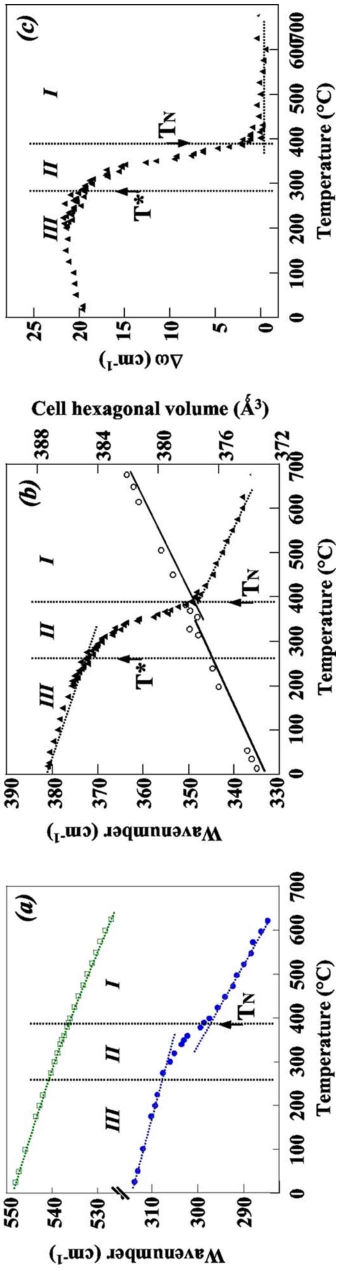

FIG. 3. (Color online) Temperature-dependent evolution of some spectral characteristics for $BiFeO_3$: (a) wave-number shift for the 315- and 550-cm^{-1} bands, (b) wave-number shift for the 380-cm^{-1} band (left), change of hexagonal cell volume (right) (Ref. 8), and (c) $\Delta\omega$ against temperature for the 380-cm^{-1} band, $\Delta\omega$ being defined as $\omega-\omega_1$ after subtraction of the linear behavior in regime I.

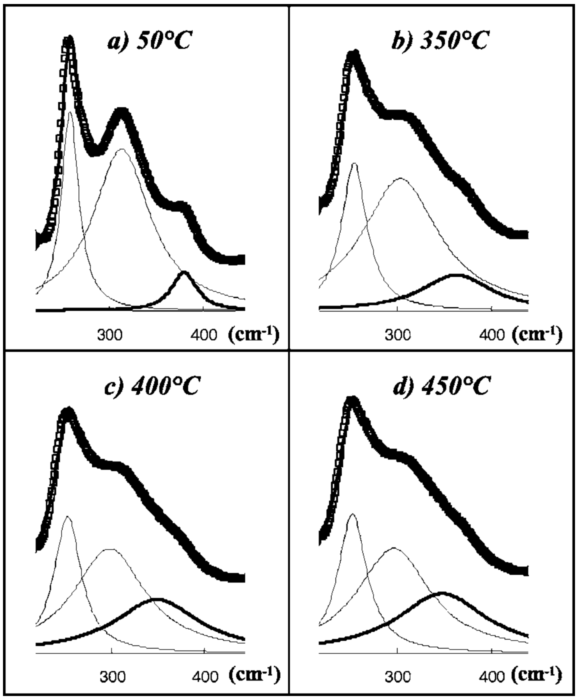

FIG. 4. Temperature-dependent spectral deconvolution for a selected wave-number window in the Raman spectra of $BiFeO_3$.

Grüneisen-type anharmonicity-related wave-number hardening. On the other hand, the application of the Grüneisen formula $\Delta\omega/\omega=\gamma\,\Delta a/a$ with available x-ray diffraction data[8] to the intermediate region II leads to a Grüneisen parameter of $\gamma\approx 30$, indicating an important anharmonicity which cannot be explained by a classical temperature behavior, but points at a further contribution.

At first sight, the considerable spectral changes at T^* suggest a structural rearrangement which has to be subtle or to occur on a local level since it is not detected by x-ray diffraction. Although we cannot formally exclude a change in space group at T^*, such a scenario is unlikely due the absence of any new spectral signature (i.e., new bands, band splitting, etc.). The work in the literature allows ruling out a further magnetic phase transition, and we have neither evidence nor reason to consider an electronic rearrangement.

A possible source of the observed anomaly at T_N is magnetostriction. Diffraction experiments on $BiFeO_3$ show upon cooling indeed a sudden change (increase) in the lattice parameters at T_N [Fig. 3(b)].[8] However, the observed change in the lattice parameter is by far too small to cause the observed phonon anomaly and, moreover, an increase in volume should rather lead to a decrease in wave number.

The observed phonon anomaly near T_N for BFO is reminiscent of similar (though smaller) observations near magnetic phase transitions in other oxides. For some of them, $SrRuO_3$ (Ref. 14), $A_2Mn_2O_7$ (A=T1,ln,Y) (Ref. 15) or $La_{0.7}Ca_{0.3}MnO_3$ (Ref. 16), the observed anomaly has been attributed to a strong electron-phonon coupling where the free carriers (or polarons) contribute in an important manner to the effective force constant. We do not expect that a ferroelectric insulator such as $BiFeO_3$ is described by the same physics.

On the other hand, the observed coupling between spin and phonon degrees of freedom in systems like MF_2 (M=Fe,Mn) (Ref. 17), $Y_2Ru_2O_7$ (Ref. 18), $LaTiO_3$ (Ref. 19), or $ZnCr_2O_4$ (Ref. 20) is closer to our observation. The qualitative behavior of the above materials is similar to what is observed for BFO, but the change in wave number observed for BFO is significantly larger. A useful approach for the understanding of spin-dependent phonon frequencies of the latter and other materials is based on an initial model by Baltensperger and Helmann, which considers the modulation of the magnetic exchange integral by the ionic displacement of the involved phonon mode.[21] Based on this approach, it has been proposed that the phonon frequencies in magnetic materials are affected by the correlation of spins of nearest-neighbor pairs.[17,21] Such a scenario should be considered to explain also the observed anomaly in BFO, but we note that the amplitude of the anomaly is very large compared to what is known for other magnetic materials. The observation of the anomaly around T_N indeed suggests that spin-phonon coupling is a contributing mechanism, but it is unlikely that a spin-phonon coupling alone can explain the observed values. A second argument for the latter comes from the fact that two different regions exist (II and III), although the phonon shift from spin-phonon coupling is expected to be proportional to the spin-spin correlation function. One possible origin for both the observed large anomaly and the two different regimes is a further contribution—for example, the coupling to another order parameter which does change with temperature. In the case of multiferroics we can expect a further contribution coming from the coupling to the ferroelectric (and/or ferroelastic) order parameters. A magnetoelectric coupling in terms of Landau theory has been discussed by Smolenskii and Chupis[22] who expressed the thermodynamic potential F as follows:

$$F = F_0 + \alpha P^2 + \beta/2P^4 - PE + \alpha M^2 + \beta/2M^4 - MH + \gamma P^2 M^2 + \cdots, \qquad (1)$$

where P and M are the polarization and magnetization, respectively. The coupling between magnetic and ferroelectric order parameters is described by the term $\gamma P^2 M^2$. For $BiFeO_3$, our work shows that Eq. (1) should be extended by an additional $\frac{\gamma}{6}P^6$ term, which takes into account the first-order nature of the ferroelectric-to-paraelectric phase transition.

Kimura *et al.*[23] have analyzed Eq. (1) for the multiferroic $BiMnO_3$ and have proposed that the temperature dependence of the electric order parameters can be neglected at the magnetic transition, provided that the magnetic and ferroelectric phase transitions are separated apart. This condition is well respected for $BiMnO_3$ ($T_{FM}=-160$ °C, $T_C=480$ °C), and for this material the authors show that the observed physical properties below T_{FM} are proportional to the square of the magnetic order parameter.

It is natural to link the observed anomaly of BFO to its multiferroic character. In order to verify this idea we have recently undertaken a similar high-temperature Raman experiment on the orthoferrite $EuFeO_3$ (EFO), which has a similar magnetic behavior and critical Néel temperature, but which is *not* ferroelectric. This experiment on EFO shows only a small anomaly around T_N, which is one order of magnitude smaller than the strong anomaly observed for BFO.[24] Such an observation offers a further argument to the proposition that the multiferroic character might well play a key role in the strong phonon anomaly observed for BFO.

The remarkable coupling in BFO might be related to the fact that the magnetic and ferroelectric order temperatures in BFO are closer together when compared to the well-separated temperatures for other multiferroics. This leads BFO to a situation where the temperature dependence of the ferroelectric order parameter can no more be neglected at T_N, and thus the magnetic phase transition takes place within a phase that presents lattice instabilities. Within this context we should recall that the ferroelectric-paraelectric phase transition is not soft-mode driven, which indicates that the definition of the ferroelectric order parameter in BFO is not trivial and clearly deserves further attention. More experimental and theoretical work is needed to unambiguously identify the physical mechanisms leading to the anomalies reported here. First-principles calculations of the phonon spectrum with models including magnetic superexchange interactions as well as lattice instabilities could lead to a better understanding of the magnetoelectric coupling.

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