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Raman studies of spin-phonon coupling in hexagonal BaFe₁₂O₁₉

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Phonon softening in hexagonal BaFe₁₂O₁₉ single crystal is observed in temperature dependent polarized Raman spectroscopy. The phonon softening is significantly enhanced below ~80 K, at which the magnetization in a magnetic field along *c*-axis shows a clear change in the temperature dependence, indicating a magnetic phase transition near 80 K. Possible interpretations of the anomalous temperature dependence of the phonon frequencies–phonon softening behaviors are discussed. The phonon softening would be correlated to local structural and magnetic phase transition in hexagonal BaFe₁₂O₁₉, in which the spin-phonon coupling would have major contribution for the phonon softening. We also discuss that the spin-phonon coupling would be affected by both the spin ordering and the individual phonon vibration in magnetic material. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4812575>]

I. INTRODUCTION

M-type hexagonal barium ferrite, BaFe₁₂O₁₉, has attracted much research interest over the past 50 years because of its applications in permanent magnets, microwave devices, and recording media.^{1–6} In addition, interesting multiferroic properties of M-type hexaferrites have been found recently.^{7–9} Hexagonal BaFe₁₂O₁₉ has a very complex crystal structure (space group P6₃/mmc), with 64 ions per unit cell on 11 different symmetry sites. Raman scattering spectroscopy has been widely used to study the crystal lattice vibrations. Group theory predicts that there are 42 Raman active Γ -point phonon modes (11A_{1g} + 14E_{1g} + 17E_{2g}) in hexagonal BaFe₁₂O₁₉. The Raman studies of the Γ -point phonon modes of hexagonal BaFe₁₂O₁₉ have been well investigated.^{4,10–12} Hexagonal BaFe₁₂O₁₉ also has a highly complex exchange-coupled magnetic structure. Complexity comes from the large number of magnetic ions in the basis, the number of crystallographically distinct magnetic ion sites, and the resulting of exchange integrals coupling the ions on the various sublattices.¹³ Raman scattering spectroscopy also offers a unique opportunity as a sensitive probe for the spin dynamics and studying the effect of magnetic ordering on the corresponding magnetic properties, a Raman study of spin-waves in hexagonal BaFe₁₂O₁₉ was recently investigated.¹⁴

The study of coupling between phonon and spin ordering has attracted great research interest; and the existence of spin-phonon coupling has been observed in a large variety of magnetic materials including perovskite manganites,^{15–23}

superconducting compounds,^{24,25} chromium spinels,^{26–28} multiferroic BiFeO₃, lead iron niobate,^{29–31} etc. However, to our knowledge, the spin-phonon coupling in hexagonal BaFe₁₂O₁₉ has not been reported; although hexagonal BaFe₁₂O₁₉ has been known as a permanent magnet for half a century. Recently, simultaneous occurrence of big ferroelectricity (FE) and strong ferromagnetism (FM) has been observed in hexagonal BaFe₁₂O₁₉.⁹ Due to the FM-FE and/or spin-phonon couplings, we expect the Raman spectra to show interesting temperature dependent behavior.

In this paper, we present a study of phonon softening in hexagonal BaFe₁₂O₁₉ single crystal through temperature dependent polarized Raman scattering. Our results show that both A_{1g} and E_{2g} phonon modes have phonon softening behaviors, while the value of phonon softening depends on individual phonon mode. We discuss that the major contribution of the phonon softening would involve a magnetic phase transition and spin-phonon coupling. The phonon softening is significantly enhanced below ~80 K. At the same temperature, the magnetization in a magnetic field along *c*-axis shows a clear change in the temperature dependence. This indicates a magnetic phase transition near 80 K in hexagonal BaFe₁₂O₁₉.

II. EXPERIMENT

The hexagonal BaFe₁₂O₁₉ single crystal was grown in a platinum crucible using a high temperature furnace. The primary reagents of BaCO₃ and Fe₂O₃ with the respective mol. % according to the composition were used for the growth. The blended powder was filled in a platinum crucible and

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calcined with the following steps: (1) quickly heated from room temperature to 1390 °C with increase of 200 °C per hour, (2) slowly heated to 1420 °C with 5 °C/h, (3) very slowly heated to 1450 °C with 2 °C/h, (4) kept at 1450 °C for 1 h, (5) very slowly cooled to 1340 °C with 0.6 °C/h, and (6) quickly cooled to room temperature with 100 °C/h. The obtained crystal was slowly separated by leaching in hot dilute nitric acid from the platinum crucible.

Raman scattering spectra of the sample were obtained in a backscattering configuration with a Jobin Yvon T64000 triple spectrometer in the single mode. The 671 nm laser was used as the excitation source with a laser power of ~ 1 mW on the surface of the sample. The beam diameter on the sample was ~ 50 μm . The laser beam power density was low enough to avoid laser heating. A long-pass filter was used so that the spectrum at lower frequency below 200 cm^{-1} was blocked. The scattered signal was detected by a liquid-nitrogen-cooled CCD detector. All the spectra have been calibrated in the frequency by using a standard neon source. The sample was mounted in a helium closed cycle cryostat and the sample temperature was varied from 10 to 300 K.

Temperature-dependent magnetizations of the sample were obtained with a Quantum Design magnetic property measurement system in the temperature range 10–300 K. The sample was zero-field cooled (ZFC) to 10 K. Magnetization measurements, with the field parallel and perpendicular to the c axis, were performed while warming the sample up to 300 K under $H = 1000$ Oe.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the temperature dependent Raman spectra of the hexagonal $\text{BaFe}_{12}\text{O}_{19}$ single crystal sample under the $z(xx)\bar{z}$ and $z(yx)\bar{z}$ configurations, respectively. The polarization dependence of the Γ -point phonon modes has been investigated by Kreisel *et al.*⁴ In the $z(xx)\bar{z}$ configuration, both A_{1g} and E_{2g} phonon modes are allowed; while in the $z(yx)\bar{z}$ configuration, only E_{2g} phonon modes are allowed. We have assigned our observed phonon modes by comparing with those reported by Kreisel *et al.*

Figures 2 and 3 present the temperature dependence of phonon frequencies for a few Raman peaks in the $z(xx)\bar{z}$ and $z(yx)\bar{z}$ configuration, respectively. In Figures 2(a)–2(c), we have plotted three Raman peaks at ~ 347 cm^{-1} ($E_{2g} + A_{1g}$ mode), 627 cm^{-1} (A_{1g} mode), and 694 cm^{-1} (A_{1g} mode). In Figures 3(a) and 3(b), we have plotted two E_{2g} phonon modes at ~ 347 cm^{-1} and 540 cm^{-1} . These Raman peaks are chosen because they have strong intensities and no interfering Raman peaks nearby. (The A_{1g} peak ~ 694 cm^{-1} has a shoulder peak at ~ 730 cm^{-1} , its peak position would be less accurate than other peaks. We choose this peak since it is correlated to vibrations of Fe–O bonds of FeO_5 bi-pyramid, which has a local structural transition near 80 K.) As can be seen in Figs. 2 and 3, all these Raman peaks have anomalous temperature dependent behaviors. Other Raman peaks also show similar temperature changes (not presented), while either their intensities are weak or there are interfering peaks nearby.

The anomalous temperature dependence of the phonon frequencies–phonon softening would indicate a phase

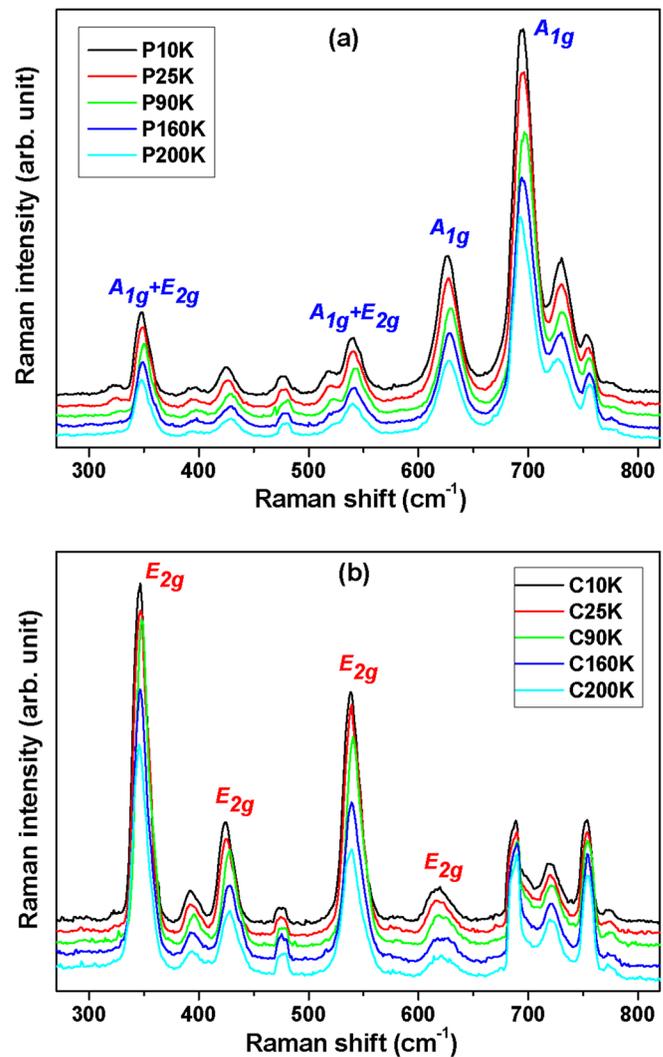


FIG. 1. Temperature dependent polarized Raman spectra of hexagonal $\text{BaFe}_{12}\text{O}_{19}$ single crystal, in (a) $z(xx)\bar{z}$ and (b) $z(yx)\bar{z}$ configurations. Only five representative spectra are shown in each figure. The spectra are shifted along y-axis for clarity.

transition near 80 K in hexagonal $\text{BaFe}_{12}\text{O}_{19}$. Both experimental observations and theoretical calculations had suggested a local structural transition of FeO_5 bi-pyramid in hexagonal $\text{BaFe}_{12}\text{O}_{19}$ near the same temperature, 80 K.^{4,32,33} This local structural transition would affect the Fe–O bond in FeO_5 bi-pyramid; thus, the phonon mode correlated to vibrations of Fe–O bonds of FeO_5 bi-pyramid could show anomalous phonon frequency changes at this temperature. In Figs. 2 and 3, only the A_{1g} mode ~ 694 cm^{-1} is correlated to vibrations of Fe–O bonds of FeO_5 bi-pyramid; while the other modes are correlated to vibrations of Fe–O bonds of FeO_6 octahedra.^{4,12} If the phonon softening is mainly correlated to this local structural transition of FeO_5 bi-pyramid, we would expect that the A_{1g} mode ~ 694 cm^{-1} has much stronger phonon softening than other modes. However, our results do not support this expectation, as can be seen in Figs. 2 and 3. Therefore, the local structural transition of FeO_5 bi-pyramid would not have major contribution on the phonon softening, especially for the phonon modes which are not correlated to FeO_5 bi-pyramid.

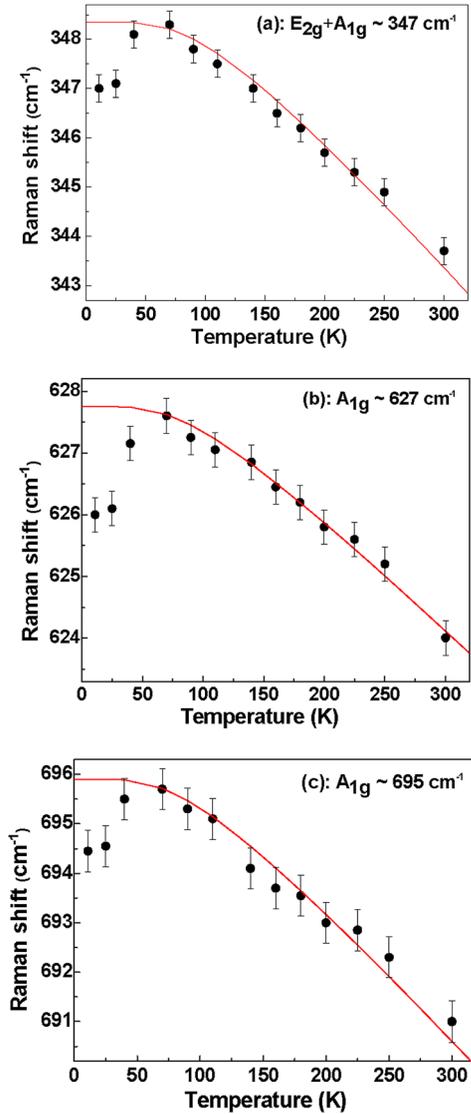


FIG. 2. Temperature dependence of phonon frequencies for three Raman peaks at (a) ~ 347 cm^{-1} , (b) ~ 627 cm^{-1} , and (c) ~ 695 cm^{-1} in $z(xx)\bar{z}$ configuration. The solid line is corresponding to the fitting using the anharmonic decay model.

In a recent study of spin-waves in hexagonal $\text{BaFe}_{12}\text{O}_{19}$, we found that magnon scattering intensity enhances rapidly below ~ 200 K; and below ~ 80 K, the magnon scattering becomes much stronger than above 80 K.¹⁴ This study suggested two magnetic phase transitions near 200 K and 80 K, and below 80 K the spin would become much more highly ordered than at 200 K.¹⁴ In addition, in multiferroic BiFeO_3 , it was reported that near 200 K and 140 K, there would be spin reorientation transitions.^{29,34} These results indicate that for Fe-ion magnetic materials, there could have additional magnetic phase transitions below Néel temperature. For hexagonal $\text{BaFe}_{12}\text{O}_{19}$, a magnetic phase transition would occur near the same temperature (80 K) as the local structural transition, or the magnetic phase transition would be induced by the local structural transition. Therefore, we suggest that the major contribution to the phonon softening would be originated from a magnetic phase transition, i.e., spin-phonon coupling, although the local structural transition may have some

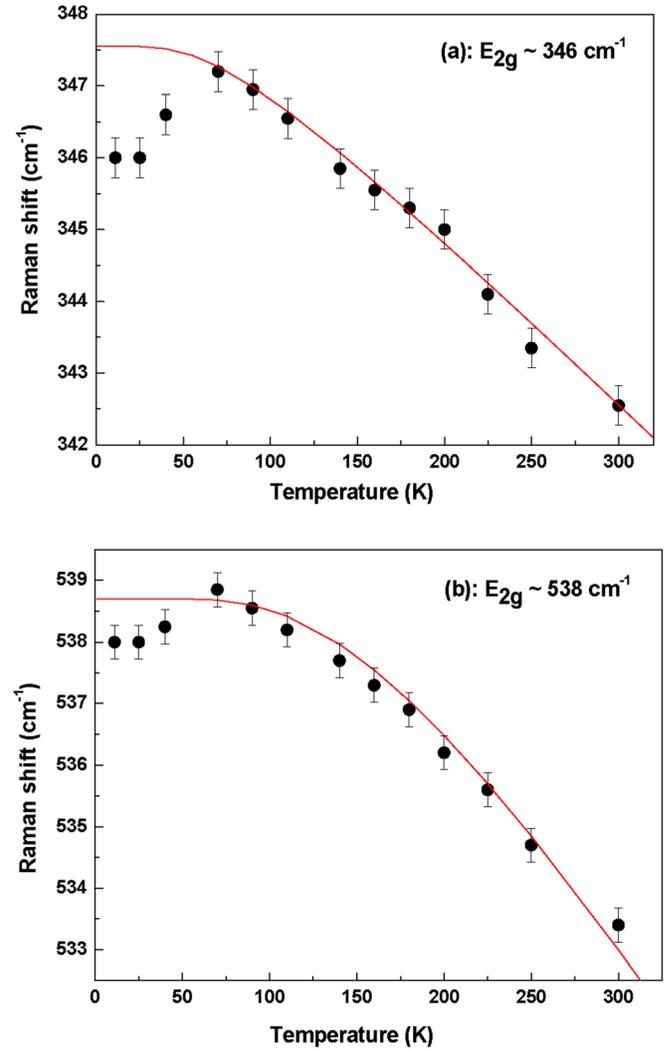


FIG. 3. Temperature dependence of phonon frequencies for two Raman peaks at (a) ~ 346 cm^{-1} and (b) ~ 538 cm^{-1} in $z(yx)\bar{z}$ configuration. The solid line is corresponding to the fitting using the anharmonic decay model.

contribution to the phonon softening. Our suggestion is consistent with the magnetization measurements, which clearly indicate a magnetic phase transition near 80 K (as shown in Fig. 4).

In magnetic materials, the frequency change of a phonon mode with temperature can be written as¹⁵

$$\omega(T) = \omega_0 + \Delta\omega_{\text{lat}}(T) + \Delta\omega_{\text{anh}}(T) + \Delta\omega_{e-ph}(T) + \Delta\omega_{s-ph}(T). \quad (1)$$

The first term on the right-hand side is the harmonic frequency of the phonon. The second term is the contribution to the phonon frequency due to the lattice expansion/contraction. The third term is the intrinsic anharmonic contribution. The fourth term accounts for the effect of renormalization of the phonon frequency due to electron-phonon coupling, which would be negligible in hexagonal $\text{BaFe}_{12}\text{O}_{19}$. The last term is the spin-phonon coupling contribution, caused by the modulation of the exchange integral by lattice vibrations. In general, the lattice expansion contribution is much smaller than the intrinsic anharmonic contribution, especially at low

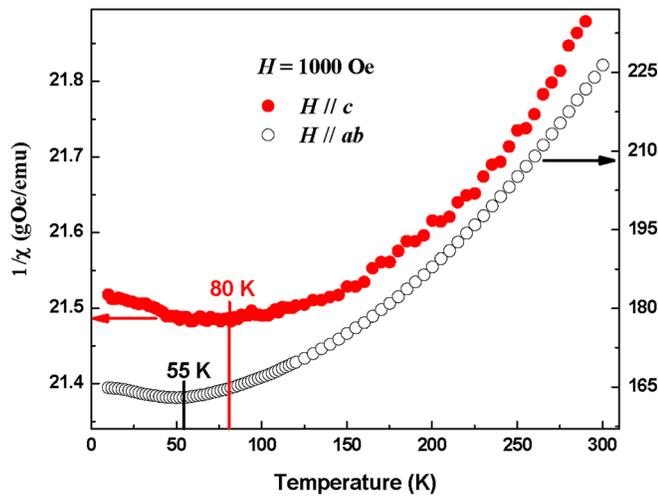


FIG. 4. Temperature dependent reciprocal susceptibility of hexagonal $\text{BaFe}_{12}\text{O}_{19}$ single crystal with a field of 1000 Oe being parallel ($H // c$) and perpendicular ($H // ab$) to the c -axis.

temperatures. Usually phonon can decay into two or three phonons, with a higher probability of the former. In the phonon decay, conservation of energy and momentum has to be obeyed, with a higher probability of decaying into same energy phonons. For two-channel-phonon-decay of same energies, the anharmonic contribution can be written as^{35,36}

$$\Delta\omega_{anh}(T) = -A \left(1 + \frac{2}{e^x - 1} \right) \quad (2)$$

in which $x = \hbar\omega_0/2k_B T$ and A is anharmonic constant. In Figures 2 and 3, the solid lines are corresponding to the fitting using above anharmonic decay model.

As illustrated in Figs. 2 and 3, at low temperatures, a significant deviation from the behavior predicted by phonon decay occurs below ~ 80 K. A softening of the phonon frequencies is clearly observed for both A_{1g} and E_{2g} phonon modes. This phonon softening would be contributed by the $\Delta\omega_{s-ph}(T)$ term, thus suggests a spin-phonon coupling in hexagonal $\text{BaFe}_{12}\text{O}_{19}$. To model the spin-phonon coupling, Granado *et al.*¹⁵ proposed a mechanism of phonon modulation of the exchange integral, which was applied to explain the phonon softening in orthorhombic manganites. Simply, the spin-phonon contribution $\Delta\omega_{s-ph}(T)$ can be written as^{37,38}

$$\Delta\omega_{s-ph}(T) = \gamma \langle \vec{S}_i \cdot \vec{S}_j \rangle, \quad (3)$$

where γ is the spin-phonon coupling constant and $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ is the scalar spin correlation function. γ can be positive or negative and is different for different phonon modes. As temperature decreases, the spin correlations build up and hence the spin-phonon coupling becomes important at lower temperatures. Therefore, renormalization of the phonon frequency below magnetic transition temperatures would be expected.

In the above spin-phonon coupling model, it has been assumed that the coupling is dominated through spin-spin interaction (exchange integral). In Fe thin film, spin-orbit interaction could also induce spin reorientation transition due to the anisotropy energy gain, which could be larger

than the exchange energy gain (spin-spin interaction) because of surface effect. However, the spin reorientation transition induced by the spin-orbit interaction is only significant when the film is thinner than 7 monolayers.³⁹ Therefore, the spin-phonon coupling through spin-orbit interaction would be negligible in $\text{BaFe}_{12}\text{O}_{19}$ single crystal. We may safely apply the spin-phonon coupling model in Eq. (3) to our hexagonal $\text{BaFe}_{12}\text{O}_{19}$ single crystal sample.

Figures 2 and 3 indicate that the spin-phonon coupling in hexagonal $\text{BaFe}_{12}\text{O}_{19}$ is strongly enhanced below ~ 80 K, with its maximum value occurring near 20 K. In a Mössbauer study of hexagonal $\text{BaFe}_{12}\text{O}_{19}$,⁴⁰ it was shown that the quadrupole splitting of the subspectrum corresponding to the bipyramidal lattice site started to increase below ~ 200 K, and below ~ 80 K, the splitting became more significant, and continued increasing systematically with the maximum value occurring near 20 K. In our previous study of spin-waves of hexagonal $\text{BaFe}_{12}\text{O}_{19}$,¹⁴ it was indicated that above ~ 200 K, there would exist strong spin fluctuation, and the spins would become significantly ordered when cooled below ~ 80 K. Therefore, the anomalous behavior observed in this study—significant phonon softening below ~ 80 K with the maximum value near 20 K—is consistent with the Mössbauer study and our previous spin-wave study. However, near 200 K, no measurable changes were observed in Figs. 2 and 3 could be attributed to the following two reasons. First, at high temperatures ~ 200 K, there would be strong spin fluctuation, thus the scalar spin correlation function $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ would be much smaller than the value at the low temperatures ~ 80 K. Second, at high temperatures ~ 200 K, the thermal expansion term $\Delta\omega_{latt}(T)$ would have more contribution on the phonon frequencies than that at low temperatures ~ 80 K. Therefore, although the spin-phonon coupling would still have some weak effect on the phonon modes frequencies at high temperatures ~ 200 K, it could not be clearly identified.

Our Raman results indicated that near 200 K and 80 K, there would be magnetic phase transitions in hexagonal $\text{BaFe}_{12}\text{O}_{19}$. For the magnetic ordering of ferrites, there are several possibilities;⁴¹ Gorter⁴² predicted a ferrimagnetic ordering picture for hexagonal $\text{BaFe}_{12}\text{O}_{19}$. It had been reported that hexagonal $\text{BaFe}_{12}\text{O}_{19}$ has a high Curie temperature (Néel temperature) above ~ 700 K.^{13,43,44} The reported Curie temperature (Néel temperature) of hexagonal $\text{BaFe}_{12}\text{O}_{19}$ is significantly higher than the magnetic phase transition temperatures indicated by our Raman results. Very similar results were also observed in multiferroic BiFeO_3 ,^{29,34} which has a Néel temperature of ~ 643 K; while previous Raman studies suggested that near 200 K and 140 K, there would have additional magnetic phase transitions. Both of these materials have high Néel temperature and have Fe ion spin ordering. These observations suggest that for Fe ion magnetic material, its magnetic property could be strongly affected by the temperature effect, and below Néel temperature, there could be additional magnetic phase transitions.

To confirm additional magnetic phase transition below Néel temperature in hexagonal $\text{BaFe}_{12}\text{O}_{19}$, we have investigated the temperature dependence of magnetization with the magnetic field parallel and perpendicular to the c -axis. The temperature dependence of the reciprocal susceptibilities

along c -axis and ab plane is plotted in Fig. 4. As can be clearly seen in Fig. 4, the temperature dependence of the reciprocal susceptibility along the c -axis is changing its slope near 80 K. This may imply that there would be a magnetic phase transition near 80 K. And along the ab plane, the magnetic transition seems to occur near 55 K. The different temperature dependence of magnetization between along c -axis and ab plane would be due to the different magnetic structure along c -axis and ab plane. The magnetization is dominated by the c -axis component; thus for the phonon modes which are coupled with spin, they would show softening behavior near 80 K. For the phonon modes which could also couple with spin along ab plane, they would show somewhat different phonon softening transition temperature. Therefore, we conclude that the magnetization results agree well with the Raman results, further suggesting that the phonon softening behaviors in hexagonal $\text{BaFe}_{12}\text{O}_{19}$ would be correlated to spin-phonon coupling.

Hexagonal $\text{BaFe}_{12}\text{O}_{19}$ has highly complex crystal and magnetic structure. At the moment, the origin of the additional magnetic phase transition is not understood. In multiferroic BiFeO_3 , it was suggested that the additional magnetic phase transition would be correlated to spin reorientation.^{29,34} Recently, in isostructural $\text{SrCr}_9\text{Ga}_{19-9x}\text{O}_{19}$ compound, it was found that the spin-phonon coupling could control magnetic relaxation. However, it was found that only phonons at 7 meV, not other frequencies, could drive magnetic relaxation.⁴⁵ The origin of the additional magnetic phase transition in hexagonal $\text{BaFe}_{12}\text{O}_{19}$ would need further experimental and theoretical studies.

Comparing with hexagonal $\text{BaFe}_{12}\text{O}_{19}$, multiferroic BiFeO_3 has much simpler crystal and magnetic structure. Yet, multiferroic BiFeO_3 and hexagonal $\text{BaFe}_{12}\text{O}_{19}$ have very similar magnetic and spin-phonon coupling behaviors. Both multiferroic BiFeO_3 and hexagonal $\text{BaFe}_{12}\text{O}_{19}$ have two similar additional magnetic phase transitions below Néel temperature (BiFeO_3 : ~ 200 K and 140 K, $\text{BaFe}_{12}\text{O}_{19}$: ~ 200 K and 80 K). In addition, phonon and magnon modes in multiferroic BiFeO_3 also show softening behavior about $1\text{--}2\text{ cm}^{-1}$ below ~ 140 K, and the value of softening also depends on individual mode of phonon and magnon.⁴⁶ Recently, the phonon and magnetic properties of multiferroic BiFeO_3 have attracted much interest.⁴⁶⁻⁴⁹ We suggest that further comparison study of hexagonal $\text{BaFe}_{12}\text{O}_{19}$ with multiferroic BiFeO_3 would be helpful for understanding highly complex crystal and magnetic structure of the hexagonal $\text{BaFe}_{12}\text{O}_{19}$.

Generally, the spin-phonon coupling would occur near the magnetic transition temperature (Néel temperature or Curie temperature). We have discussed above that for Fe ion magnetic material, the spin-phonon coupling could only be clearly identified much below the Néel temperature. Contrarily, in hexagonal manganites YbMnO_3 (Ref. 23) and double perovskite $\text{La}_2\text{NiMnO}_6$,¹⁷ it was found that spin-phonon coupling could occur much above Néel temperature; and in orthorhombic LaTeMnO_3 ,¹⁶ spin-phonon coupling was observed slightly above Curie temperature. All these manganites have Mn ion spin ordering. This indicates that Mn ion spin ordering would be weakly affected by the temperature effect, and could persist much above the magnetic

phase transition temperature (Néel temperature or Curie temperature). In our previous studies of magnon scattering in hexagonal manganites RMnO_3 ($R = \text{rare earth}$),^{50,51} we have observed that magnon scattering could persist above Néel temperature, consistent with the spin-phonon coupling result.

Manganites are generally considered having strong spin-phonon interaction, which have been recently highlighted by both theory and experiment.⁵²⁻⁵⁴ A recent optical conductivity measurement showed a very large phonon softening ~ 2 meV, i.e., 16 cm^{-1} in perovskite manganites $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$.⁵⁴ Previous Raman measurements showed variant phonon softening of $0\text{--}8\text{ cm}^{-1}$ of various manganites and phonon modes.¹⁵⁻²³ Our results show that the phonon softening in hexagonal $\text{BaFe}_{12}\text{O}_{19}$ is about $1\text{--}2\text{ cm}^{-1}$. Therefore, the spin-phonon coupling in hexagonal $\text{BaFe}_{12}\text{O}_{19}$ would be much weaker than that in manganites.

In order to further confirm the phonon softening behaviors in hexagonal $\text{BaFe}_{12}\text{O}_{19}$ are correlated to spin-phonon coupling, it would be helpful to compare the temperature dependent Raman studies of hexagonal $\text{BaFe}_{12}\text{O}_{19}$ with a non-magnetic isostructural compound, for example, $\text{MAl}_{12}\text{O}_{19}$ ($M = \text{Ba, Pb, Sr, Ca, Mg, etc.}$), or M-type hexaferrites with non-magnetic ion substitution. It was found that when Fe ions were substituted by non-magnetic Sc or In ions in $\text{PbFe}_{12}\text{O}_{19}$ hexaferrite, the magnetic property showed a rapid fall.⁵⁵ Therefore, in M-type hexaferrite with non-magnetic ion substitution, the phonon-softening behavior would be significantly weakened. However for $\text{BaAl}_{12}\text{O}_{19}$, it was first considered to be a single compound with the same magnetoplumbite structure of M-type hexaferrites;^{56,57} but later, it was found that this compound actually exists as two distinct phases, different from the magnetoplumbite structure.^{58,59}

We have discussed that the spin-phonon coupling in different magnetic materials is strongly affected by the property of spin ordering, which would be expected straightforwardly, since the spin-phonon coupling term $\Delta\omega_{s-ph}(T)$ is directly correlated to $\langle \vec{S}_i \cdot \vec{S}_j \rangle$. We would also expect that different phonon modes would have different spin-phonon coupling behavior. First, different phonon modes would have different coupling constant γ , even if they are coupled with same spin-spin interaction. Second, different phonon modes may be coupled with different spin-spin interactions if the magnetic material has a complex magnetic structure. Figure 4 shows that the spin-spin interactions parallel and perpendicular to the c -axis have very distinct behaviors. Thus, the phonon modes involving crystal vibrations parallel and perpendicular to the c -axis would have different spin-phonon coupling behaviors.

The different spin-phonon coupling behaviors of different phonon modes have been clearly observed in Figs. 2 and 3. Similar results were also reported in previous studies of spin-phonon coupling in various other magnetic materials.¹⁵⁻³⁰ Further understanding of the different phonon spin-phonon coupling behaviors would require a detailed knowledge of both the crystal and the magnetic structures of the magnetic material. However, hexagonal $\text{BaFe}_{12}\text{O}_{19}$ has highly complex crystal and magnetic structures. Even in magnetic materials with much simpler crystal and spin-ordering structures, different phonon modes showed very distinct spin-phonon coupling behaviors.^{18,19,23}

IV. CONCLUSION

In conclusion, we present a study of phonon softening in hexagonal BaFe₁₂O₁₉ single crystal. The temperature dependence of both A_{1g} and E_{2g} phonon modes shows anomalous temperature changes—a significant softening of phonon frequencies below ~80 K. Possible origins of the phonon softening are discussed, and we suggest that spin-phonon coupling would have the major contribution. The strength of spin-phonon coupling depends on individual phonon mode, and it is significantly enhanced below ~80 K. This suggests that there exists a magnetic phase transition near 80 K in hexagonal BaFe₁₂O₁₉, which is consistent with our magnetization measurements.

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