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Phonon anomalies and magnetic excitations in BaFe₂Se₂O

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We report temperature- and magnetic field-dependent Raman scattering study of the spin-ladder compound BaFe₂Se₂O. Temperature evolution of the B_{1g} modes self energies revealed anomalous behavior at about 100 K and 240 K with strong temperature dependent Fano asymmetry. Furthermore, A_g modes integrated intensity exhibit additional change in tendency at about 50 K. All the observed anomalies can be traced back to spin-phonon interaction contributions as well as multiple magnetic phase transitions present in BaFe₂Se₂O also detected in the [Raman continuum](#) induced by the spin fluctuations. Moreover, absence of magnetic field dependence of the magnetic mode observed at 436 cm⁻¹ and small linewidth and high intensity are different from the magnetic modes at about 650 cm⁻¹. This suggests two-magnon continuum and a two-magnon bound state resonance for this mode.

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I. INTRODUCTION

Quantum spin ladders have attracted much interest because of their fascinating properties and their possible relevance to the phase diagram of high-temperature superconducting cuprates¹⁻⁴. The ground state properties and the quasiparticle spectrum of the two-leg spin ladder have been studied theoretically⁵⁻⁹ and experimentally¹⁰⁻¹⁴. Generally these system may host various competing magnetic phases that are in close proximity.

Raman scattering offers a unique and powerful tool for probing lattice, spin and charge excitations as well as interplay between them⁴. In the undoped spin ladder compound La₆Ca₈Cu₂₄O₄₁, the ladders contribute to a very broad two-triplet Raman line-shape whose position is slightly different for leg-leg and rung-rung polarizations¹⁵ in accordance with theoretical models¹⁶. However, in the spin-ladder and charge-ordered compound Sr₁₄Cu₂₄O₄₁, only a particularly sharp peak is observed at the same frequency for both polarizations^{12,15}. Here, the spin ladder (antiferromagnetic dimer) structure magnon related modes appears in the form of singularities of one dimensional density of two-magnon states¹¹.

Iron-based compound BaFe₂Se₂O is an experimental realization of a two-leg ladder structure¹⁷⁻¹⁹. In this compound, all iron ions are in the Fe²⁺ oxidation state with a high spin $S = 2$. The Fe₂Se₂O planes containing weakly coupled ladders are stacked along the c crystallo-

graphic axis. The ladder legs and rungs are along the b and a crystallographic axis, respectively. The basic magnetic properties of BaFe₂Se₂O have been characterized by magnetic susceptibility and specific-heat measurements^{17,18}. The magnetic susceptibility shows a broad maximum at $T_{max} \approx 450$ K and three successive magnetic phase transitions at $T \approx 240$ K, 115 K and 43 K with T_{max} explained as due to the short-range correlation of the local moments¹⁷ and the three magnetic phase transitions explained as either due to the antiferromagnetic phase transition (240 K) or due to the formation of spin singlet dimers (115 and 43 K)¹⁸. Surprisingly, the specific heat measurements indicate that the magnetic entropy up to 300 K is much smaller than the expected value. Local-spin-density-approximation (LSDA) calculations¹⁷ suggest that the interaction along the rungs J is more than three times stronger than the inter-ladder interaction J' whereas the interaction along the legs J'' can be neglected. Lattice dynamics study of BaFe₂Se₂O was recently reported by Popović *et al.*¹⁹. They also observed a magnetic excitation related structure in the form of a magnon continuum with peaks corresponding to the singularities in the one-dimensional density of magnon states. In order to clarify the unusually large intensity of the lower-energy (magnon) peak and of origin of the B_{1g} modes line-shape asymmetry, a systematic Raman study, particularly in magnetic fields, is highly required.

In this paper, we report temperature- and field-dependent Raman scattering measurements on BaFe₂Se₂O. The temperature-dependent Raman spectra indicate absence of a structural phase transition between 10 and 300 K, consistent with a moderate

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spin-phonon coupling. The Raman continuum observed only in the parallel polarization suggests strong spin fluctuations, and allows us to identify magnetic phase transitions at about 50 K, 100 K and 240 K. The intensity of the sharp magnetic mode at 436 cm^{-1} exhibits a strong non-monotonic field-dependent behavior with no observable energy shift with external magnetic fields up to 9 T. It is interpreted in terms of the two-magnon continuum and a two-magnon bound state resonance. The present study provides the fundamental lattice and spin dynamics information on $\text{BaFe}_2\text{Se}_2\text{O}$ and deepen the understanding of magnetic excitations in the low-dimensional spin systems.

II. EXPERIMENTS

$\text{BaFe}_2\text{Se}_2\text{O}$ single crystals used in this study were grown using the self-flux method. The details of crystal growth can be found elsewhere¹⁸. The average stoichiometry was checked using energy-dispersive X-ray spectroscopy (EDS, Oxford X-Max 50). The average atomic ratios determined from EDS are Ba:Fe:Se = 1.0:1.9(2):2.0(2), close to the ratio of stoichiometric $\text{BaFe}_2\text{Se}_2\text{O}$. The presence of oxygen was confirmed for $\text{BaFe}_2\text{Se}_2\text{O}$, but the exact amount could not be quantified because of experimental limitations.

Freshly cleaved samples of (001) orientation were transferred into a UHV cryostat with a vacuum of better than 10^{-8} mbar. Temperature-dependent Raman spectra were collected with a Jobin Yvon LabRam HR800 spectrometer equipped with a volume Bragg grating low-wavenumber suite, a liquid-nitrogen-cooled back-illuminated charge-coupled device detector and a 633 nm laser (Melles Griot) with $\Gamma_\sigma < 0.1 \text{ cm}^{-1}$. The laser was focused into a spot of $\sim 5 \mu\text{m}$ in diameter on the sample surface, with a power $< 100 \mu\text{W}$, to avoid overheating. Magnetic field-dependent Raman spectra were collected with a Jobin Yvon T64000 spectrometer also equipped with a liquid-nitrogen-cooled back-illuminated CCD. A 532 nm diode-pumped solid-state laser (Torus 532; Laser Quantum) was used as an excitation source. The laser was focused onto the samples with a spot size of 5-10 μm in diameter. The laser power was maintained at a level of 300 μW and monitored with a power meter (Coherent Inc.). Magnetic fields were generated up to 9 T using a superconducting magnet (Cryomagnetics) that has a room-temperature bore that is suitable for a microscope lens. The magnetic field direction was perpendicular to the (001) plane of the sample.

In this paper, the Porto notation $i(jk)l$ is used for the scattering geometry, where i and l denote the direction and j and k the polarization of the incident and scattered light, respectively, and u stands for unpolarized light.

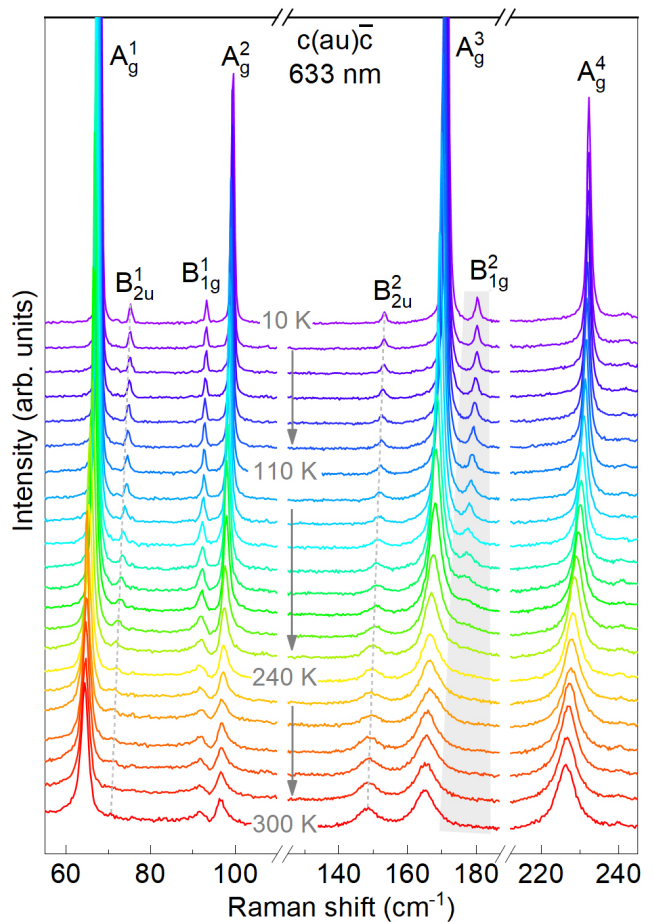


FIG. 1. Identification and temperature dependence of phonon modes in $\text{BaFe}_2\text{Se}_2\text{O}$. No change of crystal structure fingerprint was observed in the phonon spectra down to 10 K.

III. RESULTS AND DISCUSSION

A. Lattice dynamics and spin-phonon coupling

$\text{BaFe}_2\text{Se}_2\text{O}$ crystallizes in the orthorhombic crystal structure, described with space group $Pmmm$, with Ba and O atoms having C_{2v} site symmetry whereas Fe and Se atoms having C_s site symmetry¹⁹. The symmetry analysis yields total of eighteen Raman-active modes $\Gamma_{\text{Raman}} = 6A_g + 2B_{1g} + 6B_{2g} + 4B_{3g}$, out of which, according to the Raman tensors below and the selection rules, only eight ($6A_g + 2B_{1g}$) are observable for our scattering geometry.

$$A_g = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}, \quad B_{1g} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$B_{2g} = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}, \quad B_{3g} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix}.$$

Fig. 1 shows temperature evolution of $\text{BaFe}_2\text{Se}_2\text{O}$ Raman spectra in the temperature range between 10 K and

300 K, in which eight phonon modes are observed. According to the lattice dynamical calculations¹⁹, four A_g and two B_{1g} modes can be well assigned, as shown in Fig. 1. In addition to A_g and B_{1g} symmetry modes, two peaks at about 75.2 cm^{-1} and 153.3 cm^{-1} were also observed, which we previously attributed to new phonon modes due to the possible change of crystal symmetry accompanying the magnetic phase transition at $T_N = 240 \text{ K}$ ¹⁹. As can be seen in Fig. 1 these peaks are also observable in our data even above T_N , indicating different origin. Energies are consistent with B_{2u}^1 and B_{2u}^2 infrared active phonon modes, theoretically predicted by density functional theory calculations¹⁹ and we assign them accordingly. Their observability in Raman data may stem from the release of symmetry selection rule by the structural imperfections. In our previous paper¹⁸, Mössbauer data suggested oxygen deficiency, i.e. O_{1-x} composition for $\text{BaFe}_2\text{Se}_2\text{O}$. This might be the source of structural imperfections.

First, we focus on B_{1g} phonon modes, which display a pronounced asymmetry at high temperatures ($T > T_N$) that is suppressed at low temperatures ($T \ll T_N$), as can be seen in Fig. 2(a). Having in mind small instrumental broadening, the analysis of the line-shape was performed by using Fano function alone^{20,21}: $I(\omega) = I_0(q + \varepsilon)^2 / (1 + \varepsilon^2)$, where $\varepsilon = (\omega - \omega_0) / \Gamma$, ω_0 is the bare phonon frequency, Γ is the linewidth, and q is the asymmetry parameter²². Frequency shift, linewidth and Fano asymmetry parameter $|1/q|$ for both modes as a function of temperature are presented in Fig. 2(b), 2(c) and 2(d), respectively. Whereas they exhibit very similar temperature dependence, upon heating from 10 K small deviation from the "standard" anharmonic type of behavior can be noticed at about $T_1=100 \text{ K}$ accompanied by the appearance of the line-shape asymmetry. Further heating results in a significant renormalization of the phonon self energies around T_N with the Fano asymmetry parameters reaching maximum value in the same temperature region.

The pronounced Fano asymmetry observed for the B_{1g} modes above T_N (Fig. 2(d)) indicates strong coupling to a continuum of excitations. Here we attribute the continuum to the magnetic scattering stemming from the spin fluctuation, which will be further discussed below. In comparison, an electronic mechanism for the continuum is unlikely as $\text{BaFe}_2\text{Se}_2\text{O}$ is electrically insulating with a transport gap of 1.86 eV ¹⁷. According to the lattice dynamical calculations¹⁹, the B_{1g} modes are mainly due to the vibration of Fe and Se atoms along the b axis which mediate the magnetic interaction. Therefore, one could expect B_{1g} modes to couple to the magnetic scattering.

The coupling of B_{1g} modes to the spin system is also reflected in the abnormal behaviors of their linewidth. To demonstrate this, we have included in Fig. 2(c) plots of the behavior expected from anharmonicity, $\Gamma(T) = \Gamma_0(1 + 2/(e^{\hbar\omega/2k_B T} - 1))$. The fit strongly deviates already around 170 K, implying an additional relaxation mechanism which we ascribe to spin-phonon coupling.

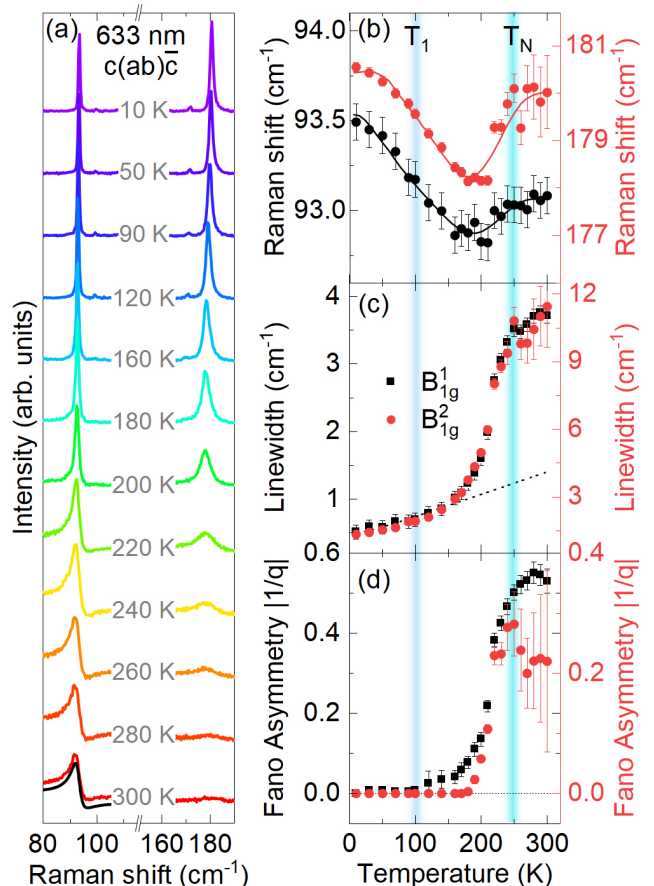


FIG. 2. Anomalies of B_{1g} modes induced by spin-lattice coupling. (a) Temperature dependence of Raman spectra for the $c(ab)\bar{c}$ polarization configuration, in which only the B_{1g} modes can be observed. The solid black line is a fit to a Fano line-shape. Temperature dependence of the (b) frequency shift, (c) linewidth and (d) Fano asymmetry parameters $|1/q|$ of B_{1g}^1 (left axis, black) and B_{21g}^2 (right axis, red) modes. The solid lines in (b) represent a fit to Eq. (1) and the dotted line in (c) represents the behavior expected from anharmonicity.

Such coupling is very pronounced in low-dimensional spin dimer systems, as well as in two- and three-dimensional frustrated spin systems^{23–25}.

In order to estimate the spin-phonon coupling constant in $\text{BaFe}_2\text{Se}_2\text{O}$, we may approximate phonon frequency temperature dependence as:

$$\omega(T) = \omega(0) - C \left(1 + \frac{2}{e^x - 1} \right) + \lambda \langle S_i S_j \rangle, \quad (1)$$

where $\omega(0)$ is the harmonic frequency of an optical mode at zero temperature, $x = \hbar\omega(0)/2k_B T$, λ is the spin-phonon coupling constant, $\langle S_i S_j \rangle$ represents the spin-spin correlation function and C is an anharmonic constant. The second term in Eq. (1) describes the anharmonic phonon contribution based on symmetrical optical phonon decay into acoustic phonons²⁶ whereas the third term represents the contribution from the spin-phonon coupling based on the Baltensperger and Helman

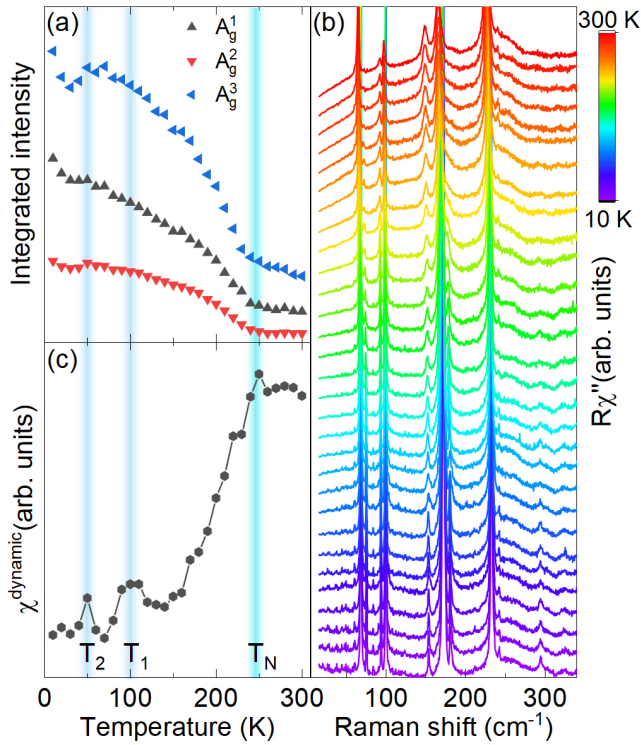


FIG. 3. (a) Integrated intensity of the A_g^1 , A_g^2 and A_g^3 symmetry modes as a function of temperature. (b) Temperature evolution of Raman susceptibility data for BaFe₂Se₂O obtained in parallel scattering configuration. The **pronounced Raman continuum evolution** is observable only in parallel (i.e. (aa) or (bb)) and absent in cross polarization configurations (i.e. (ab) or (ba)) (not shown). (c) Temperature dependence of dynamical susceptibility $\chi^{dynamic}(T)$ obtained from the Raman data.

model^{27,28}. If we take into account only the nearest-neighbour interactions the spin-spin correlation function $\langle S_i S_j \rangle_\chi$ can be written as²⁵

$$\langle S_i S_j \rangle_\chi = \frac{k_B T \chi_m(T)}{N_A g^2 \mu_B^2} - \frac{S(S+1)}{3}, \quad (2)$$

where $g = 2$, $S = 2$ and the magnetic susceptibility $\chi_m(T)$ is given in Ref. 18. We can now analyze the B_{1g} symmetry modes frequency temperature dependence within the Eq. (1) (see solid lines in Fig. 2(b)). This yields the spin-phonon coupling constants $\lambda(B_{1g}^1) = 1.8$ cm⁻¹, $\lambda(B_{1g}^2) = 12.8$ cm⁻¹ and the anharmonic constant $C(B_{1g}^1) = 0.33$ cm⁻¹, $C(B_{1g}^2) = 4.76$ cm⁻¹. The individual contribution due to anharmonic and spin-phonon coupling can be found in the Fig. A1 of the Appendix. Obtained spin-phonon coupling constants are smaller than those in the spin-Peierls system CuGeO₃, where spin-phonon coupling constants of $\lambda_{103} = -10$ cm⁻¹, $\lambda_{215} = 40$ cm⁻¹, $\lambda_{366} = -21$ cm⁻¹, $\lambda_{812} = -8$ cm⁻¹ were found²⁹. Thus moderate spin-phonon coupling constants in BaFe₂Se₂O may account for the absence of a structural phase transition at the magnetic phase transition.

Now we turn our attention to the A_g symmetry modes. As can be seen from the Fig. 3(a), integrated intensity temperature dependence of the analyzed A_g modes exhibits clear discontinuity at T_N . In addition, another change in tendency has been observed at about $T_2 = 50$ K.

Whereas the phonon anomalies at T_N can be directly traced back to the spin dynamics, the origin of the phonon anomalies at T_1 and T_2 is not clear. To clarify this, we analyze the **Raman continuum** that non-monotonically develops in the A_{1g} channel with temperature [see Fig. 3(a)], as expected for the (quasi) one-dimensional spin systems³⁰⁻³². Directly from the Raman data, dynamic Raman susceptibility³³ can be calculated using Kramers-Kronig relation $\chi^{dynamic} = \lim_{\omega \rightarrow 0} \chi(q=0, \omega) \propto \int_0^\infty \frac{\chi''}{\omega} d\omega$. Since we do not attempt to quantitatively analyze the spin fluctuation contributions, which falls beyond the scope of our work, but to pinpoint possible magnetic phase transition, we approximate $\chi^{dynamic}(T)$ as an integral of the Raman conductivity data after excluding the contributions from phonons. As can be seen in Fig. 3(c), $\chi^{dynamic}(T)$ strongly increases upon approaching T_N after which it saturates in the paramagnetic phase where the spins are not correlated. At low temperatures it develops two peak like features coinciding with observed anomalies in the lattice dynamic thus indicating their spin dynamics related origin. Furthermore, $\chi^{dynamic}(T)$ exhibits good agreement with the previously reported magnetic susceptibility data¹⁸, indicating additional magnetic phase transitions in BaFe₂Se₂O at low temperatures.

B. Two-magnon Raman scattering

The two asymmetric peaks at 436 cm⁻¹ and 653 cm⁻¹ [see Fig. 4] have been reported before and assigned as a magnetic excitation related structure **due to their special polarization and temperature dependent characterizations**¹⁹. However, extremely high intensity of the 436 cm⁻¹ (M0) mode suggests additional mechanism that comes into play, other than those manifested with the 653 cm⁻¹ mode. In particular, compared with the linewidth of two-magnon modes in other 2-dimensional (2D) spin systems, the M0 linewidth of only ~ 5 cm⁻¹ at 15 K is quite unusual for a 2D spin ladder system. For example, the linewidth of the two-magnon mode is ~ 800 cm⁻¹ for Sr₂Cu₂O₂Cl₂³⁴, while it is ~ 500 cm⁻¹ in La₆Ca₈Cu₂₄O₄₁¹³. To the best of our knowledge, the sharpest two-magnon mode so far was found in CaV₂O₅ with a width of more than 50 cm⁻¹¹⁰, still one order of magnitude larger than that in BaFe₂Se₂O.

To clarify the origin of the unusual M0 mode, the magnetic field- and temperature-dependent Raman experiments have been performed on BaFe₂Se₂O crystals [Fig. 4(a) and Fig. A2 of the Appendix]. The **field-dependence of the energy, intensity of the M0 mode are summarized in Fig. 4(b) and 4(c)**. It can be seen

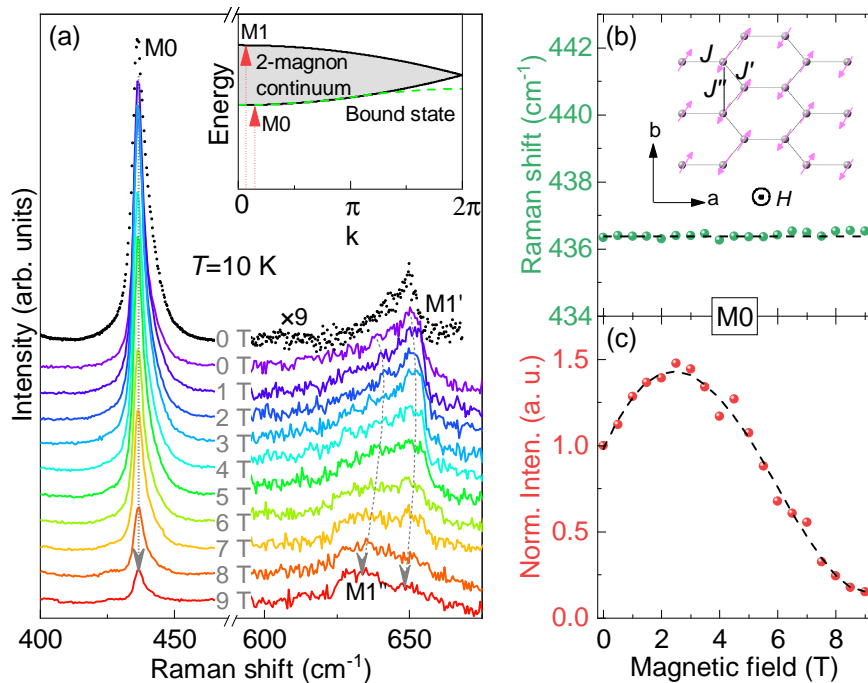


FIG. 4. Identification of magnetic excitations in $\text{BaFe}_2\text{Se}_2\text{O}$. (a) Field dependent Raman spectra, measured at 10 K with 532 nm laser line (solid lines). The spectrum (dotted line) collected at 0 T with 633 nm laser are also shown for comparison. Inset: Schematic spin excitation spectrum of $\text{BaFe}_2\text{Se}_2\text{O}$. The green dashed line represents a possible two-magnon bound state. Field-dependence of the (b) energy and (c) intensity of the M0 mode. Inset of (b): Schematic representation of the periodic magnetic structure in the (ab) plane. J represents Fe-O-Fe AFM exchange interaction along the rungs, J' is the inter-ladder Fe-Se-Fe AFM exchange interaction. J'' is the ferromagnetic Fe-Se-Fe exchange interaction along the ladder legs and can be neglected.

that both M0 energy and linewidth are nearly field-independent, whereas intensity exhibits a strong non-monotonic field dependence. The intensity slightly increases with magnetic fields below 3 T, but quickly drops down above 3 T and almost vanishes for $B = 9$ T. Closer inspection of the 653 cm^{-1} peak magnetic field dependent spectra reveals its two peak nature (M1' and M1''), see Fig. 4). Both peaks harden up to 3 T after which they soften. Whereas M1' intensity follows the M0 mode behavior, M1'' experience constant gain of intensity. The strong field-dependence of M0, M1' and M1'' as well as their special polarization and temperature-dependent characterizations¹⁹ confirms that these modes are indeed magnon-related, but not due to some structural imperfections.

In general, several theoretical scenarios can be considered to account for the strength and sharpness of the magnon modes in 2D system: (i) back-folding of the triplet dispersion due to charge ordering¹³; (ii) large anisotropy of the magnetic exchanges along rung and leg directions³⁵; (iii) the resonance between the two-magnon continuum and a two-magnon bound state^{16,36}. In $\text{BaFe}_2\text{Se}_2\text{O}$, the origin of dispersion back-folding can be excluded because of its electrically insulating nature. Although, the large anisotropy between J'' and J explains the observation of the M0 mode at the given en-

ergy, it alone can not account for the intensity and its magnetic field dependence. This kind of behavior can be observed in the presences of the resonance between two-magnon continuum and a two-magnon bound state.

In low dimensional antiferromagnets, strong magnon-magnon interaction induces a magnetic bound state^{31,37-40} that merges with the two-magnon continuum at zero momentum (schematically shown in Fig. 4). This allows a resonance at the bottom of the continuum and contributes to the asymmetric line-shape³⁶. Such a resonance can well explain the strength, sharpness and asymmetry of M0 mode. The field dependence of M0 mode intensity provides further support for the picture. External magnetic fields usually lead to a spin canting or even a spin flop/flip transition⁴¹ and consequently modulate the magnon excitation spectrum. In $\text{BaFe}_2\text{Se}_2\text{O}$, the modulation of the magnon excitation spectrum is evidenced by the energy shift of M1' and M1'' modes [Fig. 4]. Quantitative understanding of the M0, M1' and M1'' modes magnetic field dependence requires more theoretical work in the future and goes beyond the scope of the paper.

IV. SUMMARY

In summary, BaFe₂Se₂O temperature- and field-dependent Raman scattering study has been performed. Temperature evolution of the Raman active modes indicates that there is no structural phase transition accompanying the magnetic phase transitions. Observed anomalies in the phonon spectra can be traced back to a moderate spin-phonon interaction contributions as well as multiple magnetic phase transitions present in BaFe₂Se₂O also detected in the [Raman continuum](#) induced by the spin fluctuations. The anomalous intensity of the M0 peak is attributed to the contribution from the two-magnon continuum and a two-magnon bound state

resonance. The present study provides the fundamental lattice and spin dynamics information on BaFe₂Se₂O and is of significance for the understanding of magnetic excitations in the low-dimensional spin systems.

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Appendix A: Anharmonic and spin-phonon contributions to phonon mode energies

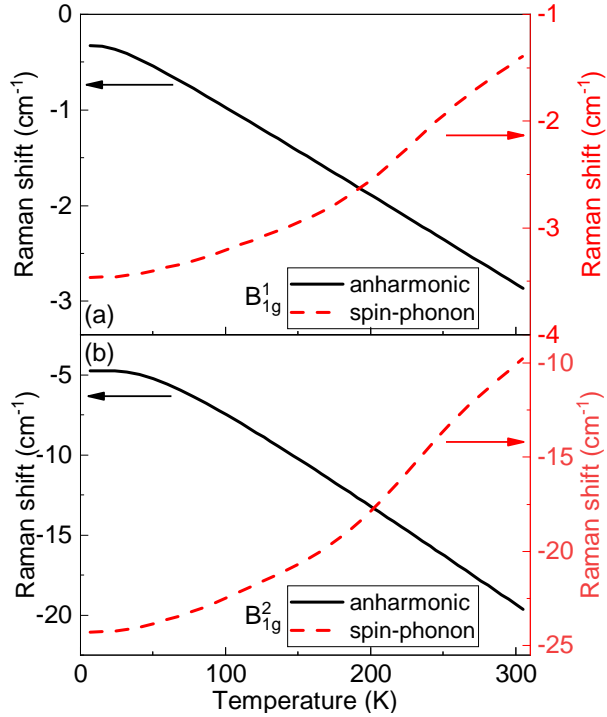


FIG. A1. Anharmonic (solid line) and spin-phonon (dashed line) contribution to the temperature dependence of the energy of (a) B_{1g}^1 and (b) B_{1g}^2 phonon modes obtained by fitting Eq. (1) to the experimental data.

Appendix B: Temperature and field dependent Raman spectra

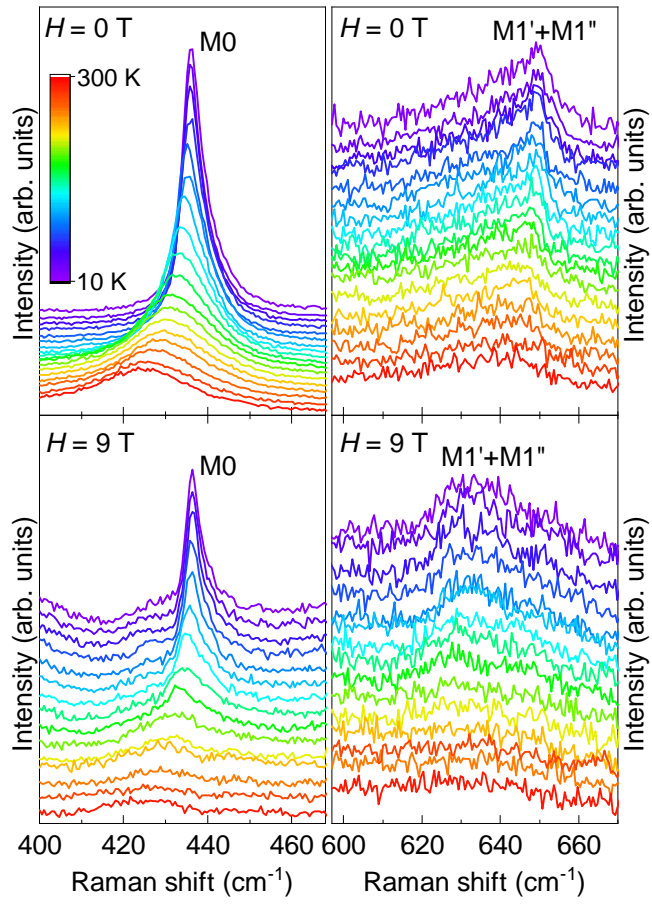


FIG. A2. Temperature-dependent spectra of the M0, M1 and M1 modes at 0 T and 9 T.