Raman scattering in superconducting NdO$_{1-x}$F$_x$BiS$_2$ crystals

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Abstract
The recently discovered layered BiS$_2$-based superconductors are of great interest due to their structural similarity to cuprate and iron-pnictide superconductors. We performed Raman scattering measurements on two superconducting crystals NdO$_{0.5}$F$_{0.5}$BiS$_2$ ($T_c = 4.5$ K) and NdO$_{0.4}$F$_{0.6}$BiS$_2$ ($T_c = 4.8$ K). We assigned observed Raman phonon modes with the aid of first-principles calculations. The asymmetric phonon mode around 118 cm$^{-1}$ reveals a small electron–phonon coupling constant $\lambda \sim 0.16$, which is insufficient to generate superconductivity at $\sim$4.5 K.

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(Some figures may appear in colour only in the online journal)

Introduction
The discovery of BiS$_2$-based superconductors has inspired a new wave of research [1–5]. Similar to cuprate and iron-pnictide superconductors, these new superconductors have two-dimensional conducting BiS$_2$ layers as key building blocks, which are considered to be responsible for superconductivity (SC). The BiS$_2$-based compounds are actually very similar to FeSe superconductors in structure and exhibit semiconducting behavior at temperatures depending on the doping level [6, 7]. As one of the most common elementary excitations in solids, lattice vibrations are vital to studies of many fundamental physical properties and interactions such as mechanical and thermal properties, electron–phonon (e–ph) coupling and other phonon-involved scattering processes. Phonon dispersion in BiS$_2$-based superconductors has initially been studied by neutron scattering [8]. Raman measurements have also been conducted recently [9]. However, a comprehensive assignment of the observed Raman modes is still lacking.

The electronic properties of REO$_{1-x}$F$_x$BiS$_2$ (RE = rare earth) compounds have been the subject of many theoretical and experimental investigations. First-principles calculations predicted a Fermi surface showing a nesting along the ($\pi, \pi, 0$) direction at half filling. This may induce phonon instability or a charge density wave (CDW), which implies that superconductivity in the BiS$_2$ system may be driven by strong e–ph coupling [10–12]. However, infrared optical spectroscopy shows no sign of a CDW transition [13], and neutron scattering measurements do not show significant change in phonon density across the SC transition [8], which suggests that the e–ph coupling in a BiS$_2$-based system is not as strong as predicted. Furthermore, rectangular-like Fermi pockets around X points have been revealed by angle resolved photoemission spectroscopy (ARPES) experiments. The measured band filling is smaller than the calculated one, against the picture of Fermi surface nesting [14, 15]. The smaller...
band filling may explain why the observed e–ph coupling is weaker than the calculated value.

In this work, we conducted Raman scattering experiments on superconducting single crystals NdO0.5F0.5BiS2 (Tc = 4.5 K) and NdO0.7F0.3BiS2 (Tc = 4.8 K). The transition temperatures were determined by resistivity measurement [15]. The observed Raman modes are assigned with the assistance of first-principles calculations. The A1g mode at 118 cm⁻¹ exhibits an asymmetric lineshape which is attributed to Breit–Wigner–Fano (BWF) resonance (or Fano resonance) driven by e–ph coupling [16, 17]. The fitting of the Fano lineshape gives the strength of the e–ph coupling constant λ ∼ 0.16 at Γ point, which gives a near-zero Tc using the density of states (DOS) at Fermi surface N(EF) derived from electronic specific heat coefficient [18]. This may suggest that the paring glue in the BiS2 system is beyond e–ph coupling.

Experiments and methods

Superconducting single crystals NdO0.5F0.5BiS2 (Tc = 4.5 K) and NdO0.7F0.3BiS2 (Tc = 4.8 K) were grown using KCl flux. Details of crystal growth and characterization can be found elsewhere [19, 20]. The sample size is typically about 0.5 × 0.5 × 0.1 mm. The crystals can be easily cleaved to obtain flat and shining ab planes. To minimize the impact of possible impurities on surfaces, we repeated the cleavage of the crystals at least two times before they were placed into the cryostat. For each cleavage, Raman spectra were recorded and compared. No sign of impurity is seen in the spectra, which is consistent with the structural characterization of these materials [7]. Raman measurements were performed in a high-vacuum closed-cycle cryostat with anti-vibration design (10 ∼ 300 K, ∼10⁻⁸ mbar). Raman spectra were collected with an HR800 spectrometer (Jobin Yvon) equipped with a liquid nitrogen cooled CCD and volume Bragg gratings. The volume Bragg gratings were made on a special multi-componton silicate glass (BragGlass™) which has a permanent refractive index change after exposure to UV radiation followed by a thermal development, and can be used to effectively eliminate the laser line. Micro-Raman backscattering configuration was adopted. A 632.8 nm laser was focused on sample surfaces using a 50× objective lens with a spot size of ∼5 μm. Laser power was kept below 1 mW to avoid overheating.

In order to identify the Raman-active modes found in experiments, we carried out first-principles calculations by using the QUANTUM-ESPRESSO (QE) package [21]. The ultra-soft pseudopotentials [22] were employed to describe the electron–ion interactions. The generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) [23] formalism was adopted for the exchange and correlation functional. The kinetic energy cutoff and the charge density cutoff for the plane-wave basis were 800 eV and 8000 eV, respectively. For the Brillouin zone integration, the k points were sampled on a 12 × 12 × 4 grid. The Fermi surface was broadened using the Gaussian smearing technique with a width of 0.05 eV. Variable-cell calculations were performed until zero pressure was reached and all of the forces acting on atoms were less than 0.01 eV Å⁻¹.

Results and discussions

Low-temperature Raman spectra of NdO0.5F0.5BiS2 and NdO0.7F0.3BiS2 are shown in figure 1. The spectra from both crystals are similar. This implies that although their nominal fluorine contents seem quite different, the actual composition of the two samples may be very close due to the bismuth deficiency [15]. It is consistent with the fact that both crystals have very close superconductivity (SC) transition temperatures. The crystal symmetry has a space group P4/nmm (#129). Symmetry analysis shows that there are ten Raman-active modes (4A1g + B1g + 5Eg) at the gamma point. No multi-phonon bands or forbidden modes are observed in the spectra which indicates that 1.96 eV may not be the resonance frequency of these samples. The corresponding vibration patterns are illustrated in figure 2. The observed Raman modes are well assigned in combination with first-principles calculations as shown in figure 2. The calculated phonon frequencies are close to those from [8] and summarized in table 1. We think the broad hump between 0 ∼ 400 cm⁻¹ in both channels may originate from electronic excitations between the bands split by spin–orbit coupling and leave it as an open question.

Among the observed Raman modes, the two peaks located at 70 cm⁻¹ and 117.5 cm⁻¹, only visible in the parallel polarization configuration (ε∥/εc, see figure 1), are identified as A1g symmetry. The 2A1g phonon mode exhibits a clear asymmetric lineshape, indicating an apparent

![Figure 1](image1.png)

![Figure 2](image2.png)
e–ph coupling. The small peaks around 38 cm\(^{-1}\) and 79 cm\(^{-1}\) in cross polarization (\(e_{\perp} \ll e_{s}\)) are attributed to \(E_g\) modes according to first-principles calculations (see table 1). The modes are normally prohibited in the present scattering geometry but may leak into the measurements on \(ab\) planes, perhaps due to a slight tilt of sample surfaces. There are two unidentified tiny peaks in cross polarization. One is located at around 111.5 cm\(^{-1}\) (marked by \# in figure 1) which may be attributed to intensity leakage of the strongest \(2A_{1g}\) mode in parallel polarization. The other peak at 56 cm\(^{-1}\) (marked by *) may be a leakage of the Raman-inactive mode. In fact, around this energy, a peak of phonon DOS has been observed by neutron scattering measurements [8]. The \(2E_g\) and \(B_{1g}\) modes are from cooperative vibrations of O/F atoms. Both modes are clearly broader than others, which is consistent with O/F disorder. It implies that the O/F disorder does not induce

**Table 1.** Assignments of Raman modes from NdO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\). The calculated phonon frequencies are in good agreement with experiments. \(S_1\) and \(S_2\) denote sulfur atoms in the BiS plane and out of plane, respectively. Results from [9] are also listed.

| Symmetry | Calc. Freq. (cm\(^{-1}\)) | Exp. Freq. (this work) (cm\(^{-1}\)) | Exp. Freq. [9] (cm\(^{-1}\)) | Vibrating atoms |
|----------|--------------------------|-------------------------------------|-----------------------------|----------------|
| \(1E_g\) | 32.7                     | 38                                  |                             | Bi and \(S_1\) |
| \(1A_{1g}\) | 69.0                     | 70.7(10 K)                          | 52.6(300 K)                 | Bi, \(S_1\) and \(S_2\) |
| \(2E_g\) | 76.0                     | 79.1(10 K)                          |                             | \(S_2\), Nd and O/F |
| \(2A_{1g}\) | 127.5                    | 117.5(10 K)                         | 112.4(300 K)               | Nd and \(S_1\) |
| \(E_g\)  | 143.3                    |                                     |                             | \(S_1\) and \(S_2\) |
| \(A_{1g}\) | 158.1                    |                                     |                             | \(S_1\) and \(S_2\) |
| \(E_g\)  | 167.6                    |                                     |                             | \(S_1\) and \(S_2\) |
| \(1B_{1g}\) | 283.4                    | 299.7                               |                             | O/F |
| \(3A_{1g}\) | 312.0                    | 346.8                               |                             | \(S_2\) |
| \(E_g\)  | 354.0                    |                                     |                             | O/F |

Figure 2. Vibration patterns of Raman-active modes in NdO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\). The calculated and experimental mode frequencies are listed below each pattern.
Figure 3. Temperature dependent Raman spectra from NdO$_{0.5}$F$_{0.5}$BiS$_2$ and NdO$_{0.7}$F$_{0.3}$BiS$_2$. Representative Lorentzian and Fano fittings for (a) and (b), respectively, are shown as black curves for the lowest temperature spectra at the bottom of each panel. The grey dotted lines show the tilted backgrounds on which the Raman peaks, $1A_{1g}$ and $2A_{1g}$, are displayed in detected.

Figure 4. Temperature dependence of the frequencies of $1A_{1g}$ (a) and $2A_{1g}$ modes in NdO$_{0.5}$F$_{0.5}$BiS$_2$ (a) and (c)) and NdO$_{0.7}$F$_{0.3}$BiS$_2$ (b) and (d)). The red lines are anharmonic fittings using formula (1).

Temperature dependence of the two strongest Raman peaks, $1A_{1g}$ and $2A_{1g}$, are displayed in figure 3. Both modes show a smooth temperature evolution without observable anomalies in the temperature range of 10 to 300 K. However, their lineshapes are clearly different. The $1A_{1g}$ mode has a well-defined Lorentzian lineshape (see figure 3(a)), while the $2A_{1g}$ mode displays an asymmetric Fano lineshape (see figure 3(b) and the analysis below).

Generally the anharmonic effects in a crystal can be divided into three types, two of them (the thermal expansion and one phonon interaction with another) have opposite contributions and almost cancel out in many real systems [24, 25]. Figure 4 further shows the temperature dependence of phonon frequencies. Both modes can be well described by anharmonic phonon decay process [26]

$$\omega = \omega_0 - C \left(1 + \frac{2}{\hbar \omega_p \varepsilon q^2 \Gamma}\right), \quad (1)$$

where $\omega_0$, $\hbar \omega_p$ and $C$ are the phonon frequency extrapolated to 0 K, Boltzmann constant, and fitting constant which represents the coupling strength between phonons, respectively. The smooth temperature evolution indicates that there is no structural phase change over the measured temperature range, which is in agreement with the absence of a CDW transition [13]. The frequencies of the two modes extrapolated to 0 K (70.5 cm$^{-1}$ and 118.94 cm$^{-1}$, respectively) are almost the same in both crystals, which suggests that the chemical composition in NdO$_{0.5}$F$_{0.5}$BiS$_2$ and NdO$_{0.7}$F$_{0.3}$BiS$_2$ are very close.

The asymmetric $2A_{1g}$ mode exhibits a typical Breit–Wigner–Fano (BWF) lineshape which results from quantum interference between a discrete phonon state and a relatively broad continuum of electronic transitions. The Fano equation reads [16, 27]

$$I(\varepsilon, q) = I_0 (q + \varepsilon)^2 / \left(1 + \varepsilon^2\right), \quad \varepsilon = (\omega - \omega_p) / \Gamma, \quad (2)$$

in which $I_0$ is a scaling factor, $\omega_p$ is the uncoupled mode frequency, $\Gamma$ is the broadening parameter, and $q$ reflects the degree of lineshape asymmetry and is related to e–ph coupling strength. The larger the $q$, the smaller the coupling, and the more symmetric the peak is. In the case of $q \to \infty$, $1/q \to 0$, the peak will display a Lorentzian lineshape. In the entire temperature range that we probed, the $2A_{1g}$ mode displays a Fano lineshape with $q$ varying between −4 and −6. This means that a finite e–ph coupling exists above SC transition temperatures.

The e–ph coupling constant $\lambda$ can be determined from phonon broadening $\Gamma_{e-ph}$ [28] which may be obtained from the measured FWHM of phonon modes, the jump of phonon frequencies at SC transition [28, 29], or the asymmetry factor $q$ [30]. It is rather complicated to derive $\Gamma_{e-ph}$ from $q$ [30]. Measuring the frequency jump across the SC transition seems to be a relatively reliable way to estimate intrinsic phonon broadening. However, such a jump is not available in our measurements since our experimental setup can only access 10 K which is higher than the SC transition temperatures of these two materials. Here we estimate $\Gamma_{e-ph}$ from the measured phonon linewidths $\Gamma$. Figure 5 shows the dependence of $\Gamma$ (obtained from Fano lineshape fitting given by equation (2)) as a function of temperature in the two materials we studied. The total linewidth $\Gamma$ is contributed by anharmonic phonon decay, e–ph coupling, and temperature-independent impurity scattering. It can be described by the
where the anharmonic phonon broadening extrapolated to 0 K, $\omega_0 = 118.9 \text{ cm}^{-1}$ is the phonon frequency at 0 K. $\Gamma_{e-ph}$ and $\Gamma_{imp}$ are the broadening caused by e–ph coupling and impurity scattering, respectively. We assume that the widths of anharmonic phonon broadening and impurity scattering of the $^{1}A_{1g}$ and $^{2}A_{1g}$ phonon branches are approximately the same. Then we take the width of the symmetric $^{1}A_{1g}$ mode extrapolated to 0 K as the contribution from anharmonic phonon broadening and impurity scattering of the $^{2}A_{1g}$ mode at 0 K. Hence, we estimate that the e–ph coupling linewidth $\Gamma_{e-ph}(0 \text{ K}) \approx \Gamma^{(^{1}A_{1g}, 0 \text{ K})} - \Gamma^{(^{2}A_{1g}, 0 \text{ K})} \approx 9.3 \text{ cm}^{-1} - 4.0 \text{ cm}^{-1} = 5.3 \text{ cm}^{-1}$ for Nd$_{0.5}$F$_{0.5}$BiS$_{2}$. The experimental DOS at the Fermi surface, $N_{exp}(E_f) \approx 5.5$ states/eV/spin/formula (formula = one Nd$_{0.5}$F$_{0.5}$BiS$_{2}$), can be derived from electronic specific heat measurements [18]. The e–ph coupling constant is expressed as [28]

$$\lambda = \frac{\Gamma_{e-ph}}{\pi N(E_f) \hbar \omega_0},$$

(4)

where $N(E_f)$ is the bare DOS at the Fermi energy and is given by $N_{exp}(E_f)/\lambda(1 + \lambda)$ [31, 32].

Equation (4) gives $\lambda \approx 0.16$. The coupling strength leads to $T_c$ approaching zero using Allen–Dynes formula [33, 34],

$$T_c = \frac{\omega_0}{1.20} e^{\left(\frac{1.04 (1 + \lambda)}{\lambda - \mu^{\ast} (1 + 0.62 \lambda)}\right)},$$

(5)

where $\mu^{\ast}$ is the Coulomb pseudopotential parameter and a typical value of 0.1 is used in our case [35–37]. If we take $\Gamma_{e-ph}$ as the total linewidth $\sim 9.3 \text{ cm}^{-1}$ (0 K) without subtracting the anharmonic and impurity broadening, we get $\lambda \sim 0.47$ and $T_c \sim 1.1 \text{ K}$. This $T_c$ value is still much smaller than the experimental ones, which implies that the pairing glue for the new superconductors may not be the e–ph coupling. It should be pointed out that the estimation of the e–ph coupling constant follows the conventional procedure in Raman measurements and may represent the average coupling strength for a particular phonon branch [38–40]. The exact determination of the coupling constant requires more momentum–resolved measurements, such as electron energy loss spectrum and neutron scattering. We note that in [9] the authors employed a calculated DOS rather than an experimental one, which gives an e–ph coupling constant of $\sim 0.68$ and a $T_c$ of $\sim 5 \text{ K}$.

In summary, we measured polarized Raman scattering spectra of Bi$_2$S$_3$–based SC single crystals Nd$_{0.5}$F$_{0.5}$BiS$_{2}$ ($T_c = 4.5 \text{ K}$) and Nd$_{0.7}$F$_{0.3}$BiS$_{2}$ ($T_c = 4.8 \text{ K}$) from 10 K to 300 K. The observed Raman modes are assigned with the aid of first–principles calculations. Investigation of the Fano–type $^{2}A_{1g}$ mode gives an electron–phonon coupling constant $\lambda \sim 0.16$, which is not strong enough to produce superconductivity at $\sim 4.5 \text{ K}$.

Acknowledgments

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