Phonon spectra and superconductivity of the BiS$_2$-based compounds LaO$_{1-x}$F$_x$BiS$_2$

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Abstract – Using the density-functional perturbation theory with structural optimization, we investigate the electronic structure, phonon spectra, and superconductivity of the BiS$_2$-based layered compounds LaO$_{1-x}$F$_x$BiS$_2$. For LaO$_{0.5}$F$_0.5$BiS$_2$, the calculated electron-phonon coupling constant is equal to $\lambda = 0.8$, and the obtained $T_c \simeq 9.1$ K is very close to its experimental value, indicating that it is a conventional electron-phonon superconductor.

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The recent discovery of superconductivity in the BiS$_2$-based compounds has attracted much attention due to their layered crystal structure and physical properties similar to cuprate and Fe-based superconductors. The Bi$_4$O$_3$S$_3$ superconductor was found to exhibit metallic transport behavior and to show a zero-resistivity state below 4.5 K [1]. Soon after, another type of BiS$_2$-based systems, ReO$_{1-x}$F$_x$BiS$_2$ (Re = La, Ce, Pr, and Nd), were reported to be superconducting with transition temperatures $T_c$ equal to 10.6, 3.0, 5.5, and 5.6 K, respectively [2–5]. For Bi$_4$O$_3$S$_3$ (ReO$_{1-x}$F$_x$BiS$_2$), superconductivity can be obtained by electrons doping into the insulating parent compound Bi$_6$O$_8$S$_5$ (ReOBiS$_2$). Experimental and theoretical studies indicated that these materials exhibit multiband behavior with dominant electron carriers originating mainly from the Bi 6$p$ orbitals [1,6–12].

In this letter we report the calculated results for electronic structure of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0$, 0.5, and 1), phonon dispersions and electron-phonon coupling of superconducting LaO$_{0.5}$F$_0.5$BiS$_2$. From the first-principles calculation, it is shown that the parent compound LaOBiS$_2$ is a band insulator with an energy gap of $\sim 0.8$ eV, similar to the case of cuprate superconductors. Upon F doping, the Fermi level moves up and the system appears a metallic nature. We obtain electron-phonon coupling constant $\lambda = 0.8$ and superconducting transition temperature $T_c \simeq 9.1$ K in LaO$_{0.5}$F$_0.5$BiS$_2$, indicating that this compound can be explained as a conventional phonon-mediated superconductor, quite different from the Fe-based materials [13,14] but somewhat similar to the Ni-based compounds [15,16].

We used the full-potential linearized augmented plane-wave method implemented in the WIEN2K package [17] for the lattice parameter optimization and electronic structure calculations. The generalized gradient approximation (GGA) presented by Wu and Cohen [18] was used for the exchange-correlation energy calculations. This GGA is a nonempirical approximation that gives significant improvements of calculations for lattice constants and crystal structures. The phonon dispersions were obtained in linear response via the QUANTUM-ESPRESSO program [19] and ultrasoft pseudopotentials. The GGA of Perdew-Burke-Ernzerhof [20] was adopted for the exchange-correlation potentials with a cutoff of 60 Ry for the wave functions and 600 Ry for the charge density. The electronic integration was performed over a $8 \times 8 \times 8$ $k$-point mesh. Dynamical matrices and the electron-phonon interaction coefficients were calculated on a $4 \times 4 \times 4$ $q$-point grid. A dense $24 \times 24 \times 24$ grid was used for evaluating an accurate electron-phonon interaction matrix.

LaO$_{1-x}$F$_x$BiS$_2$ with $x = 0$ or 1 is crystallized in the ZrCuSiAs-type tetragonal structure ($P4/nmm$) with La, Bi, S1 in the Bi planes, S2 in between Bi-S1 and La-O(F) planes, and O(F) being at the positions $2c(0.5, 0, z_{La})$, $2c(0.5, 0, z_{Bi})$, $2c(0.5, 0, z_{S1})$, $2c(0.5, 0, z_{S2})$, and $2c(0.5, 0, z_{S2})$, and
Table 1: Various optimized structural parameters for LaO$_{1-x}$F$_x$BiS$_2$ with $x = 0, 0.5$, and 1.

|                  | LaOBiS$_2$ | LaO$_{0.5}$F$_{0.5}$BiS$_2$ | LaFBiS$_2$ |
|------------------|------------|-----------------------------|------------|
| $a$ (Å)          | 4.0677     | 4.1091                      | 4.1524     |
| $c$ (Å)          | 14.3085    | 13.4196                     | 12.9554    |
| $V$ (Å$^3$)      | 236.75     | 226.59                      | 223.38     |
| $z_{La}$         | 0.0890     | 0.1073                      | 0.1276     |
| $z_{Bi}$         | 0.6309     | 0.6145                      | 0.6090     |
| $z_{S1}$         | 0.3945     | 0.3844                      | 0.3691     |
| $z_{S2}$         | 0.8073     | 0.8128                      | 0.8163     |
| $d_{Bi-S1}$ (Å)  | 2.8993     | 2.9056                      | 2.9499     |
| $d_{Bi-S2}$ (Å)  | 2.5231     | 2.6621                      | 2.6862     |

2$a$(0, 0, 0), respectively. The F substitution at the O sites in LaO$_{0.5}$F$_{0.5}$BiS$_2$ reduces the symmetry to a space group of $P-4m2$. Starting from the lattice parameters ($a = 4.0527$ Å and $c = 13.3237$ Å) reported by Mizuguchi et al. [2], we have performed the full structural optimization including the lattice parameters and atomic positions, the obtained results being summarized in table 1. It is found that, with doping F from $x = 0$ to $x = 1$, the $a$ value increases gradually but the $c$ value decreases, accompanied with a decrease of primitive cell volume $V$. By making a comparison in the atomic bond length between LaO$_{0.5}$F$_{0.5}$BiS$_2$ and LaOBiS$_2$, one finds that the Bi-S2 bond expands due to F doping while $d_{Bi-S1}$ for the Bi-S1 bond remains almost unchanged.

The calculated band structures and electronic density of states (DOS) are shown in fig. 1. The contribution of orbital states to the band structure are characterized by different colors: blue (Bi-$p$), red (S1-$p$), and green (O-$p$ and S2-$p$). For LaOBiS$_2$, the Fermi level is located at the upper edge of valence bands with an energy gap of $\sim 0.8$ eV, indicating an insulating behavior. The valence bands spread from around $-6$ eV to 0 and consist of the $p$ states of the O and S atoms. While the La-$d$ and La-$f$ states lie above 4 eV, far away from the Fermi level, the Bi-$p$ and S1-$p$ states dominate the conduction bands. For doped LaO$_{0.5}$F$_{0.5}$BiS$_2$, the Fermi level enters the conduction bands coming from the Bi-$p$ and S1-$p$ states, so that the Bi-S1 layers dominantly contribute to the electronic conduction. As shown in fig. 1(b), the present Fermi level crosses four bands of electron pockets, and so LaO$_{0.5}$F$_{0.5}$BiS$_2$ has electron carriers, which is well consistent with the Hall resistance measurements [10].

The DOS at the Fermi level is equal to $N(E_F) = 1.22\text{eV}^{-1}$ on a per formula unit both spins basis, and the corresponding bare susceptibility and specific heat coefficient are given by $\chi_0 = 4.0 \times 10^{-5}$ emu/mol and $\gamma_0 = 3.0 \text{mJ/molK}^2$, respectively. For LaFBiS$_2$, the Fermi level further enters the conduction bands and the energy gap increases to $\sim 1.1$ eV. Meanwhile, the DOS at the Fermi level increases to $N(E_F) = 1.84\text{eV}^{-1}$ per formula unit both spins, yielding $\chi_0 = 6.0 \times 10^{-5}$ emu/mol and $\gamma_0 = 4.5 \text{mJ/molK}^2$.

The calculated phonon dispersions of LaO$_{0.5}$F$_{0.5}$BiS$_2$ are plotted in fig. 2(a), in which there are 30 phonon bands extending up to $\sim 450\text{cm}^{-1}$ and the point group...
the radius of the circle is proportional to the magnitude of \( \omega_{q\nu} \cdot \lambda_{q\nu} \) for each mode, which represents the contribution to \( T_c \). The \( \omega_{q\nu} \cdot \lambda_{q\nu} \) circles are mostly distributed over the low-frequency phonon branches. The largest couplings are concentrated around the \( M \) and \( A \) points. It is these low-frequency phonon modes that dominate the contribution to \( T_c \). In MgB2, by comparison, the \( \lambda_{q\nu} \) circles that contribute to \( T_c \) spread mostly over the higher frequency region (see fig. 1 of ref. [21]). The corresponding phonon density of states (PDOS), Eliashberg spectral function \( \alpha^2 F(\omega) \), electron-phonon coupling \( \lambda(\omega) \) and projected PDOS are shown in fig. 3. There are three distinct peaks centered at \( \sim 70 \text{ cm}^{-1} \) (\( A_1 \) mode at the \( \Gamma \)-point), \( \sim 190 \text{ cm}^{-1} \) (\( E_1 \) and \( E_2 \) modes at the \( \Gamma \)-point), and \( \sim 250 \text{ cm}^{-1} \) (\( B_2 \) mode at the \( \Gamma \)-point), respectively, corresponding to four thick lines from lower to upper in fig. 2(a). As shown in fig. 2(b), the \( A_1 \) mode corresponds to the vertical vibrations with the upper and lower BiS2-layers (La-layers) beating against each other. The \( E \) mode corresponds to the in-plane stretching vibrations with motion along the \( x(y) \)-axis. In the \( B_2 \) mode, the La, Bi, and S1 atoms vibrate along the same \( z \)-direction, opposite to the vibration direction of the S2, O, and F atoms. From fig. 3, one can see that the bands around 70 cm\(^{-1}\) comes mainly from the PDOS contributions of the Bi and La motion, the peak at 190 cm\(^{-1}\) mainly corresponds to the S character, and that at 250 cm\(^{-1}\) corresponds to F, O and S character. The calculated Eliashberg spectral function has peaks consistent with the PDOS at the low-frequency regime, and is evidently enhanced in the intermediate frequency regime. In the density-functional perturbation theoretical (DFPT) calculations, the Eliashberg spectral function depends directly on the electron-phonon matrix element:

\[
\alpha^2 F(\omega) = \frac{1}{N(E_F)N_k} \sum_{kq} \left| g_{nk,m(k+q)}^\nu \right|^2 \times \delta(\epsilon_{nk})\delta(\epsilon_{m(k+q)})\delta(\omega - \omega_{q\nu}).
\]

Here, \( N_k \) is the number of \( k \)-points used in the summation, \( N(E_F) \) is the density of states at the Fermi level, and \( \omega_{q\nu} \) are the phonon frequencies. The electron-phonon matrix element \( |g_{nk,m(k+q)}^\nu| \)\(^2\) is defined by the variation in the

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**Table 2:** Phonon mode frequencies (cm\(^{-1}\)) at \( \Gamma \) and \( M \) points in LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\). I: infrared active, R: Raman active.

| \( B_2 \) (I + R) | \( E \) (I + R) | \( A_1 \) (R) | \( M \) (0.5, 0.5, 0) |
|-----------------|-----------------|--------------|------------------|
| 0               | 0               | 74.8         | 153.6            |
| 65.4            | 39.3            | 138.3        | 181.3            |
| 145.4           | 44.0            | 168.4        | 184.1            |
| 249.4           | 78.4            | 305.9        | 243.8            |
| 270.1           |                 |              | 345.1            |
| 412.2           |                 |              |                  |

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**Fig. 2:** (Color online) (a) Calculated phonon dispersion curves of LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\). The radius of the circles is proportional to \( \omega_{q\nu} \cdot \lambda_{q\nu} \) for each phonon mode, which represents the contribution to \( T_c \). The \( \omega_{q\nu} \cdot \lambda_{q\nu} \) circles are mostly distributed over the low-frequency phonon branches. The largest couplings are concentrated around the \( M \) and \( A \) points. It is these low-frequency phonon modes that dominate the contribution to \( T_c \). In MgB\(_2\), by comparison, the \( \lambda_{q\nu} \) circles that contribute to \( T_c \) spread mostly over the higher frequency region (see fig. 1 of ref. [21]). The corresponding phonon density of states (PDOS), Eliashberg spectral function \( \alpha^2 F(\omega) \), electron-phonon coupling \( \lambda(\omega) \) and projected PDOS are shown in fig. 3. There are three distinct peaks centered at \( \sim 70 \text{ cm}^{-1} \) (\( A_1 \) mode at the \( \Gamma \)-point), \( \sim 190 \text{ cm}^{-1} \) (\( E_1 \) and \( E_2 \) modes at the \( \Gamma \)-point), and \( \sim 250 \text{ cm}^{-1} \) (\( B_2 \) mode at the \( \Gamma \)-point), respectively, corresponding to four thick lines from lower to upper in fig. 2(a). As shown in fig. 2(b), the \( A_1 \) mode corresponds to the vertical vibrations with the upper and lower BiS\(_2\)-layers (La-layers) beating against each other. The \( E \) mode corresponds to the in-plane stretching vibrations with motion along the \( x(y) \)-axis. In the \( B_2 \) mode, the La, Bi, and S1 atoms vibrate along the same \( z \)-direction, opposite to the vibration direction of the S2, O, and F atoms. From fig. 3, one can see that the bands around 70 cm\(^{-1}\) comes mainly from the PDOS contributions of the Bi and La motion, the peak at 190 cm\(^{-1}\) mainly corresponds to the S character, and that at 250 cm\(^{-1}\) corresponds to F, O and S character. The calculated Eliashberg spectral function has peaks consistent with the PDOS at the low-frequency regime, and is evidently enhanced in the intermediate frequency regime. In the density-functional perturbation theoretical (DFPT) calculations, the Eliashberg spectral function depends directly on the electron-phonon matrix element:

\[
\alpha^2 F(\omega) = \frac{1}{N(E_F)N_k} \sum_{kq} \left| g_{nk,m(k+q)}^\nu \right|^2 \times \delta(\epsilon_{nk})\delta(\epsilon_{m(k+q)})\delta(\omega - \omega_{q\nu}).
\]

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the electronic structure and Fermi surface have a similar two-dimensional character. Superconductivity in MgB$_2$ is understood to be caused by the strong interaction between zone-centered holes in the B-B bonding $\sigma$ band and the relative softness of the optical bond-stretching modes [21,24]. Although the calculated $\lambda$s in both compounds are close to each other, $T_c$ evaluated in MgB$_2$ is much higher than $T_c = 9.1$ K obtained here in LaO$_{0.5}$F$_{0.5}$BiS$_2$. For example, $\lambda \simeq 0.7$, $\omega_n \simeq 700$ K, and so $T_c \simeq 22$ K in MgB$_2$ [24]; and $\lambda \simeq 0.87$, $\omega_n \simeq 540$ K, and also $T_c \simeq 22$ K [25]. Such a big difference in the calculated value of $T_c$ between LaO$_{0.5}$F$_{0.5}$BiS$_2$ and MgB$_2$ stems from the fact that the former $\omega_n$ is much lower than the latter $\omega_n$. As shown in fig. 2(a) and discussed above, the main contributions to $T_c$ for LaO$_{0.5}$F$_{0.5}$BiS$_2$ come from the low-frequency phonon modes, whereas those for MgB$_2$ come from the high-frequency ones.

In summary, the present first-principles calculations indicate that LaO$_{1-x}$F$_x$BiS$_2$ changes from a band insulator at $x = 0$ to a band metal upon doping. Similar to LaFeAsO$_{1-x}$F$_x$, electrons in LaO$_{1-x}$F$_x$BiS$_2$ are doped from the LaO(F) redox layer to the superconducting BiS$_2$ layers. The $p$-orbital states of the Bi-S layers play an important role in the electron transformation due to their domination of the DOS at the Fermi level. From the phonon calculations for LaO$_{0.5}$F$_{0.5}$BiS$_2$, we obtain a strong electron-phonon coupling of $\lambda = 0.8$ and a superconducting transition temperature of $T_c = 9.1$ K, the latter being very close to its experimental value. It then follows that LaO$_{0.5}$F$_{0.5}$BiS$_2$ is a conventional electron-phonon superconductor.

For LaO$_{1-x}$F$_x$BiS$_2$, we have shown that the electronic states near the Fermi level are dominantly from the hybridized $p$ orbital states of the Bi and S1 atoms, and the electron-phonon coupling comes mainly from the contribution of the Bi and S phonons around the M and A points at the low-frequency branches. These facts indicate that the BiS$_2$ layers play an important role in the transport and superconducting properties, similar to the CuO$_2$ layers of the cuprates or Fe-As layers of the Fe-based superconductors.

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