Effects of stoichiometric doping in superconducting Bi-O-S compounds

Corentin Morice¹, Emilio Artacho¹,²,³, Siân E Dutton¹, Daniel Molnar¹, Hyeong-Jin Kim¹ and Siddharth S Saxena¹

¹ Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK
² Nanogune and DIPC, Tolosa Hiribidea 76, 20018 San Sebastián, Spain
³ Basque Foundation for Science, Ikerbasque, 48011 Bilbao, Spain

E-mail: cm712@cam.ac.uk, ea245@cam.ac.uk and sss21@cam.ac.uk

Received 4 December 2014, revised 10 February 2015
Accepted for publication 19 February 2015
Published 13 March 2015

Abstract
Newly discovered Bi-O-S compounds remain an enigma in attempts to understand their electronic properties. A recent study of Bi₄O₄S₃ has shown it to be a mixture of two phases, Bi₂O₂S₂ and Bi₃O₂S₃, the latter being superconducting (Phelan et al. 2013 J. Am. Chem. Soc. 135 5372–4). Using density functional theory, we explore the electronic structure of both the phases and the effect of the introduction of extra BiS₂ bilayers. Our results demonstrate that the S₂ layers dope the bismuth-sulphur bands and this causes metallisation. The bands at the Fermi level are of clear two-dimensional character. One band manifold is confined to the two adjacent, square-lattice bismuth-sulphur planes, a second manifold is confined to the square lattice of sulphur dimers. We show that the introduction of extra BiS₂ bilayers does not influence the electronic structure. Finally, we also show that spin–orbit coupling does not have any significant effect on the states close to the Fermi level at the energy scale considered.

Keywords: superconductivity, BiS₂-based, DFT

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

1. Introduction
The recent discovery of superconductivity in two new compounds, Bi₄O₄S₃ [1–4] and LaOₓF₁−ₓBiS₂ [5–8], has raised great interest. All those compounds share the same structure: a stacking of alternating BiS₂ bilayers and spacer layers. Superconductivity is thought to arise from doping of the BiS₂ bilayers. Electron doping in Sr₁−ₓLaₓFBiS₂ [9] and La₁−ₓMₓOBiS₂ (M = Ti, Zr, Hf, Th) [10] results in superconductivity. The versatility of the La(O,F)BiS₂ system has been demonstrated by replacement of La with a range of lanthanide Ln³⁺ ions [11–15]—a maximum Tc of 10.6 K is reported in LaOₓF₁−ₓBiS₂ for x = 0.5.

Electronic structure calculations have mainly focused on the LaOₓF₁−ₓBiS₂ (x = 0, 0.5) materials partially due to uncertainties in the composition of the Bi-O-S superconducting phase [17, 18]. These calculations indicated that the superconducting electrons are a mixture of bismuth 6pₓ,y and sulphur 3pₓ,y states [17, 18]. These form 8 bands, four of which sit under the Fermi level, when the other four either are above the Fermi level or cross it. The electronic and thermodynamic properties of this group of materials are indeed exciting and enigmatic and suggestions range from spin-fluctuation mediated superconductivity [19], to proximity to ferroelectricity and charge density wave (CDW) instabilities [20, 21].

The coupling mechanism has been investigated in various ways. Electron–phonon interactions have been calculated in La(O,F)BiS₂ and yield a large electron–phonon coupling constant, suggesting superconductivity in this compound is strongly coupled and conventional [20–22]. Renormalisation-group calculations suggested triplet pairing and weak topological superconductivity [23, 24], a possibility studied in the context of quasiparticle interference [25]. Random phase approximation was applied to a two-orbital model [18], leading to an extended s-wave or d-wave pairing [19, 26].

The first superconductor of this family to be discovered, Bi₄O₄S₃, was studied in great detail [27–33]. Nevertheless,
there were still doubts concerning its structure. However Phelan et al recently published an extensive study of the chemistry of these compounds and concluded that Bi$_2$O$_2$S$_3$ was actually a two-phased material [34]. The two phases are Bi$_2$O$_2$S$_2$ and Bi$_3$O$_2$S$_3$, the latter being assigned as the superconducting one. Single crystals of the superconducting phase have recently been synthesised [35].

Composed of BiS$_2$, S$_2$ and Bi$_2$O$_2$ layers, the latter being a spacer layer (figure 1). Bi$_2$O$_2$S$_2$ is made of alternating BiS$_2$ bilayers and S$_2$ layers, all separated by Bi$_2$O$_2$ spacer layers, whereas in Bi$_3$O$_2$S$_3$ only the two BiS$_2$ bilayers are present. Here, we call BiS plane a two-dimensional squared lattice containing bismuth and sulphur atoms. We call BiS$_2$ bilayer a structure containing two BiS planes and extra sulphurs localised on top or under each bismuth atom of the BiS planes. Figure 2 illustrates the difference between BiS plane and BiS$_2$ bilayer.

Experimental results [34] suggest that superconductivity is suppressed by the inclusion of additional BiS$_2$ bilayers disrupting the alternation of S$_2$ and BiS$_2$ sheets, which we call extra BiS$_2$ bilayers. Phelan et al studied these extra BiS$_2$ bilayers in detail, in particular displaying TEM data that shows without ambiguity the variations in stacking.

In this paper we explore the electronic structure of the recently experimentally determined superconducting and non-superconducting phases of the Bi-O-S compounds. The role of introducing additional BiS$_2$ bilayers in the superconductor Bi$_3$O$_2$S$_3$ is also investigated, as suggested by Phelan et al in their experimental work [34]. Like in the La(O,F)BiS$_2$ systems we find that the BiS$_2$ bilayers play a critical role in conduction. Our analysis indicates that the S$_2$ sheets give rise to electron carriers in the bismuth-sulphur bands. These electrons are localised within the BiS planes rather than through the BiS$_2$ bilayer. Interruption of the BiS$_2$, S$_2$ stacking sequence is shown not to influence the electronic structure.

2. Methods

Band structures and density of states for Bi$_2$O$_2$S$_2$ and Bi$_3$O$_2$S$_3$ were calculated, using the SIESTA method [36, 37], implementing the generalized gradient approximation (GGA) in the shape of the Perdew, Burke and Ernzerhof (PBE) functional. It uses norm-conserving pseudopotentials to replace the core electrons, while the valence electrons are described using atomic-like orbitals as basis states at the double zeta polarized level. In the case of the two known structures, experimentally determined structural parameters were used in our calculations [34]. Spin polarized calculations were found to be unnecessary. We used a k-point grid of $16 \times 16 \times 5$ for Bi$_2$O$_2$S$_2$, of $16 \times 16 \times 2$ for Bi$_3$O$_2$S$_3$ and of $16 \times 16 \times 1$ for the two other structures, after showing the electronic structure was well converged using them. We used an electronic temperature of 7 K and a real space mesh cutoff of 300 Ry for the real-space integration, necessary to calculate the matrix elements for some terms of the Hamiltonian. The convergence of these parameters was also checked.

In order to estimate the influence of spin–orbit coupling, we also performed all electron calculations on Bi$_3$O$_2$S$_3$ using full-potential linearised augmented plane waves, including spin–orbit coupling through a second-variational scheme, as implemented in the Elk program [38]. We used the PBE functional and the same k-point grid we used with SIESTA, along with a carefully converged high-quality set of parameters.

3. Crystal structure

In order to simulate how extra BiS$_2$ bilayers perturb the electronic structure, we also investigated materials where the relative number of BiS$_2$ bilayers and S$_2$ layers was changed, as suggested by experiment, in particular by TEM data [34]. We did not use relaxed structures in order to keep consistency with the structures directly measured with x-rays.

In Bi$_3$O$_2$S$_3$, the stacking is $2 \times$ BiS$_2$/Bi$_2$O$_2$/S$_2$/Bi$_2$O$_2$/$2 \times$ BiS$_2$/Bi$_3$O$_2$/S$_2$/Bi$_3$O$_2$ (figure 1). The sequence is repeated twice because of symmetry: S$_2$ layers shift the Bi$_2$O$_2$ layers next to them on the x and y axis. Therefore the unit cell

Figure 1. Crystal structure of Bi$_2$O$_2$S$_2$, Bi$_3$O$_2$S$_3$, Bi$_3$O$_2$S$_3$ with one extra BiS$_2$ bilayer per unit cell of Bi$_3$O$_2$S$_3$ and Bi$_2$O$_2$S$_3$ with one extra BiS$_2$ bilayer per two unit cell of Bi$_3$O$_2$S$_3$, represented with Vesta [16]. They are formed of a stacking of BiS$_2$, S$_2$ and Bi$_2$O$_2$ layers, the latter being a spacer layer. These structures implement four different S$_2$/BiS$_2$ ratios: 0, 1, 2/3, 4/5. The black squares represent the unit cells used in the calculations.
Figure 2. BiS plane seen from above (top), in perspective (middle) and BiS₂ bilayer seen in perspective (bottom) represented with Vesta [16]. One BiS₂ bilayer contains two BiS planes and one extra S atom on top (or below) each Bi atom. The Bi-S-Bi angle is highlighted in the middle plot.

has to be doubled so that the stacking of one cell on another is possible.

To modify the ratio of S₂ layers over BiS₂ bilayers, we added a BiS₂ bilayer, with its corresponding Bi₂O₂ spacer layer, at the top of Bi₃O₂S₃. We therefore obtain the following stacking:

\[ 2 \times \text{BiS}_2 / \text{Bi}_2 \text{O}_2 / \text{S}_2 / \text{Bi}_2 \text{O}_2 / 2 \times \text{BiS}_2 / \text{Bi}_2 \text{O}_2 / \text{S}_2 / \text{Bi}_2 \text{O}_2 / 2 \times \text{BiS}_2 / \text{Bi}_2 \text{O}_2. \]

This can be done because BiS₂ bilayers, unlike S₂, do not shift Bi₂O₂ layers laterally. The stacking sequence is therefore not disturbed by the added block. Similarly we also constructed a structure in which an additional BiS₂ bilayer was included every two units cells. In total, we calculated the electronic structure of compounds with four different S₂ / BiS₂ ratios: 0, 1/3, 2/3 and 4/3.

The structure of BiS₂ bilayers is different in Bi₂OS₂ and Bi₃O₂S₃, the most noticeable difference being the Bi-S-Bi angle in the BiS planes (figure 2), which is larger in the parent phase. We thus have had to choose which BiS₂ bilayer to add in the compounds with a modified stacking: Bi₁O₂S₁⁺BiS₂ and 2xBi₂O₂S₂⁺BiS₂ (figure 1). We did calculations for both and the results were extremely similar (e.g. the bands are less than 0.1 eV apart). The results discussed below are the ones for Bi₃O₂S₃’s BiS₂ bilayers, as the extra BiS₂ bilayers appear in this compound.

4. Electronic structure

The band structures calculated with Elk and SIESTA are in very close agreement (figure 3, right hand side). The influence of spin–orbit coupling is very limited, with a difference under 0.15 eV between energy levels with and without spin–orbit coupling (figure 3, left hand side). The presence or absence of spin–orbit coupling has no impact on any of the features of the electronic structure discussed below. In the following we concentrate on electronic structures calculated with SIESTA.

4.1. Band structures

Bi₂OS₂ and Bi₃O₂S₃ only differ by the replacement in the second compound of one out of two BiS₂ bilayer by an S₂ layer. In terms of stoichiometry, as noted by Phelan et al [34], Bi₂OS₃ can be written BiOBiS₂, just as the parent phase of the lanthanum compound, LaOBiS₂.

The band structure of Bi₁O₂S₁ (figure 4) has features close to the Fermi energy which are similar to those of the undoped LaOBiS₂ phase [17, 18]. For all band structures calculated, of specific interest is the set of bands crossing or just above the Fermi level near the R and X points and approaching the Fermi level between the A and Z points (figure 4). These were also found in LaOₓF₁−ₓBiS₂ [17, 18] and were shown in these compounds to be composed of bismuth 6pₓ,y and sulphur 3pₓ,y orbitals. Partial density of states calculations enabled us to confirm that in all the compounds considered in this study these bands are composed of bismuth 6pₓ,y and sulphur 3pₓ,y orbitals, confirming the assignment done in [18] (figure 4).

In the first case, Bi₁O₂S₁, these BiS bands are just above the Fermi level, at around 0.3 eV at their minimum. This is very close to the corresponding minimum in LaOBiS₂ (0.2 eV) [17, 18]. The gap is 0.7 eV wide, twice as large as in the LaOBiS₂ case (0.37 eV) [17, 18].

In Bi₃O₂S₃, one of these BiS bands crosses the Fermi level near the R and X points, just as in LaO₀.₅F₀.₅BiS₂ [17, 18], causing Bi₃O₂S₃ to be metallic, unlike Bi₂OS₂. At these points it interacts with two other bands. These are in great majority composed of S 3p states, as the projected density of states shows (‘projected’ refers to decomposing the total density of states in contributions from the different basis orbitals of the different atoms). These bands are not present in the parent phase, Bi₂O₂S₂; they come from the S₂ layer. These two bands therefore correspond to the partly filled π antibonding states in the S₂ dimers. If fully occupied, this would formally correspond to S₂⁻⁻ dimers.

4.2. Local densities of states

To confirm these bands are coming from the S₂ layer, we plotted the local density of states (‘local’ refers to decomposing the total density of states into real space), integrated in the range of energies between −1.5 eV and 0 eV (figure 5). The chosen range of energies contains the bands we are interested in.
The results are quite clear: it is indeed the S$_2$ layer that gathers all the electron density. Moreover, this density is organised as a torus oriented along the $z$ axis around each S atom (the fact that the density decreases near the atom comes from the pseudopotentials), which shows that the orbitals lying at or just above the Fermi level correspond mainly to $p_x$, $p_y$ electrons on the S$_2$ dimers (oriented along $z$). The concentration of the electron density on the atoms rather than on the S–S bond could be indicative of a weakening of the S–S interaction.

We also plotted the local density of states in real space for the range of energies between 0 eV and 1.5 eV (figure 5). This range contains the characteristic bands present in all the BiS$_2$-based compounds. We can clearly see that the charges are localised in the BiS$_2$ bilayer, more precisely in the two BiS planes. The S atoms in the BiS$_2$ bilayer which are outside the BiS planes gather as few electrons in that range of energy as the S atoms in the S$_2$ layer.

4.3. Pinning of the Fermi level

In the band structures of Bi$_3$O$_2$S$_3$ with and without extra BiS$_2$ bilayer, we observe that the top S$_2$ band touches the Fermi level, without crossing it, approximately at equal distance from A and Z. Interestingly, this band is perfectly flat along the $z$ direction: this S$_2$ related band has very marked two-dimensional character and therefore it shows the characteristic discontinuous 2D Van Hove singularity (very clear at the Fermi level in the three lower panels of figure 4), which seems to be pinning the Fermi level. Such a discontinuity is suggestive of possible instabilities along the (1,1,0) direction.

4.4. Influence of extra BiS$_2$ bilayers

The electronic structure of Bi$_3$O$_2$S$_3$ with an extra BiS$_2$ bilayers is very close to that of Bi$_3$O$_2$S$_3$ (figure 4). The only difference is that some bands below the S$_2$ bands are raised slightly. It has strictly no impact on the bands close to the Fermi level.

5. Conclusions

The main conclusions of this study are:

(i) The key result of this study is that, in spite of it being a nominally stoichiometric composition (no doping), the S$_2$ layers in the Bi$_3$O$_2$S$_3$ compound act as effective dopants of the parent insulating compound. They push a $p_x$, $p_y$-like band of the S$_2$ layer onto the bottom of the conduction band, thereby transferring part of the electron density from the S$_2$ dimers to the BiS planes. This doping is in agreement with experiments, that show that Bi$_3$O$_2$S$_3$ is metallic [34]. Furthermore, the experimental observation of an anomalously short S–S distance in the S$_2$ layers is also consistent with electron depletion of the S$_2$ layer. Indeed, a substantial residual force is observed for the S atoms in the S$_2$ layer in the direction of elongating the distance, which suggests that the real system has a larger depletion of electrons from the S$_2$ bands than the one obtained in the calculations.

(ii) The electronic structure close to the Fermi level is not modified by extra BiS$_2$ bilayers. This indicates that the changes in the superconducting state caused by these are not related to the electronic structure.

(iii) Finally, the calculations of density of states in real space indicate that the BiS bands, shown to be central for superconductivity in these compounds [18], actually come from the BiS planes. Therefore finding other structures having such planes would be very interesting in order to tune their interactions differently and maybe transform their behaviour.
Figure 4. Band structures and densities of states projected onto the basis orbitals for Bi (red), S (green) and O (lilac) for the four simulated compounds. From top to bottom, they correspond to the structures from left to right in figure 1. The two last compounds are simulations of extra BiS$_2$ bilayers for two different frequencies in Bi$_3$O$_2$S$_3$. In Bi$_3$O$_2$S$_3$ without extra BiS$_2$ bilayer, we plot the partial density of states for the bismuth 6$p_{x,y}$ (light blue) and sulphur 3$p_{x,y}$ orbitals (black). In each case, the $p_x$ and $p_y$ orbitals are indistinguishable. At the Fermi level, they each contribute approximately half of the density of state of the corresponding specie. These projections have been omitted in the other plots for clarity. The $y$-axis has been chosen so that the Fermi level is at zero energy.

In summary, we studied in detail the electronic structure of the newly discovered superconductor Bi$_3$O$_2$S$_3$. We find the bismuth-sulphur bands corresponding to the BiS planes are doped by the S$_2$ dimers, unlike the other superconducting members of the BiS$_2$ family which are non-stoichiometric. We studied the influence of extra BiS$_2$ bilayers on this material and found it does not influence the electronic structure. Finally, the fact that the electrons responsible for superconductivity are
Figure 5. Local density of states of Bi$_2$O$_2$S$_3$ in real space integrated in the energy ranges $[-1.5, 0]$ (a) and $[0,1.5]$ (b), plotted with XCrySDen [39]. Framed is a 3D plot of an isosurface centred on the S–S dimer. In the first case, the S$_2$ layer gathers most of the density. In the second case it is the BiS planes, without the extra S atoms, that gather the density. Half of the atoms represented are not in the plane corresponding to the density plot.

localised in the 2D bands of BiS planes suggests the possibility of other superconductors with BiS structural units.

Acknowledgments

We would like to thank D Sanchez-Portal for his help with particular features of SIESTA, Arman Khojakhmetov for his exploratory work and G G Lonzarich, R Needs, S Rowley, S Haines, C Liu and A Amigues for fruitful discussions. We acknowledge the support from EPSRC, Corpus Christi College, Darwin College, Jesus College, Cambridge Central Asia Forum, Cambridge Kazakhstan Development Trust and KAZATOMPROM. SED would like to thank the Winton Program for the Physics of Sustainability. Part of this work was performed using the Darwin Supercomputer of the University of Cambridge High Performance Computing Service, using Strategic Research Infrastructure Funding from the Higher Education Funding Council for England and funding from the Science and Technology Facilities Council.

References

[1] Mizuguchi Y, Fujihisa H, Gotoh Y, Suzuki K, Usui H, Kuroki K, Demura S, Takano Y, Izawa H and Miura O 2012 BiS$_2$-based layered superconductor Bi$_2$O$_2$S$_3$ Phys. Rev. B 86 220510
[2] Singh S K, Kumar A, Gahtori B, Shruti K, Sharma G, Patnaik S and Awana V P S 2012 Bulk superconductivity in bismuth oxy sulfide Bi$_2$O$_2$S$_3$ J. Am. Chem. Soc. 134 16504–7
[3] Takatsu H, Mizuguchi Y, Izawa H, Miura O and Kadowaki H 2012 Bulk superconductivity in Bi$_2$O$_2$S$_3$ revealed by specific heat measurement J. Phys. Soc. Japan 81 125002
[4] Tan S G, Li L J, Liu Y, Tong P, Zhao B C, Lu W J and Sun Y P 2012 Superconducting and thermoelectric properties of new layered superconductor Bi$_2$O$_2$S$_3$ Phys. C: Supercond. 483 94–6
[5] Awana V P S, Kumar A, Jha R, Singh S K, Pal A, Shruti K, Saha J and Patnaik S 2013 Appearance of superconductivity in layered LaO$_{1-x}$F$_x$BiS$_2$ Solid State Commun. 157 21–3
[6] Deguchi K et al 2013 Evolution of superconductivity in LaO$_{1-x}$F$_x$BiS$_2$ prepared by high-pressure technique Europhys. Lett. 101 17004
[7] Kotegawa H, Tomita Y, Tou H, Izawa H, Mizuguchi Y, Miura O, Demura S, Deguchi K and Takano Y 2012 Pressure study of BiS$_2$-based superconductors Bi$_2$O$_2$S$_3$ and La(O,F)BiS$_2$ J. Phys. Soc. Japan 81 103702
[8] Mizuguchi Y, Demura S, Deguchi K, Takano Y, Fujihisa H, Gotoh Y, Izawa H and Miura O 2012 Superconductivity in novel BiS$_2$-based layered superconductor LaO$_{1-x}$F$_x$BiS$_2$ J. Phys. Soc. Japan 81 114725
[9] Lin X et al 2013 Superconductivity induced by la doping in Sr$_{1-x}$La$_x$F$_x$BiS$_2$ Phys. Rev. B 87 020504
[10] Yazici D, Huang K, White B D, Jeon I, Burnett V W, Friedman A J, Lum I K, Nallaiyan M, Spagna S and Maple M B 2013 Superconductivity induced by electron doping in La$_{1-x}$M$_x$OBiS$_2$ (M = Ti, Zr, Hf, Th) Phys. Rev. B 87 174512
[11] Demura S et al 2013 New member of BiS$_2$-based superconductor NdO$_{1-x}$F$_x$BiS$_2$ J. Phys. Soc. Japan 82 033708
[12] Jha R, Kumar A, Singh S K and Awana V P S 2013 Synthesis and superconductivity of new BiS$_2$ based superconductor PrO$_{1-x}$F$_x$BiS$_2$ J. Supercond. Novel Magn. 26 499–502
[13] Jha R, Kumar A, Singh S K and Awana V P S 2013 Superconductivity at 5 K in NdO$_{1-x}$F$_x$BiS$_2$ J. Appl. Phys. 113 056102
[14] Xing J, Li S, Ding X, Yang H and Wen H-H 2012 Superconductivity appears in the vicinity of semiconducting-like behavior in CeO$_{1-x}$F$_x$BiS$_2$ Phys. Rev. B 86 214518
[15] Yazici D, Huang K, White B D, Chang A H, Friedman A J and Maple M B 2013 Superconductivity of F-substituted LaOBiS$_2$ (Ln = La, Ce, Pr, Nd, Yb) compounds Phil. Mag. 93 673–80
[16] Momma K and Izumi F 2011 VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data J. Appl. Crystallogr. 44 1272–6
[17] Shein I R and Ivanovskii A L 2013 Electronic band structure and fermi surface for new layered superconductor LaO$_{1-x}$F$_x$BiS$_2$ in comparison with parent phase LaOBiS$_2$ from first principles J. Phys.: Condens. Matter 25 312202

[18] Usui H, Suzuki K and Kuroki K 2012 Minimal electronic models for superconducting BiS$_2$ layers Phys. Rev. B 86 220501

[19] Martins G B, Moreo A and Dagotto E 2013 RPA analysis of a two-orbital model for the BiS$_2$-based superconductors Phys. Rev. B 87 081102

[20] Yildirim T 2013 Ferroelectric soft phonons, charge density wave instability and strong electron-phonon coupling in BiS$_2$ layered superconductors: a first-principles study Phys. Rev. B 87 020506

[21] Wan X, Ding H-C, Savrasov S Y and Duan C-G 2013 Electron–phonon superconductivity near charge-density-wave instability in LaO$_{1-x}$F$_x$BiS$_2$: density-functional calculations Phys. Rev. B 87 115124

[22] Li B, Xing Z W and Huang G Q 2013 Phonon spectra and superconductivity of the BiS$_2$-based compounds LaO$_{1-x}$F$_x$BiS$_2$ Europhys. Lett. 101 47002

[23] Yao H and Yang F 2013 Topological odd-parity superconductivity at type-II 2D Van Hove singularities (arXiv:1312.0077)

[24] Yang Y, Wang W-S, Xiang Y-Y, Li Z-Z and Wang Q-H 2013 Triplet pairing and possible weak topological superconductivity in bis-based superconductors Phys. Rev. B 90 094519

[25] Gao Y, Zhou T, Huang H, Tong P and Wang Q-H 2014 Testing the d$_{x^2-y^2}$-wave pairing symmetry by quasiparticle interference and knight shift in BiS$_2$-based superconductors Phys. Rev. B 90 054518

[26] Zhou T and Wang Z D 2013 Probing the superconducting pairing symmetry from spin excitations in BiS$_2$ based superconductors J. Supercond. Novel Magn. 26 2735–40

[27] Srivatsava P, Shrutii and Patnaik S 2014 Structural, electromagnetic and thermoelectric properties of Bi$_2$O$_3$S$_3$ superconductor Supercond. Sci. Technol. 27 055001

[28] Sathish C I, Feng H L, Shi Y and Yamaura K 2013 Superconductivity in bismuth oxytsulfide Bi$_2$O$_3$S$_3$ J. Phys. Soc. Japan 82 074703

[29] Shrutii, Srivastava P and Patnaik S 2013 Evidence for fully gapped strong coupling s-wave superconductivity in Bi$_2$O$_3$S$_3$ J. Phys.: Condens. Matter 25 312202

[30] Li S, Yang H, Fang D, Wang Z, Tao J, Ding X and Wen H 2013 Strong coupling superconductivity and prominent superconducting fluctuations in the new superconductor Bi$_3$O$_4$S$_3$ Sci. China Phys. Mech. Astron. 56 2019–25

[31] Biswas P K, Amato A, Baines C, Khasanov R, Luetskens H, Lei H, Petrovic C and Morenzoni E 2013 Low superfluid density and possible multigap superconductivity in the BiS$_2$-based layered superconductor Bi$_2$O$_3$S$_3$ Phys. Rev. B 88 224515

[32] Selvan G K, Kanagaraj M, Muthu S E, Jha R, Awana V P S and Arumugam S 2013 Phys. Status Solidi RRL 7 510

[33] Jha R and Awana V P S 2014 Effect of se doping in recently discovered layered Bi$_2$O$_3$S$_3$ superconductor Phys. C: Supercond. 498 45–9

[34] Phelan W A, Wallace D C, Arpino K E, Neilson J R, Livi K J, Seabourne C R, Scott A J and McQueen T M 2013 Stacking variants and superconductivity in the BiOS system J. Am. Chem. Soc. 135 5372–4

[35] Shao J, Liu Z, Yao X, Pi L, Tan S, Zhang C and Zhang Y 2014 Bulk superconductivity in single-phase Bi$_3$O$_2$S$_3$ Phys. Status Solidi RRL 8 845–8

[36] Artacho E et al 2008 The SIESTA method; developments and applicability J. Phys.: Condens. Matter 20 064208

[37] Soler J M, Artacho E, Gale J D, Garcia A, Junquera J, Ordejon P and Sanchez-Portal D 2002 The SIESTA method for ab initio order-n materials simulation J. Phys.: Condens. Matter 14 2745

[38] http://elk.sourceforge.net/

[39] Kokalj A 2003 Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale Comput. Mater. Sci. 28 155–68