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Abstract: $Bi_4O_4S_3$ was the first superconductor discovered in the BiS_2 family of novel superconductors. The subfamily of Bi-O-S systems now expanded and was probed both theoretically and experimentally. Here we review the experimental work done on the Bi-O-S compounds, and compare it with theoretical results obtained using ab-initio methods. In particular we calculate the charge carrier density using an ab-initio calculated density of states, and find a really close agreement with experimental data.

Keywords: Superconductivity, BiS_2-based, $Bi_4O_4S_3$, $Bi_3O_2S_3$

1 Introduction

The discovery of superconductivity in $Bi_4O_4S_3$, quickly followed by the one in La(O,F)BiS_2, opened up a new research field on novel superconductors [1, 2]. This new family of superconductors was quickly shown to be based on the same layer of bismuth and sulphur atoms which concentrates the superconducting electrons[3, 4]. This group of superconductors is now named after this layer, the BiS_2 family of superconductors.

This family can be divided in two subfamilies: one formed of compounds only containing bismuth, oxygen and sulphur atoms, which we call Bi-O-S systems. The other subfamily, which branched out of research on La(O,F)BiS_2, has been studied extensively. Magnetic order and charge density wave order have been found, both theoretically and experimentally [5–15].

The electronic structure of these materials has been probed using density functional theory [3, 4, 12, 14, 16, 17]. The coupling mechanism for superconductivity has been investigated in various ways. Electron-phonon interactions have been calculated in *Ln*(O,F)BiS_2, and yield a large electron-phonon coupling constant, suggesting that superconductivity in this compound is strongly coupled and conventional [13, 14, 18, 19]. Renormalisation-group calculations suggested triplet pairing and weak topological superconductivity [20, 21], a possibility studied in the context of quasiparticle interference [22]. The random phase approximation was applied to a two-orbital model [4], leading to extended s-wave, d-wave or g-wave (at low doping) pairing [23–25]. Electron-electron interactions were found to stabilise extended s-wave pairing [26]. Probing these symmetries experimentally could be achieved as different pairing symmetries induce qualitatively different resonance states [27]. A one-dimensional model has been considered following ARPES results pointing to the one-dimensional character of these systems [28, 29]

In this paper we review the experimental work and ab-initio theoretical work on Bi-O-S systems, and compare the results obtained. We also go beyond the theoretical work published to bring closer together simulations and measurements and compare the obtained values of the charge carrier density.

2 The Bi-O-S subfamily

Superconductivity was first measured in $Bi_4O_4S_3$ using transport and magnetisation measurements [2, 30], and later using specific heat measurements [31], which confirmed the superconductivity was a bulk effect in this material.

Further work on the crystallography of $Bi_4O_4S_3$ demonstrated that this compound is actually a mixture of two phases, Bi_2OS_2 and $Bi_3O_2S_3$ [32]. The first one is insulating while the second one is metallic and is responsible for the superconductivity measured in $Bi_4O_4S_3$. Bi_2OS_2 has the same structure as $LaOBiS_2$, where the lanthanum atom is replaced with bismuth. $Bi_3O_2S_3$ has the same

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stacking if one replaces one BiS_2 layer out of two by a layer of sulphur dimers.

Stacking faults, meaning the incidental lack of this sulphur dimers layer in the stacking sequence of $Bi_3O_2S_3$, have been shown experimentally to suppress superconductivity [32]. This disruption of the stacking can also be considered as inclusions of Bi_2OS_2 in $Bi_3O_2S_3$, making logical this suppression of superconductivity.

After separating the two phases in $Bi_4O_4S_3$, it was shown theoretically that the BiS_2 layer was effectively doped by the sulphur dimers layer [16]. Subsequent work undertook to dope Bi_2OS_2 with fluorine [33, 34]. The F substituted compound, $Bi_2(O,F)S_2$ was successfully shown to be superconducting. The optimal doping for solid state doping was shown to be of 24%, at which the superconducting transition temperature was 3.5 K [34]. Topotactic synthesis of $Bi_2(O,F)S_2$ enhanced the transition temperature, which reached 5.1 K [33]. The upper critical field was shown to be much lower than the one in stoichiometric compounds [34].

This subfamily has also been studied under a very different angle. Indeed Bi_2OS_2 has been shown to have very interesting photoelectric properties [35].

Finally, the last compound in this subfamily so far is $Bi_6O_8S_5$, which was considered as the insulating parent phase of $Bi_4O_4S_3$. However, recent work found it to be superconducting at a temperature of 4.2 K [36]. Further work in order to elucidate its exact structure might help understanding better its position in the family.

3 Experimental review

Unlike the compounds with a lanthanide oxide spacer layer, some of which display magnetic ordering, Bi-O-S compounds have been shown not to exhibit any magnetic ordering [37], nor any magnetic anomaly in the superconducting state [38].

The phase diagrams of $Bi_3O_2S_3$ and $Bi_4O_4S_3$ have been studied further by doping, applying pressure and applying a magnetic field. Superconductivity was indeed suppressed by doping the bismuth sites with less than 2.5% of silver [39], and lowered by doping the sulphur sites with selenium [40]. The first one was interpreted as a shift of the Fermi level to lower energies, which would be the opposite effect of fluorine doping in the BiS_2 family. The superconducting transition temperature was also lowered by applying hydrostatic pressure, at a moderate rate of the order of one Kelvin per GPa [37, 41, 42]. Finally, the upper critical magnetic field is about 5 T [43].

The Debye temperature has been estimated to be 182 K [44]. The thermoelectric figure of merit was measured to be about 0.03 at 300 K, indicating a strong thermoelectric effect in this context [45]. Thermopower measurements showed that $Bi_3O_2S_3$ is semimetallic [37]. The charge carrier density was measured to be 1.45×10^{19} cm^{-3} at 50 K [44].

The superconducting state has been investigated by measuring Hall resistivity which was shown to be non linear with respect to magnetic field, pointing towards a multiband effect [30, 44]. This was further supported by Seebeck measurements which detected two different types of carriers [45].

The ratio of the gap and the superconducting transition temperature has been measured using scanning tunneling spectrum (STS) and tunnel diode oscillator (TDO) [43, 46]. They found a ratio of 16.6 and 7.2 respectively. Both are well above the BCS value of 3.53, indicating that superconductivity in these compounds is strong coupling. The discrepancy between the two methods could be due to some surface states, to which STS is know to be very sensitive. However, the specific heat jump at T_c has been shown to be close to the BCS weak coupling limit [44].

The symmetry of the superconducting order parameter was investigated using TDO and muon-spin rotation and relaxation (μSR). The TDO data is well described using a single gap s-wave model, whereas the μSR data point more towards a two-gap s-wave symmetry [38, 46].

The experimental evidence thus points towards a conventional phonon-driven s-wave superconductivity, with multiband effects.

4 Comparison with ab-initio calculations

Ab-initio calculations were performed recently on Bi_2OS_2, $Bi_3O_2S_3$ and two structures of the latter compound including stacking faults [16]. It was shown that the sulphur dimers effectively dope the bismuth-sulphur layer. Moreover, the superconducting electrons are not present in the whole BiS_2 layer but only on the bismuth sulphur planes, stressing the two-dimensionality of superconductivity in this family. Finally, the stacking faults did not modify the band structure strongly, pointing towards a phononic cause in the suppression of superconductivity.

The calculated band structure is in very good agreement with experimental data. First, thermopower measurements confirmed the semimetallic character of $Bi_3O_2S_3$ [37]. Moreover, the multiband behaviour

[30, 44, 45] clearly corresponds to the band structure obtained from ab-initio methods.

In order to check the agreement further, we estimated the carrier density by integrating the total density of states calculated previously [16] over a range of energy of 50 K around the Fermi level, and divided by the volume of the unit cell. This gives us a charge carrier density of 2.63×10^{19} cm^{-3} at 50 K, in remarkable agreement with the experimental value of 1.45×10^{19} cm^{-3} [44].

The second main result of the ab-initio calculations is the confinement of the superconducting electrons to the BiS planes. Unfortunately, no experiment in the Bi-O-S subfamily enables us to draw a comparison. However, ARPES measurements on Ce(O,F)BiS_2 and Nd(O,F)BiS_2 are consistent with this confinement [47, 48]. Finally, the influence of stacking faults on superconductivity needs further exploration.

5 Conclusion

We reviewed the experimental work done on Bi-O-S system and compared it with recent ab-initio calculations. The agreement is very satisfactory, albeit questions on the suppression of superconductivity by the inclusion of stacking faults remain. We calculated the charge carrier density using ab-initio calculations of the density of states and found a remarkable agreement with experimental measurements, lending support to the idea that it is the S_2 dimers that dope the nominally stoichiometric compound.

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