Electronic structure, disconnected Fermi surfaces and antiferromagnetism in the layered pnictide superconductor Na$_x$Ba$_{1-x}$Ti$_2$Sb$_2$O

David J Singh
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6056, USA
E-mail: singhdj@ornl.gov

New Journal of Physics 14 (2012) 123003 (11pp)
Received 1 October 2012
Published 7 December 2012
Online at http://www.njp.org/
doi:10.1088/1367-2630/14/12/123003

Abstract. We report electronic structure calculations for BaTi$_2$Sb$_2$O and discuss the results in relation to the observed superconductivity of this material when hole doped with Na. The Fermi surface shows several sheets. These include a nested nearly two-dimensional cylinder. There are also two sheets, which are three dimensional, in spite of the layered crystal structure. A magnetic instability associated with Fermi surface nesting is found. A sign-changing s-wave state, different from the one in the Fe-based superconductors, is predicted within a scenario of spin-fluctuation mediated superconductivity.

The discovery of high temperature superconductivity in Fe-based compounds [1] has lead to renewed interest in non-oxide superconductors. Recently, Doan et al [2] reported superconductivity in Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O, 0.05 ≤ x ≤ 0.33 and $T_c$ up to 5.5 K. The structure of the parent compound, BaTi$_2$Sb$_2$O, as determined by x-ray refinement [2], is shown in figure 1. This structure shares a number of common features with the Fe-based superconductors. Specifically, it is a layered structure containing square planes of transition element atoms, in this case Ti.
Like the Fe-based superconductors, there are two transition metal atoms per chemical unit cell. As may be seen, the two Ti in the BaTi$_2$Sb$_2$O unit cell are related by a translation of $[1/2, 1/2]$, followed by a $90^\circ$ rotation, and not by the glide of the Fe$_2$As$_2$ layers in the Fe-based superconductors. Superconductivity was also very recently reported by Yajima et al [3] in undoped BaTi$_2$Sb$_2$O with a bulk $T_c$ of 0.8 K.

The nearest neighbor Ti–Ti distance is 2.91 Å, which is only somewhat larger than the nearest neighbor distance of 2.51 Å in Ti metal, implying the possibility of important direct Ti–Ti bonding, as for the Fe lattice in Fe-based superconductors [4]. Also similar to the Fe-based superconductors each Ti atom is coordinated by four pnictogens, although in the present case the geometry is that of approximate square planes with Ti at the center, instead of approximate tetrahedra and furthermore, no Fe-based superconductor is known where the pnictogen is Sb. Furthermore, the Ti are also coordinated by O in the present compound. Each Ti has two O nearest neighbors. Thus as shown in the right panel of figure 1, if one considers only Ti–O hopping, one obtains a bipartite lattice consisting of two independent sets of one-dimensional (1D) ...Ti–O–Ti–O... chains, running respectively along $x$ and $y$. Similarly if one considers only Ti–Sb hopping one also obtains 1D chains, ...Ti–Sb$_2$–Ti–Sb$_2$..., running along $y$ and $x$, where Sb$_2$ denotes an Sb above the plane and an Sb below the plane. Such 1D objects might therefore form the basis of a strongly nested electronic structure. However, as mentioned, the short Ti–Ti nearest neighbor distance suggests metal–metal bonding, which would couple the two sub-lattices. Furthermore, the Sb atoms are arranged in linear chains along the $c$-axis with Sb–Sb distances of $\sim c/2 = 4.05$ Å, which is short enough that $c$-axis hopping could be important, especially assisted by the Ba. Returning to the metal–metal bonding, one sees that the bonds run along the diagonal directions in the two Ti atom unit cells, i.e. forming a square network oriented at 45$^\circ$ to the ...Ti–O–Ti–O... and ...Ti–Sb$_2$–Ti–Sb$_2$... chains.

Experiments [2] show that stoichiometric BaTi$_2$Nb$_2$O has a transition at $T_s = 54$ K, similar to several other related compounds [5–9]. This transition has strong signatures in resistivity, susceptibility and specific heat. The microscopic mechanism for this transition has not been demonstrated, but it is described as either a charge density wave (CDW) or a spin density wave (SDW). This is consistent with electronic structure calculations for the compound Na$_2$Ti$_2$Sb$_2$O, which show a nested Fermi surface [10].

In any case, as Na is substituted for Ba in Na$_x$Ba$_{1-x}$Ti$_2$Sb$_2$O, $T_s$ is systematically suppressed and superconductivity arises with $T_c$ of up to 5.5 K [2]. Importantly,
superconductivity co-exists with the phase corresponding to \( T_s \) including near the maximum \( T_c \). Superconductivity occurs for \( 0.05 \leq x \leq 0.33 \), which nominally amounts to average Ti valences between \( T_i^{3.025} \) and \( T_i^{3.165} \), assuming that Sb occurs as \( Sb^{−4} \). Titanates with valences between 4+ and 3+ are known to have electron–phonon superconductivity as in the case of electron doped SrTiO\(_3\) [11], but they can also be magnetic and exhibit non-trivial correlation effects as in e.g. TiOCl and LaTiO\(_3\) [12, 13].

Here we report first principles studies of BaTi\(_2\)Sb\(_2\)O in relation to magnetism and superconductivity. We find that like its sister compound Na\(_2\)Ti\(_2\)Sb\(_2\)O, the Fermi surface is nested. This nesting leads to peaks in the susceptibility that are incommensurate but near the \( X \) points. These peaks are strong enough to result in an actual magnetic instability, which we confirm by direct calculations. This shows that \( T_s \) is most likely an SDW instability. Therefore the superconductivity of doped BaTi\(_2\)Sb\(_2\)O is in proximity to an antiferromagnetic SDW phase. This leads to a specific prediction of the pairing state in a spin-fluctuation mediated scenario, in particular a sign changing s-wave state, but not the same one as in the Fe-based superconductors [14].

The electronic structure was calculated using standard density functional theory based on the Perdew, Burke and Ernzerhof generalized gradient approximation [15]. For this purpose we used the general potential linearized augmented planewave (LAPW) method including local orbitals [16] as implemented in the WIEN2k code [17]. The LAPW sphere radii were 2.4 bohr for Ba and Sb, 2.15 bohr for Ti and 1.7 bohr for O. The calculations are based on the experimental crystal structure [2]. This structure contains one internal coordinate, \( z_{Sb} = 0.2514 \) corresponding to the Sb height. The value obtained from total energy minimization of \( z_{Sb} = 0.2522 \) is very close to the experimental value. This is in contrast to the large discrepancies found in the Fe-based superconductors in standard non-magnetic density functional calculations [18]. We used well converged LAPW basis sets, including additional local orbitals, along with dense Brillouin zone samplings, as high as a \( 48 \times 48 \times 24 \) mesh for the primitive tetragonal cell.

The calculated band structure is shown in figure 2 and the corresponding electronic density of states (DOS) is shown in figure 3 along with projections. These calculations were done relativistically, including spin–orbit, but spin–orbit does not have a large effect. It does, however, affect the details at \( E_F \). A comparison of the DOS with and without spin–orbit is given in figure 4.

The value of the DOS at the Fermi energy (with spin–orbit) is \( N(E_F) = 4.26 \text{eV}^{-1} \) on a per formula unit basis. This corresponds to a bare specific heat \( \gamma = 10.0 \text{mJ mol}^{-1}\text{K}^{-2} \) and bare Pauli susceptibility \( \chi_0(q = 0) = 1.37 \times 10^{-4} \text{emu mol}^{-1} \). The calculated Drude plasma energies are \( h\Omega_{p,xx} = 2.71 \text{eV} \) and \( h\Omega_{p,zz} = 2.14 \text{eV} \) for the in-plane and c-axis directions, respectively. For isotropic scattering this implies a resistivity anisotropy of \( \sim 1.6 \), meaning that from a transport point of view this is a very 3D material. This is reminiscent of what was found previously by Pickett [10] for the related compound Na\(_2\)Sb\(_2\)Ti\(_2\)O.

The DOS shows that the O 2p derived bands lie between \( \sim -7 \) and \( -5 \text{eV} \), while the Sb 5p bands are in the energy range \(-4 \) to \(-1 \text{eV} \), all with respect to \( E_F \). Therefore, these shells are nominally full. Also there are no Ba derived occupied valence bands. Thus Sb is a trivalent anion in this compound and Ti is in its trivalent d\(^1\) state. The DOS around \( E_F \) is derived primarily from Ti d states, hybridized with Sb p.

The orbital character is illustrated in figure 5, which shows the band structure in a 1 eV range around \( E_F \) emphasizing the character of different d-orbitals in a so-called ‘fat bands’
Figure 2. Calculated band structure of BaTi$_2$Sb$_2$O including spin orbit. The Fermi energy is denoted by the horizontal line at 0 eV.

Figure 3. Electronic density of states and projections onto the LAPW spheres.

scheme, where the bands are shown with symbols having a size that is a small value to make all bands visible plus an enhancement of the size proportional to the projection of given orbital character onto the LAPW sphere. As may be seen, there are three d orbitals—d$_{z^2}$, d$_{x^2-y^2}$ and d$_{xy}$—that contribute significantly at $E_F$. There is strong d$_{xy}$ character in this mixture.

The Fermi surface is shown in figure 6 and the dependence on band filling is given in figure 7. There are three sheets of Fermi surface. The first is a very 2D, square electron cylinder around the zone center. As seen in the fat bands plot, the band making up this cylinder contains
a mixture of the three d orbitals that participate at $E_F$. There is a 3D complex shaped electron section around the $\Gamma - Z$ line. This section has $d_{z^2}$ character. Finally, there is a large 3D hole section around $X$. Like the square cylinder electron section, this part of the Fermi surface has mixed character derived from the three active d-orbitals, though the dominant character is $d_{z^2}$. Since the electron count is even, this section compensates the two electron sections. This basic structure is preserved as the Fermi level is lowered within the range corresponding to superconductivity in Na$_x$Ba$_{1-x}$Ti$_2$Sb$_2$O. The hole section grows, while the two electron sections shrink. Importantly, the square cylindrical shape of the 2D section is preserved.

An important aspect of the Fermi surface is that the square section, as well as the edges of the $X$ centered electron section are nested along the [1,1] direction. The 2D nesting vector is approximately $(0.24, 0.24)(2\pi/a)$. [1,1] is the orientation of the Ti square lattice. In this lattice, the $d_{xy}$ orbitals are along the Ti–Ti bond directions, and may be expected to give nested bands. Actually, the nested electron section has strong $d_{xy}$, but also as mentioned involves the other two active d orbitals. In any case, qualitatively the nesting found should lead to two ridges in the bare susceptibility $\chi_0$ running along the diagonals in the zone. The intersection near the $X$ points would give a prominent peaks in $\chi_0(q)$ near the X points. This in fact is the case. Figure 8 shows the bare Lindhard $\chi_0$ calculated with the neglect of the matrix element approximation, similar to calculations presented for the Fe-based superconductors [14]. As seen there are diagonal ridges in the real part of $\chi_0$, with a prominent peak at $X$. This peak will be further increased by the random phase approximation (RPA) enhancement, $\chi(q) = \chi_0(q)/(1-I(q)\chi_0(q))$ (here $I(q)$ is written as a Stoner term, but in correlated materials it takes the form of the Hubbard parameter $U$).

The real part of $\chi$ governs magnetic ordering as well as providing the pairing interaction in spin-fluctuation induced superconductivity [19, 20]. We discuss it further below. The imaginary part of $\chi_0$, like the real part, shows ridges with intersections near $X$, but the structure is more complex. This structure in both the real and imaginary parts of $\chi$, i.e. intersecting ridges with peaks at the intersections, is a consequence of the Fermi surface structure, particularly the square cylinder shape. This Fermi surface amounts to the intersection of two 1D sections. The result is similar to the antiferromagnetic peak in the triplet superconductor Sr$_2$RuO$_4$ [21, 22], but different from the Fe-based superconductors where the nesting arises from matching of electron and hole Fermi surface sections.

Figure 4. Comparison of the DOS around $E_F$ with and without spin orbit.
Figure 5. Fat bands plot for different d orbital characters near $E_F$. The coordinate system is such that $d_{z^2}$ is directed along the $c$-axis, and $x$ and $y$ are along the $a$-axis and $b$-axis, such that $d_{xz}$ is towards the nearest Sb and $y$ is in the direction of the O neighbors.

We did direct self-consistent calculations to look for a magnetic ground state. We find a magnetic instability at the $X$ point. These calculations were done including spin–orbit with the moment directed along the $c$-axis. We find an instability, with small Ti moments inside the LAPW spheres of $0.2\mu_B$. This is much smaller than the $\sim 2\mu_B$ characteristic of the Fe-based superconductors in similar calculations using the experimental crystal structure [18]. We also checked for a nearest neighbor antiferromagnetic state, which would correspond to a zone center instability. However, we did not find such a state.

The magnetic structure is shown in figure 9. This a so-called double stripe structure. It lowers the symmetry from tetragonal to orthorhombic and contains both ferromagnetic and antiferromagnetic Ti–Ti bonds, as shown. This may be expected to result in a spin-dimerization, with coupling to the lattice, perhaps consistent with neutron scattering results showing lattice anomalies at $T_s$ in Na$_2$Ti$_2$Sb$_2$O [8]. The actual magnetic structure may be incommensurate, as the moments are small and as mentioned, the intersection of the ridges in $\chi(q)$ is off the $X$
Figure 6. Calculated Fermi surfaces of BaTi$_2$Sb$_2$O spin orbit. The shading is by velocity, with blue representing low velocity. The approximately square cylindrical sections around the zone corner ($M$, $A$) are electron sections as is the complex shaped section around $\Gamma$ and $Z$. The other section around $R$ is a hole section.

Figure 7. $c$-axis view of the Fermi surface as in figure 6, but with shifted Fermi energies. The corresponding band fillings are $-0.38$ e ($-0.10$ eV), $-0.23$ e ($-0.05$ eV), 0 e (0 eV) and 0.20 e (0.05 eV).

Another indication that the actual ground state may be a more complex incommensurate magnetic structure is that in our calculations without imposed symmetry for the $X$ point instability we find slightly different moments on the two Ti sites of each spin (the magnetic unit cell contains four Ti atoms, two spin-up and two spin-down).

In any case, we find a significant coupling of the magnetic order to the electrons at the Fermi energy. In particular, even though the moments are small, the DOS near $E_F$ is
substantially reduced in the ordered state. We find $N(E_F) = 3.42 \, \text{eV}^{-1}$ per formula unit for the X point ordered state as compared to $N(E_F) = 4.26 \, \text{eV}^{-1}$ without magnetic order. As in the Fe-based superconductors [23], and in contrast to cuprates, the antiferromagnetic state near superconductivity is metallic, both in experiment [2] and in the present density functional calculations.

One of the reasons why unconventional superconductivity attracts so much attention is that it is a rare phenomenon. In particular, the vast majority of known superconductors are conventional electron–phonon superconductors, and in particular conventional electron–phonon superconductivity is known in titanates. Unlike the Fe-based superconductors, the maximum $T_c = 5.5 \, \text{K}$ observed in BaTi$_2$Sb$_2$O is not so high as to preclude conventional superconductivity. However, the close proximity to an antiferromagnetic state provides an indication that this may not be the case. In particular, spin-fluctuations provide a repulsive interaction in a singlet channel, opposite to the attractive electron–phonon interaction. Therefore the net superconducting interaction will be $\lambda = \lambda_{ep} - \lambda_{sf}$, where ep and sf denote electron–phonon and spin-fluctuation contributions, respectively. As such the wide coexistence, of magnetic and superconducting order in the composition dependent phase diagram argues against (but does not fully exclude) conventional superconductivity. An argument against an unconventional state would be that scattering due to disorder in the alloy should suppress an unconventional state. However, the disorder in the present case is in the Ba layer, and as mentioned Ba does not contribute significantly to the electronic structure near $E_F$, and furthermore, as mentioned the
bands are rather flat, which means that the superconducting coherence length will be relatively short, again reducing the effect of disorder.

As such, we discuss the possibility of a spin-fluctuation mediated unconventional superconducting state. In such a scenario, the pairing interaction is related to the real part of the actual RPA enhanced \( \chi(q) \) and is repulsive for a singlet state and attractive for a triplet state \([19, 20, 24]\). As mentioned, in BaTi$_2$Sb$_2$O the susceptibility is peaked near X. Identification of the superconducting state amounts to matching the pairing interaction with the Fermi surface structure, so that opposite sign order parameters occur on parts connected by peaks in the repulsive (singlet case) interaction or parts connected by peaks in the attractive (triplet case) interaction have the same sign order parameter, while maintaining consistency with the overall triplet or singlet parity. We find that the best match is obtained for a singlet state as depicted in figure 10. In this state the two sections of Fermi surface with similar orbital character, namely the square section and the large section around X, have opposite sign as expected in such a scenario.

As seen, this is a sign-changing s-wave state, although not the same one as in the Fe-based superconductors. It consists of a state where the two electron sections of the Fermi surface have opposite sign order parameter to the large hole section. The motivation for this state is that it has sign changes between all pairs of Fermi surface sections that are separated by \((0, \pi/a)\) and \((\pi/a, 0)\), where the susceptibility is peaked. Similar to the Fe-based superconductors, the SDW and this superconducting state are competing instabilities of the Fermi surface. However, the SDW antiferromagnetism found for BaTi$_2$Sb$_2$O is much weaker than that in the Fe-based superconductors. It is unclear what role correlation effects beyond standard density functional calculations play in these titanates. The fact that the transition at \(T_s\) is a metal–metal transition in spite of the integral band filling suggests that they are not so strong as in e.g. the cuprates. This of course is an expected result considering that the d orbitals in Ti$^{3+}$ ions are more extended than those in Cu$^{2+}$. One possible effect of Coulomb correlations will be to enhance the small moments found here. It will be of interest to perform neutron diffraction experiments both to confirm whether the transition is in fact an SDW and to quantify the magnitude of the moments. In this regard, Subedi has recently presented electron–phonon calculations \([25]\) that are consistent with electron–phonon superconductivity and so either scenario is possible here.
Returning to Na$_2$Ti$_2$Sb$_2$O, that material [26], which has been studied more extensively than BaTi$_2$Sb$_2$O, has not been reported to show superconductivity, but does have a transition, likely of SDW or CDW character and a similar phenomenology to BaTi$_2$Sb$_2$O. The transition in Na$_2$Ti$_2$Sb$_2$O is at higher temperature, $T_s \sim 114–120$ K [5–8]. From a structural point of view, Na$_2$Ti$_2$Sb$_2$O has similar Ti$_2$Sb$_2$O layers to BaTi$_2$Sb$_2$O, but these are stacked differently along the $c$-axis so that the Sb–Sb linear chains in the Ba compound are broken up yielding a body centered tetragonal structure. The band structure, which as mentioned has similarities to the present compound, was investigated by Pickett using density functional theory, and in a tight binding framework by de Biani et al [27]. The arsenide, Na$_2$Ti$_2$As$_2$O has a transition at $T_s \sim 320$ K [6]. Other related compounds may be (SrF)$_2$Ti$_2$Sb$_2$O, which has an apparently similar phase transition at $T_s \sim 198$ K and (SmO)$_2$Ti$_2$Sb$_2$O with $T_s \sim 230$ K [28]. BaTi$_2$As$_2$O also has been reported and has similar transition at $T_s \sim 200$ K. Considering the superconductivity of BaTi$_2$Sb$_2$O, it will be of great interest to study these compounds in more detail and especially their properties if the SDW can be suppressed, e.g. by pressure, doping or chemical substitutions. It will be particularly interesting to study the pressure dependence in BaTi$_2$Sb$_2$O and related materials.

In conclusion, we find that BaTi$_2$Sb$_2$O has an SDW instability associated with Fermi surface nesting. The close proximity of the superconducting phase that emerges with Na doping to this antiferromagnetic phase suggests the possibility of unconventional spin-fluctuation mediated superconductivity. We find that the susceptibility is peaked near the $X$ point. Matching this structure of the susceptibility with the Fermi surface suggests the possibility of a sign-changing s-wave superconducting state of a different nature than the Fe-based superconductors.

Acknowledgments

This work was supported by the US Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. I am grateful to Bernd Lorenz for helpful discussion and communication of results and to Igor Mazin and Douglas Scalapino for useful discussions on spin fluctuations in relation to superconductivity.

References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[2] Doan P, Gooch M, Tang Z, Lorenz B, Moeller A, Tapp J, Chu P C W and Guloy A M 2012 J. Am. Chem. Soc. 134 16520
[3] Yajima T, Nakano K, Takeiri F, Ono T, Hosokoshi Y, Matsushita Y, Heister J, Kobayashi Y and Kageyama H 2012 J. Phys. Soc. Japan 81 103706
[4] Singh D J and Du M H 2008 Phys. Rev. Lett. 100 237003
[5] Axtell E A III, Ozawa T, Kauzlarich S M and Singh R R P 1997 J. Solid State Chem. 134 423
[6] Liu R H, Tan D, Song Y A, Li Q J, Yan Y J, Ying J J, Xie Y L, Wang X F and Chen X H 2009 Phys. Rev. B 80 144516
[7] Ozawa T C and Kauzlarich S M 2004 J. Cryst. Growth 256 571
[8] Ozawa T C, Pantoja R, Axtell E A III, Kauzlarich S M, Greedan J E, Bieringer M and Richardson J W Jr 2000 J. Solid State Chem. 153 275
[9] Ozawa T C and Kauzlarich S M 2008 Sci. Tech. Adv. Mater. 9 033003
[10] Pickett W E 1998 Phys. Rev. B 58 4335
[11] Koonce C S, Cohen M L, Schooley J F, Hosler W R and Pfeiffer E R 1967 Phys. Rev. 163 380
[12] Saha-Dasgupta T, Lichtenstein A and Valenti R 2005 Phys. Rev. B 71 153108
[13] Khaliullin G and Maekawa S 2000 Phys. Rev. Lett. 85 3950
[14] Mazin I I, Singh D J, Johannes M D and Du M H 2008 Phys. Rev. Lett. 101 057003
[15] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[16] Singh D J and Nordstrom L 2006 Planewaves Pseudopotentials and The LAPW Method 2nd edn (Berlin: Springer)
[17] Blaha P, Schwarz K, Madsen G, Kvasnicka D and Luitz J 2001 WIEN 2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Vienna: Tech. Univ. Wien)
[18] Mazin I I, Johannes M D, Boeri L, Koepernik K and Singh D J 2008 Phys. Rev. B 78 085104
[19] Berk N F and Schrieffer J R 1966 Phys. Rev. Lett. 17 433
[20] Moriya T and Ueda K 2003 Rep. Prog. Phys. 66 1299
[21] Mazin I I and Singh D J 1999 Phys. Rev. Lett. 82 4324
[22] Braden M, Sidis Y, Bourges P, Pleuty P, Kulda J, Mao Z and Maeno Y 2002 Phys. Rev. B 66 064522
[23] Sebastian S E, Gillett J, Harrison N, Lau P H C, Singh D J, Mielke C H and Lonzarich G G 2008 J. Phys.: Condens. Matter 20 422203
[24] Scalapino D J 2010 Physica C 470 S1
[25] Subedi A 2012 arXiv:1210.0499
[26] Adam A and Schuster H U 1990 Z. Anorg. Allg. Chem. 584 150
[27] de Biani F F, Alemany P and Canadell E 1998 Inorg. Chem. 37 5807
[28] Liu R H, Song Y A, Li Q J, Ying J J, Yan Y J, He Y and Chen X H 2010 Chem. Mater. 22 1503