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PHYSICAL REVIEW B **67**, 180505(R) (2003)

First-principles characterization of the electronic structure of the molecular superconductor β-(BEDT-TTF)$_2$IBr$_2$

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The electronic structure of the molecular superconductor β-(BEDT-TTF)$_2$IBr$_2$ has been studied by means of first-principles density functional calculations. The calculated transverse cross section of the Fermi surface is in excellent agreement with that reconstructed from magnetoresistance measurements. It is shown that the cylindrical Fermi surface exhibits warping (the dispersion along the interlayer direction is of the order of 0.8–1.7 % of the dispersion in the conducting plane) and that it does not contain any additional small pocket. These features provide support for a recent proposal concerning the much debated question of the origin of the slow magnetoresistance oscillations exhibited by this material.

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The organic donor molecule bis(ethylenedithio)- tetrathiafulvalene (BEDT-TTF) gives rise to a number of metallic and superconducting salts with inorganic anions, which have been the focus of continued attention and debate for almost two decades. A common structural pattern to practically all of these materials is that they have layers of donor BEDT-TTF molecules alternating with layers of the anions in one crystallographic direction (see, for instance, Fig. 1).[1] Since the BEDT-TTF layers are those responsible for the electrical conductivity, these materials are very anisotropic quasi-two-dimensional (Q2D) metals. This fact and the possibility to grow high purity single crystals have led to an impressive number of physical studies of these salts.[2] A key aspect in understanding the physics of their normal and superconducting states is the nature of the band structure and the shape of the Fermi surface (FS). The Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) effects have been extensively used in order to provide experimental information about the FS.[3–7] A wealth of interesting data concerning magnetic quantum oscillations as well as a number of semiclassical magnetotransport phenomena has been obtained, stimulating advances in the theory of the Q2D SdH and dHvA effects.[3–5]

In this context, the absence of detailed high-level first-principles studies of the electronic structure of these materials may be surprising. Certainly, the success of simple tight-binding treatments in providing an understanding of the gross features of the FS of many of these salts[5] can be part of the reason. In addition, the large unit cells and the mixed type of bonding associated with their molecular nature face the computational physicists with a real challenge. However, accurate first-principles calculations are needed at this stage of the research in order to better exploit the experimental information, to test existing theoretical models, and to suggest new experiments. With this in mind we have initiated a general study of the electronic structure of molecular conductors and carefully studied the conditions to be fulfilled by a computational approach in order to be both accurate and applicable to solids with unit cells as large as those of TTF-TCNQ, the Bechgaard salts, the α, β, or κ salts of BEDT-TTF, etc., in order to provide a solid computational framework. We recently have shown[8] that this kind of computations appropriately describe the change from metallic to weakly activated conductivity in single component molecular conductors induced by a subtle chemical modification.

Here we report our results concerning the molecular superconductor β-(BEDT-TTF)$_2$IBr$_2$,[9] a material subject to intense interest because of the much debated question of the origin of the slow magnetoresistance oscillations.[3–5] It does not exhibit superstructure transitions or metal-to-insulator instabilities, being metallic down to $\geqslant$2K, at which temperature it exhibits a superconducting transition.[9] This relatively simple behavior has made it the target of many dHvA and SdH studies. The slow oscillations of magnetoresistance were initially discovered in this material,[10] and later they were also observed in β-(BEDT-TTF)$_2$I$_3$,[11] κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$,[12] and κ-(BEDT-TSF)$_2$C(CN)$_3$.[13] These oscillations were supposed to originate from small pockets of the FS because their behavior strongly resembles that of the SdH effect. However, the origin of such slow oscillations has remained one of the more elusive features of the electronic structure of these materials until recently, when Kartsovnik *et al.*[14] proposed that those of β-(BEDT-TTF)$_2$IBr$_2$ originate from the warping of the cylindrical FS. But no high-level first-principles characterization of the FS of the material is available. The tight-binding FS for this material is in reasonable agreement with experiment as far as the anisotropy in the conducting plane is concerned.[6,15] This method is, however, unable to treat the interlayer interactions properly, a major drawback in the present context. First-principles calculations of the augmented spherical-wave type were used to study the isostructural and physically related β-(BEDT-TTF)$_2$I$_3$ salt,[16] which after all [with β-(BEDT-TTF)$_2$IBr$_2$] is the simplest BEDT-TTF based salt. The results concerning the Fermi surface differed dramatically from experiment. Later, another first-principles study using the pseudofunction method was applied to β-(BEDT-TTF)$_2$IBr$_2$.[17] However, except for the band dispersion along a few selected directions of reciprocal space no detailed information was reported. Thus, no computational data can be confronted with the recent work by Kartsovnik *et al.*[14]

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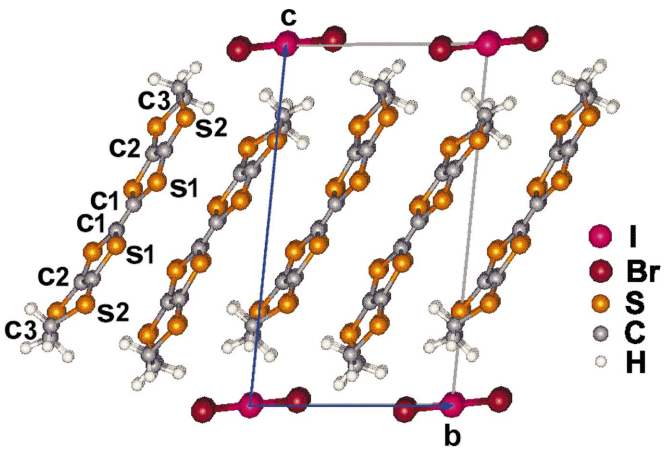

FIG. 1. (Color) Crystal structure of β-(BEDT-TTF)$_2$IBr$_2$ showing the alternation of layers along the c direction. The different types of C and S atoms in the BEDT-TTF donor molecule are labeled. The energy is relative to the Fermi level.

The present calculations were carried out by the density functional theory (DFT) (Refs. 18 and 19) using a numerical atomic orbital approach,[20] which has been recently developed and designed for efficient calculations in large systems and implemented in the SIESTA code.[20,21] We have used the generalized gradient approximation for the exchange-correlation energy and, in particular, the functional of Perdew, Burke, and Ernzerhof.[22] Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials[23] factorized in the Kleinman-Bylander form.[24] The nonlinear core-valence exchange-correlation scheme[25] is used for all elements with the exception of the hydrogen atom. We have used the following type of basis set: triple-ζ for the s orbitals of I, Br, S, and C atoms; triple-ζ plus single polarization functions for the s orbital of H; triple-ζ plus double polarization functions for the p orbitals of I and Br; and triple-ζ plus single polarization functions for the p orbitals of S and C, as obtained with an energy shift of 2 meV.[20,21] The integrals of the self-consistent terms of the Kohn-Sham Hamiltonian are obtained with the help of a regular real space grid in which the electron density is projected. The grid spacing is determined by the maximum kinetic energy of the plane waves that can be represented in that grid. In the present work, we used a cutoff of 250 Ry. The Brillouin zone was sampled using a grid of $4\times3\times2$ Monkhorst-Pack[26] k points for the determination of density matrix and projected density of state and a set of 20000 k points for the determination of FS and density of states.

The conducting donor layers of β-(BEDT-TTF)$_2$IBr$_2$ extend in the (a,b) plane and are built from parallel chains of BEDT-TTF along the $(a+b)$ direction. The calculated band structure and density of states (DOS) near the Fermi level are shown in Figs. 2 and 3. As shown there, the anion contributions are practically nil in the region displayed (Fig. 3). The two bands of Fig. 2 are almost exclusively built from the highest occupied molecular orbital (HOMO) of BEDT-TTF. There are two such bands because the unit cell of β-(BEDT-TTF)$_2$IBr$_2$ contains two donor molecules.

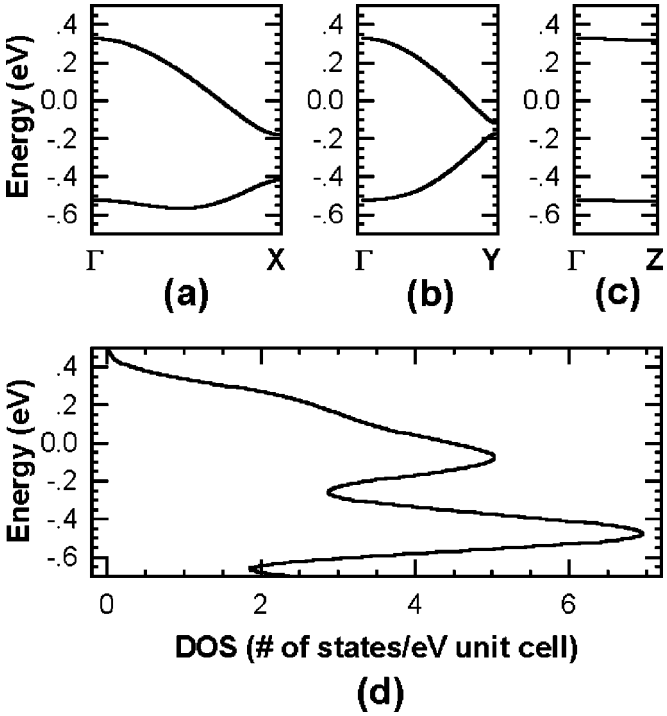

FIG. 2. (a), (b), and (c) Calculated band structures, and (d) density of states (DOS) for β-(BEDT-TTF)$_2$IBr$_2$. $\Gamma=(0,0,0)$, $X=(1/2,0,0)$, $Y=(0,1/2,0)$, and $Z=(0,0,1/2)$ in units of the triclinic reciprocal lattice vectors. The energy is relative to the Fermi level.

As shown in Fig. 1, there are different types of S and C atoms in the BEDT-TTF donor. The analysis of the DOS shows that the H and the outer C3 atoms practically do not contribute to the two bands and thus to the DOS at the Fermi level (Fig. 3). The largest contribution is that of the inner S1 atoms followed by that of the inner C1 atoms. Note that there are four S1 atoms but only two C1 atoms per molecule, so

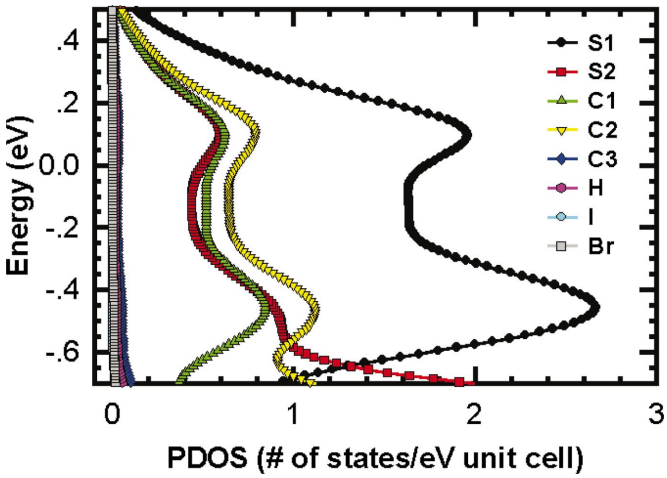

FIG. 3. (Color) Projected density of states (PDOS) of β-(BEDT-TTF)$_2$IBr$_2$ in terms of the different types of atoms. The different contributions plotted refer to the total contribution for a given type of atom.

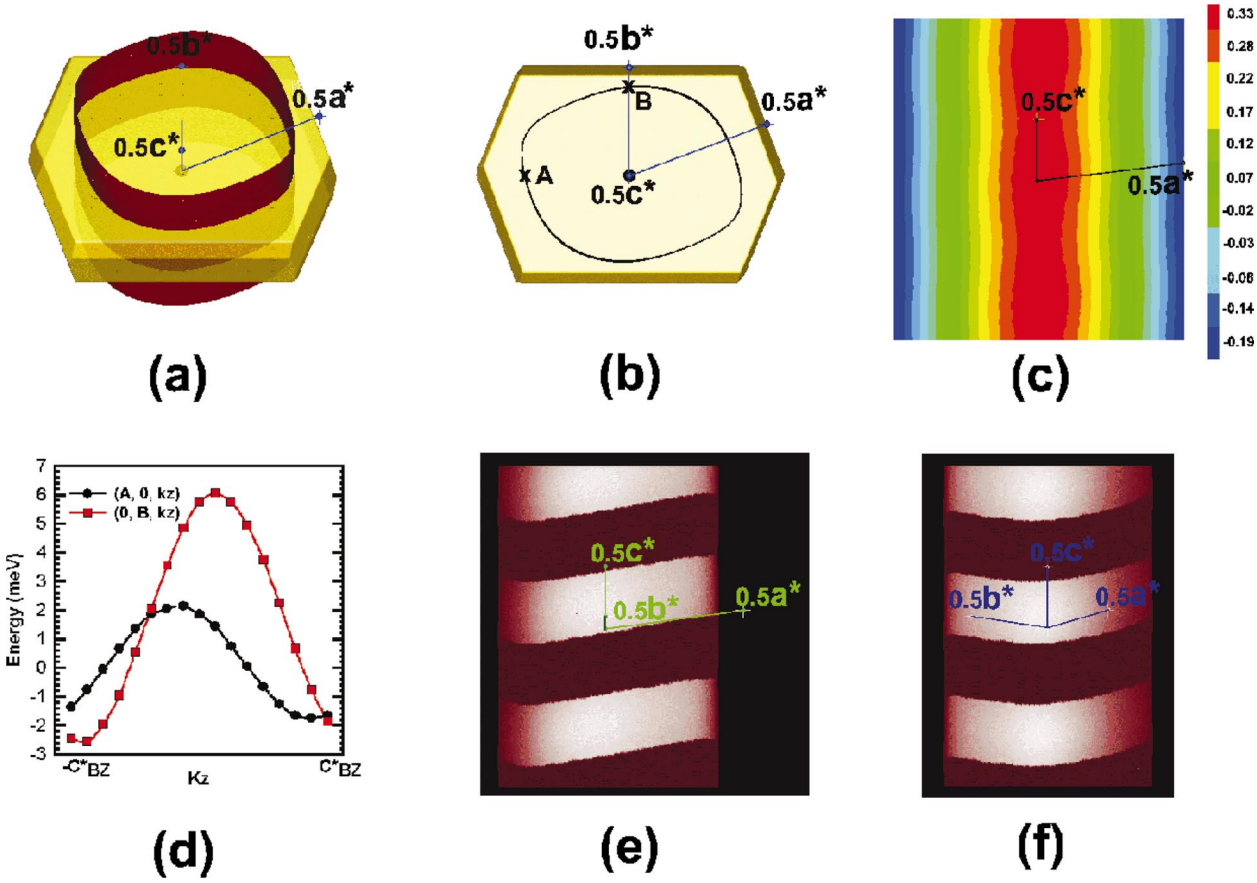

FIG. 4. (Color) Calculated Fermi surface for β-(BEDT-TTF)$_2$IBr$_2$. (a) Three-dimensional FS. (b) FS and Brillouin zone viewed along the c^* direction. (c) Eigenvalues of the k points in the (a^*, c^*) plane passing through the Γ point. The numbers in the color scale are in eV. (d) Band dispersion along the lines parallel to the c^* direction passing through the points **A** and **B** marked in (b). The energies in (c) and (d) are relative to the Fermi level. (e) and (f) Graphical representations of the FS warping (see text).

that the DOS per atom is only a little bit larger for the S1 atoms. The contributions of the S2 atoms are approximately three times smaller than those of the inner S1 atoms, and those of the C2 atoms approximately two times smaller than those of the inner C1 atoms (recall that there are two C1 atoms but four C2 atoms per molecule). The relative contributions of the carbon atoms are in excellent agreement with those derived from a ^{13}C high-resolution NMR study of the isostructural β-(BEDT-TTF)$_2$I$_3$.[27] The contributions of the S1, S2, C1, and C2 atoms are almost exclusively due to the π-type orbitals (i.e., the p_z orbitals). The band dispersions of Fig. 2 are typical of a Q2D metal and are very close to those obtained by the tight-binding methods.[15] To the best of our knowledge there is not a precise experimental estimation of the band width but from a Drude analysis of the reflectance spectra it was estimated that the dispersion along the chain direction $(a+b)$ is 0.63 eV.[28]

The calculated DOS at the Fermi level is 4.65 electrons per eV and per unit cell. Again, we have not found data to make a direct comparison, but for the isostructural β-(BEDT-TTF)$_2$I$_3$ superconductor a value of 13.6 electrons per eV and per unit cell was reported from spin susceptibility measurements.[29] On the basis of comparison between the spin susceptibility and optical data it was proposed that there was a susceptibility enhancement factor of 3 at room temperature and ambient pressure. Our result provides confirmation for this proposal assuming that the DOS at the Fermi level is very similar in the two salts, something which is expected from structural reasons. The previous analysis of the DOS provides a basis to understand the success of tight-binding methods as far as the in-plane band structure is concerned. The relative weight of the different contributions is very similar in the region of the two bands, giving evidence that only the HOMO of the BEDT-TTF is implicated in these bands. The shape of the HOMO of BEDT-TTF provided by these methods is in close agreement with the relative atomic contributions to the DOS near the Fermi level, and thus the relative anisotropy of the electronic interactions is satisfactorily described by these methods.

In Fig. 4 we report a detailed characterization of the FS of β-(BEDT-TTF)$_2$IBr$_2$. As expected from the band structure it is a typical Q2D FS with a cylinder like shape [Fig. 4(a)]. The transverse cross-section of the FS cylinder is however somewhat distorted from a purely elliptical shape [Fig. 4(b)]. The calculated transverse cross-section is in excellent agreement with that reconstructed from the magnetoresistance data.[6,30] As shown by the chart of the eigenvalues of the k points in the (a^*,c^*) plane passing through the Γ point [Fig. 4(c)], the cylinder like FS must be warped. This warping is not uniform but changes along the closed line of the trans-

verse cross section as shown in Fig. 4(d) for two different points marked **A** and **B** in Fig. 4(b). The dispersion along the c^* direction reaches values around 9 meV and varies considerably. This warping leads to a FS as depicted in Figs. 4(e) and 4(f). In order to clarify the kind of warping, the region of k space giving negative values of $d\epsilon/dc^*$ (ϵ is the eigenvalue at c^*) is encoded by a bright color and the region of k space giving positive values is encoded by a dark color. It is clear that the striped bands of colors are inclined with respect to the c^* direction [see Figs. 4(e) and 4(f)] a feature which harmonizes with the results of the magnetoresistance reconstruction of the FS.[6,30] The present study shows without any ambiguity that the FS of β-(BEDT-TTF)$_2$IBr$_2$ does not contain any small closed pockets of carriers which could be the origin of the slow oscillations. It also suggests that the dispersion along the interlayer direction is of the order of 0.8–1.7 % of that in the conducting plane. Let us note that slow oscillations have not been found for other BEDT-TTF salts exhibiting cylinder like features in their FS such as those of the α-(BEDT-TTF)$_2M$Hg(XCN)$_4$ family (M=K, Tl, Rb; X=S, Se).[1] We have carried out computations of the same quality for α-(BEDT-TTF)$_2$KHg(SCN)$_4$, and found a considerably smaller warping along the interlayer direction.

The two facts, together, the absence of additional closed pockets of carriers and the warping as reported here provide a firm computational basis to a very recent proposal[14] that the slow oscillations in β-(BEDT-TTF)$_2$IBr$_2$ originate from the warping of its cylindrical FS. In addition, the present work opens the way towards a more in depth characterization of the electronic structure of β-(BEDT-TTF)$_2$IBr$_2$ by allowing the comparison of the calculated and experimental fine details of the FS and band structure.

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