

# First-principles study of the neutral molecular metal Ni(tmdt)<sub>2</sub>

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The electronic structure of the molecular solid Ni(tmdt)<sub>2</sub>, the only well characterized neutral molecular metal to date, has been studied by means of first-principles density functional calculations. It is shown that these calculations correctly describe the metallic vs semiconducting behavior of molecular conductors of this type. The origin of the band overlap leading to the metallic character and the associated Fermi surfaces has been studied.

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With the successful marriage of the molecular donor TTF (tetrathiafulvalene) and the molecular acceptor TCNQ (tetracyanoquinodimethane),<sup>1</sup> the long date challenge of being able to prepare a solid exhibiting metallic properties but being built exclusively from molecular species was realized. The discovery of superconductivity a few years later in another molecular solid, (TMTSF)<sub>2</sub>PF<sub>6</sub> (TMTSF: tetramethyltetraselenafulvalene),<sup>2</sup> launched an enormous interest in these systems leading to the discovery of many molecular conductors exhibiting very interesting new physical phenomena.<sup>3</sup> Because of their molecular nature these solids are associated with relatively weak transfer integrals and intrasite repulsion energies. This leads to the existence of several ground states relatively close in energy and consequently, to very rich phase diagrams.<sup>4</sup> An essential requirement for the induction of metallic behavior in these solids is some kind of electron transfer (either direct or electrochemically induced) leading to the partial emptying and/or filling of at least one band. Therefore, molecular metals were thought to be always (at least) two-component systems. Thus, the recent report by Tanaka *et al.*<sup>5</sup> concerning the metallic behavior in a single-component neutral molecular solid, Ni(tmdt)<sub>2</sub> (tmdt: trimethylenetetrathiafulvalenedithiolate), is certainly a remarkable achievement which can open new alleys in molecular conductors physics.<sup>6</sup>

As a consequence of the molecular nature of these solids, the intermolecular forces leading to the spread of the molecular energy levels into bands, are considerably weaker than the intramolecular bonding forces which determine the molecular energy levels of the donor and acceptor. Thus, it was for a long time commonly accepted that the partially filled bands of these salts can be adequately described by considering just the highest occupied molecular orbital (HOMO) of the donor and/or the lowest unoccupied molecular orbital (LUMO) of the acceptor. Since only one orbital *per molecular species* is then involved in the relevant part of the band structure of these solids (i.e., the levels near the Fermi level), they can be described as *one-band systems*. Indeed, most of the presently known molecular conductors are one-band systems. The notion that molecular metals are one-band systems was challenged<sup>7</sup> back in 1989 when some

of us proposed that some molecular conductors containing the Ni(dmit)<sub>2</sub> [see Fig. 1(b); dmit: 1,3-dithia-2-thione-4,5-dithiolate] electron acceptor could be *two-band systems* [i.e., that *both* the HOMO and LUMO of Ni(dmit)<sub>2</sub> were leading to partially filled bands]. Very soon this proposal received experimental support (diffuse X-ray scattering,<sup>8</sup> <sup>13</sup>C Knight shift,<sup>9</sup> magnetic susceptibility,<sup>10</sup> etc.). An obvious consequence of this proposal was that molecular metals *must not necessarily be* two-component systems. For some molecular

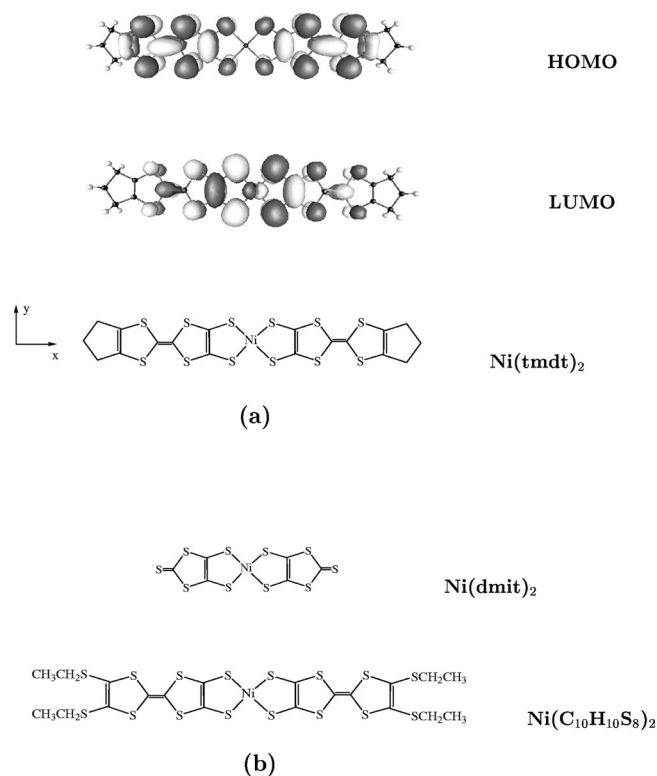


FIG. 1. Some relevant bis(dithiolene) systems used in the search for molecular conductors. (a) Shows schematically the structure of Ni(tmdt)<sub>2</sub>, and isosurface plots of its HOMO and LUMO levels (indicating the sign of the wave functions with different tones). (b) Shows a scheme of the structure of Ni(dmit)<sub>2</sub> and Ni(C<sub>10</sub>H<sub>10</sub>S<sub>8</sub>)<sub>2</sub>.

species in the solid state, there is the possibility of an internal electron transfer which thus can make unnecessary the presence of the doping species. The structural and electronic requirements for the realization of a two-band behavior were explored,<sup>11–14</sup> and metal bis(dithiolene) systems were proposed to be the more promising species in order to lead to single-component molecular metals.<sup>14</sup> Consequently, although Tanaka *et al.*<sup>5</sup> apparently did not notice these developments, the discovery by these authors is certainly a remarkable experimental achievement but hardly an unexpected one since Ni(tmtdt)<sub>2</sub> is a metal bis(dithiolene) species [see Fig. 1(a)].

Theoretical studies of the electronic structure of solids like Ni(tmtdt)<sub>2</sub> can certainly play a key role in the search for new neutral molecular metals and the rationalization of their physical properties. In their original report, Tanaka *et al.*<sup>5</sup> presented a tight-binding study of the Fermi surface of Ni(tmtdt)<sub>2</sub> in which the HOMO-LUMO energy difference was treated as a parameter (i.e., the band structure calculations were carried out by varying this energy difference). Since the band overlap leading to the metallic type behavior results from a very fine balance between the strength of the intermolecular interactions and the initial HOMO-LUMO gap, these calculations cannot be considered accurate enough in order to discuss this type of problems. Here we report a first principles density functional study of the band structure and Fermi surface of Ni(tmtdt)<sub>2</sub>. The calculations were carried out using a numerical atomic orbitals density functional theory (DFT)<sup>15,16</sup> approach, which has been recently developed and designed for efficient calculations in large systems and implemented in the SIESTA code.<sup>17–21</sup> We have used the generalized gradient approximation to DFT and, in particular, the functional of Perdew, Burke, and Ernzerhof.<sup>22</sup> Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials<sup>23,24</sup> factorized in the Kleinman-Bylander form.<sup>25</sup> We have used a split-valence double- $\zeta$  basis set including polarization orbitals for all atoms, as obtained with an energy shift of 10 meV.<sup>20</sup> 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 135 Ry, which yields to a spacing between the grid points of around 0.13 Å. The Brillouin zone (BZ) was sampled using a grid of (4×3×2)  $k$  points.<sup>26</sup> We have checked that the results are well converged with respect to the real space grid, the BZ sampling and the range of the atomic orbitals.

The x-ray crystal structure reported by Tanaka *et al.*<sup>5</sup> has been used in the calculations. A projection of this structure along the  $b$  direction is shown in Fig. 2. It is clear that there is a number of S···S contacts along the  $b$  direction which will lead to  $\sigma$  type overlap interactions between the  $\pi$  type orbitals of the molecules. In addition, there are also several lateral S···S contacts. As a consequence, there really is a three-dimensional (3D) network of S···S interactions which will spread the molecular levels (mostly the  $\pi$  type ones) into bands.

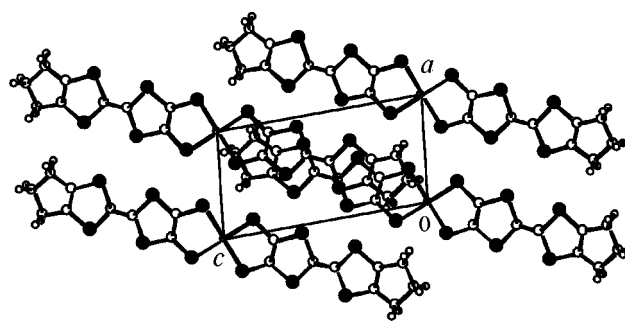


FIG. 2. Projection of the Ni(tmtdt)<sub>2</sub> crystal structure along the  $b$  direction.

As mentioned, the metallic behavior in this system should arise from the overlap between the bands originating from the HOMO and LUMO. Calculations for an isolated Ni(tmtdt)<sub>2</sub> molecule indicate that these levels are separated by an energy gap of 0.36 eV. The nature of these two levels is shown in Fig. 1(a). This HOMO-LUMO energy gap is calculated to be considerably larger (0.75 eV) for Ni(dmit)<sub>2</sub> [see Fig. 1(b)] which apparently was the metal bis(dithiolene) system more prone to lead to molecular solids exhibiting a two-band behavior. The HOMO and LUMO of Ni(tmtdt)<sub>2</sub> [as for Ni(dmit)<sub>2</sub><sup>7,14</sup>] originate from the in-phase and out-of-phase combinations of the same  $\pi$  type orbital of the two identical tmtdt organic ligands. The  $d_{xz}$  orbital of the nickel atom has the appropriate symmetry to mix in an antibonding way<sup>27</sup> into the out-of-phase combination leading to the LUMO of Fig. 1(a). However the nodal properties of the ligand orbital (i.e., the different sign for the nearest sulfur and carbon  $p_z$  orbitals) are such that the overlap, and thus, the mixing, is relatively weak. In addition, the Ni  $d$  type orbitals cannot mix into the in-phase combination because they do not have the appropriate symmetry with respect to the three pseudosymmetry planes. Thus, the HOMO of the system [see Fig. 1(a)] is practically a purely ligand  $\pi$  type orbital and the HOMO-LUMO energy gap is the result of the metal-ligand antibonding interaction. As mentioned above, the overlap interactions of the Ni  $d_{xz}$  orbital with the nearest carbon and sulfur  $p_z$  orbitals partially cancel and consequently, the HOMO-LUMO gap is relatively small. This is what makes metal bis(dithiolenes) potential two-band systems. That this gap is considerably reduced in Ni(tmtdt)<sub>2</sub> with respect to Ni(dmit)<sub>2</sub> is an obvious consequence of the increase in the delocalization of the ligand  $\pi$  type orbital leading to the HOMO and LUMO, since this increase leads to a decrease of the coefficients of the  $p_z$  orbitals of the above mentioned carbon and sulfur atoms via the orbital normalization, and consequently, to a decrease of the metal-ligand interaction.

The calculated band structure near the Fermi level for the Ni(tmtdt)<sub>2</sub> molecular solid is reported in Fig. 3. Since there is only one Ni(tmtdt)<sub>2</sub> molecule per unit cell, there are just one HOMO (middle) and one LUMO (upper) bands in Fig. 3. The widths of these bands are 0.655 eV and 0.540 eV, respectively. Since the addition of the two half-widths is larger than the initial HOMO-LUMO gap, the two bands overlap (0.19 eV) thus leading to the metallic character of this solid.

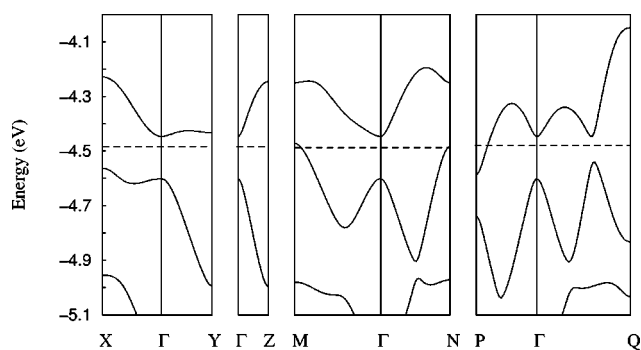


FIG. 3. Band structure calculated for  $\text{Ni}(\text{tmdt})_2$  where the dashed line refers to the Fermi level.  $\Gamma=(0,0,0)$ ,  $X=(1/2,0,0)$ ,  $Y=(0,1/2,0)$ ,  $Z=(0,0,1/2)$ ,  $M=(1/2,1/2,0)$ ,  $N=(1/2,0,1/2)$ ,  $P=(0,1/2,1/2)$ , and  $Q=(1/2,1/2,1/2)$ , in units of the triclinic reciprocal lattice vectors.

In fact, there is a substantial HOMO-LUMO mixing in several parts of the BZ, so that it is not possible to rationalize in simple terms the shape of these bands along different directions of the BZ on the basis of simple (and usual) overlap arguments. However, what is clear from Fig. 3 is that  $\text{Ni}(\text{tmdt})_2$  must be a 3D metal. This is a consequence of both the delocalization of the HOMO and LUMO and the existence of a 3D network of  $\text{S} \cdot \cdot \cdot \text{S}$  interactions (see Fig. 2). The calculated Fermi surfaces are shown in Fig. 4 (calculations for a mesh of 512  $k$  points equally spaced in the irreducible

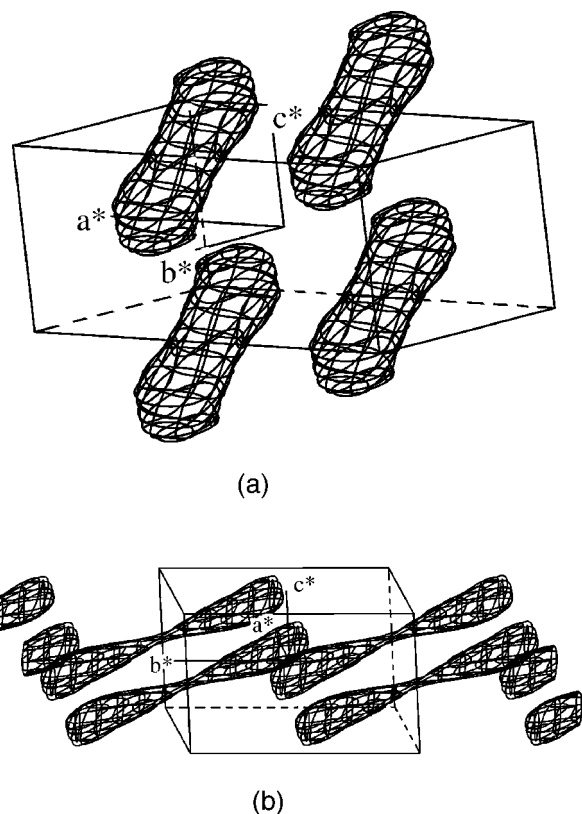


FIG. 4. Fermi surface calculated for  $\text{Ni}[\text{tmdt}]_2$ : (a) electron pockets, centered around  $(0, b^*/2, c^*/2)$  and (b) hole pockets, centered around  $(a^*/2, b^*/2, 0)$ .

part of the BZ were used for determination of these surfaces). Both the electron [Fig. 4(a)] and hole [Fig. 4(b)] pockets are closed 3D objects which would be very interesting to study by magnetoresistance measurements. The shape of these pockets is such that they should exhibit angle-dependent oscillations. It should be pointed out that the hole pockets can be considered as resulting from the condensation of two identical objects with a weak overlap so that they could split in two separate ones as a result of minor structural changes. In the absence of a low temperature crystal structure, this fact should be kept in mind for the correct interpretation of the magnetoresistance measurements. The 3D nature of the Fermi surface agrees well with the small resistivity anisotropy reported for  $\text{Ni}(\text{tmdt})_2$ .<sup>5</sup>

Let us note that this Fermi surface is very different from that reported by Tanaka *et al.*<sup>5</sup> based on approximate tight-binding calculations. This is not so surprising in view of the delicate balance between the initial HOMO-LUMO gap and the strength of the different intermolecular interactions which ultimately lead to the small band overlap. In the tight-binding calculations none of the two factors are free from adjustment (i.e., the initial HOMO-LUMO gap is arbitrarily fixed as it is the constant relating the overlap and effective transfer integrals) so that these calculations cannot be of real value for this specific problem. In contrast, the present first principles calculations seem to be well adapted to describe the electronic structure of these materials. For instance, Narvor *et al.*<sup>6</sup> previously reported that the very strongly related nickel bis(dithiolene) material  $\text{Ni}(\text{C}_{10}\text{H}_{10}\text{S}_8)_2$  [see Fig. 1(b)] is a semiconductor with a small energy gap (approximately 0.10 eV as deduced from the conductivity measurements). Our calculations fully agree with this observation since the HOMO and the LUMO bands are now calculated to be separated by a small energy gap of 0.054 eV. The reason for the semiconducting behavior of this material is entirely due to the differences in the crystal packing (i.e., difference in the intermolecular interactions) since the molecular HOMO-LUMO gaps are practically identical (0.36 vs 0.37 eV).

The report by Tanaka *et al.*<sup>5</sup> will certainly make the search for neutral molecular metals an active topic of research in the near future and thus a warning is in order here. The decrease of the molecular HOMO-LUMO gap by increasing the delocalization of the organic ligands, is certainly an important aspect of the strategy but it is just part of it. As mentioned before, the delocalization of the  $\pi$  type orbital of the ligand leads to the decrease of the HOMO-LUMO gap via the decrease of the coefficients of the  $p_z$  orbitals of the carbon and sulfur atoms near the nickel atom, simply because of the orbital normalization. However, the decrease of the coefficients occurs for the  $p_z$  orbitals of all atoms contributing to the organic ligand orbital. This means that the effective transfer integrals associated with the different intermolecular interactions of the crystal (which are roughly proportional to the associated overlap integrals) may also decrease (assuming the same intermolecular geometry), something which goes against the realization of the band overlap needed for the metallic behavior. In other words it is

the relative rate of decrease of the initial HOMO-LUMO gaps and the effective transfer integrals which is important to control. Thus, in general, a decrease in the molecular HOMO-LUMO gap will only be effective if the crystal structure can adjust in such a way that the intermolecular transfer integrals do not decrease very much. Several strategies to alter the initial HOMO-LUMO gap in metal bis(dithiolenes) can be envisioned. The transfer integrals are however more difficult to predict because they depend on the actual details of the crystal structure. However, model studies with appro-

priate first-principles based transfer integrals and HOMO-LUMO gap, as those reported here, should have an important role in a rational search for new single-component molecular metals.

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