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First-principles study of the electronic structure of the organic solids $(\mathrm{CH}_3)_4\mathrm{N}[M(\mathrm{dmit})_2]_2$ ($M=\mathrm{Ni}$ and Pd): Role of dimerization and the stability of the formation of a dimer

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The electronic structures of organic solids $(\mathrm{CH}_3)_4\mathrm{N}[\mathrm{Ni(dmit)}_2]_2$ and β-$(\mathrm{CH}_3)_4\mathrm{N}[\mathrm{Pd(dmit)}_2]_2$ (dmit=2-thioxo-1,3-dithion-4,5-dithiolate) are studied by first-principles calculations based on the density functional theory. We have found that the electronic structure of the Ni salt shows strong one-dimensional character, while that of the Pd salt shows two-dimensional character. These results agree with experimental results. We show that the differences mainly come from the degree of dimerization. By calculating the stable structure of the isolated dimer, we have found that the difference of the degree of dimerization is due to the different character of $M(\mathrm{dmit})_2$ itself. [S0163-1829(99)50808-4]

The electronic structures of organic solids are determined by two hierarchical interactions, strong intramolecule and weak intermolecule interactions. The molecular orbitals (MO's) and their energy levels for the isolated molecule come from the strong intramolecule interaction and in most cases they can be considered as unchanged even in solids. In fact, the electronic structures of organic solids have often been successfully analyzed by the tight binding (TB) calculation using only the highest occupied molecular orbitals (HOMO's) or the lowest unoccupied molecular orbitals (LUMO's), which are calculated for the isolated molecule by using extended Hückel approximation.[1,2] On the other hand, intermolecule interactions determine the network of the electron's hopping in the solids. In some organic solids, there are two different kinds of intermolecule interactions, namely strong intradimer and weak interdimer interactions. The presence of dimerized structures splits each MO levels into two levels, those of bonding and antibonding MO's. Dimerized structures often play important roles for the physical properties of organic solids.[3,4]

The title compounds are unique in the sense that the intradimer interactions are as strong as intramolecule interactions. This means that the energy separations of bonding and antibonding MO's are as large as those between MO's. Actually, the optical reflectance experiments for the Pd salts[5] suggest that the level of bonding LUMO is lower than that of antibonding HOMO. The electronic structures of the title compounds have been analyzed by TB calculations considering both LUMO and HOMO of the isolated $M(\mathrm{dmit})_2$ molecule. However, when intradimer interactions are large to the same extent as intramolecule interactions, such TB calculations are not reliable. They cannot obtain the reliable LUMO-HOMO energy separation Δ and the effective Δ in the solids, which are crucial for the electronic structure of the solids. More elaborate calculations considering the effect of the structure in the solids including the effects of cations $(\mathrm{CH}_3)_4\mathrm{N}$ are highly desired. Our calculations are based on the density functional theory within the generalized gradient approximation.[6] Although such calculations are relatively expensive, they can clarify the details of the electronic structure and the subtle difference among the related materials.[7] Further, they can determine the crystal structure fairly accurately.[8] In this paper we will show that the electronic structures of the two title compounds are qualitatively different and that the above qualitative differences of the electronic structure come from the different stable structures of the isolated dimer. Theoretical structure determination is necessary for the study of the stability of the formation of a dimer.

The family of $M(\mathrm{dmit})_2$ related materials show various crystal structures and exhibit a large variety of transport and magnetic properties.[9,10] Especially, as we will see below, they show various dimensionality in the transport properties. The structure of $M(\mathrm{dmit})_2$ molecule is shown in Fig. 1. This molecule is formed by connecting two dmit molecules by a metallic M atom. The title compounds, $(\mathrm{CH}_3)_4\mathrm{N}[\mathrm{Ni(dmit)}_2]_2$ and β-$(\mathrm{CH}_3)_4\mathrm{N}[\mathrm{Pd(dmit)}_2]_2$, are isostructural to each other and the space group is C2/c. They have a layered structure along the c axis, anion layers made from $M(\mathrm{dmit})_2$ molecules, and cation layers from $(\mathrm{CH}_3)_4\mathrm{N}$ clusters (see Fig.1 in Ref. 11). The formal charge of $M(\mathrm{dmit})_2$ molecule is -0.5 for both cases. There are two equivalent anion layers in the unit cell, where $M(\mathrm{dmit})_2$ molecules stack face to face along $[110]$ and $[1\bar{1}0]$ directions. Dimerized structure along the stacking direction can be seen especially in the Pd salt.[12] Their physical properties at ambient pressure are qualitatively different although both salts show superconducting behavior under pressure. For the Ni salt, the temperature dependence of the resistivity shows metallic behavior at least for $T>100\,\mathrm{K}$.[11,13,14] At lower temperatures the resistivities are sample dependent and the phase is not clear at present.[15] In contrast to the temperature dependence of the resistivity, the polarized reflectance spectra experiments[5] are not sample dependent and they show Drude-like behavior down to 20 K. By analyzing the anisotropy of the plasma frequency within

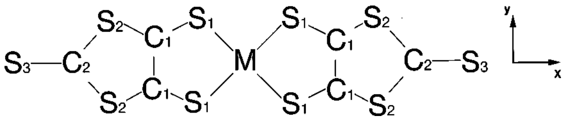

FIG. 1. Structure of $M(\mathrm{dmit})_2$ molecule. Indices of atoms are also shown in the figure.

the *ab* plane, it is suggested that the Ni salt shows strong one-dimensional (1D) character along the stacking direction. This strong 1D character is also confirmed by the thermoelectric power measurements.[5] On the other hand, the resistivity temperature dependence of the Pd salt does not show clear metallic behavior around 300 K and it shows nonmetallic behavior at lower temperatures.[12] The NMR studies suggest that the antiferromagnetic phase is realized below 12 K.[16] Under pressure, the resistivities of the Pd salt shows metallic behavior at high temperatures and it becomes superconductor at low temperatures when the pressure of 6–9 kbar is applied.[17] It is pointed out that the reflectance spectra in the infrared region is fairly isotropic within the *ab* plane compared with the Ni salt.[18] In addition, by analyzing the optical conductivity results, it is suggested that the bonding LUMO bands are lower than the antibonding HOMO bands.[5,18] The target of our present study is to clarify what makes the above qualitative differences between the Ni and Pd salts.

Our calculations are based on the generalized gradient approximation[6] in the density functional theory. Ultrasoft pseudopotentials[19] are used for the *p* states of C and N, *d* states of Ni and Pd, and an *s* state of H. For other states, we employ the optimized norm-conserving pseudopotentials.[20] The cutoff energies for the wave functions and charge density are 25 and 225 Ry, respectively. We do not consider the spin polarized case. In this paper most calculations have been done by using experimental structures.[12,21] We have also optimized the atomic positions of the title compounds and have found that the errors in interatomic distances are about 1% of the experimental ones. Details of the accuracy for the theoretical structure determination will be reported in a forthcoming paper, together with the study of pressure effects for the Pd salt.

First we have calculated the electronic structure of the isolated neutral $M(\mathrm{dmit})_2$ ($M=$Ni and Pd) molecule.[22] The character of the calculated LUMO and HOMO for both molecules is almost the same as those shown in Fig. 1 of Ref. 23, where extended Hückel calculations are used. The energy separation Δ between these two orbitals is 0.73 eV for the $\mathrm{Ni(dmit)_2}$ and 0.59 eV for the $\mathrm{Pd(dmit)_2}$. The present Δs and the difference of the Δ between two molecules are both much larger than those in Ref. 23 ($\Delta \sim 0.4$ eV, and the difference is about 0.07 eV). It should be noted that one can consider LUMO (HOMO) as the antibonding (bonding) state between two MOs of dmit through *d* orbitals of *M* atom. Because of its symmetry b_{1u}, HOMO has no contributions from *d* orbitals of the *M* atom. TB calculations based on the extended Hückel approximation suggest that LUMOs tend to form 1D bands along the stacking direction.[24] The LUMO-LUMO overlap integral perpendicular to the stacking direction is small because of LUMO's symmetry b_{2g} and the way of packing, although there are short *S*-*S* contacts along this direction. As HOMO's have the different symmetry from LUMO's, they tend to form 2D bands within the anion layer.

The band structure of $\mathrm{(CH_3)_4N[Ni(dmit)_2]_2}$ is shown in Fig. 2. First we can see that the dispersion of the bands near the Fermi level is very weak along the Γ-Z and V-L lines, implying that the interlayer interaction is very weak in this system. Our present results agree with the experimental results for the anisotropy of the resistivity. We have also calculated the energy levels of the isolated neutral $\mathrm{Ni(dmit)_2}$ molecule and dimer. This energy diagram shows that two bands around the Fermi level come from the bonding LUMO of the $\mathrm{Ni(dmit)_2}$ dimer. From the band structure along V-Γ line, which corresponds to the direction perpendicular to [110], we can see that one of the bonding-LUMO bands shows appreciable dispersion while the other shows very weak dispersion. This fact means that within a certain anion layer the electronic structure near the Fermi level shows strong 1D character along the stacking direction ([110] or $[1\bar{1}0]$). The structure of bonding-LUMO bands in Fig. 2 can be reproduced by using TB calculation with some fitted parameters and we have obtained two planar Fermi surfaces with different directions. The width of bonding-LUMO bands in Fig. 2 is about 0.27 eV and the effective hopping integral along the stacking direction $t_\perp$ is approximately estimated as 0.14 eV. This agrees with the experimental values of 0.10 eV from the reflectance spectra[25,26] and 0.12 eV from the thermoelectric measurements.[5]

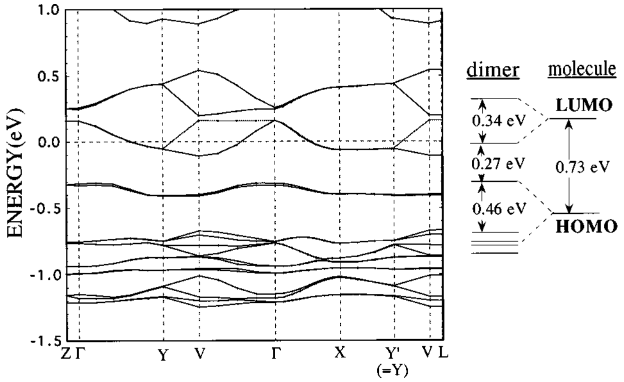

FIG. 2. Band structure of $\mathrm{(CH_3)_4N[Ni(dmit)_2]_2}$. Z, Γ, Y, V, X, Y', and L refer to (0 0 1), (0 0 0), (0 y 0), $(\frac{1}{2}\,\frac{1}{2}\,0)$, (1 0 0), (1 1 $-y$ 0), and $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$, respectively. Here $y=(a^2+b^2)/(2a^2)$, where a and b are lattice parameters. The energy levels of $\mathrm{Ni(dmit)_2}$ molecule and dimer are also shown in the right part of the figure.

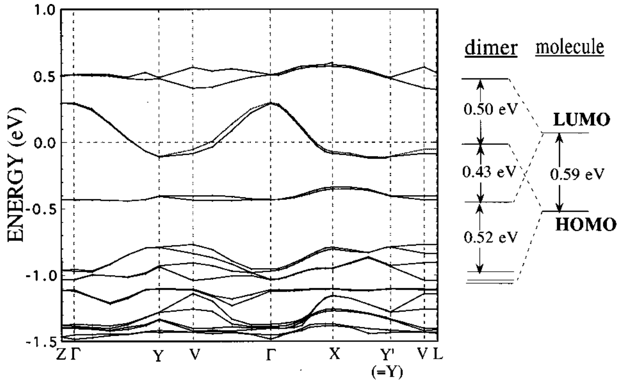

FIG. 3. Band structure of β-$\mathrm{(CH_3)_4N[Pd(dmit)_2]_2}$. The labels of k space are the same as those in Fig. 2. The energy levels of $\mathrm{Pd(dmit)_2}$ molecule and dimer are also shown in the right part of the figure.

The electronic structure of β-$\mathrm{(CH_3)_4N[Pd(dmit)_2]_2}$ shown in Fig. 3 is qualitatively different from that of the Ni salt.[27] Especially, the band structure along V-Γ and Γ-X line is completely different from Fig. 2. The fact that the two bands

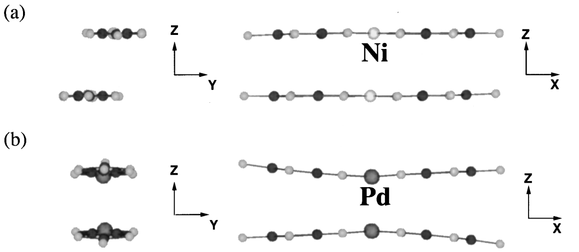

FIG. 4. Intradimer alignment in the (a) Ni and (b) Pd salts.

around the Fermi level are almost degenerate along V-Γ line means that the eigenstates near the Fermi level show very small anisotropy within the anion layer. The two Fermi surfaces, which are obtained by the TB fitting to the calculated band structure, are fairly isotropic within the ab plane. By comparing the band structure with the energy levels of the isolated molecule and dimer, we can see that the eigenstates near the Fermi level come from the antibonding HOMO of the Pd(dmit)$_2$ dimer, which are higher than the bonding-LUMO bands. The energy separation between bonding- and antibonding-LUMO bands and the one between two HOMO bands are both about 1.0 eV. These values may correspond to the experimental value 1.3 eV, where a strong peak is observed in the conductivity spectra.[18]

The above qualitative differences of the electronic structure between the Ni and Pd salts come mainly from the differences of the internal coordinates, especially the degree of dimerization. Interplanar distances of two $M(\mathrm{dmit})_2$ molecules between dimers and within a dimer are 3.58 Å and 3.53 Å for the Ni salt, while they are 3.81 Å and 3.28 Å for the Pd salt. We have calculated the electronic structure of the Pd salt with artificial weak dimerization and have found that the electronic structure becomes similar to that of the Ni salt.

The degree of dimerization determines which MO is responsible for the eigenstates around the Fermi level and thus determines the dimensionality in the transport properties. Further, it is worthwhile to note that the stacking mode within a dimer is quite different between the Ni and Pd salts (Fig. 4). We may call the way of stacking within a dimer for the Ni salt as the staggered mode and the one for the Pd salt as the eclipsed mode. As LUMO and HOMO have many nodes within the molecule,[24] there are many stacking modes which obtain the local maximum of the absolute value of the intermolecule overlap integrals.

The difference in the dimer formation brings about the difference in the network of intermolecule hopping integrals even along the stacking direction. For the Ni salt, hopping integrals between LUMO's of the neighbor molecules along the stacking direction are arranged like $t_1, -t_1', t_1, -t_1', \ldots, (t_1 \simeq t_1')$. As the intradimer and interdimer stacking modes are different, their hopping integrals have different signs. The band energy of the above alternately stacking system is almost the same as the one of the uniform stacking ($t_1, t_1, t_1, t_1, \ldots,$ network) system. As the title compounds are 2:1 salts, the alternately stacking system is stabilized by the interaction with the cations. On the other hand, the electronic structure near the Fermi level for the Pd salt comes from the $t_2, dt, t_2, dt, \ldots, (|t_2| \gg |dt|)$ network, where t_2 and dt are the intra and interdimer hopping integrals between HOMO's of the neighbor molecules along the stacking direction. The intradimer hopping integral of the Pd salt t_2 is about three times larger than that of the Ni salt t_1. To make such large hopping integrals, Pd(dmit)$_2$ molecules must bend at the Pd site to suppress the repulsions between dmit molecules. Thus it is impossible to make interdimer interaction dt large to the same extent as t_2.

It is a question whether the difference in the dimer formation between the Ni and Pd salts comes from the difference in characters of the $M(\mathrm{dmit})_2$ molecules solely or together with the effects of cation. This is important because many compounds with different cations have been synthesized and their various physical properties, especially their pressure effects,[28] have been reported so far. To answer the above question, we have calculated the optimized structure, total energy and the electronic structure of the isolated dimer with additional one electron.[29] For the optimization of the atomic positions, we have considered two initial configurations: (a) the structure of the dimer in the solid of the Ni salt and (b) the one for the Pd salt (Fig. 4). The results of the calculations are the following. First, we have found that the optimized structure of the Pd(dmit)$_2$ dimer in the mode (b) is almost the same as the one in the solid. For example, the difference of Pd-Pd distance is about 0.02 Å. We have also found for the Ni case that the optimized structure in the mode (a) is not so largely different from the one in the solid. Second, by comparing the total energy, we have found that the mode (a) is stable in the Ni case (0.16 eV) while the mode (b) is stable in the Pd case (0.11 eV). The above two results mean that the effects of cations are small for the structure of a dimer, especially for the Pd case. Finally, it should be noted that the bonding and antibonding HOMO for both modes and for both Ni and Pd cases have appreciable contributions from d orbitals (mainly $3z^2-r^2$) of Ni or Pd atoms. As we have mentioned before, HOMO of the isolated molecule does not include d contributions because of its symmetry. However, such symmetry does not hold for dimers and we cannot neglect this effect. This fact suggests that it is not reliable to calculate the electronic structure of the solids by considering only HOMO and LUMO of the isolated molecule.

The following three aspects play important roles for the Pd(dmit)$_2$ dimer to favor the mode (b) (eclipsed stacking mode): (1) d orbitals of Pd atom are larger, (2) bonds between Pd atom and dmit molecules are weaker, and (3) Δ of Pd(dmit)$_2$ is smaller. (1) is important to obtain large intradimer interactions for the mode (b). We have found that interactions between d orbitals within a dimer have substantial contributions although the intradimer interactions come mainly from S_1-S_1 contact. Intradimer interactions through d orbitals for the Pd salt must be larger than that of the Ni salt. In fact the energy separation between bonding and antibonding LUMO (HOMO) for the Pd case is 0.14 eV (0.05 eV) larger than that for the Ni case in the mode (b). (2) is responsible for the small energy loss to deform $M(\mathrm{dmit})_2$ in the mode (b). In order to make small interatomic distances between two M atoms without the distortion of dmit molecules, $M(\mathrm{dmit})_2$ molecule must bend at M site to suppress the intermolecule dmit-dmit repulsion. (3) is the result of (2). Remind that HOMO (LUMO) can be considered as a bonding (antibonding) orbital of two molecular orbitals of dmit molecules through M atom. The gain of the band energy for the mode (b) compared with the mode (a) can be roughly estimated by the energy to bring one electron from antibonding HOMO to bonding LUMO. In this sense, (3) is crucial for the Pd salt to form the (b) mode.

In summary, we have studied the electronic structure of $(CH_3)_4N[Ni(dmit)_2]_2$ and β-$(CH_3)_4N[Pd(dmit)_2]_2$ by first-principles calculations based on the density functional theory. The character of the eigenstates near the Fermi level is quite different between these two materials. The eigenstates near the Fermi level for the Ni salt show strong 1D character and they come mainly from LUMO of the $Ni(dmit)_2$ molecule, while those for the Pd salt show 2D character and come from HOMO. The calculated band width and interband energy separations agree with experimental results. We have discussed that the differences of the band structure are due to the different way of stacking $M(\mathrm{dmit})_2$ molecules within a dimer. We have also found that the stable structures of the isolated dimers are almost the same as those in the solid for both the Ni and Pd cases. This fact means that the effects of cations are small for the dimer formation and the above differences come from the different character of $M(\mathrm{dmit})_2$ molecule itself.

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