Electronic Structure of a Single-Component Molecular Conductor [Pd(dddt)$_2$] (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) under High Pressure

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We examined high-pressure electronic structure of a single-component molecular conductor [Pd(dddt)$_2$] (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) at room temperature, based on the crystal structure determined by single crystal synchrotron X-ray diffraction measurements at 5.9 GPa. The monoclinic unit cell contains four molecules that form two crystallographically independent molecular layers. A tight-binding model of 8 × 8 matrix Hamiltonian gives an electronic structure as a Dirac electron system. The Dirac point describes a loop within the first Brillouin zone, and a nodal line semimetal is obtained. The noticeable property of the Dirac cone with a linear dispersion is shown by calculating density of states (DOS). The Dirac cone in this system is associated with the crossing of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) bands, which originates from the direct interaction between different molecular layers. This is a newly found mechanism in addition to the indirect one [J. Phys. Soc. Jpn., 86, 064705 (2017)]. The Dirac points emerge as a line, when the HOMO and LUMO bands meet on the surface and the HOMO-LUMO couplings are absent. Such a mechanism is verified using a reduced model of 4 × 4 matrix Hamiltonian. The deviation of the band energy ($\delta E$) at the Dirac point from the Fermi level is very small ($\delta E < 0.4$meV). The nodal line is examined by calculating the parity of the occupied band eigen states at TRIM (Time Reversal Invariant Momentum) showing that the topological number is 1.

1. Introduction

Molecular conductors have simple and clear electronic structures where a simple extended Hückel tight-binding (TB) band picture is applicable. This is mainly because only one kind of frontier molecular orbital (HOMO or LUMO) in each molecule contributes to the formation of a conduction band in conventional molecular conductors, where HOMO and LUMO denote highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. In recent years, however, the number of molecular conductors that cannot be categorized as a single-orbital system is increasing. This means that we should expand our perception toward a multi-orbital system where more than two molecular orbitals in the same molecule contribute to electronic properties and the orbital degree of freedom plays an essential role.

A typical example of the multi-orbital system is single-component molecular conductor. Molecules usually have a closed-shell electronic structure, which is the reason why they are stable in an isolated state. Therefore, it was believed that neutral closed-shell molecules do not self-assemble to form a metallic bond in a crystal and, therefore, electron transfer between the frontier molecular orbital and other chemical species is indispensable for a metallic molecular crystal. Resultant molecular metals are not single-component anymore, but they include other cations or anions to keep the charge neutrality.

If the energy difference between HOMO and LUMO is small enough, however, an overlap of the fully occupied HOMO band and the empty LUMO band can be possible and an intramolecular electron transfer leads these bands to partially filled states. This idea has been confirmed by the observation of electron and hole Fermi surfaces in an ambient-pressure single-component molecular metal [Ni(tmdt)$_2$] (tmdt = trimethylene-trithiinfulvalenedithiolate) by detecting the de Haas-van Alphen effect. After this breakthrough, various single-component molecular conductors were developed by using metal dithiolene complexes. In metal dithiolene complexes with a planar central core, the HOMO is destabilized due to the absence of contribution from the metal d orbitals and the HOMO-LUMO gap is small (< 1 eV) in general. Even in the case of metal dithiolene complexes, however, the HOMO and LUMO bands are mostly separated from each other and a metallic state rarely emerges at ambient pressure. In a molecular crystal with a soft lattice, the application of high pressure can effectively enhance intermolecular transfer integrals and thus induce the overlap of the HOMO and LUMO bands. Indeed, an increasing number of single-component molecular metals have been found under high pressure. Notably, an improvement of the DAC (Diamond Anvil Cell) technique that provides high-quality quasi hydrostatic pressure drove the research forward. Superconductivity in a single-component molecular crystal was also achieved under high pressure generated by DAC. We thus realized a metallic/superconducting state in single-component molecular crystals. In these

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single-component molecular systems that we now focus on, molecules maintain their original molecular properties even in the high-pressure metallic state, and it is anticipated that the emergence of a metallic state itself can be well understood in the framework of the conventional TB band theory. It should be recognized that the deeper goal of the physical research on single-component molecular conductors is not just to obtain a conventional metallic state. What is really being put to the test is the possibility of unique physical properties that are built in the multi-orbital system.

In this sense, the discovery of a nodal line semimetal state in a single-component molecular conductor [Pd(dddt)$_2$] (dddt = 5,6-dihydro-1,4-dithin-2,3-dithiolate) under high pressure has paved the way for the development of multi-orbital molecular conductors. Indeed, after this discovery, the semimetal with open pockets, which means that the system is a nodal-line semimetal, is an insulator at ambient pressure. The application of hydrostatic pressure using the DAC technique suppressed resistivity and activation energy. The temperature-independent resistivity observed at 12.6 GPa triggered theoretical studies using first-principles calculations based on density functional theory (DFT). The energy band structure for the optimized high-pressure structure indicates the emergence of the Dirac cones at 8 GPa, which is consistent with the zero-gap behavior observed in the resistivity measurement. The TB model based on extended Hückel molecular orbital calculations revealed that the Dirac cone formation is associated with the multi-orbital character and the Dirac point describes a loop in the three-dimensional Brillouin zone. The small deviation of the energy on the loop from the Fermi level gives hole and electron bands even in the high-pressure metallic state, and it is anticipated that the emergence of a metallic state itself can be well understood in the framework of the conventional TB band theory. It should be recognized that the deeper goal of the physical research on single-component molecular conductors is not just to obtain a conventional metallic state. What is really being put to the test is the possibility of unique physical properties that are built in the multi-orbital system.

2. Tight-binding model

We carried out synchrotron X-ray diffraction measurements at several pressure points and found that there is no drastic structural phase transition up to 8 GPa. The cell volume measured at 5.9 GPa (1152.8 Å$^3$) is close to the one obtained by the DFT calculation for the 8 GPa structure (1147.5 Å$^3$), which is the reason why we focus on the 5.9 GPa structure. The determined cell parameters and atomic coordinates are listed in Appendix A.

Figure 1 shows the molecular arrangement and intermolecular couplings in the [Pd(dddt)$_2$] crystal. The unit cell contains four molecules (1, 2, 3, and 4), and each central Pd atom is located on the inversion center. The [Pd(dddt)$_2$] molecules uniformly stack along the b axis that is perpendicular to the ac plane. Crystallographically equivalent molecules form two kinds of layers, layer 1 (molecules 1 and 3) and layer 2 (molecules 2 and 4), both of which are parallel to the ab plane.

We construct a TB model for [Pd(dddt)$_2$] using frontier molecular orbitals of four molecules in the unit cell, HOMOs (H1, H2, H3, H4) and LUMOs (L1, L2, L3, L4). The TB model Hamiltonian is given by

$$H_{\text{TB}} = \sum_{i,j=1}^{N} \sum_{\alpha,\beta} t_{i,j,\alpha,\beta} | i, \alpha \rangle \langle j, \beta | + \sum_{k} h_{\alpha,\beta}(k) | k, \alpha \rangle \langle k, \beta | = \sum_{k} \langle \Phi(k) | \hat{H}(k) | \Phi(k) \rangle ,$$

where $t_{i,j,\alpha,\beta}$ are transfer energies between nearest-neighbor sites and $| i, \alpha \rangle$ is a state vector. $\alpha, \beta = H_1, H_2, \cdots, L_3, L_4$. $h_{\alpha,\beta}(k)$ denotes a Fourier transform of $h_{i,j,\alpha,\beta}$ with a complex conjugate relation $h_{\alpha,\beta}(k) = h_{\beta,\alpha}^*(k)$, where $k = k_x a^* + k_y b^* + k_z c^*$, and $2\pi k_z = ka, 2\pi k_y = kb$, and $2\pi k_x = kc$.

The energy difference between HOMO and LUMO is...
taken as $\Delta E = 0.696$ eV.

Interlayer and intralayer transfer energies in matrix elements $h_{\alpha, \beta}^c(k)$ are shown in Table I, which are estimated by the extended Hückel method. The interlayer transfer energies in the $c$ direction are given by $a$ (molecules 1 and 2, and molecules 3 and 4) and $c$ (molecules 1 and 4, and molecules 2 and 3). The intralayer transfer energies parallel to the $ab$ plane are given by $p$ (molecules 1 and 3), $q$ (molecules 2 and 4), and $b$. These transfer energies are classified by HOMO-HOMO (H), LUMO-LUMO (L), and HOMO-LUMO (HL).

These transfer energies are rather different from those of the previous model based on the theoretically optimized structure at 8 GPa. Notably, there are significant contributions from the direct interlayer HOMO-LUMO couplings, which provide elements $h_{11,22}^c$, $h_{11,14}^c$, $h_{13,12}^c$, and $h_{13,14}^c$ and those being the complex conjugate elements. In the previous model,\(^{11}\) however, these elements are negligibly small and then discarded. The indirect interlayer HOMO-LUMO couplings play an important role in the Dirac cone formation instead. This is obtained by a second order perturbation in terms of the intralayer HOMO-LUMO and interlayer LUMO-LUMO or HOMO-HOMO couplings, e.g., a combination of $h_{11,1,2}$ and $h_{1,1,1,2}$. The direct interlayer HOMO-LUMO couplings also give the off-diagonal elements of a reduced model of $4 \times 4$ Hamiltonian, which is to be discussed later. Since the symmetry of the HOMO (H) (LUMO (L)) is odd (even) with respect to the Pb atom, the matrix element of H-L (H-L and L-L) is the odd (even) function with respect to $k$.

The energy band $E_j(k)$ and the wave function $\Psi_j(k)$, $(j = 1, 2, \ldots, 8)$ is calculated from

$$\hat{H}(k)\Psi_j(k) = E_j(k)\Psi_j(k),$$

where $E_1 > E_2 > \cdots > E_8$. Since the energy band formed by fully occupied HOMOs and empty LUMOs is half-filled, we examine the gap defined by

$$E_g(k) = \min(E_4(k) - E_5(k)),$$

for all $k$ in the Brillouin zone. The Dirac point $k_D$ is obtained from $E_g(k_D) = 0$, which leads to a nodal line.

We also examine the nodal line using an effective Hamiltonian given by

$$H_{\text{eff}}(k) = \left( \begin{array}{ccc} f_0(k) + f_4(k) & f_2(k) & f_0(k) - f_5(k) \\ f_4(k) & f_2(k) & f_0(k) + f_5(k) \\ f_0(k) - f_5(k) & f_4(k) & f_2(k) \end{array} \right),$$

where $f_0(k)$, $f_4(k)$, and $f_2(k)$ are calculated as follows. Hamiltonian is divided into three $8 \times 8$ matrices as

$$\hat{H} = \hat{H}_{\text{H-H}} + \hat{H}_{\text{L-L}} + \hat{H}_{\text{H-L}},$$

where $[\hat{H}_{\text{H-H}}]_{\alpha, \beta} = h_{\alpha, \beta}$ with $\alpha, \beta = \text{H1, H2, H3, H4}$ and 0 otherwise, $[\hat{H}_{\text{L-L}}]_{\alpha, \beta} = h_{\alpha, \beta}$ with $\alpha, \beta = \text{L1, L2, L3, L4}$ and 0 otherwise, $[\hat{H}_{\text{H-L}}]_{\alpha, \beta} = h_{\alpha, \beta}$ with $\alpha = \text{H1, H2, H3, H4}$ (or L1, L2, L3, L4) and $\beta = \text{L1, L2, L3, L4}$ (or H1, H2, H3, H4) and 0 otherwise. We define $E_{\text{HLL}}(k)$ (or $E_{\text{HHL}}(k)$) as the maximum (minimum) eigenvalue of HOMO (LUMO), which are obtained from $\hat{H}_{\text{H-H}} [\Psi_{\text{H}}] = E_{\text{HLL}}(k) [\Psi_{\text{H}}]$ and $\hat{H}_{\text{H-L}} [\Psi_{\text{L}}] = E_{\text{HHL}}(k) [\Psi_{\text{L}}]$. Note that $[\Psi_{\text{H}}]$ and $[\Psi_{\text{L}}]$ are eigenvectors at each $k$. Thus, we obtain $f_0(k) = (E_{\text{HLL}}(k) + E_{\text{LHL}}(k))/2$, $f_4(k) = (E_{\text{HLL}}(k) - E_{\text{LHL}}(k))/2$, and $f_2(k) = \langle \Psi_{\text{H}} | r H_{\text{H-L}} | \Psi_{\text{L}} \rangle = \langle \Psi_{\text{L}} | H_{\text{H-L}} | \Psi_{\text{H}} \rangle$. Quantities $f_0(k)$, $f_2(k)$, and $f_4(k)$ can be taken as real.\(^{34}\) Note that $f_0(k) = f_0(-k)$, and $f_2(k) = f_2(-k)$ owing to the time reversal symmetry and $f_4(k) = -f_4(-k)$ owing to the different parity of HOMO and LUMO. The nodal line is obtained from $f_3(k) = 0$ and $f_2(k) = 0$. In the next section, we examine these surfaces of $f_2(k) = 0$ and $f_3(k) = 0$ in the three-dimensional momentum space.

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**Fig. 1.** (Color online) Molecular arrangement and intermolecular couplings that explain crystal structure of [Pd(dddt)$_2$].\(^{11}\)
3. Results

3.1 Band structure with Dirac cone

In Fig. 2, the energy band structure is shown, where the origin of the energy is taken at the Fermi energy $E_F$. In spite of rather large differences in transfer energies, the essential shape of the band structure, including the nodal line semimetal state, is very similar to that of the previous model. The band crossing occurs on the line between TRIMs $\Gamma$ and $Y$. The corresponding energy is slightly lower than the Fermi energy ($E_F$) leading to an electron pocket.

Here we mention the Dirac point obtained from $E_4(k_D) = 0$, i.e., $E_4(k_D) = E_5(k_D)$, which provides a line in the three-dimensional momentum space. Figure 3 shows Dirac points forming a closed line (loop), which is symmetric with respect to $k_y = 0$. Compared with the previous case of Ref. 11, the loop is almost coplanar and located within the first Brillouin zone. The variation of the energy at the Dirac point along the line is very small as shown in the next paragraph.

Results of the calculation are summarized as follows. The energy band of the $8 \times 8$ model in Fig. 2 reproduces the overall behavior of the previous result that is obtained based on the DFT. This is partially because the nature of main transfer energies including $b_{1H}$ and $b_{2L}$ does not change. Dirac points form a nodal loop in the first Brillouin zone (Fig. 3). The axis of the cone changes along the line and the axis at $k_z = 0$ is almost perpendicular to that at $k_y = 0$. The energy at the Dirac points varies along the nodal line but the deviation from the Fermi energy is very small, $\sim \pm 0.4$ meV, which is smaller (electron pocket) around $k_z = 0$ and larger (hole pocket) around $k_y = 0$. Thus the electronic state is expected to have a two-dimensional character of the Dirac cone, as shown later in DOS.

In order to consider a role of the direct interlayer HOMO-LUMO couplings in the Dirac cone formation, we examine a reduced $4 \times 4$ Hamiltonian obtained from Eq. (1) by discarding states $[H2], [H4], [L1]$, and $[L3]$ i.e.,

$$H_{red} = \sum_k \sum_{\alpha',\beta'} h_{\alpha',\beta'}(k) |k, \alpha'\rangle \langle k, \beta'|$$

$$= \sum_k \Phi_4(k) \hat{H}_{4x4}(k) \Phi_4(k),$$

with $\alpha', \beta' = H1, H3, L2$, and $L4$ and $\langle \Phi_4(k) | = \langle H1\rangle \langle H3\rangle \langle L2\rangle \langle L4\rangle$). This reduced model of $4 \times 4$ Hamiltonian well reproduces the four energy bands of Fig. 2 around the Fermi level (Figs. 4(a) and 4(b)). This means that the Dirac points originate from the HOMO bands in layer 1 and the LUMO bands in layer 2. Figures 4(c) and 4(d) show that the Dirac cone vanishes, when the HOMO-LUMO couplings becomes zero ($h_{H1L2} = h_{H1L4} = h_{H3L2} = h_{H3L4} = 0$). From Figs. 4(b) and 4(d), it turns out that the Dirac points (nodal line) emerge when the HOMO and LUMO bands meet without the HOMO-LUMO couplings on the special points ( the Dirac points). That is, the nodal line is an intersection of the surface of $f_2(k) = 0$ and that of $f_3(k) = 0$, each of which forms a cylinder and a plane in the three-dimensional momentum space, respectively (Fig. 5). Note that Fig. 5 displays a qualitative behavior, since the surfaces, i.e. $f_2(k)$ and $f_3(k)$ are evaluated by the perturbation method.

Further, the global band structure of Fig. 6, in which the direct HOMO-LUMO couplings corresponding to the $4 \times 4$ model are discarded, still resembles that of Fig. 2. This fact also suggests an additional mechanism of forming the Dirac point by inducing a HOMO-LUMO interaction through a process of 2nd order perturbation as demonstrated in Ref. 10. We return this point later in the discussion of DOS.

3.2 DOS

We examine the density of states (DOS), $D(\omega)$ per unit cell, which is defined by

$$D(\omega) = \frac{1}{N} \sum_k \delta(\omega - E_{\gamma}(k)).$$

A chemical potential $\mu$ corresponding a half-filled band is obtained from $4 = \int_{\mu}^{\infty} d\omega \ D(\omega)$.

Figure 7 shows DOS for both $8 \times 8$ Hamiltonian (line (1)) and $4 \times 4$ Hamiltonian (line(2)), where the latter
that the direct HOMO-LUMO interaction is crucial for the present Dirac electron. This can be understood by comparing with the line (3), which is obtained by discarding the direct HOMO-LUMO interaction in 8 × 8 Hamiltonian (Eq. (1)). The line (3) corresponds to the energy band of Fig. 6, and is similar to that in the previous paper.\cite{12} There is a qualitative difference in DOS between the line (1) and line (3) in the sense that the linear dependence of DOS around \( \omega - \mu \) in lines (1) and (2) suggests almost a zero-gap state (ZGS) and is robust, i.e., displaying a wide energy region of linear dependence due to the direct HOMO-LUMO interaction, which is in contrast to that of the line (3) without the direct HOMO-LUMO interaction. A detailed analysis close to \( \omega = \mu \) shows that the deviation of \( D(\omega) \) form the linear dependence occurs in the narrow region of \(|\omega - \mu| < 0.001\) suggesting that the variation of the energy on the nodal line is less than 0.001.

Here we note that such a linear dependence of DOS has been found in two-dimensional organic conductor \( \alpha \)-ET\(_2\)I\(_3\), which is the first material of Dirac electron.
in molecular conductor. \(^{30-32}\) The similarity of DOS for Pd(dddt\(_2\)) and that for \(\alpha\)-ET\(_2\)\(I_2\) suggests that such a three-dimensional nodal line semimetal shares a common feature with two-dimensional Dirac cone.

Further, we note that the linear dependence is given by \(D(\omega) = K |\omega - \mu|\) with a coefficient \(K \propto v^{-2,33}\) where \(v\) denotes an averaged velocity of the Dirac cone. Since \(K\) of the lines (1) and (2) is smaller than that of the line (3), the former velocity is larger than the latter one suggesting that \(f_2(k)\) in Eq. (4) of the former is larger than that of the latter. This is reasonable since the direct HOMO-LUMO interaction is present in lines (1) and (2) but is absent in the line (3).

### 3.3 Parity at TRIM

In order to analyze the Dirac point, we consider the parity at the TRIM given by \(G/2\) with \(G\) being the reciprocal lattice vector, where \(G/2 = (0, 0, 0), (1/2, 0, 0), (0, 1/2, 0), (0, 0, 1/2)\), and \((1/2, 1/2, 0)\) correspond to the \(\Gamma\), X, Y, and M points and \(G/2 = (0, 0, 1/2), (1/2, 0, 1/2), (0, 1/2, 1/2)\), and \((1/2, 1/2, 1/2)\) correspond to the Z, D, C, and E points, respectively.

The inversion with respect to a Pd atom of the molecule 1 in the crystal structure gives the matrix for the translation of the basis (H1, H2, \(\cdots\), L4), \(\hat{P}(G/2)\), expressed as\(^{11}\)

\[
\hat{P}(k) = \begin{pmatrix}
\hat{P}_1(k) & 0 \\
0 & -\hat{P}_1(k)
\end{pmatrix},
\]

(8)

where \(\hat{P}_1(k)\) denotes a \(4 \times 4\) matrix,

\[
\hat{P}_1(k) = \begin{pmatrix}
-1 & 0 & 0 & 0 \\
0 & -X Y Z & 0 & 0 \\
0 & 0 & -X Y & 0 \\
0 & 0 & 0 & -Z
\end{pmatrix}.
\]

(9)

A relation \((\hat{P}(k))_{H_j H_i} = -(\hat{P}(k))_{H_j L_j}\) for \(j = 1, 2, 3, 4\) comes from a fact that the HOMO has ungerade symmetry and the LUMO has gerade symmetry. The eigenvalue and eigenfunction of \(\hat{P}(k)\) are obtained from \((\alpha = H_1, H_2, \cdots, L4)\)

\[
\hat{P}(k) u_{\alpha}(k) = p_{\alpha}(k) u_{\alpha}(k),
\]

(10)

where \(p_{\alpha}(k) = \langle \hat{P}(k) \rangle_{\alpha, \alpha}, u_{H_1}(k) = u_1 = (1, 0, 0, 0, 0, 0, 0, 0, 0)^t, u_{H_2} = u_2 = (0, 1, 0, 0, 0, 0, 0, 0, 0)^t, \cdots,\) and \(u_{L_4} = u_8 = (0, 0, 0, 0, 0, 0, 0, 0, 1)^t\). At the TRIM, one obtains \(p_{\alpha}(G/2) = p_{\alpha} = \pm 1\), which gives an even (odd) parity. The parity \(p_{\alpha}(G/2)\) is listed in Table II. From Eq. (8), it is obvious that \(\hat{P}(G/2) = 0\), i.e., the number of the even parity is the same as that of the odd parity.

Since \(\hat{P}(G/2), \tilde{H}(G/2) = 0\), \(\Psi_j(G/2)\) in Eq. (11) is also an eigenfunction of \(\hat{P}(G/2)\). The corresponding equation at the TRIM is given by

\[
\hat{P}(G/2) \Psi_j(G/2) = E_P(j, G/2) \Psi_j(G/2),
\]

(11)

with \(E_P(j, G/2) = \pm 1\), which denotes an even (odd) parity. In terms of \(u_l(G/2), \Psi_j(G/2)\) is expressed as

\[
\Psi_j(G/2) = \sum_i d_{j,i}(G/2) u_l(G/2).
\]

(12)

Since \(\hat{P}(G/2) u_l(G/2) = p_l(G/2) u_l(G/2)\) with \(p_l(G/2) = \pm 1\), it turns out that \(d_{j,i}(G/2) = 0\) for \(p_l(G/2) \neq E_P(j, G/2)\). Thus, the wave function for \(E_P(j, G/2)\) is given by a linear combination of the base \(u_l(G/2)\), which has the same parity as \(E_P(j, G/2)\).

From Eqs. (11) and (12), \(E_P(j, G/2)\) is estimated as

\[
E_P(j, G/2) = \Psi_j(G/2)^\dagger \hat{P}(G/2) \Psi_j(G/2) = \sum_{l=1}^{8} p_l(G/2) |d_{j,i}|^2,
\]

(13)

which is utilized for the present numerical calculation. \(E_P(j, G/2)\) is shown as a function of \(E_i(G/2)\) for the respective TRIM. The sign of some elements in Table III, is different from that of the previous calculation.\(^{11}\) However, as shown later, the resultant conditions for the Dirac points are unchanged, since both share a common feature of a nodal line. Note that \(\sum_j p_{E_j}(G/2) = 0\) for the respective TRIM. For the wave function \(\Psi_j(G/2)\) in Eq. (11) at the \(\Gamma\) and M points, the even (odd) parity corresponds to LUMO (HOMO).

In order to examine the nodal loop between \(E_4(k)\) and \(E_5(k)\), we calculate \(P_5\) \(\delta = 1\) for \(k_z = 0, \delta = 2\) for \(k_y = 0, \delta = 3\) for \(k_x = 0.5\), which is defined as\(^{11}\)

\[
P_1 = \sum_{j=5}^8 P_{E_j}(\Gamma) P_{E_j}(X) P_{E_j}(Y) P_{E_j}(M),
\]

(14a)

\[
P_2 = \sum_{j=5}^8 P_{E_j}(Z) P_{E_j}(\Gamma) P_{E_j}(X) P_{E_j}(D),
\]

(14b)

\[
P_3 = \sum_{j=5}^8 P_{E_j}(Z) P_{E_j}(D) P_{E_j}(E) P_{E_j}(C).
\]

(14c)

Since we examine the Dirac point of the level crossing between \(E_4\) and \(E_5\) bands owing to a half-filled band, we take \(j = 5, 6, 7,\) and 8. Each \(P_5\) denotes a quantity assigned on a plane including the four corresponding TRIMs. The condition for the Dirac point between \(E_4\) and \(E_5\) is given by \(P_5 = \pm 1\).\(^{15}\) When \(P_5 = -1\), the number of pairs of Dirac points between \(E_4\) and \(E_5\) is odd,\(^{36,37}\) implying that the topological number is 1. The condition for a nodal line is given by\(^{11}\)

\[
P_1 P_3 = -1,
\]

(15)

Note that Eqs. (14a), (14b), and (14c) describe the condition of the Dirac point on the planes of \(k_z = 0\) (TRIM with the \(\Gamma, X, Y, \text{and } M\) points) and \(k_y = 0\) (TRIM with the Z, \(\Gamma, X, \text{and } D\) points), and \(k_z = 0.5\) (TRIM with the Z, D, C, and E points), respectively. The nodal closed loop is found for \(P_1 = -1, P_2 = -1,\) and \(P_3 = 1\). Note
the parity for nodal line semimetal of [Pt(dmdt)$_2$] with open line$^{16}$ is given by $P = 1^{17}$ instead of Eq. (15).

Here we examine the reduced 4 × 4 Hamiltonian with the base of H1, H3, L2, and L4 by discarding the elements corresponding to H2, H4, L1, and L3. Instead of eight bands, we obtain four bands $E_1(k)$, $E_2(k)$, $E_3(k)$, and $E_4(k)$. In this case, the inversion matrix is given by

$$
P_{4 \times 4}(k) = \begin{pmatrix}
-1 & 0 & 0 & 0 \\
0 & -XY & 0 & 0 \\
0 & 0 & XYZ & 0 \\
0 & 0 & 0 & Z
\end{pmatrix}.
$$

(16)

The parities are listed in Table IV. Noting that the filled band is given by $E_j$ with $j$ = 3 and 4, we obtain also the closed nodal line since $P(k_z = 0) = -1$, $P(k_x = 0) = -1$, and $P(k_x = \pi) = 1$.

Here we comment on the parity of the 4 × 4 reduced Hamiltonian, which is different from the conventional one. A relation $\sum_{G} \bar{P}(G) = 0$ holds for the latter case but does not for $G = Z$ and E of the former, in which Pd atom is not the inversion center due to discarding H2, H4, L1, and L3. Thus, we construct an effective 8 × 8 Hamiltonian by adding 4 bases of H2, H4, L1, and L3 with only site energies, which are much higher (lower) than $E_j$, ($j = 1, \cdots, 4$) for H2 and H4 (L1 and L3). In this case, energies are obtained as $E_a > E_b \gg E_1 > E_2 > E_3 > E_4 \gg E_c > E_d$, where $E_1, \cdots, E_4$ are the same as those of 4 × 4 Hamiltonian. We obtain the additional parity as $(P_{E(\Gamma)}$, $P_{E(X)}$, $P_{E(Y)}$, $P_{E(M)}$, $P_{E(Z)}$, $P_{E(D)}$, $P_{E(C)}$, $P_{E(E)}) = (-, -, -, -, -, -, -)$ for $E = E_4$, $(+, +, +, +, +, +, -)$ for $E = E_0$, $(+, +, +, +, +, +, +)$ for $E = E_d$, respectively. It turns out that the resultant parity satisfies $\sum_{G} \bar{P}(G) = 0$ and the parity relevant to $E_1, E_2, E_3$ and $E_4$ remains the same as Table IV.

4. Conclusions

We have examined a nodal line semimetal in a single component molecular conductor [Pd(dddt)$_2$] under high pressure, which consists of two layers of HOMO and LUMO. Based on the synchrotron X-ray diffraction measurements at 5.9 GPa, we derive the TB model with both 8 × 8 and 4 × 4 matrix Hamiltonians. We have shown a mechanism of the nodal line formation, which is obtained as an intersection between a crossing plane of the HOMO and LUMO bands and a plane of vanishing HOMO-LUMO interactions. Compared with our previous paper, a new finding is a crucial role of the direct HOMO-LUMO interaction between layer 1 and layer 2, which results in the robust Dirac cone within an energy height of ~ 0.01 eV. Such a fact was verified by calculating DOS, which also provides a width of energy band along the nodal line less than 0.4 meV. Finally, in the aspect of topology, we examined the parity for the nodal line in both 8 × 8 and 4 × 4 matrix Hamiltonians. The former one is essentially the same as the previous one, while the latter is different from the conventional 4 × 4 matrix Hamiltonian but can be interpreted in a consistent way.

Acknowledgements

We acknowledge Diamond Light Source for time on Beamline I19-2 under Proposal MT20934-1 and we thank Dr. Dave Allan and Dr. Lucy Saunders for their assistance. This work was supported by JSPS KAKENHI Grant, JP16H06346.

Appendix A: Crystal data of [Pd(dddt)$_2$] at 5.9 GPa

Space group: $P2_1/n$

Lattice constants: $a_0 = 16.48$, $b_0 = 4.3102$, $c_0 = 17.480$ Å, $\beta_0 = 111.84^\circ$
Based on these data, fractional atomic coordinates are shown in Table A-1.

In the calculation, we define the following new cell \( a = (a_o + c_o), b = -b_o, c = c_o \).

**Appendix B: Matrix elements of Hamiltonian**

Matrix elements for HOMO-HOMO (H-H) are given by

\[
\begin{align*}
    h_{H1,H1} & = b_{1H}(Y + \bar{Y}), \\
    h_{H1,H2} & = a_{1H}(XZ + Y) + a_{2H}(1 + XYZ), \\
    h_{H1,H3} & = p_{H}(1 + Y + X + XY), \\
    h_{H1,H4} & = c_{1H}(1 - \bar{Z}) + c_{2H}(Y + \bar{Y}Z), \\
    h_{H2,H2} & = b_{2H}(Y + \bar{Y}), \\
    h_{H2,H3} & = c_{1H}(1 + \bar{Z}) + c_{2H}(Y + \bar{Y}Z), \\
    h_{H2,H4} & = q_{H}(\bar{X}Z + \bar{Y}Z + \bar{X}Y\bar{Z}), \\
    h_{H3,H3} & = b_{1H}(Y + \bar{Y}), \\
    h_{H3,H4} & = a_{1H}(1 + \bar{X}Y\bar{Z}) + a_{2H}(\bar{X}Z + Y), \\
    h_{H4,H4} & = b_{2H}(Y + \bar{Y}), \\
\end{align*}
\]

Matrix elements for HOMO-LUMO (H-L) are given by

\[
\begin{align*}
    h_{H1,L1} & = c_{1H}(1 - \bar{Z}) + c_{2H}(Y - \bar{Y}Z), \\
    h_{H2,L1} & = a_{1H}(\bar{X}Z - \bar{Y}) + a_{2H}(1 - \bar{X}Y\bar{Z}), \\
    h_{H2,L2} & = b_{2H}(Y - \bar{Y}), \\
    h_{H2,L3} & = c_{1H}(\bar{Z} - 1) + c_{2H}(\bar{Y} - Y\bar{Z}), \\
    h_{H2,L4} & = q_{1H}(\bar{X}Y\bar{Z} - \bar{Z}) + q_{2H}(\bar{X}Y\bar{Z} - \bar{Z}), \\
    h_{H3,L1} & = p_{1H}(\bar{X} - \bar{Y}) + p_{2H}(\bar{X}Y - 1), \\
    h_{H3,L2} & = c_{1H}(1 - \bar{Z}) + c_{2H}(Y - \bar{Y}Z), \\
    h_{H3,L3} & = b_{1H}(\bar{Y} + \bar{Y}), \\
    h_{H3,L4} & = a_{1H}(1 - \bar{X}Y\bar{Z}) + a_{2H}(Y - \bar{X}Z), \\
    h_{H4,L1} & = c_{1H}(1 - \bar{X}Y\bar{Z}) + c_{2H}(Y - \bar{X}Z), \\
    h_{H4,L4} & = b_{2H}(\bar{Y} - Y),
\end{align*}
\]

Matrix elements for LUMO-LUMO (L-L) are given by

\[
\begin{align*}
    h_{L1,L1} & = \Delta E + b_{1L}(Y + \bar{Y}), \\
    h_{L1,L2} & = a_{1L}(XZ + Y) + a_{2L}(1 + XYZ), \\
    h_{L1,L3} & = p_{L}(1 + Y + X + XY), \\
    h_{L1,L4} & = c_{1L}(1 + \bar{Z}) + c_{2L}(Y + \bar{Y}Z), \\
    h_{L2,L2} & = \Delta E + b_{2L}(Y + \bar{Y}), \\
    h_{L2,L3} & = c_{1L}(1 + \bar{Z}) - c_{2L}(\bar{Y} + Y\bar{Z}), \\
    h_{L2,L4} & = q_{L}(\bar{X}Z + \bar{Y}Z + \bar{X}Y\bar{Z} + \bar{Z}), \\
    h_{L3,L3} & = \Delta E + b_{1L}(Y + \bar{Y}), \\
    h_{L3,L4} & = -a_{1L}(1 + \bar{X}Y\bar{Z}) - a_{2L}(\bar{X}Z + Y), \\
    h_{L4,L4} & = \Delta E + b_{2L}(Y + \bar{Y}).
\end{align*}
\]
14) Z. Liu, H. Wang, Z. F. Wang, J. Yang, and F. Liu, Phys. Rev. B \textbf{97}, 155138 (2018).
15) Y. Suzumura, T. Tsumuraya, R. Kato, H. Matsuura, and M. Ogata, J. Phys. Soc. Jpn. \textbf{88}, 124704 (2019).
16) B. Zhou, S. Ishibashi, T. Ishii, T. Sekine, R. Tkehara, K. Miyagawa, K. Kanoda, E. Nishibori, and A. Kobayashi, Chem. Commun. \textbf{55}, 3327 (2019).
17) R. Kato and Y. Suzumura, J. Phys. Soc. Jpn. \textbf{89}, 044713 (2020).
18) T. Kawamura, D. Ohki, B. Zhou, A. Kobayashi, and A. Kobayashi, J. Phys. Soc. Jpn. \textbf{89}, 074704 (2020).
19) S. Murakami, New J. Phys. \textbf{9}, 356 (2007).
20) A. A. Burkov, M. D. Hook, and L. Balents, Phys. Rev. B \textbf{84}, 235126 (2011).
21) Y. Kim, B. J. Wieder, C. L. Kane, and A. M. Rappe, Phys. Rev. Lett. \textbf{115}, 036806 (2015).
22) A. Yamakage, Y. Yamakawa, Y. Tanaka, and Y. Okamoto, J. Phys. Soc. Jpn. \textbf{85}, 013708 (2016).
23) C. Fang, H. Weng, X. Dai, and Z. Fang, Chinese Physics B \textbf{25}, 117106 (2016).
24) Y. Suzumura and A. Yamakage, J. Phys. Soc. Jpn. \textbf{87}, 093704 (2018).
25) S.-Y. Yang, H. Yang, E. Derunova, Stuart S. P. Parkin, B. Yan, and Mazhar N. Ali, Advances in Physics, X \textbf{3}, 1414631 (2018).
26) M. Hirayama, R. Okugawa, T. Miyake, and S. Murakami, Nat. Commun. \textbf{8}, 14022 (2017).
27) M. Hirayama, R. Okugawa, and S. Murakami, J. Phys. Soc. Jpn. \textbf{87}, 041002 (2018).
28) A. Bernevig, H. Weng, Z. Fang, and X. Dai, J. Phys. Soc. Jpn. \textbf{87}, 041001 (2018).
29) H. B. Cui, R. Kato, T. Minamidate, and H. H.-M. Yeung, to be submitted.
30) A. Kobayashi, S. Katayama, K. Noguchi, and Y. Suzumura, J. Phys. Soc. Jpn. \textbf{73}, 3135 (2004).
31) S. Katayama, A. Kobayashi, and Y. Suzumura, J. Phys. Soc. Jpn. \textbf{75}, 054705 (2006).
32) S. Katayama, A. Kobayashi, and Y. Suzumura, Eur. Phys. J. B \textbf{67}, 139 (2009).
33) S. Katayama, A. Kobayashi, and Y. Suzumura, J. Phys. Soc. Jpn. \textbf{75}, 023708 (2006).
34) F. Piéchon and Y. Suzumura, J. Phys. Soc. Jpn. \textbf{82}, 123703 (2013).
35) C. Herring, Phys. Rev. \textbf{52}, 365 (1937).
36) L. Fu and C.L. Kane, Phys. Rev. B \textbf{76} (2007) 045302.
37) F. Piéchon and Y. Suzumura, J. Phys. Soc. Jpn. \textbf{82}, 033703 (2013).