Molecular orbital polarization in $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$: microscopic route to metal-metal transition without spontaneous symmetry breaking

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Ordered phases such as charge- and spin-density wave states accompany either full or partial gapping of Fermi surface (FS) leading to a metal-insulator or metal-metal transition (MMT). However, there are examples of MMT without any signatures of symmetry breaking. One example is $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$, where a partial gapping of FS is observed but a density wave ordering has not been found. Here we propose a microscopic mechanism of such a MMT which occurs due to a momentum dependent spin-orbit coupled molecular orbital polarization. Since a molecular $d$ orbital polarization is present due to a small spin-orbit coupling of Ti, there is no spontaneous symmetry breaking involved. However, a sharp increase of polarization happens above a critical electron interaction which gaps out the $d$ orbital FS and reduces the density of states significantly, while the rest of FS associated with Sb $p$ orbitals is almost intact across MMT. Experimental implications to test our proposal and applications to other systems are also discussed.

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FIG. 1. (Color online) Schematic figures illustrating evolution of electronic structures in NTSO upon inclusion of spin-orbit coupling (SOC) and on-site Coulomb interaction $U$. (a) and (b) show schematic band structures near three special $k$ points and Fermi surfaces without and with the presence of SOC. As depicted in (c), the Coulomb interaction enhances the polarization ($\lambda$) of the spin-orbit coupled molecular orbital (SO-MO) states near M point. Line colors depict the orbital character as shown in the figure, and thicker lines represent the states affected by inclusion of SOC.

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Introduction – Fermi surface (FS) is one of the most important concepts in solid state physics, and exists in every metal, semimetal, and doped semiconductors. Many ordered phases such as charge- and spin-density waves, and superconductivity can be regarded as FS instabilities. Such ordered phases accompany broken symmetries involving either translation, time-reversal, or charge conservation symmetries. As a consequence, either full or partial gapping of FS occurs with anomalies in spin susceptibility, specific heats, and resistivity at a critical temperature $T_c$[1].

However, there are examples of metallic systems which undergo a phase transition to a metallic state with a partial gapping of FS at lower temperatures without any detection of spontaneous symmetry breaking. A widely studied example is $\text{URu}_2\text{Si}_2$ where both $f$ and $d$ orbitals are relevant and a low-temperature metallic phase is associated with a hidden order, implying difficulties of identifying the order parameter[2, 3]. A less studied material is $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ (NTSO), where a partial gapping of FS is observed but a density wave ordering has not been found. Here we propose a microscopic mechanism of such a MMT which occurs due to a momentum dependent spin-orbit coupled molecular orbital polarization. Since a molecular $d$ orbital polarization is present due to a small spin-orbit coupling of Ti, there is no spontaneous symmetry breaking involved. However, a sharp increase of polarization happens above a critical electron interaction which gaps out the $d$ orbital FS and reduces the density of states significantly, while the rest of FS associated with Sb $p$ orbitals is almost intact across MMT. Experimental implications to test our proposal and applications to other systems are also discussed.

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In this work, we provide a microscopic route to MMT without spontaneous symmetry breaking in NTSO [15]. Fig. 1 illustrates our proposal; a momentum-dependent polarization of molecular orbitals (MO), which is induced by the cooperation of spin-orbit coupling (SOC) and the on-site Coulomb interaction inherent in Ti 3$d$ orbital, gaps out a significant fraction of FS while leaving the rest of FS intact, so that the system remains metallic. As shown in Fig. 1(a), the system has three Fermi surfaces with atomic Sb $p$, Ti $d$, and MO originating from Ti $d$ orbitals at $\Gamma$, $X$, and M points in the Brillouin
zone, respectively. Degeneracies at $\Gamma$ and $M$ points are protected by crystal and SU(2) spin rotational symmetries, thus introduction of SOC of $Sb$ $p$ and $Ti$ $d$ lifts degeneracies at $\Gamma$ and $M$ respectively. Due to the smallness of Ti SOC, it makes a tiny gap at $M$ point and the MO states evolve into spin-orbit coupled MO (SO-MO) states as shown in Fig. 1(b). Inclusion of the Coulomb interaction sharply enhances the SO-MO polarization, such that a significant gap opens at $M$ point, reducing the FS area in $\Gamma$ and $X$ points to balance the charge as shown in Fig. 1(c). Neither lattice nor time-reversal symmetry (TRS) are broken in the resulting metallic state. Due to the lack of spontaneously broken symmetry MMT is a first-order phase transition, which we will discuss later. The spin-orbit coupled and anisotropic nature of the SO-MO states can explain the strong anisotropies in electronic and magnetic responses observed in recent experiments[9, 14]. While our theory is applied to NTSO, it can be generalized to a system with different orbital characters which compose FS, and undergoes a partial gapping of FS across MMT.

Structure and ab-initio calculations – Crystal structure of NTSO consists of neighboring $Ti_2Sb_2O$ layers with Na ions intercalated in between. As shown in Fig. 2(a), each $Ti_2Sb_2O$ layer is composed of a $Ti_2O$ square lattice and two $TiSb_2$ ribbons perpendicular to each other, with the unit cell containing two Ti sites in a NTSO layer ($Ti1$ and $Ti2$ shown in Fig. 2). The space group for the whole unit cell, which contains two NTSO layer, is $I4/mmm$ (No. 139), and for an isolated NTSO layer the layer group is $P4/mmm$ (No. 123).

Previous ab-initio studies showed that, strong hybridization between the $Ti$ $d$ and $Sb$ $p$ orbitals yields dispersive bands for both states so that the system has multiple Fermi surfaces with $d$ and $p$ orbital character as shown in Fig. 1[10, 11]. Contrary to the $p$ orbital pocket at $\Gamma$, which shows three-dimensional shape, the $d$ orbital pockets show weak dispersion along the layer-normal direction and considered as quasi-two-dimensional Fermi surfaces. While we simplify the system by choosing an isolated NTSO layer as a unit cell, comparison between the band structures from the full and our two-dimensional unit cells in Supplementary Material[16] shows almost unaffected $d$ bands near the zone boundary by the layer stacking.

Fig. 2(a) shows the $Ti$ $d$ orbitals which contribute to the bands near the Fermi level: $\{ |d_{xy}\rangle_1, |d_{xy}\rangle_2\}$ and $\{ |d_{xy}\rangle_3, |d_{xy}\rangle_4\}$ for $Ti1$ and $Ti2$ respectively, where the subscripts 1 and 2 denote the Ti atoms to which the orbitals belong. The hybrid $|d_{xy}\rangle_1,|d_{xy}\rangle_2$ orbitals are defined as linear combinations of $e_g$ orbitals such that $|d_{xy}\rangle_1 = -a|d_{x^2-y^2}\rangle_1 - b|d_{3z^2-r^2}\rangle_1$ and $|d_{xy}\rangle_2 = +a|d_{x^2-y^2}\rangle_2 - b|d_{3z^2-r^2}\rangle_2,$ where the real coefficients $a$ and $b$ are determined by the ligand fields. Note that, $|d_{xy}\rangle_1,|d_{xy}\rangle_3$ are dominated by $|d_{3z^2-r^2}\rangle_1$ and $|d_{xy}\rangle_2,|d_{xy}\rangle_4$ respectively in our system, and $|d_{xy}\rangle_1$ and $|d_{xy}\rangle_3$ are transformed to $-|d_{xy}\rangle_2$ and $|d_{xy}\rangle_2$ respectively by the $C_4$ rotation depicted in the figure. Left panel of Fig. 2(b) shows the bands without SOC where the orbital weights of $Sb$ $p$ and $|d_{xy}\rangle_1,|d_{xy}\rangle_2$ states are represented as the size of the corresponding symbols. The $|d_{xy}\rangle_1,|d_{xy}\rangle_2$ weight is concentrated on the X-M line as shown in the right panel in the figure.

Both the $\Gamma$ and $M$ points have $D_{4h}$ point group symmetry which allows the presence of quadratic band touching points located just below the Fermi level, as can be seen in Fig. 2(b). At $\Gamma$ point, the band touching consists of $Sb$ atomic $p_x$ and $p_y$ orbitals where degeneracy of the orbitals is compatible with the $Sb$ site symmetry ($C_{4v}$). On the contrary, the band touching at $M$ point has dominant $d$ character and described by molecular orbitals (MO). Without considering spin, two degenerate Bloch states at $M$ point which we denote as $|\alpha\rangle$ and $|\beta\rangle$ are expressed as follows,

$$|\alpha\rangle = \sum_R e^{ik_M \cdot R} \left( |d_{xy}\rangle_{R,1} + |d_{xy}\rangle_{R,2} \right),$$

$$|\beta\rangle = \sum_R e^{ik_M \cdot R} \left( -|d_{xy}\rangle_{R,1} - |d_{xy}\rangle_{R,2} \right),$$

where $k_M = \left( \frac{\pi}{2}, \frac{\pi}{2} \right)$, $R$ and $\{1, 2\}$ are indices for Bravais lattice and Ti sublattices respectively. Fig. 2(c) shows the
Like the Sb dotted squares depict the primitive and the enlarged unit cell. Schematic illustrations of the states, where the dashed and dotted squares depict the primitive and the enlarged unit cell. Like the Sb \(p_x\) and \(p_y\) orbitals at \(\Gamma\) point, they belong to the \(E_u\) irreducible representation, which are odd under spatial inversion and transforms as \((C_4)_v^2|\alpha\rangle = C_4|\beta\rangle = -|\alpha\rangle\). There is additional degeneracy due to the \(SU(2)\) symmetry in the spin subspace without the presence of SOC, so the band touching at M point is fourfold degenerate and protected by the \(SU(2)\) and crystal symmetries. Unless either the spin or the crystal symmetry is lifted, the degeneracy at M point remain robust, and our LDA+\(U\) calculation without including SOC and keeping paramagnetic constraint confirms it (See Supplementary Material).

Degeneracy lifting at \(\Gamma\) and \(M\) points via SOC – Below we discuss the effect of SOC. Intuitively, one expects a relatively large impact of SOC on Sb \(p\) orbitals while negligible on Ti \(d\) orbitals, as SOC in Ti is only about 20 meV. Indeed degenerate bands near \(\Gamma\) point made of \(p\) orbitals are split, and the gap between the two is about 0.4 eV. Each band is characterized by total angular momenta \(j = 1/2\) and \(3/2\) made of \(|L_z = \pm 1\rangle = |p_x \pm ip_y\rangle\) and spin-1/2 due to ligand field splitting of layer structure. As SOC is introduced, the \(SU(2)\) symmetry in the spin space is lifted, and the fourfold degeneracy at \(\Gamma\) is split into \(j = 1/2\) and 3/2 doublets as shown in Fig. 3(a). Hereafter we denote the orbital and total angular momenta for the atomic and MO states as lowercase and capital letters respectively.

Similarly, at M point, quenching of planar orbital moment components happens in the MO space \(|\{\alpha\}, |\beta\}\rangle\). Projecting the Ti total angular momentum operators \(\hat{L} \equiv \hat{L}^{11} \oplus \hat{L}^{11'} \oplus \hat{L}^{12} \oplus \hat{L}^{12'}\) onto the space yields \(L_z\) as the only nonvanishing component, which is diagonalized with the basis choice of \(|L_z^{\pm}\rangle \equiv |\alpha \mp i\beta\rangle\) where \(L_{z}^{\pm} \approx \pm \sqrt{3}\) in this system [17]. In the presence of Ti SOC, the \(|L_z^{\pm}\rangle\) states are split into two spin-orbit coupled MO (SO-MO) doublets which are characterized by total angular momenta \(J = (|L_z^{\pm}| + \frac{1}{2}) \equiv J^{+}\) and \((|L_z^{\pm}| - \frac{1}{2}) \equiv J^{-}\). Note that both \(J^{+}\) and \(J^{-}\) form doublets with \(J^z = \pm (|L_z^{\pm}| + \frac{1}{2})\) and \(J_z = \pm (|L_z^{\pm}| - \frac{1}{2})\), respectively, and \(J^{+}\) doublet is higher in energy than \(J^{-}\) by 20 meV at M point as shown in the inset of Fig. 3(a).

Molecular orbital polarization enhanced by on-site Coulomb interaction – The size of the gap opening can be quantified by defining the MO polarization operator \(\hat{p} \equiv \hat{n}_{j^-} - \hat{n}_{j^+}\), where \(\hat{n}_{j^\pm}\) are number operators for the \(J^\pm\) subspaces. SOC in the MO space can be rewritten by employing the MO polarization operator as \(\hat{H}_{SO} = -\lambda_{Ti}/2\). Due to the minus sign, \(\hat{H}_{SO}\) favors positive MO polarization, but its magnitude is tiny because of the small \(\lambda_{Ti} \sim 20\) meV as can be seen in the PDOS of Fig. 3(a). However, once the degeneracy at M is lifted, the size of the splitting can be further enhanced, and inclusion of on-site Coulomb interaction does the role in this case.

Like \(\hat{H}_{SO}\), the LDA+\(U\) correction to the Ti on-site potential introduced by the Coulomb interaction can be projected onto the MO space. It can be rewritten in terms of \(\hat{p}\) as follows:

\[
\hat{V}_U \equiv U_{\text{eff}} \left[\frac{1}{2} - \frac{\langle \hat{n} \rangle}{4}\right]\hat{n} - \frac{\langle \hat{p} \rangle}{2}\hat{p},
\]

where \(U_{\text{eff}} \equiv U - J\) is the effective Coulomb interaction parameter, \(\hat{n} \equiv \hat{n}_{j^+} + \hat{n}_{j^-}\) is the total number operator, and expectation values are obtained by integrating over the Brillouin zone (detailed derivation is in Supplementary material). Combining it with \(\hat{H}_{SO}\), apart from the trivial constant term, yields

\[
\hat{H}_{SO} + \hat{V}_U = -\frac{\lambda_{Ti} + U_{\text{eff}}\langle \hat{p} \rangle}{2}\hat{p},
\]

so that the MO polarization \(\langle \hat{p} \rangle\) initiated by SOC can be further increased under the presence of \(U_{\text{eff}}\). Right panel in Fig. 3(a) shows the band structure and PDOS projected onto the SO-MO states with the presence of \(U_{\text{eff}} = 3\) eV. The gap at M point is allowed due to the loss of \(SU(2)\) symmetry via SOC, and is greatly enhanced by the inclusion of the Coulomb interaction. A normalized MO polarization \(P \equiv \langle \hat{p} \rangle / \langle \hat{n} \rangle\) as a function of \(U_{\text{eff}}\) is plotted in Fig. 3(b). One can see an abrupt change in \(P\) near \(U_{\text{eff}} = 2.2\) eV, where the bottom of the \((|L_z^{\pm}| + \frac{1}{2})\) band crosses the Fermi level and the electron-like Fermi pocket near M point disappears. Fig. 3(c) compares the Fermi surfaces with and without including \(U_{\text{eff}} = 3\) eV. To compensate the removal of the M point electron pocket, the size of hole-like pocket near X point also decreases, resulting
the half-reduction of the Fermi surface area. Such reduction of Fermi surface area, or equivalently the reduction of DOS at the Fermi level, is observed in several magnetic susceptibility and resistivity measurements\[6, 7, 9].

We also comment on the X pocket, which is less affected by the inclusion of $U_{\text{eff}}$ than the M pocket despite its dominant $|d_{x^2-y^2}\rangle_{1,2}$ character. Since the X pocket coexists with the $p$-originated $\Gamma$ pocket, the size of X pocket is determined by the on-site energy of $|d_{x^2-y^2}\rangle_{1,2}$ orbitals relative to that of Sb $p$. The $V_{ij}$ term, however, behaves as an effective SOC for the SO-MO states, and its contribution to the $|d_{x^2-y^2}\rangle_{1,2}$ on-site energy is not significant so that the X pocket remains even after inclusion of the Coulomb interaction. This is confirmed by examining the change of the on-site energies from the Wannier orbital calculations for the Ti $d$ states. Note also that, the Sb $j=3/2$ and $1/2$ states near $\Gamma$ are well polarized due to the large $\lambda_{\text{SO}}$, so they are less affected by the inclusion of $U_{\text{eff}}$.

**Discussion and Conclusion** – The notion of orbital polarization in transition metal compounds, which is induced by the Coulomb interaction in degenerate $d$ orbitals, usually accompanies symmetry lowering by the orbital-lattice coupling such as Jahn-Teller effect\[19–23]. In metallic systems, an orbital polarization also occurs\[24], but does not accompany a MMT for a fixed charge filling. The SO-MO polarization in our work is distinguished from previous studies since it accompanies a phase transition without spontaneous symmetry reduction.

For experimental validation of our proposal, one can take advantage of the anisotropy in the SO-MO states. Since the total angular momentum of the SO-MO states are fixed to be perpendicular to the Ti$_2$O plane, i.e. the absence of the in-plane angular momentum component, one direct consequence of the SO-MO formation is an anisotropic response to the external magnetic fields. A recent report on the magnetic susceptibility of NTSO shows such anisotropic behavior, where the $H//z$ susceptibility data shows drastic enhancement compared to the $H//xy$ result below the transition temperature\[9]. Such behavior is hard to understand in the conventional charge-density wave picture, but is consistent with our SO-MO polarization scenario; due to the absence of the $L_{x,y}$ components in the SO-MO space, the states should be more susceptible to $H//z$ compared to the in-plane fields.

Measuring the branching ratio in Ti $L_2$ and $L_3$ edge x-ray absorption spectroscopy (XAS) below $T_c$ can be another way to experimentally validate the MO polarization scenario\[25]. Note that, the unoccupied SO-MO state has total angular momentum of $j^+=\{(l^2+(1/2)}\}$, which is close to 5/2, for each Ti site. As a result, $L_3$ edge XAS is expected to show higher intensity more than twice that of $L_2$ edge, so that the ratio between the $L_3$ and $L_2$ channels should be larger then the statistical ratio 2:1. Also, phase-sensitive tools such as resonant x-ray scattering may probe the presence of SO-MO states, which revealed the presence of the spin-orbit-entangled $j_{\text{SO}}=1/2$ states in several iridate compounds with strong SOC\[26, 27].

Finally, we would like to mention the nature of the phase transition at $T_c$. Specific heat versus temperature data indicate significant loss of entropy at the transition. Previously this was considered as a signature of continuous phase transition by the density wave formation, but this feature can be explained within our SO-MO polarization scenario which results in entropy change by the reduction of the Fermi surface area. Since this process does not spontaneously break any symmetries in NTSO, it should be a first-order transition. We found a metastable phase with $P\sim 0$ in the regime $2.3 \leq U_{\text{eff}} \leq 4$ eV and its presence is robust independent of parameters and code choices (see Supplementary Material for details on the metastable state). Remarkably, hysteresis behavior in resistivity with unknown origin was reported previously\[7], indicating a possible first-order phase transition.

In summary, we propose an alternative scenario for the MMT in NTSO based on the SO-MO polarization induced by SOC and the Coulomb interaction. Our picture can be generalized to other systems with FS with mixed orbital characters and spontaneous phase transition with partial gapping out of FS without a symmetry breaking. Also, our picture calls attention to the role of SOC in 3$d$ transition metal compounds, which was considered insignificant in understanding the physics of such systems. Indeed, there are several reports about the role of the ostensibly small SOC, which cooperate with the Coulomb interaction and becomes a crucial element for the underlying physics\[28, 29]. Further studies on the role of SOC in previously known transition metal systems with high crystal symmetries can be an interesting future subject in this regard.

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[15] In this work we employed two ab-initio density functional theory codes: OPENMX[30, 31] and Vienna ab-initio Simulation Package[32, 33]. Note that we did not incorporate magnetism in our calculations. Detailed parameter set adopted in both of the calculations are in Supplementary Material.
[16] See Supplementary Material for computational detail and further information on electronic structures.
[17] Since $|de_{g}|_{1,2}=\mp a|d_{x^2-y^2}|_{1,2} -b|d_{3z^2-r^2}|_{1,2}$, the eigenvalues $L^\pm_\sigma$ are given as $\pm 2a^2/(a^2 + b^2)$. Our result gives roughly $a:b = 3:1$, which yields $L^\pm_\sigma \approx \pm \sqrt{3}$.
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