Large magnetoresistance and non-zero Berry phase in the nodal-line semimetal MoO$_2$

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We performed calculations of the electronic band structure and the Fermi surface as well as measured the longitudinal resistivity $\rho_{xx}(T,H)$, Hall resistivity $\rho_{xy}(T,H)$ and quantum oscillations of the magnetization as a function of temperature at various magnetic fields for MoO$_2$ with monoclinic crystal structure. The band structure calculations show that MoO$_2$ is a nodal-line semimetal when spin-orbit coupling is ignored. It was found that a large magnetoresistance reaching 5.03 $\times 10^{4}$% at 2 K and 9 T, its nearly quadratic field dependence and a field-induced up-turn behavior of $\rho_{xx}(T)$, the characteristics common for many topologically non-trivial as well as trivial semimetals, emerge also in MoO$_2$. The observed properties are attributed to a perfect charge-carrier compensation, evidenced by both calculations relying on the Fermi surface topology and the Hall resistivity measurements. Both the observation of negative magnetoresistance for magnetic field along the current direction and the non-zero Berry phase in de Haas-van Alphen measurements indicate that pairs of Weyl points appear in MoO$_2$, which may be due to the crystal symmetry breaking. These results highlight MoO$_2$ as a new platform materials for studying the topological properties of oxides.

I. INTRODUCTION

Since the discovery of first topological insulators fifteen years ago [1–3], the important role of the topology of electronic bands in condensed matter materials has been broadly recognized. In addition to topological insulators, semimetallic topological phases with a variety quasiparticles related to the Dirac [4, 5], Weyl [6, 7], nodal-line [8–10], nodal-chain [11, 12], nodal-link [13–15] band degeneracies, have been proposed and confirmed experimentally in a few dozens of materials. Topological electronic materials, as new quantum states of matter, attracted a lot of attention in the past ten years due to their promise for the development of devices with new functionalities. The search for novel topological phases and materials has become one of the most dynamic active directions of research in condensed matter physics and materials science. Recently, a number of groups [16–19] predicted thousands candidate topological materials by performing systematic high-throughput computational screening across the databases of known materials. However, the topological nature of most of these candidate topological materials yet has to be confirmed by experiments. According to the predictions, many conventional materials including those currently used in electronic devices, sensors, and as energy materials, also host topological phases. It thus becomes important to re-evaluate the physical properties of these materials from the topological view in anticipation of new technological applications.

MoO$_2$ has been widely investigated as a promising catalyst [20] for electro-catalytic or photocatalytic hydrogen evolution in aqueous solution, as an efficient electrode material for lithium ion batteries [21] and as a materials for supercapacitors [22]. On the other hand, in order to uncover the mechanism of the metal-insulator transition in early transition metal oxides such as VO$_2$ [23], a well-known phenomenon originating from strong electronic correlations, both the crystal and electronic structure of MoO$_2$ have been studied [24, 25]. Compared to the 3$d$ electrons in VO$_2$, the reduced localization of the 4$d$ electrons in MoO$_2$ results in metallic character with a weak electronic correlations. Recently, Zhang et al. [18] pointed out that MoO$_2$ is a nodal-line semimetal when considering spin-orbital coupling (SOC) is neglected.

In this paper, we present calculations of the electronic band structure and the Fermi surface (FS) as well as measured the longitudinal resistivity $\rho_{xx}(T,H)$, Hall resistivity $\rho_{xy}(T,H)$ and quantum oscillations of the magnetization as a function of temperature at various magnetic fields for MoO$_2$ with monoclinic crystal structure. We further reveal a nearly quadratic field dependence of magnetoresistance (MR) reaching a large value of 5.03 $\times 10^{4}$% at 2 K and 9 T, as well as a field-induced up-turn behavior of $\rho_{xx}(T)$ in this material, the characteristics common for many other topologically non-trivial as well as trivial semimetals. The observed properties are attributed to a perfect charge-carrier compensation, evidenced by both calculations relying on the Fermi surface topology and the Hall resistivity measurements. Both the observation of negative MR for magnetic field along the current direction and the non-zero Berry phase in de Haas-van Alphen (dHvA) measurements indicate that
pairs of Weyl points appear in MoO$_2$, which may be due to the crystal symmetry breaking.

II. EXPERIMENTAL METHODS AND CALCULATIONS

MoO$_2$ single crystals were grown by a chemical vapor transport method. Polycrystalline MoO$_2$ prepared previously was sealed in an evacuated quartz tube with 10 mg/cm$^3$ TeCl$_3$ as a transport agent, then heated for two weeks at 1020 K, in a tube furnace with a temperature gradient of 50 K. Grey crystals with typical dimensions $1.5 \times 1.0 \times 0.2$ mm$^3$ and a (110) easy cleavage plane [see Fig. 1(b)] were obtained at the cold end of the tube. The composition was confirmed to be Mo : O = 1 : 2 by using the energy dispersive x-ray spectrometer (EDXS). The crystal structure was determined by a powder x-ray diffractometer (XRD, Rigaku Gemini A Ultra), created by grinding pieces of crystals [see Fig. 1(c)]. It was confirmed that MoO$_2$ crystallizes in a monoclinic structure (space group P2$\bar{1}$/c, No. 14). The lattice parameters, $a = 5.618(2)$ Å, $b = 4.867(1)$ Å and $c = 5.637(2)$ Å are obtained by using Rietveld refinement to XRD data (weighted profile factor R$_{wp}$ = 8.62%, and the goodness-of-fit $\chi^2$ = 3.466), as shown in Fig. 1(c). Longitudinal electrical resistivity ($\rho_{xx}$), Hall resistivity ($\rho_{xy}$) and magnetization measurements were carried out using a Quantum Design Physical Property Measurement System (PPMS, 9 T) or Magnetic Property Measurement System (MPMS, 7 T). The band structure was calculated using the Vienna $ab$ initio simulation package (VASP) [26, 27] with generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [28] for the exchange-correlation potential. A cutoff energy of 520 eV and a $13 \times 15 \times 13$ k-point mesh were used to perform the bulk calculations.

III. RESULTS AND DISCUSSIONS

As a starting point, we discuss the results of our electronic structure calculations that provide a broad overview of MoO$_2$ and extend the initial finding of the nodal-line semimetal phase in this material [18]. In order to address the topological character of MoO$_2$, we calculate its band structure and the Fermi surface (FS). As shown in Fig. 1(d), there are three different FS sheets: two hole-like surfaces near the Y point, which occupy 9% and 2% of the Brillouin zone volume (sheets 1 and 2), respectively, and a peanut-shaped electron-like surface centered around the $\Gamma$ point that occupies 11% of the Brillouin zone volume (sheet 3). The latter FS sheet has two loopholes near the B points, whereas it is closed along the $\Gamma$-A direction. The same volume (11%) of the first Brillouin zone occupied by both electron-like and hole-like pockets indicates that monoclinic MoO$_2$ is a compensated semimetal. All FS sheets have been correctly identified using angle-resolved photoemission spectroscopy (ARPES), dHvA measurements and electronic structure calculations [24]. We then identified the nodal-line band degeneracies in the band structure of this material using the open-source code WannierTools [29], which is based on the Wannier tight-binding model constructed using Wannier90 [30]. In the absence of SOC, the band degeneracies in MoO$_2$ are nodal lines and rings rather than point degeneracies. In other words, the band crossings exist along certain closed loops in the three-dimensional momentum space. In particular, two circular nodal rings and four nodal lines in the $\Gamma$-B-Y plane are formed. All of the nodal lines and rings are formed by the electron and hole pockets connected by nodal points near the Fermi energy. We then use irreducible representations of the bands to analyze the nodal lines [31]. As shown in Fig. 1(e), two bands touch at $(0, 0.146, 0.246)$ along the $\Gamma$-B path in momentum space. At this touching point, the irreducible representations of two bands are $A'$ and $A''$ which are two different irreducible representations of point group $C_{2v}$ [32]. According to Schur’s lemma, the two bases belonging to two different irreducible representations are orthogonal to each other, hence the bands cross without gap when SOC is ignored, resulting in a nodal-line semimetal phase. Whether the topological phase transition into the Weyl phase upon introducing SOC occurs due to some crystal symmetry breaking, e.g. resulting from oxygen vacancies, element substitution or applied pressure remains to be addressed theoretically.

Next, we focus on resistivity $\rho_{xx}$ measured for MoO$_2$ sample 1 (S1) at various temperatures ($T$) and in different magnetic fields ($\mu_0H$) with current $I \perp c$ axis, and $H \perp (110)$ plane. As shown in Fig. 2(a), resistivity measured at $\mu_0H = 0$ T exhibits a metallic behavior with $\rho(2 K) = 0.09 \mu\Omega \text{cm}$, and $\rho(300 K) = 96 \mu\Omega \text{cm}$, thus the residual resistivity ratio (R RR) $\rho(300 K)/\rho(2 K) \approx 1067$, indicating that this MoO$_2$ crystal (S1) has a high quality. Due to the values of resistance at low temperature reaching the measurement limitation of PPMS, $\rho_{xx}(T)$ below 20 K is not smooth. Similar to many topological and trivial topological semimetals [33–38], MoO$_2$ exhibits extremely large magnetoresistance. As shown in Fig. 2(a), an up-turn in $\rho_{xx}(T)$ curves under applied magnetic field occurs at low temperatures: $\rho_{xx}$ increases with decreasing $T$ and then saturates. The inset in Fig. 2(b) shows MR as a function of temperature at various magnetic fields, with the conventional definition $MR = \frac{\Delta \rho}{\rho(0)} = [\frac{\rho(H)-\rho(0)}{\rho(0)}] \times 100\%$. The normalized MR, shown in Fig. 2(b), has the same temperature dependence for various fields, excluding the suggestion of a field-induced metal-insulator transition [39, 40] at low temperatures, as discussed in our work addressing the topologically trivial semimetal $\alpha$-WP$_2$ [41], and the work...
of Thoutam et al. [42] on the type-II Weyl semimetal WTe$_2$. Figure 2(c) displays $\rho_{xx}(T,H)$ measured at 0 and 7 T, as well as the difference $\Delta \rho_{xx} = \rho_{xx}(T,7T) - \rho_{xx}(T,0T)$. The data clearly shows that the resistivity in applied magnetic field consists of two components, $\rho_0(T)$ and $\Delta \rho_{xx}$, with opposite temperature dependences. As discussed by us for $\alpha$-WP$_2$ [41] and by Wang et al. for WTe$_2$ [43], the resistivity can be written as

$$\rho_{xx}(T,H) = \rho_0(T)[1 + \alpha(H/\rho_0)^n].$$ (1)

The second term is the magnetic-field-induced resistivity $\Delta \rho_{xx}$, which follows Kohler's rule with two constants $\alpha$ and $m$. $\Delta \rho_{xx}$ is proportional to $1/\rho_0$ (when $m = 2$) and competes with the first term upon changing temperature, possibly giving rise to a minimum in $\rho(T,H)$ curves. Figure 3(a) shows MR as a function of field at various temperatures. The measured MR is extremely large at low temperatures, reaching $5.03 \times 10^4\%$ at 2 K and 9 T, and does not show any sign of saturation up to the highest field (9 T) applied in our measurements. The inset in Fig. 3(a) displays MR of crystals S1 and S2 with different RRR values of 1067 and 400, respectively. It is obvious that the magnitudes of MR are strongly dependent on the quality of samples, which was also observed in Dirac semimetal PtBi$_2$ [44], $\beta$-WP$_2$ [45], and $\alpha$-WP$_2$ [41]. As discussed above, MR can be described by the Kohler scaling law [46]

$$MR = \frac{\Delta \rho_{xx}(T,H)}{\rho_0(T)} = \alpha(H/\rho_0)^n.$$ (2)

As shown in Fig. 3(b), all MR data from $T = 2$ to 100 K collapse onto a single straight line when plotted as MR $\sim H/\rho_0$ curve, with $\alpha = 0.14 (\rho \Omega \text{cm/T})^{1.8}$ and $m = 1.8$ obtained by fitting. The nearly quadratic field dependence of MR observed for this nodal-line semimetal MoO$_2$ is attributed to the perfect electron-hole compensation, that is an effect of the Fermi surface topology [47] evidenced by the FS calculations mentioned above, as well as the Hall resistivity measurements discussed below, both are common characteristics for most topologically non-trivial and trivial semimetals [41, 43, 48, 49].

We also measured the anisotropy of longitudinal resistance at $T = 2$ K, and $\mu_B H = 3, 6$, and 9 T with $I \perp c$ axis, and by rotating the $H$ in the $z$-$c$ plane. Figure 4(a) shows the angular polar plot of resistance [$z$ is normal to (110) plane, see Fig. 4(b)], which exhibits mirror symmetry, i.e. $R(\theta) = R(\theta + \pi)$. The resistance data exhibits maxima at $\theta = 90^\circ$, and $270^\circ$ and minima at $\theta = 145^\circ$, and $325^\circ$, consistent with the monoclinic crystal structure. The resistance anisotropy reflects the symmetry of the projected profile of the FS onto the plane perpendicular to $I$, as shown in Fig. 4(c).

In Weyl semimetals, the presence of chiral Weyl node pairs is expected to lead to an unconventional negative MR induced by the Adler-Bell-Jackiw anomaly [50, 51] when $H$ is applied parallel to electric field $E$, i.e. the current direction $I$. In type-II Weyl semimetals [52], negative MR emerges along specific crystallographic directions, referred to as the planar orientation-dependent chi-
ral anomaly, due to the Weyl points appearing at the boundary of electron and hole pockets. To search for such chiral anomaly in MoO$_2$, we measured MR at 2 K by changing angle $\beta$ between $H$ and $I$ as shown in the inset of Fig. 5(a). Figures 5(a) and 5(b) show MR as a function of $H$ for sample 3 (S3). As $H \parallel I$ ($\beta = 90^\circ$), a negative MR was indeed observed except for a small positive peak below 3 T, which is usually attributed to the weak anti-localization phenomenon, as observed in both the type-I and type-II Weyl semimetals. A small misalignment of $H$ relative to $I$ leads to positive MR. We found that the emergence of such a negative MR behavior is sensitive to samples particularities and the direction of $I$. We believe that whether negative MR is observed or not depends on the Fermi level position and the current direction relative to Weyl points in the MoO$_2$ crystal, similar to the observations in the type-II Weyl semimetal WTe$_2$ [52]. The emergence of Weyl phase in MoO$_2$ may be due to the breaking of crystal symmetry resulting from, for example, the presence of oxygen vacancies in the crystal, but this hypothesis needs to be addressed in the future.

We now discuss the characteristics of charge carriers in MoO$_2$ relying on the Hall resistivity measurements performed on sample S1. Figure 6(a) displays $\rho_{xy}(H)$ measured at various temperatures. The linear dependence of $\rho_{xy}(H)$ with a positive slope at all temperatures indicates that the holes dominate the transport properties. This is, however, not what is expected for semimetals, in which both electron and hole carriers coexist. Follow-
FIG. 4. (a) The angular plot of resistivity at 2 K measured under various fields. (b) Scheme of applied current and magnetic field directions. Current is applied perpendicular to the c axis, \( \theta \) is the angle between z axis and \( H \). (c) Cross-section of the FS of MoO\(_2\) passing through the \( \Gamma \) point perpendicular to the current direction. The yellow and blue dashed lines correspond to electron and hole pockets, respectively. (d) Plane in momentum space resulting in the cross-section shown in panel (c).

FIG. 5. MR as a function of magnetic field measured at 2 K for various orientations of \( H \) with respect to \( I \): (a) \( \beta = 0-80^\circ \), (b) \( \beta = 86-94^\circ \).

FIG. 6. (a) Field dependence of Hall resistivity \( \rho_{xy} \) measured at different temperatures for MoO\(_2\) sample 1 (S1). (b) Charge-carrier mobilities, \( \mu_e \) and \( \mu_h \), and (inset) the carrier concentrations, \( n_e \) and \( n_h \), as a function of temperature. (c), (d), (e) and (f) Conductivity \( \sigma_{xy} \) as a function of magnetic field at 2 K, 20 K, 80 K, 120 K. The solid lines are the fits obtained using the two-band model.

Using the analysis of Ref. [53, 54] for TaAs and TaP Weyl semimetals, we fitted the Hall conductivity tensor \( \sigma_{xy} = \frac{-\rho_{xy}}{\rho_{xx}^2 + \rho_{xy}^2} \) using a two-carrier model [55]

\[
\sigma_{xy} = eBn_h\mu_h^2/(1 + \mu_h^2B^2) - eBn_e\mu_e^2/(1 + \mu_e^2B^2),
\]

where \( n_e \) and \( n_h \) denote the carrier concentrations, \( \mu_e \) and \( \mu_h \) denote the mobilities of electrons and holes, respectively. Figures 6(c)-6(f) display the fits of the \( \sigma_{xy} \) data measured at \( T = 2 \text{ K}, 20 \text{ K}, 80 \text{ K} \) and 120 K, respectively. Figure 6(b) shows the \( n_e, n_h, \mu_e \) and \( \mu_h \) values obtained by fitting over the entire temperature range 2–300 K. It is remarkable that the \( n_e \) and \( n_h \) values are almost the same below 100 K, as shown in the inset of Fig. 6(b), such as at 2 K, \( n_e = 2.91 \times 10^{19} \text{ cm}^{-3} \), and \( n_h = 2.98 \times 10^{19} \text{ cm}^{-3} \). This indicates that MoO\(_2\) is indeed a charge-carrier compensated semimetal, which is also consistent with the discussion of the calculated FS. It was pointed out in Ref. [9], that nodal-line semimetals are expected to have a higher Dirac fermion density due to the Dirac band crossings along a line or a loop compared with that in the Dirac semimetals. From the fitting of Hall resistivity using the two-band model, both electron and hole densities are estimated to be \( \sim 10^{19} \text{ cm}^{-3} \) in our sample, significantly higher than those in other Dirac semimetals such as Cd\(_3\)As\(_2\) (\( \sim 10^{18} \text{ cm}^{-3} \) [39]) and Na\(_3\)Bi (\( \sim 10^{17} \text{ cm}^{-3} \) [56]), topological insulators (\( \sim 10^{10-12} \text{ cm}^{-3} \) [57]), and graphene (\( \sim 10^{10-12} \text{ cm}^{-3} \) [58]), but comparable to that of another nodal-line
semimetal ZrSIS (∼10²⁰ cm⁻³ [9]). We can reasonably expect that high carrier density in MoO₂ also reflects the nature of Dirac band crossings along the nodal line. Due to the existence of phonon thermal scattering at higher temperatures, as shown in Fig. 6(b), it is obvious that both the \( \mu_e \) and \( \mu_h \) increase notably with decreasing temperature. It is worth noting that hole mobility \( \mu_h \) is almost one order of magnitude larger than \( \mu_e \) at lower temperatures, e.g. at 2 K \( \mu_h = 9.0 \times 10^4 \) cm²/Vs and \( \mu_e = 1.2 \times 10^4 \) cm²/Vs.

Finally, the nodal-line semimetal of MoO₂ is supported by our measurements of the quantum oscillation of magnetization. Figure 7(a) displays the isothermal magnetization measured at various temperatures (1.8–4.0 K) up to 7 T \((\mu_0 H \parallel c \text{ axis})\) exhibiting pronounced dHvA oscillations. In Fig. 7(b), we present the oscillation components of magnetization obtained after subtracting the background. Strong oscillations with amplitudes of 0.2 \( \sim 0.3 \) emu/mol at 1.8 K are clearly seen. From the fast Fourier transform (FFT) analyses, we obtained two frequencies 1369 T \((F_\alpha)\) and 1435 T \((F_\beta)\) as shown in Fig. 7(c). In general, the oscillating magnetization of 3D systems can be described by the Lifshitz-Kosevich (LK) formula [59, 60] with the Berry phase [61]

\[
\Delta M \propto -B^{1/2} R_T R_D R_S \sin[2\pi(F/B - \gamma - \delta)],
\]

\[
R_T = \alpha T \mu/B \sinh(\alpha T \mu/B),
\]

\[
R_D = \exp(-\alpha T \mu/B),
\]

\[
R_S = \cos(\pi \gamma \mu/2),
\]

where \( \mu \) is the ratio of effective cyclotron mass \( m^* \) to free electron mass \( m_0 \), \( T_D \) is the Dingle temperature, and \( \alpha = (2\pi^2 k_B m_0)/(\hbar e) \). The phase factor \( \delta = 1/8 \) or \(-1/8 \) for 3D systems. The effective mass \( m^* \) can be obtained by fitting the temperature dependence of the oscillation amplitude \( R_T(T) \) as shown in Fig. 7(d). For \( F_\alpha \) 1369 T and \( F_\beta = 1435 \) T, the obtained \( m^* \) is 0.463 \( m_0 \) and 0.498 \( m_0 \), respectively, which is smaller than that of MoP₂ (1.6 \( m_0 \)) [62], but larger than that of the nodal-line semimetals ZrSIS (0.16 \( m_0 \)) [63] and ZrSIsSe (0.082 \( m_0 \), ZrSiTe (0.093 \( m_0 \)) [9]. Using the fitted \( m^* \) as a known parameter, we can further fit the oscillation patterns at given temperatures [e.g., \( T = 1.8 \) K, see Fig. 7(e)] to the LK formula with two frequencies, from which quantum mobility and the Berry phase can be extracted. The fitted values of \( T_D \) are of 2.05 K and 0.91 K, which corresponds to the quantum relaxation times \( \tau_q = \hbar/(2\pi k_B T_D) \) of 0.6 ps and 1.3 ps; and quantum mobility \( \mu_q (e\tau/m^*) \) of 2300 cm²/Vs and 4600 cm²/Vs for \( F_\alpha \) and \( F_\beta \), respectively, as listed in Table I. The LK fit also yields a phase factor \(-\gamma - \delta - 0.21 \) \((F_\alpha)\), from which the Berry phase \( \phi_B \) is determined to be 0.83 \( \pi \) for \( \delta = 1/8 \) and 0.33 \( \pi \) for \( \delta = -1/8 \). The phase factor for \( F_\beta \) is 0.35, with \( \phi_B = 1.95\pi \) \((\delta = 1/8)\) and 1.45 \( \pi \) \((\delta = -1/8)\).

The Berry phase can also be obtained from the commonly used Landau level fan diagram [64] (i.e., the LL indices \( n \) plotted as a function of the inverse of magnetic field \( 1/B_n \)). According to customary practice, the integer LL indices \( n \) should be assigned when the Fermi level lies between two adjacent LLs [65], where the density of state near the Fermi level DOS \( (E_F) \) reaches a minimum. Given that the oscillatory magnetic susceptibility is proportional to the oscillatory DOS at the Fermi level (i.e. \( \Delta(dM/dB) \propto \Delta DOS(E_F) \)) and that the minima of \( \Delta M \) and \( \Delta(dM/dB) \) are shifted by \( \pi/2 \), the minima of \( \Delta M \) should be assigned to \( n - 1/4 \). The established LL fan diagram based on this definition is shown in Fig. 7(f). The extrapolation of the linear fit in the fan diagram yields an intercept \( n_0 = 0.24 \), which appears to correspond to a Berry phase \( \phi_B = 2\pi(0.24+\delta) \) of 0.73\( \pi \) \((\delta = 1/8)\) and 0.22\( \pi \) \((\delta = -1/8)\) for the \( F_\alpha \) band. This is consistent with the results of the LK formula. The non-zero Berry phase for two bands indicates that monoclinic MoO₂ to be a topological nodal-line semimetal.
TABLE I. The obtained parameters by fitting dHvA data for MoO$_2$

| Parameters | $F_\alpha$(LK) | $F_\beta$(LK) | $F_\alpha$(Landau fan) | $F_\beta$(Landau fan) |
|-----------|---------------|---------------|-----------------------|-----------------------|
| Frequency (T) | 1369 | 1435 | | |
| $m^*/m_0$ | 0.463 | 0.498 | | |
| $T_D$ (K) | 2.05 | 0.91 | | |
| $\tau_q$ (ps) | 0.6 | 1.3 | | |
| $\mu_q$ (cm$^2$/Vs) | 2300 | 4600 | | |
| $\varphi_B(\delta=+1/8)$ | 0.83$\pi$ | 1.95$\pi$ | 0.73$\pi$ | 2.05$\pi$ |
| $\varphi_B(\delta=-1/8)$ | 0.33$\pi$ | 1.45$\pi$ | 0.22$\pi$ | 1.55$\pi$ |

IV. CONCLUSION

In summary, we performed electronic structure calculations and measured the longitudinal resistivity, Hall resistivity and quantum oscillations of magnetization of the monoclinic phase of MoO$_2$ single crystals. It was found that MoO$_2$ exhibits many common characteristics for topological and trivial semimetals, such as large values of MR, reaching 5.03 $\times$ 10$^4$ % at 2 K and 9 T, its nearly quadratic field dependence, and a field-induced up-turn behaviour of $\rho_{xx}$($T$). Both the calculated Fermi surface and Hall resistivity measurements attribute these magneto-transport properties to perfect charge-carrier compensation. Interestingly, we observed an unconventional negative MR when the magnetic field was applied along the I direction in some samples as well as the non-zero Berry phase in the dHvA measurements. These results indicate that pairs of Weyl points appear in MoO$_2$, which may be due some source of crystal symmetry breaking, e.g. resulting from the presence of oxygen vacancies. These results highlight MoO$_2$ as an interesting new material for studying the topological properties of oxides.

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[1] C. Kane, Phys. Rev. Lett. 95, 226801 (2005).
[2] B. Bernevig, Phys. Rev. Lett. 96, 106802 (2006).
[3] L. Fu, Phys. Rev. Lett. 103, 266801 (2009).
[4] Z. Liu, B. Zhou, Y. Zhang, Z. Wang, H. Weng, D. Prabhakaran, S.-K. Mo, Z. Shen, Z. Fang, X. Dai, et al., Science 343, 864 (2014).
[5] Z. Wang, H. Weng, Q. Wu, X. Dai, and Z. Fang, Phys. Rev. B 88, 125427 (2013).
[6] C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skourski, J. Woynitz, Z. Liu, et al., Nat. Phys. 11, 645 (2015).
[7] B. Lv, H. Weng, B. Fu, X. Wang, H. Miao, J. Ma, P. Richard, X. Huang, L. Zhao, G. Chen, et al., Phys. Rev. X 5, 031013 (2015).
[8] L. An, X. Zhu, W. Gao, M. Wu, W. Ning, and M. Tian, Phys. Rev. B 99, 045143 (2019).
[9] J. Hu, Z. Tang, J. Liu, X. Liu, Y. Zhu, D. Graf, K. Myhro, S. Tran, C. N. Lau, J. Wei, et al., Phys. Rev. Lett. 117, 016602 (2016).
[10] E. Emmanouilidou, B. Shen, X. Deng, T.-R. Chang, A. Shi, G. Kotliar, S.-Y. Xu, and N. Ni, Phys. Rev. B 95, 245113 (2017).
[11] T. Bzdusek, Q. Wu, A. Ruegg, M. Sigrist, and A. A. Soluyanov, Nature 538, 75 (2016).
[12] R. Yu, Q. Wu, Z. Fang, and H. Weng, Phys. Rev. Lett. 119, 036401 (2017).
[13] Z. Yan, R. Bi, H. Shen, L. Lu, S.-C. Zhang, and Z. Wang, Phys. Rev. B 96, 041103 (2017).
[14] W. Chen, H.-Z. Lu, and J.-M. Hou, Phys. Rev. B 96, 041102 (2017).
[15] M. Ezawa, Phys. Rev. B 96, 041202 (2017).
[16] M. Vergniory, L. Elcoro, C. Felser, B. Bernevig, and Z. Wang, arXiv preprint arXiv:1807.10271 (2018).
[17] G. Autès, Q. Wu, N. Mounet, and O. V. Yazyev, Materials Cloud Archive , doi:10.24435/materialscloud:2019.0019/v2 (2019).
[18] T. Zhang, Y. Jiang, Z. Song, H. Huang, Y. He, Z. Fang, H. Weng, and C. Fang, Nature 566, 475 (2019).
[19] F. Tang, H. C. Po, A. Vishwanath, and X. Wan, Nature 566, 486 (2019).
[20] Y. Zhao, Y. Zhang, Z. Yang, Y. Yan, and K. Sun, SCI TECHNOL ADV MAT 14, 043501 (2013).
[21] L. Zhou, H. B. Wu, Z. Wang, and X. W. Lou, ACS Appl. Mater. Interfaces 3, 4853 (2011).
