



Topological nodal line in ZrTe_2 demonstrated by nuclear magnetic resonance

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In this work, we report nuclear magnetic resonance (NMR) combined with density functional theory studies of the transition metal dichalcogenide ZrTe_2 . The measured NMR shift anisotropy reveals a quasi-two-dimensional behavior connected to a topological nodal line close to the Fermi level. With the magnetic field perpendicular to the ZrTe_2 layers, the measured shift can be well-fitted by a combination of enhanced diamagnetism and spin shift due to high-mobility Dirac electrons. The spin-lattice relaxation rates with external field both parallel and perpendicular to the layers at low temperatures match the expected behavior associated with extended orbital hyperfine interaction due to quasi-two-dimensional Dirac carriers. In addition, calculated band structures also show clear evidence for the existence of a nodal line in ZrTe_2 between Γ and A. For intermediate temperatures, there is a sharp reduction in spin-lattice relaxation rate that can be explained as due to a reduced lifetime for these carriers, which matches the reported large change in mobility in the same temperature range. Above 200 K, the local orbital contribution starts to dominate in an orbital relaxation mechanism revealing the mixture of atomic functions.

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I. INTRODUCTION

In recent years, there has been great interest in layered transition metal dichalcogenides (TMDCs), comprised of a wide range of transition metal (Mo, W, Ta, Zr, Hf, etc.) and chalcogen (S, Se, or Te) elements. The TMDC family offers platforms for exploring striking physical phenomena and exotic electronic device applications [1]. Among TMDCs, ZrTe_2 has been relatively little investigated; however, recent work [2–4] has indicated interesting topological features in this material both in the normal state and as a doped superconductor. Also, other zirconium tellurides have been of considerable interest. For instance, ZrTe_5 shows interesting topological properties and unique physical properties such as the chiral magnetic effect [5] and the three-dimensional quantum Hall effect [6]. ZrTe_5 also exhibits a topological phase transition separating the strong and weak topological insulator states [7–9] with a temperature-driven valence- and conduction-band inversion associated with this topological phase transition [7]. The layered material ZrTe_3 has also been long studied due to interesting behavior such as a charge density wave phase transition [10]. Recently, theoretical calculations indicated distinctive topological behavior in ZrTe , which possesses triple-point fermions coming from the threefold-degenerate crossing points formed by the crossing of a double-degeneracy band and a nondegeneracy band [11].

Regarding ZrTe_2 , theoretical predictions from several groups give rather different results [2–4,12–14], including several [2,12] predicting ZrTe_2 to be a simple metal; however, recent experimental evidence appears to contradict this result. In addition, recent angle-resolved photoemission spectroscopy (ARPES) studies [4] have presented evidence

of massless Dirac fermions observed in the ZrTe_2 bulk phase, while recent density functional theory (DFT) calculations [3,4] have also supported the topological semimetal prediction, thus indicating that ZrTe_2 may have promising prospects for quantum device applications. Nuclear magnetic resonance (NMR) spectroscopy is particularly sensitive to electronic carriers near the Fermi level, based on the observation of spectral shifts and also nuclear relaxation times, and thus it provides an effective means to characterize the behavior of the Dirac carriers in this system.

In this work, we have studied ZrTe_2 using NMR techniques combined with DFT computations, and the results indicate a strongly diamagnetic response of Dirac carriers circulating within the ZrTe_2 layers, but with a quasi-two-dimensional (2D) behavior that becomes modified as the temperature increases at low T . By observing the differences in NMR shifts and spin-lattice relaxation rates for both the $B \parallel c$ and $B \perp c$ orientations, we find that the low-temperature results correspond to a nodal line extending in the direction perpendicular to the layers.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

The ZrTe_2 single crystals (crystal structure shown in Fig. 1) were prepared using chemical vapor transport. The stoichiometric mixture of Zr and Te powder was sealed in a quartz tube with iodine being used as transport agent (2 mg/cm^3). Platelike single crystals with metallic luster were obtained via vapor transport growth with a temperature gradient from 950 to 850°C . Cameca SXFive microprobe measurements indicate a uniform phase $\text{Zr}_{0.99}\text{Te}_2$.

NMR experiments utilized a custom-built spectrometer at a fixed field $B \approx 9 \text{ T}$. Many individual crystals were stacked with the c axes aligned, and the sample was measured with the field parallel to c ($B \parallel c$) and in the basal plane ($B \perp c$).

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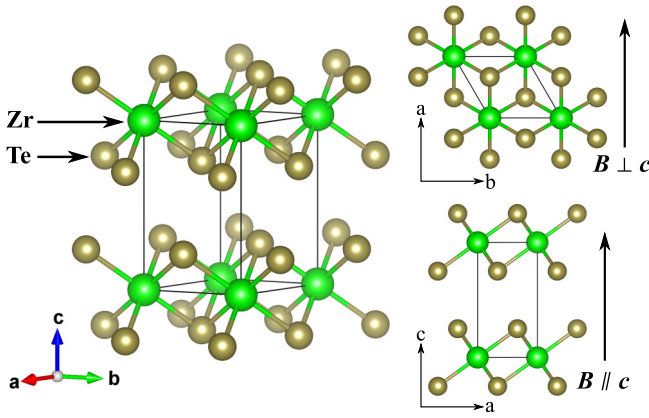


FIG. 1. Crystal structure of 1T-ZrTe₂ with $P-3m1$ space group, showing van der Waals-bonded layered structure.

The a -axis orientation was not identified for these crystals. ¹²⁵Te (nuclear spin $I = 1/2$ and gyromagnetic ratio $\gamma = -8.51 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$) shifts were calibrated by aqueous Te(OH)₆ and adjusted for its $\delta = 707$ ppm paramagnetic shift to the dimethyltelluride standard [15].

The band structure and density of states calculations were carried out in the framework of the DFT by employing the augmented plane wave (APW) plus local orbital (APW + lo) method [16] with the Perdew-Burke-Ernzerhof (PBE) potential [17] as implemented in the WIEN2K code [18]. A mesh of 1000 k -points was employed in the irreducible wedge of the hexagonal Brillouin zone [see Fig. 4(d)] corresponding to the grids of $10 \times 10 \times 10$ in the Monkhorst-Pack [19] scheme. The cutoff parameter of $k_{\text{max}} = 7/R_{\text{MT}}$ inside the interstitial region was used for the expansions of the wave functions in terms of the plane waves.

III. EXPERIMENTAL AND COMPUTATIONAL RESULTS

A. Shift

Consistent with the single local environment for Te in the 1T-ZrTe₂ structure, there is only one peak observed in the

¹²⁵Te spectra, as shown in Fig. 2(a). The angular dependence of the NMR shift (with θ defined between the ab layer and the magnetic field B) is shown in Fig. 2(b). The room-temperature shift was fitted [red curve in Fig. 2(b)] to

$$K = K_{\text{iso}} + \frac{3 \cos^2 \theta - 1}{2} \Delta K, \quad (1)$$

where $K_{\text{iso}} = 2767 \pm 3$ ppm is the isotropic shift and $\Delta K = -530 \pm 4$ ppm. By symmetry, the shift will not depend on orientation in the basal plane, which is confirmed by the absence of additional inhomogeneous line broadening for this orientation [Fig. 2(a)]. Reference [20] gives $\delta_{\text{iso}} = 1825$ ppm with Te(OH)₆ as a reference, which corresponds to 2532 ppm, a similar shift to that reported here, considering the large width measured in Ref. [20].

Figures 2(c) and 2(d) show the temperature dependence of the ¹²⁵Te shift for $B \parallel c$ and $B \perp c$ ($K_{\parallel c}$ and $K_{\perp c}$), respectively. The shifts were obtained by identifying the highest intensity position of the measured single-peak ¹²⁵Te spectra. Both $K_{\parallel c}$ and $K_{\perp c}$ decrease monotonically versus T , with K_{iso} corresponding to the linear fits [shown in Figs. 2(c) and 2(d)] changing by 0.34 ppm/K. At low T , $K_{\parallel c}$ shows a sharp decrease as T approaches zero, while for $K_{\perp c}$ there is a clear change in the opposite direction close to 50 K, where the shift is nearly temperature-independent. These results are indicative of quasi-2D Dirac-node behavior as is discussed in Sec. IV A.

The carrier concentration shown in Ref. [4] is on the order of 10^{19} cm^{-3} , which indicates that the large measured shifts are mostly chemical shifts due to electronic states away from the Fermi energy (ε_F); however, the temperature dependence is dominated by Knight shifts due to carriers at ε_F , and for convenience we label the observed shift, which is the sum of these shift terms, as K .

B. Spin-lattice relaxation

Spin-lattice relaxation results, measured by inversion recovery, could be well fitted to a single exponential $M(t) = (1 - Ce^{-t/T_1})M(\infty)$, giving $1/T_1 T$ values shown in Figs. 3(a)

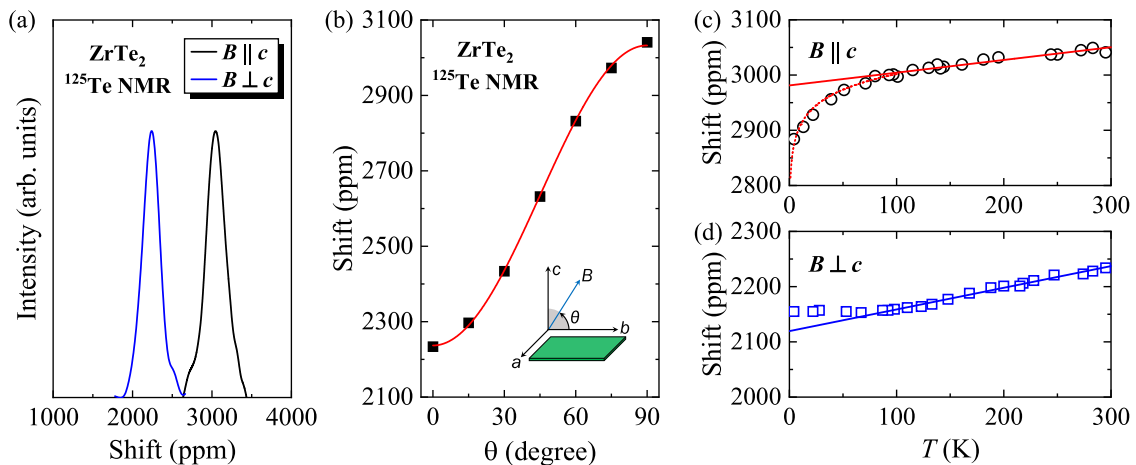


FIG. 2. (a) ¹²⁵Te line shapes of ZrTe₂ at room temperature. (b) Angular dependence of shift at room temperature. The red solid curve is a fit to Eq. (1). Shift vs temperature for (c) $B \parallel c$ (magnetic field perpendicular to the layers) with linear and $\ln(T)$ curves as guides to the eye and (d) $B \perp c$ (magnetic field parallel to the layers).

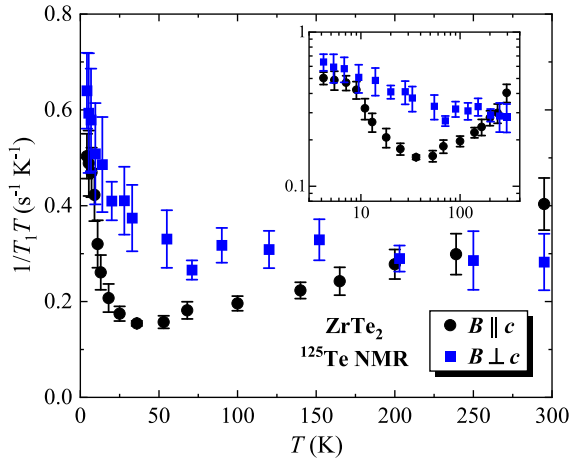


FIG. 3. $1/T_1 T$ vs T for both orientations $B \parallel c$ (perpendicular to the layers) and $B \perp c$ (parallel to the layers). Inset: $1/T_1 T$ vs T in log scale.

and 3(b). The results decrease rapidly at low temperatures as T increases, especially $(1/T_1 T)_{\parallel c}$, which changes rather quickly at temperatures near 15 K. Near 50 K, which is also the temperature at which $K_{\perp c}$ exhibits a change in behavior, the relaxation results also exhibit a characteristic change, with $1/T_1 T$ leveling off, and $1/T_1 T$ exhibiting a minimum near 40 K and then steadily increasing. In metals $1/T_1 T$ is often dominated by s -electron Fermi contact and proportional to $g^2(\varepsilon_F)$. However, similarly to ZrTe₅ [21], we find that the Dirac states in ZrTe₂ are dominated by Te p -orbitals, along with Zr d -states, as confirmed by the DFT results, which are described in the next section. These produce a dominant orbital contribution to $1/T_1 T$, and we will further demonstrate that the largest term is due to the high-mobility Dirac carriers.

C. DFT computations

From reports by several groups [2–4,12–14], there have been some conflicting opinions about the topological nature of ZrTe₂ as detected in DFT results. Reference [14] suggests a semimetallic state of ZrTe₂ without any topological nature. Reference [4] suggests that ZrTe₂ is a topological semimetal, consistent with its ARPES results. References [3,4] indicate a Dirac point at Γ with the Dirac node close to the chemical potential and an electron pocket at M in the conduction band. The lattice parameters used in Ref. [4] are about 1–2 % expanded from experimental values. However, these parameters were obtained from a DFT energy optimization, and they provided an approximate match for the reported ARPES results, with the calculated Dirac node roughly 0.5 eV higher in energy than what is actually observed by ARPES, and with larger calculated overlaps of the pockets at L and M than what is observed. Reference [14] included a correction for the van der Waals interaction, leading to a much smaller overlap at the L and M points; however, a large gap opened throughout the Brillouin zone, in seeming contradiction with magnetotransport results [22] as well as APRES results [4]. It is likely that the well-known difficulty in predicting band energies near the gap in standard GGA functionals such as PBE is responsible for the discrepancies between the calculated results and the

observation. In TMDCs specifically DFT is well-known to underestimate the band gaps [23,24]. For further investigation, we used the lattice parameters of Ref. [4] ($a = 3.909 \text{ \AA}$ and $c = 6.749 \text{ \AA}$) for DFT calculations, with the understanding that the ε_F position is much closer to the Dirac node than predicted.

Results of the DFT calculations, with spin-orbit coupling included, are shown in Figs. 4(a)–4(c). The nearly dispersionless band from Γ to A connects to Dirac-like features at Γ (as previously identified [3,4]) and also at A , and this band is doubly degenerate except for a gap of about 20 meV very close to Γ , identified [4] as associated with a band inversion. The mapping in reciprocal space, and a schematic of the nodal line between Γ and A , are demonstrated in Figs. 4(d) and 4(e). Also note that the partial DOS results show that Te p -orbitals are mostly located at these Dirac bands away from the node, while Zr d -orbitals dominate at the node itself, and the Zr orbitals dominate the electron pockets at L and M . There is also a separate high-dispersion band crossing Γ just below the node energy.

As an estimate of the Fermi velocity for the Dirac nodal line, we analyzed the linear slope in the Γ - M and A - L directions leading up to the nodal line according to $\varepsilon = \hbar v_F k$, and we obtained 6.9 and 6.5×10^5 m/s. Based on these values, which are typical for Dirac semimetals [25], we will use the mean value, 6.7×10^5 m/s, for further analysis of the Dirac-carrier behavior. A similar value was estimated for the monolayer case [3]. The extra pockets at L and M contain ordinary electrons, and the existence of both Dirac and ordinary electrons at ε_F leads to additional complexity in this case, although experimental indications [3,4] point to a much smaller overlap between the M pocket and the Dirac valence band than what is calculated. With the $\sqrt{\varepsilon}$ -type density of states near ε_F dominated by the M pocket, we fitted to $g(\varepsilon) = \sqrt{[2\varepsilon(m^*)^3]/(\pi^2 \hbar^3)}$ and obtained an estimate of $m^* = 1.7m_e$ for this pocket. In the model discussed in Sec. IV A, the position of the Fermi level is near the edge of this pocket, and very close to the nodal line.

IV. DISCUSSION AND ANALYSIS

A. Knight shift

As shown in Figs. 2(c) and 2(d), there is an obvious difference between the measured shifts of $B \parallel c$ and $B \perp c$ orientations, especially at low temperatures. The observed low- T divergence for $K_{\parallel c}$ follows approximately a $\ln(T)$ curve, characteristic of the divergent orbital susceptibility for Dirac semimetals [26,27], although the absence of the corresponding behavior for $K_{\perp c}$ points to a quasi-2D Dirac semimetal rather than 3D point-node behavior.

To analyze this situation, first we note that the shifts will be largely due to the dominant p -electrons for Te in ZrTe₂, contributing a combination of core polarization and spin-dipolar shifts, which are due to electron spin mechanisms, as well as orbital shifts, with the latter likely dominated by the large bulk orbital response of the Dirac electrons rather than due to local orbitals. The core polarization mechanism normally contributes an isotropic shift (the same sign for both orientations), and the spin-dipolar, an anisotropic shift [second term

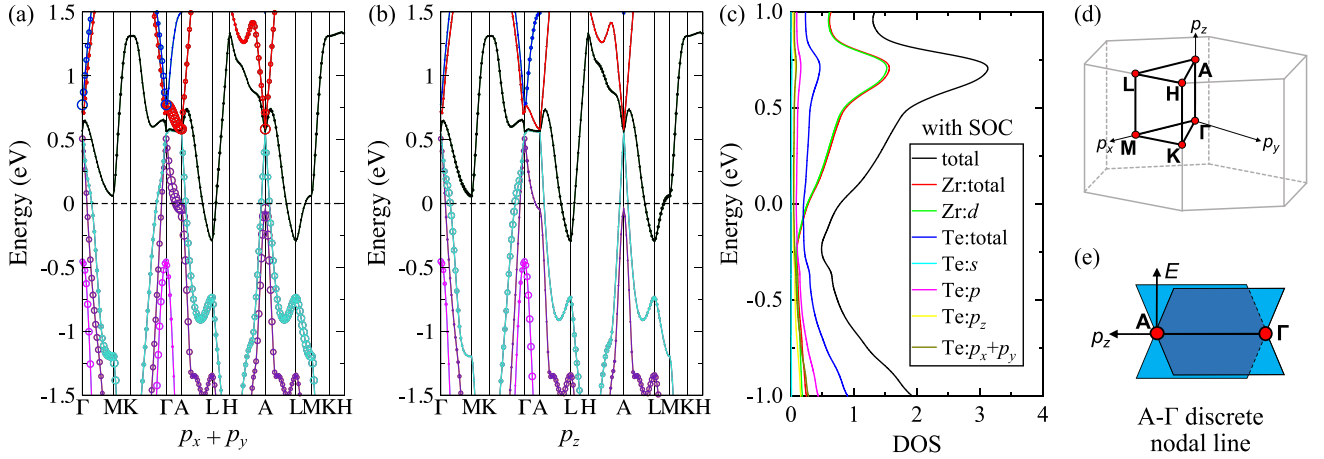


FIG. 4. Band structures of ZrTe_2 with spin-orbit coupling, with superposed circles showing weights for (a) $p_x + p_y$ and (b) p_z Te orbitals. The dashed lines represent the Fermi level. The circle size represents the partial state density of Te. (c) Density of states for ZrTe_2 . (d) 3D view of the hexagonal Brillouin zone with high-symmetry points. (e) Sketch of discrete nodal line between Γ and A.

in Eq. (1)]. However, the absence of divergent behavior for $B \perp c$ points to a different physical mechanism for the two orientations rather than shift anisotropy, and thus we analyze the $B \parallel c$ divergence in terms of the spin response of quasi-2D Dirac electrons due to the separation of Landau levels with $B \parallel c$, plus an orbital shift dominated by quasi-2D orbital currents confined to the basal plane.

For a quantitative comparison, first we consider the case of a 3D point node. The Knight shift due to the orbital interaction in a 3D massless Dirac electron case can be expressed as [27]

$$K = K_0 - \left[\frac{\mu_0 v_F e^2}{6\pi^2 \hbar} \ln \left(\frac{W}{\max\{k_B T, |\mu|\}} \right) \right] (1 - N_D), \quad (2)$$

where K_0 is a T -independent term, μ is the chemical potential measured from the Dirac node, W is a bandwidth cutoff, and N_D is a demagnetizing factor. N_D can be significant for the orbital hyperfine contribution of extended Dirac carriers, and in fact in the pure 2D limit the shift due to this mechanism will vanish [28]. Note that this is the low-field case. For v_F , we used $v_F = 6.7 \times 10^5$ m/s from the DFT results (Sec. III C). Considering the demagnetizing effect, the overall sample size (around $2 \times 2 \times 0.5$ mm³) implies a demagnetizing factor of approximately $N_D = 0.8$ for such a bulk-susceptibility contribution for the $B \parallel c$ orientation. Using these values, and assuming that $k_B T$ dominates in the logarithm of Eq. (2), we obtain a difference in shift of less than 1 ppm between the temperatures 10 and 100 K, much less than what is observed. Or, if changes in μ are on the order of $k_B T$, the results will be similarly small.

B. Quasi-2D model for the Knight shift

As an alternative we consider the shift due to the diamagnetic currents of a Dirac nodal line oriented along the c direction. In this quasi-2D case, currents are confined to the basal plane, and the diamagnetic response is equivalent to that of a 2D Dirac gas, for which we follow the treatment used for graphene [29]. Also note that the effect vanishes for $B \perp c$ due to the absence of high-mobility circulating currents perpendicular to the plane. For ZrTe_2 we modeled this system as

including a quasi-2D Dirac line, with the addition of a normal electron pocket crossing the node energy ($\varepsilon_{\text{node}}$), as indicated by DFT calculations and by ARPES measurements [4].

First, we calculate the chemical potential (μ). For the normal electron pocket we assumed an effective mass $m^*/m_e = 1$, close to the estimate for the pocket at M in DFT calculations (Sec. III C). Also for the perpendicular Fermi velocity we used the result obtained from DFT, $v_\perp = 6.7 \times 10^5$ m/s, which in the 9 T NMR field perpendicular to the layers gives Landau-level energies $\varepsilon_{\text{LL}}(N) = \pm \sqrt{(2e\hbar v_\perp^2 B |N|)} = \pm 73 \sqrt{|N|}$ meV, and a volume density of carriers per spin level $n_{\text{LL}} = B/(\Phi_0 c) = 3.3 \times 10^{18}$ cm⁻³, where $\Phi_0 = 4.14 \times 10^{-15}$ T m² is the magnetic flux quantum. The gyro-magnetic ratio is not known for these carriers, so we assumed $g = 2$. Also we assumed that a fixed density of carriers $n_{\text{total}} = 10^{19}$ cm⁻³ estimated from ARPES results [4] is divided between these band features. To solve for the chemical potential, we specified

$$n_{\text{total}} = \int_0^\infty f(\varepsilon, \mu) g_{\text{CB}}(\varepsilon) d\varepsilon + \sum_{s=-1/2}^{1/2} \sum_{N=-\infty}^{\infty} n_{\text{LL}} f(\varepsilon_N, \mu) - n_{\text{LL}} - \sum_{s=-1/2}^{1/2} \sum_{N=-\infty}^{-1} n_{\text{LL}}, \quad (3)$$

where $g_{\text{CB}}(\varepsilon) = \sqrt{(2\varepsilon m^* c^3)/(\pi^2 \hbar^3)}$ is the density of states in the normal-carrier pocket with its minimum set to $\varepsilon = 0$, $\varepsilon_N = \varepsilon_{\text{node}} + \mu_B g B s + \varepsilon_{\text{LL}}(N)$ represents the Landau level energies, and $f(\varepsilon, \mu) = 1/[1 + e^{(\varepsilon - \mu)/k_B T}]$ is the Fermi function. The extra term n_{LL} comes about because the lower $N = 0$ level is derived from the hole states, and we apply level quantization only to the Dirac states for which the large v_F pushes these states into the quantum limit. In the finite sums, we chose a very large cutoff for which the sums are numerically well-converged. In the $B \perp c$ case for which the Landau levels collapse, we replaced the sum over Landau levels in Eq. (3) with an integral over the 2D Dirac density of states $g_D(\varepsilon) = |\varepsilon - \varepsilon_{\text{node}} \pm \mu_B g B s|/[\pi c (\hbar v_\perp)^2]$ per spin,

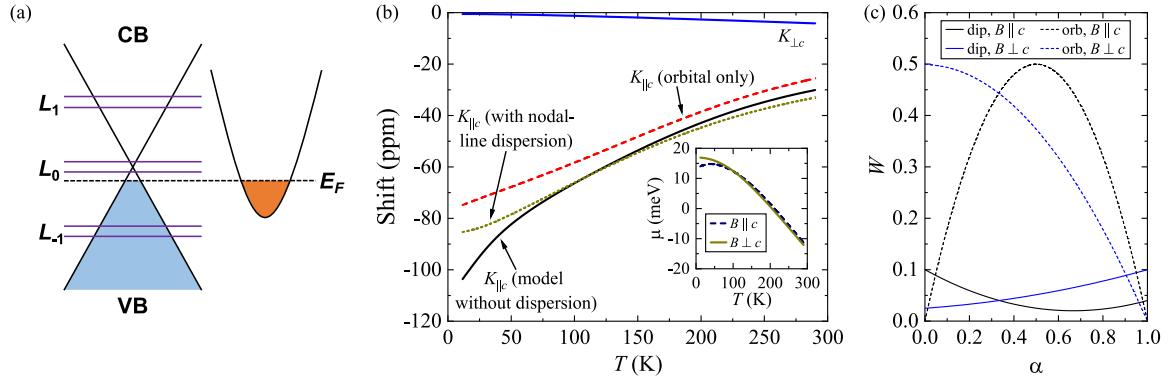


FIG. 5. (a) Sketch of Dirac band and electron pocket. (b) Simulated shifts for both orientations. Inset: chemical potential vs T . (c) $W = 1/2T_1$ is the dipolar and orbital relaxation rates divided by $2\pi(\gamma_e\gamma_n\hbar^{3/2})^2g^2(\epsilon_F)k_B T \langle r^{-3} \rangle^2$. α is the mixture of orbitals ($p_x + p_y$) vs p_z .

also normalized for hole states similarly to the last term in Eq. (3). Solving for $\mu(T)$, we obtained the results shown in the inset of Fig. 5(b) for the case $\epsilon_{\text{node}} = 12$ meV. Because of the significant carrier density n_{LL} at each Landau level energy including $N = 0$, the $B \parallel c$ field tends to pull μ into ϵ_{node} at low temperature [30], as can be seen from the results shown in the inset of Fig. 5(b). Recently anomalous magnetotransport effects were also identified in a layered Dirac material due to field-induced alignment of the chemical potential [31].

We next calculate the diamagnetic susceptibility, $\chi = \mu_0 \partial M / \partial B$, and its contribution to the NMR shift, $K = \chi(1 - N_D)$. The magnetization for $B \parallel c$ is $M = -(1/V) \partial \Omega / \partial B$ [29] with the grand potential volume density given by

$$\Omega/V = -k_B T n_{\text{LL}} \sum_{N=-m}^m \ln[1 + e^{(\epsilon_N - \mu)/k_B T}], \quad (4)$$

with m a numerical cutoff for the sum. For numerical calculation of the B derivative, we adopted the method described in Ref. [29] to normalize for the B -dependence caused by the numerical cutoff m . Using the $\mu(T)$ results shown in the inset of Fig. 5(b), we thus arrived at an estimation of χ for the $B \parallel c$ case. For the $B \perp c$ case, the diamagnetic contribution is zero since there is no splitting into Landau levels. Using the demagnetizing factor $N_D = 0.8$ estimated for our sample for $B \parallel c$, we arrived at the bulk-diamagnetic contribution to $K_{\parallel c}$ shown by the dashed curve in the main plot of Fig. 5(b). Note that in the B -derivative of Ω/V we included changes in n_{LL} and $\epsilon_{\text{LL}}(N)$, but not in the numerical solutions $\mu(T)$. The difference should be small, since for most of the temperature range the CB pocket determines the position of μ , while at low temperatures the results have the linear- T behavior equivalent to the case when μ is fixed at ϵ_{node} [29], due to the pulling effect of the magnetic field.

To calculate the spin contribution to the shift, we first calculated the Dirac-electron spin density as

$$n_{\text{spin}} = \sum_{s=-1/2}^{1/2} 2s \sum_{N=-\infty}^{\infty} n_{\text{LL}} f(\epsilon_N, \mu), \quad (5)$$

both for $B \parallel c$ and $B \perp c$ using the corresponding $\mu(T)$ values shown in the inset of Fig. 5(b). Assuming the core-polarization hyperfine contribution dominates for the Te

p -electrons participating in the Dirac node, we used the estimated [32] hyperfine field $B_{\text{cp}}^{\text{HF}} = -15$ T in calculating the spin shift as $K_{\text{spin}} = n_{\text{spin}}(B_{\text{cp}}^{\text{HF}}/9 \text{ T})(V_{\text{cell}}/2)$, with 9 T the applied NMR field and the sample volume per Te atom given by $V_{\text{cell}}/2 = 50 \text{ \AA}^3$. The results were added to the calculated T -dependent diamagnetic orbital shift, giving the spin+orbital result plotted in Fig. 5(b) (lowest curve). The results are comparable to the observed shift behavior and have the same general temperature dependence. Since there is considerable likelihood that g differs from 2 [33–36], we did not attempt a quantitative fitting; however, it appears that this model correctly captures the low- T behavior, and that a combination of spin susceptibility and orbital diamagnetism, both strongly enhanced in the quantum limit for the $B \parallel c$ orientation, is responsible for the observations.

Comparing to the 3D case discussed earlier [Eq. (2)], we can thus understand the enhanced effect for the quasi-2D case as due to two effects. First, the lack of Landau level dispersion in two dimensions means that the density of states is changed considerably by the field, which allows for a large spin polarization since a large number of states is concentrated at discrete energies. Secondly, this concentration of states in energy also enhances the diamagnetic response obtained from Eq. (4). Also note that the estimated $\mu(T)$ obtained from Eq. (3) [inset of Fig. 5(b)] should be little changed in the 3D case because of the large role of $g_{\text{CB}}(E)$, and indeed these changes in $\mu(T)$ are on the order of $k_B T$, confirming the estimate in Sec. IV A of the small expected shift in that case.

Note that in the DFT results (Fig. 4), a small dispersion appears in the nodal line, with the changes covering a range of approximately 20 meV between Γ and A. To model the effect of this behavior, we added a simple linear dispersion to the ϵ_{node} position. This was done by modifying the sum over Landau level numbers N in Eqs. (3)–(5), replacing the summands having fixed ϵ_{node} by an integrated square distribution covering a range $\epsilon_{\text{node}} \pm 10$ meV, and repeating the numerical calculations described above with otherwise identical parameters. This yielded the spin+orbital shift result shown in the dotted curve in Fig. 5(b): the main effect is a softening of the spin contribution as T approaches zero; however, the calculated magnitude is similar to that of the completely dispersionless case.

C. Relaxation mechanisms

The low- T $1/T_1$ results exhibit an anisotropy and temperature dependence that does not match the corresponding behavior of the measured shifts. Thus, we expect that the T_1 behavior is not a result of a Korringa-type spin contribution [37], which would be expected in that case. However, in contrast to the spin contribution, the orbital shift and T_1 are not governed by a Korringa relation [26], and the behavior in the low- T limit matches what is predicted [27,38] for the quasi-2D orbital case due to a mechanism governed by high-mobility carriers, which we denote here as the extended orbital mechanism, since carriers far from the nucleus dominate this process. For the quasi-2D free-electron gas (i.e., metallic layers where the electrons behave as a 2D free-electron gas), Lee and Nagaosa obtained the relaxation rates due to this mechanism when the magnetic field is applied parallel and perpendicular to the layers [38], which corresponds to a ratio between $(1/T_1T)_{\parallel c}$ and $(1/T_1T)_{\perp c}$ of 2 : 3. As shown in Fig. 3, excluding a T -independent background, the low- T $(1/T_1T)_{\parallel c}$ and $(1/T_1T)_{\perp c}$ reaches a ratio close to 2 : 3. Thus, the low- T behavior can be modeled using the extended orbital scenario.

For a quasi-2D Dirac system, the extended orbital contribution can be expressed as [27]

$$\left(\frac{1}{T_1T}\right)_{\perp c} = \frac{3}{2} \left(\frac{1}{T_1T}\right)_{\parallel c} = \frac{\mu_0^2 \gamma_n^2 e^2 k_B}{(4\pi)^2} \int_{|E| > \Delta} dE \times \left[-\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right] \frac{\sqrt{\varepsilon^2 - \Delta^2}}{\hbar^2 c v_F} \ln \frac{2(\varepsilon^2 - \Delta^2)}{\hbar \omega_0 |\varepsilon|}, \quad (6)$$

with $\varepsilon = \pm \sqrt{v_F^2 k^2 + \Delta^2}$, and c is the distance between nearest-neighbor layers. In addition, $f(\varepsilon)$ is the Fermi function and $E_g = 2\Delta$ is the gap. In the low- T limit assuming Δ is small, this readily evaluates to $\frac{(\mu_0 \gamma_n e)^2}{(4\pi)^2} \frac{k_B \mu}{\hbar^2 c v_F} \ln\left(\frac{2\mu}{\hbar \omega_0}\right)$. Comparing to the result [27] for a 3D point node in the same limits, $\frac{8\pi}{3} \frac{(\mu_0 \gamma_n e)^2}{(4\pi)^2} \frac{k_B \mu^2}{\hbar^3 v_F^3} \ln\left(\frac{2\mu}{\hbar \omega_0}\right)$, $1/T_1T$ for the quasi-2D case is the same as the 3D case multiplied by a factor $\frac{3}{8\pi} \frac{\hbar v_F}{\mu c}$. Taking $\mu = 10$ meV, $v_F = 0.67 \times 10^6$ m/s, and $c = 6.7$ Å for ZrTe₂, this is a factor of 7, with the quasi-2D situation enhanced essentially because of the increased phase space for the scattering phenomena leading to Eq. (6), which can include events with Δk covering the entire Brillouin zone in the direction perpendicular to the layers. With the low- T $(1/T_1T)_{\perp c}$ larger by a factor of about 10 as compared to that of the comparable point-node material ZrTe₅ [9], this indeed makes it plausible that the extended-orbital mechanism for high-mobility Dirac electrons is the dominant mechanism at low temperatures. In the low- T limit, the ratio $(1/T_1T)_{\perp c}/(1/T_1T)_{\parallel c}$ is smaller than the expected 3/2 given by this model; however, note that Eq. (6) was derived in the low-field limit, and it seems possible that such effects might renormalize the $(1/T_1T)_{\parallel c}$ results. In addition, while the normal-electron pocket at M is strongly dominated by Zr d -orbitals, a nonzero contribution due to Te states might also lead to a slowly varying background contribution to $1/T_1T$.

As shown in Fig. 5(b), we determined that Dirac spins can give a considerable contribution to the Knight shift due to core polarization combined with Landau level splitting for $B \parallel c$.

However, we expect the core polarization mechanism to give a rather negligible contribution to $1/T_1T$. This can be seen from the Korringa relation [32], which can provide an approximate upper limit for the spin $1/T_1T$. For ¹²⁵Te, the Korringa relation will be $(1/T_1T)_{\text{spin}} = K_{\text{spin}}^2/[2.6 \times 10^{-6} \text{ (s K)}^{-1}]$, and with $|K_{\text{spin}}|$ at low temperatures determined to be somewhat less than 100 ppm, choosing 100 ppm yields a limiting value $(1/T_1T)_{\text{spin}} = 4 \times 10^{-3} \text{ (s K)}^{-1}$. This is considerably smaller than what is observed. Note also that in the low- T limit where the Dirac spins are heavily polarized, the probability of spin-flip scattering can be reduced, further limiting $1/T_1T$. However, the extended orbital $1/T_1T$ due to high-mobility electrons is not connected to the shift via a Korringa relation, and from these considerations we determine that the spin-lattice relaxation rate of ZrTe₂ is dominated by this orbital contribution. These results will extend across the whole temperature range.

As the temperature increases past 10 K, $(1/T_1T)_{\parallel c}$ drops rather suddenly, reaching a minimum at about 40 K. This also coincides with a reported drop in the Dirac-carrier mobility, before the high- T regime sets in with different behavior [22]. We believe that the change in $(1/T_1T)_{\parallel c}$ can be understood in terms of carrier scattering effectively reducing the dimensionality of the relaxation mechanism. Reference [39] shows that the orbital $1/T_1T$ process due to high-mobility electrons, which relies upon a logarithmic divergence in the hyperfine coupling mechanism at large distances, will begin to cut off at a distance corresponding to the mean free path (ℓ) as the scattering rate increases, so that $1/T_1T$ becomes proportional to $\ln(\ell)$. With little or no dispersion for the nodal-line carriers in the direction perpendicular to the layers, the mean free path will certainly be highly anisotropic. Once this length becomes considerably reduced, $1/T_1T$ will go over to the 2D case, for which the extended orbital $(1/T_1T)_{\perp c}$ is unchanged but $(1/T_1T)_{\parallel c}$ in this mechanism vanishes [27,28]. This is not to say that the layers become completely decoupled; a large reduction in mean free path is sufficient for this change to occur.

Above the minimum, $(1/T_1T)_{\parallel c}$ again starts to increase. As seen in the inset of Fig. 5(b), the increase versus T is also accompanied by a drop in chemical potential to maintain charge balance given the large $g_{\text{CB}}(\varepsilon)$ contribution. As shown in Figs. 4(a) and 4(b), there is a split-off band at Γ just below the Dirac node, which is more strongly dominated by Te p -electrons. As μ decreases, holes will begin to appear in these states, with a significant effect on the ¹²⁵Te NMR because of their orbital weight. Aside from the $1/T_1T$ changes, there is also a change of character for the T -dependence of K , with a small increase in shift appearing for $B \perp c$. This behavior matches the observed change in magnetotransport behavior at these temperatures [22], which we believe is a Lifshitz transition corresponding to the chemical potential meeting this split-off band edge. To understand the increase in $(1/T_1T)_{\parallel c}$ at high temperatures, we show in the Appendix that in addition to the extended orbital contribution, there is a local orbital contribution [39] to $1/T_1T$ that does not rely on logarithmic divergence at extended distances, which will be larger for the $B \parallel c$ orientation as long as the Te p_z contribution exceeds the Te p_x and p_y contributions [Fig. 5(c)], which seems to be the case here. Therefore, the high-temperature behavior can

be understood in terms of an enhanced local-orbital contribution of $1/T_1T$, dominated by the split-off band, which comes into play at higher temperatures, while the extended orbital contribution decreases as a consequence of the large decrease in carrier mobility.

V. CONCLUSIONS

In conclusion, the topological nature of transition metal dichalcogenide ZrTe₂ is revealed here as a quasi-2D Dirac semimetal with a nodal line between Γ and A . For magnetic fields perpendicular to the ZrTe₂ layers, the measured shift can be well-modeled by a combination of orbital shift and spin shift due to high-mobility Dirac carriers. We also show that the low-temperature behavior of the spin-lattice relaxation rate can be explained through a quasi-2D Dirac electron model. In the intermediate temperature range, an increase in scattering of the Dirac carriers is applied to interpret the observed fast drop of the spin-lattice relaxation rate for the $B \parallel c$ orientation. With temperature increasing further, the local orbital contribution starts to dominate the spin-lattice relaxation rate with the significant contribution of a split-off band.

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APPENDIX: SPIN-LATTICE RELAXATION DUE TO ORBITAL AND DIPOLAR INTERACTIONS

The local orbital contribution to $1/T_1T$ is the mechanism typically associated with orbital hyperfine coupling in normal metals. As opposed to the extended-orbital mechanism [38,39], the local contribution is expected to be limited to orbitals belonging to the atom containing the nucleus being measured. Following the treatment of Obata [40], here we extend the calculation of $1/T_1T$ to p -electrons in the tetragonal symmetry corresponding to the threefold uniaxial symmetry for Te sites in ZrTe₂.

In the tight-binding approximation, the Bloch eigenfunctions are built up from localized atomic functions. For p -electrons, there are three independent orbital functions p_x , p_y , and p_z . With magnetic field B along a certain direction, in our case x and z , here are the mixed wave functions for uniaxial symmetry (omitting the product spin states):

$$\Psi = \begin{cases} \alpha^{1/2} p_z + (1 - \alpha)^{1/2} \frac{1}{\sqrt{2}}(p_x + p_y), & B \parallel c, \\ \alpha^{1/2} p_y + (1 - \alpha)^{1/2} \frac{1}{\sqrt{2}}(p_z + p_x), & B \perp c, \end{cases} \quad (\text{A1})$$

where α is a parameter specifying the relative amount of E symmetry (p_x and p_y) versus A_1 symmetry (p_z) for a magnetic field along z (similarly for $B \perp c$ with Ψ rotating correspondingly). For $B \parallel c$, when $\alpha = 0$, the wave function contains only p_x and p_y . With $\alpha = 1$, only p_z remains. For both dipolar interaction and orbital interaction contributions, we can thus determine the expressions of the corresponding spin-lattice relaxation rates, starting with a golden-rule relation, for which $1/T_1 = 2W = 4\pi/\hbar k_B T \langle |\Psi| \mathcal{H} |\Psi\rangle|^2 g^2(\varepsilon_F)$, where \mathcal{H} is the orbital or dipolar hyperfine interaction Hamiltonian [40], both of which are proportional to $1/r^3$ allowing the relative magnitudes to be readily compared. Also $g(\varepsilon_F)$ denotes the partial density of states at ε_F for the Te p -orbitals, which are assumed to appear in the relevant band according to the amplitudes given in Eq. (A1). We obtain the following for the case of dipolar interaction:

$$\begin{aligned} W_{\text{dip}} &= \frac{4\pi}{5} C \left(\left| \int_0^{2\pi} \int_0^\pi \Psi \Psi^* \frac{1}{2} Y_2^0 \sin \theta \, d\theta \, d\phi \right|^2 \right. \\ &\quad \left. + \left| \int_0^{2\pi} \int_0^\pi \Psi \Psi^* \frac{\sqrt{3}}{2} Y_2^{-1} \sin \theta \, d\theta \, d\phi \right|^2 \right. \\ &\quad \left. + \left| \int_0^{2\pi} \int_0^\pi \Psi \Psi^* \sqrt{\frac{3}{2}} Y_2^{-2} \sin \theta \, d\theta \, d\phi \right|^2 \right) \\ &= \begin{cases} \frac{C}{50} (9\alpha^2 - 12\alpha + 5) & (B \parallel c), \\ \frac{C}{200} (9\alpha^2 + 6\alpha + 5) & (B \perp c), \end{cases} \quad (\text{A2}) \end{aligned}$$

where Ψ is the wave function from Eq. (A1). Here $C = 2\pi (\gamma_e \gamma_n \hbar^{3/2})^2 g^2(\varepsilon_F) k_B T \langle r^{-3} \rangle^2$, where $\langle r^{-3} \rangle$ comes from the radial parts of the integrations that are not displayed in Eq. (A2). The integrals can be analytically evaluated giving the results also shown in Eq. (A2). For the case of the orbital interaction, the corresponding relations are

$$W_{\text{orb}} = \frac{C}{2} |\langle \Psi | l^{-1} | \Psi \rangle|^2 = \begin{cases} 2C\alpha(1 - \alpha) & (B \parallel c), \\ \frac{C}{2}(1 - \alpha^2) & (B \perp c). \end{cases} \quad (\text{A3})$$

These results are shown in Fig. 5(c) in the main text. As anticipated [40], the orbital term dominates in almost all cases. Also there is a crossing of terms at $\alpha = 1/3$ that represents an equal mixture of orbitals, as expected since such a mixture becomes isotropic. When α is larger than $1/3$, the local orbital contribution for $B \parallel c$ exceeds that for $B \perp c$.

- [1] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, *Nat. Rev. Mater.* **2**, 17033 (2017).
- [2] A. J. S. Machado, N. P. Baptista, B. S. de Lima, N. Chaia, T. W. Grant, L. E. Corrêa, S. T. Renosto, A. C. Scaramussa, R. F. Jardim, M. S. Torikachvili *et al.*, *Phys. Rev. B* **95**, 144505 (2017).
- [3] P. Tsipas, D. Tsoutsou, S. Fragkos, R. Sant, C. Alvarez, H. Okuno, G. Renaud, R. Alcotte, T. Baron, and A. Dimoulas, *ACS Nano* **12**, 1696 (2018).

- [4] I. Kar, J. Chatterjee, L. Harnagea, Y. Kushnirenko, A. V. Fedorov, D. Shrivastava, B. Büchner, P. Mahadevan, and S. Thirupathiah, *Phys. Rev. B* **101**, 165122 (2020).
- [5] Q. Li, D. E. Kharzeev, C. Zhang, Y. Huang, I. Pletikosić, A. V. Fedorov, R. D. Zhong, J. A. Schneeloch, G. D. Gu, and T. Valla, *Nat. Phys.* **12**, 550 (2016).
- [6] F. Tang, Y. Ren, P. Wang, R. Zhong, J. Schneeloch, S. A. Yang, K. Yang, P. A. Lee, G. Gu, Z. Qiao *et al.*, *Nature (London)* **569**, 537 (2019).

- [7] G. Manzoni, L. Gragnaniello, G. Autès, T. Kuhn, A. Sterzi, F. Cilento, M. Zacchigna, V. Enenkel, I. Vobornik, L. Barba *et al.*, *Phys. Rev. Lett.* **117**, 237601 (2016).
- [8] Z. Fan, Q.-F. Liang, Y. B. Chen, S.-H. Yao, and J. Zhou, *Sci. Rep.* **7**, 45667 (2017).
- [9] Y. Tian, N. Ghassemi, and J. H. Ross, Jr., *Phys. Rev. B* **100**, 165149 (2019).
- [10] S. Takahashi, T. Sambongi, J. W. Brill, and W. Roark, *Solid State Commun.* **49**, 1031 (1984).
- [11] Z. Zhu, G. W. Winkler, Q. S. Wu, J. Li, and A. A. Soluyanov, *Phys. Rev. X* **6**, 031003 (2016).
- [12] A. H. Reshak and S. Auluck, *Physica B* **353**, 230 (2004).
- [13] H. Guo, N. Lu, L. Wang, X. Wu, and X. C. Zeng, *J. Phys. Chem. C* **118**, 7242 (2014).
- [14] Z. Muhammad, B. Zhang, H. Lv, H. Shan, Z. u. Rehman, S. Chen, Z. Sun, X. Wu, A. Zhao, and L. Song, *ACS Nano* **14**, 835 (2019).
- [15] M. Inamo, *Chem. Lett.* **25**, 17 (1996).
- [16] G. K. H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nordström, *Phys. Rev. B* **64**, 195134 (2001).
- [17] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [18] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G. K. H. Madsen, and L. D. Marks, *J. Chem. Phys.* **152**, 074101 (2020).
- [19] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [20] I. Orion, J. Rocha, S. Jobic, V. Abadie, R. Brec, C. Fernandez, and J.-P. Amoureux, *Dalton Trans.* **20**, 3741 (1997).
- [21] H. Weng, X. Dai, and Z. Fang, *Phys. Rev. X* **4**, 011002 (2014).
- [22] H. Wang, C. H. Chan, C. H. Suen, S. P. Lau, and J.-Y. Dai, *ACS Nano* **13**, 6008 (2019).
- [23] T. Cheiwchanamngij and W. R. Lambrecht, *Phys. Rev. B* **85**, 205302 (2012).
- [24] N. A. Pike, A. Dewandre, B. Van Troeye, X. Gonze, and M. J. Verstraete, *Phys. Rev. Mater.* **2**, 063608 (2018).
- [25] N. P. Armitage, E. J. Mele, and A. Vishwanath, *Rev. Mod. Phys.* **90**, 015001 (2018).
- [26] Z. Okvátovity, H. Yasuoka, M. Baenitz, F. Simon, and B. Dóra, *Phys. Rev. B* **99**, 115107 (2019).
- [27] H. Maebashi, T. Hirotsawa, M. Ogata, and H. Fukuyama, *J. Phys. Chem. Solids* **128**, 138 (2019).
- [28] B. Dóra and F. Simon, *Phys. Rev. Lett.* **102**, 197602 (2009).
- [29] Z. Li, L. Chen, S. Meng, L. Guo, J. Huang, Y. Liu, W. Wang, and X. Chen, *Phys. Rev. B* **91**, 094429 (2015).
- [30] G. P. Mikitik and Y. V. Sharlai, *Phys. Rev. B* **101**, 205111 (2020).
- [31] S. Xu, C. Bao, P.-J. Guo, Y.-Y. Wang, Q.-H. Yu, L.-L. Sun, Y. Su, K. Liu, Z.-Y. Lu, S. Zhou *et al.*, *Nat. Commun.* **11**, 2370 (2020).
- [32] G. C. Carter, L. H. Bennett, and D. J. Kahan, *Metallic Shifts in NMR: A Review of the Theory and Comprehensive Critical Data Compilation of Metallic Materials* (Pergamon Press, New York, 1977).
- [33] S. Jeon, B. B. Zhou, A. Gyenis, B. E. Feldman, I. Kimchi, A. C. Potter, Q. D. Gibson, R. J. Cava, A. Vishwanath, and A. Yazdani, *Nat. Mater.* **13**, 851 (2014).
- [34] Y.-S. Fu, T. Hanaguri, K. Igarashi, M. Kawamura, M. S. Bahramy, and T. Sasagawa, *Nat. Commun.* **7**, 10829 (2016).
- [35] Y. Liu, X. Yuan, C. Zhang, Z. Jin, A. Narayan, C. Luo, Z. Chen, L. Yang, J. Zou, X. Wu *et al.*, *Nat. Commun.* **7**, 12516 (2016).
- [36] J. Hu, Z. Tang, J. Liu, Y. Zhu, J. Wei, and Z. Mao, *Phys. Rev. B* **96**, 045127 (2017).
- [37] C. P. Slichter, *Principles of Magnetic Resonance* (Springer, New York, 1990).
- [38] P. Lee and N. Nagaosa, *Phys. Rev. B* **43**, 1223 (1991).
- [39] A. Knigavko, B. Mitrović, and K. V. Samokhin, *Phys. Rev. B* **75**, 134506 (2007).
- [40] Y. Obata, *J. Phys. Soc. Jpn.* **18**, 1020 (1963).