Interplay of itinerant electrons and quantum Ising magnetism in a hybrid quantum material TmNi$_3$Al$_9$

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The interplay between itinerant electrons and local magnetic moments in quantum material brings rich and fascinating phenomena and stimulates the development of the theoretical framework. In this work, we perform the thermodynamic, electric transport, neutron diffraction measurements and present the physical understanding of the honeycomb lattice magnet TmNi$_3$Al$_9$. We found that the Tm$^{3+}$ ion forms an Ising-like moment, with the Ising axis normal to the honeycomb layer. An antiferromagnetic order around $T_N = 3$ K was observed, and the magnetic structure was determined by the neutron diffraction. With applying magnetic field along the easy axis, the antiferromagnetic order is gradually suppressed until the critical point around 0.9 T. A comprehensive field-temperature phase diagram was established, and enhanced critical spin fluctuations were observed in the vicinity of the critical field. The quantum Ising nature of the local moment and the coupling to the itinerant electrons are discussed.

I. INTRODUCTION

Itinerant frustration occurs widely in the hybrid quantum materials with both itinerant electrons and local moments. The frustration can come from the original exchange interaction between the local moments, or generated from the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction via the itinerant electrons.$^{1,2}$ Due to the presence of two distinct degrees of freedom and their interactions, these materials provide an interesting and rich arena for the study of the interplay between the itinerant electrons and the local moments.$^3$ The frustrated interactions on the local moments have already brought many interesting physics on themselves.$^{4-6}$ When the quantum phases and/or the magnetic orders of the local moments feedback to the itinerant electrons, more interesting physics could emerge. The magnetic order could reconstruct the band structures of the itinerant electrons and generate the non-trivial band structure topology such as the well-known magnetic Weyl semimetal.$^{7-9}$ The magnetic fluctuations at the magnetic transition can influence the physical properties of the itinerant electrons and often convert them into non-Fermi liquids with distinct transport behaviors.$^{10-13}$ The nature of the magnetic transition is further modified by the gapless itinerant fermions. Moreover, the manipulation of one degree of freedom could influence the physical properties of the other degree of freedom. Thus, the interplay between these two distinct degrees of freedom in the hybrid quantum materials could generate rather rich phenomena for both fundamental research and application purpose.$^{14}$

In this paper, we study the physical properties of a hybrid quantum material TmNi$_3$Al$_9$. In this material,
the 4f electrons of Tm$^{3+}$ ions form the local magnetic moments on a honeycomb lattice, and the rest ions provide the itinerant electrons. We report the comprehensive magnetization, heat capacity, magnetocaloric, electric transport and neutron diffraction studies of this hybrid quantum material. The crystal develops an antiferromagnetic order $\sim$ 3 K. The G-type magnetic structure is determined by the neutron diffraction with spins along the $c$-axis and ordered moments are $\sim$ 5.53(3)$\mu_B$. With applying magnetic field along its easy $c$-axis, the magnetic ordering is suppressed gradually $\sim$ 0.9 T at zero temperature where strong critical spin fluctuation was observed. This is reflected in the anomalous scaling of the electric resistivity in the transport measurement. We explain the physics from the coupling and the scattering between the itinerant electrons and the local moments.

II. EXPERIMENTAL DETAILS

High-quality TmNi$_3$Al$_9$ single crystalline samples were grown using the metallic flux method.\textsuperscript{15} The crystal structure of was characterized using a Bruker D8 Quest diffractometer with Mo-Kα radiation ($\lambda = 0.71073\text{Å}$), and the data integration and reduction were performed with the commercial Bruker APEX2 software suite. To identify the magnetic structure, neutron powder diffraction measurements with center wavelengths 1.5 Å were performed with the high-resolution time-of-flight powder diffractometer POWGEN, at the Spallation Neutron Source, Oak Ridge National Laboratory.\textsuperscript{16} A powder sample of TmNi$_3$Al$_9$, prepared by griding about 2g of single crystals, was loaded in a vanadium can for the measurements. An orange cryostat was used to cover the temperature region of 1.7 K to 300 K. The magnetic structure refinement was carried out using the software package FullProf.\textsuperscript{17} Specific heat and electrical resistivity measurements were performed on the Physical Property Measurement System. Magnetization measurements were performed using two magnetometers for different temperature ranges. For $T = 1.8$-300 K, commercial Quantum Design Magnetic Property Measurement System was used, while for $T = 0.4$-1.8 K, a Hall sensor magnetometer integrated in $^3$He insert was used.\textsuperscript{18–20}

III. RESULTS AND ANALYSIS

A. Crystal Structure and Crystalline Electrical Field Calculation

TmNi$_3$Al$_9$ has been previously reported to form a trigonal ErNi$_3$Al$_9$-type structure (space group $R\bar{3}2$), with lattice constants $a = b = 7.2576\text{Å}, c = 27.2983\text{Å}$ and $\alpha = \gamma = 90^\circ, \beta = 120^\circ$.\textsuperscript{15} In this structure, the magnetic Tm$^{3+}$ ions form a honeycomb lattice in the $ab$-plane, with the nearest-neighbor distance around 4.20 Å in-plane, and about 9.12 Å between Tm honeycomb layers (see Fig. 1). Due to the large spin-orbit coupling, the crystalline electrical field (CEF) is important for understanding the magnetism of the rare-earth ions. For TmNi$_3$Al$_9$, the 3-fold local symmetry of the Tm sites indicates that the Tm$^{3+}$ magnetic moments are either constrained in the $ab$ plane (perpendicular to the high symmetric direction), or along the $c$ axis (parallel to the high symmetric direction). Further calculation of the CEF levels was performed using the software package McPhase.\textsuperscript{21} In this local environment of Fig. 1(c), the 13-fold degenerate $J = 6 (L = 5, S = 1)$ multiplets were lifted into different doublet and singlet states. Since the Kramers theorem does not apply to Tm$^{3+}$ ions, there is no guarantee for a doublet ground state. Our calculation from the point charge model indicates a weakly-split ground state doublet with the wavefunction mostly contributed from $| \pm 6 \rangle$, which is analogous to the triangular lattice antiferromagnet TmMgGaO$_4$.\textsuperscript{22,23} This wavefunction suggests an Ising-like moment with the local Ising direction along the $c$ axis.

B. Magnetic Properties

![Fig. 2](https://example.com/figure2.png) FIG. 2. (a) The field dependent magnetization of TmNi$_3$Al$_9$, measured at $T = 1.8$ K, with the field applied along in-plane and out-plane axis. (b) Temperature dependent DC magnetic susceptibility ($\chi = M/H$) at different magnetic field for $H \parallel c$.

The field-dependent magnetization of TmNi$_3$Al$_9$ measured at 1.8 K with applied field in the $ab$-plane and along the $c$-axis, were shown in Fig. 2(a). For $H \parallel c$, the Tm$^{3+}$ moments were polarized above 2T, with the saturation moment $M_s \approx 6.97\mu_B$. This is very close to
FIG. 3. (a) Field dependent magnetization at different temperatures from 4 K down to 0.4 K for $H \parallel c$. (b) Magnetic field dependence of derivative susceptibility $dM/dH$ at temperatures 3 K, 2 K and 0.4 K. (c) Contour plot of the derivative susceptibility $dM/dH$, overlaid with the field-temperature phase boundary extracted from the peak positions of $dM/dH$.

the expected value for a pure $| \pm 6 \rangle$ ground states, where \( M_s = g_J \mu_B = 7/6 \times 6 \mu_B = 7 \mu_B \). Moreover, the measured magnetization in the ab-plane was about one order smaller, and no saturation behavior was observed up to 7 T. This is consistent with the strong Ising-like anisotropy of TmNi$_3$Al$_9$. In Fig. 2(b), we depict the temperature evolution of the magnetic susceptibility $\chi$ with an applied field along the c axis. An AFM order was observed below $T_N \approx 3$ K. Fig. 3(a) shows the field-dependent magnetization from 0.4 K to 4 K. The corresponding derivative susceptibility $dM/dH$ are presented in Fig. 3(b). Below $T_N$, a peak in $dM/dH$ was observed, indicating the phase transition from the AFM order to the high field polarized state. The contour plot of magnetic susceptibility $dM/dH$ is shown in Fig. 3(c), overlaid with the phase boundary extracted from the peak positions of $dM/dH$. The zero field AFM order is gradually suppressed at critical field around $B_c \approx 0.9$ T, suggesting a possible continuous transition. This would be unlikely for classical Ising moments where a strongly first order transition is expected, but is allowed for quantum Ising moments. This is consistent with our expectation from the intrinsic transverse field due to the weak splitting within the ground state doublet.$^{23}$ It is interesting to notice that following the peak in $dM/dH$, a broad shoulder-like anomaly was observed in the intermediate temperature range (1-2 K). This shoulder-like feature then gradually merges with the peak at lower fields as further decreasing temperatures and finally evolves into a broad peak at base temperature $\sim 0.4$ K, suggesting the strong spin fluctuations near the critical field.

C. Neutron Powder Diffraction and Magnetic Structure

To determine the AFM order, a powder neutron diffraction experiment was performed. The neutron diffraction pattern at 65 K and 2 K are shown in Fig. 4(a) and (b), respectively. Rietveld analysis confirms the trigonal structure with the space group $R\overline{3}2$, consistent with our XRD result at 300 K. This indicates there is no additional structural transition between 2 K and 300 K. For 2 K, extra intensity emerges on the diffraction reflections, especially around the low Q region, suggesting the magnetic origin. The magnetic propagation vector is determined to be $K = 0$. Symmetry-allowed magnetic space groups are analyzed by the Bilbao crystallographic server$^{24–28}$ and two possible magnetic configurations are available. One of the spin configurations is AFM, the other is ferromagnetic. By refining both nuclear and magnetic reflections at 2 K, we obtain the lattice information and magnetic structure simultaneously. The refinement confirms a G-type AFM configuration, where the spins are aligned antiferromagnetically in all a, b and c directions, as shown in Fig. 4(c). The Tm$^{3+}$ moments are along the c axis, consistent with the CEF calculation and the magnetic susceptibility measurement. The ordered moment of Tm$^{3+}$ is about 5.53(3)$\mu_B$, smaller than the saturated moment 7$\mu_B$. This is attributed to the quantum fluctuation generated by the intrinsic transverse field due to the weak splitting of the doublet that is analogous to TmMgGaO$_4$.$^{22,23}$

D. Specific Heat and Magnetic Entropy

Specific heat measurements were performed to further investigate the spin fluctuations in TmNi$_3$Al$_9$. Fig. 5(a) shows the specific heat at zero magnetic field. To remove the lattice contribution, specific heat of an isostructural nonmagnetic compound LuNi$_3$Al$_9$ extracted from Ref.$^{15}$ was used (green dashed line in Fig. 5(a)). A weak upturn in specific heat was observed below $\sim 0.5$ K, which is due to the nuclear Schottky effect, and it scales as
FIG. 4. Rietveld refinement of neutron powder diffraction patterns of TmNi$_3$Al$_9$ at (a) 65 K and (b) 2 K. The red points represent actual data and black line represent the Rietveld fitting to the data. The difference curve is shown at the bottom. (c) The magnetic structure of TmNi$_3$Al$_9$ below the ordering temperature refined from the neutron data. The arrows indicate the ordered Tm$^{3+}$ spins, which are found to point to the c axis.

$C_n \sim \alpha T^{-2}$. The pure magnetic contribution is shown in Fig. 5(b). The sharp-peak-like anomaly located around $T_N$=3 K implies the long-range AFM order. The integrated magnetic entropy is presented in Fig. 5(b), and a full entropy of $R \ln 2$ was released at the transition temperature. However, the ratio of the full released entropy at the transition decreases with increasing fields, and only about 50% of $R \ln 2$ was reached at the transition temperature with 0.8 T. These phenomena all suggest that the spin fluctuations are enhanced when the system was tuned to the critical region with applying fields.

The field-dependent specific heat is presented in Fig. 6(a)-(b). For higher temperatures, a step-like anomaly was observed across the phase boundary. With lowering temperatures, due to the constraint of the third law of thermodynamics that demands $\Delta S \to 0$ as $T \to 0$, the step-like anomaly gradually evolves into a weak peak at the critical fields (see Fig. 6(b)). Interestingly, at the mean time, as the contribution of phase transition to the specific heat gets weaker and weaker as lowering temperatures. In addition, two crossover-like peaks start to appear symmetrically around the critical field, as indicated by the empty stars in the field dependent specific heat. These crossover-like peaks get most distinguishable at temperatures ranges around 1.2 to 0.8 K, which then gradually merges into one single peak at the critical field at base temperatures below $\sim$ 0.6 K. The overall phase diagram extracted from the specific heat and magnetization with the phase boundaries and the crossover lines are summarized and over-plotted on the contour of the specific heat (see Fig. 6(c)). These crossover behaviors linearly extend to the critical field at 0.9 T, which are rarely seen in traditional magnets, such as classical
spin flip transitions when Ising spins are flipped at the critical fields. Instead, these linear crossovers are usually expected when the system is tuned to the vicinity of a quantum critical point, where great amount of spin fluctuations are present, such as been observed in many low dimensional quantum magnetic systems.\textsuperscript{29,30} Shown in Fig. 6(d) is the integrated magnetic entropy as function of field and temperature, and it is clearly seen that a lot of entropy was released around the a broad 'V'-shape area in the vicinity of the critical field.

E. Electrical Transport Properties

Electrical resistivity of TmNi\textsubscript{3}Al\textsubscript{9} with field along the crystal c axis was performed to reveal the impact of the local moment on itinerant electrons. Fig. 7(a) is the temperature-dependent resistivity $\rho(T)$ at various fields from 0 T to 2 T. Metallic behaviors are observed with the residual resistivity as low as 0.08 $\mu\Omega\cdot$cm when temperature approaches to 0.4 K in zero fields, and the ratio of the room-temperature resistivity to the residual resistivity is about $\rho_{300K}/\rho_{0.4K}$ $\approx$ 100. A sharp drop of the resistivity around $T_N \approx$ 3 K is observed, where the scatterings from the local moment fluctuations are greatly reduced in the long-range AFM state.

With increasing fields, the transition temperature gradually decreases as expected from the previous magnetization and specific heat measurements. It is worth to notice that the residual resistivity changes with increasing fields. This is most significant in the field-dependent magnetic resistivity of Fig. 7(b). At the base temperature 0.4 K, where the dominant contribution is from the residual resistivity, a broad maximum developed centered around 0.9 T, which on the other side reflects the great enhancement of the spin fluctuation in the vicinity of the criticality. The low temperature resistivity near the criticality even shows a non-Fermi liquid like linear temperature dependent behavior. The contour plot of the resistivity is shown in Fig.7(c). Very interestingly, this contour plot is very similar to the contour plot of the field temperature dependent magnetic entropy presented in Fig. 6(d). The Tm\textsuperscript{3+} local moments are well localized in TmNi\textsubscript{3}Al\textsubscript{9}, and Kondo effect plays little role here. This similarity between the resistivity and the magnetic entropy is not just accidental, which further confirms that the resistivity is mostly contributed from the spin fluctuation scattering of the Tm\textsuperscript{3+} local moments.
To summarize, the single crystals of TmNi$_3$Al$_9$ with the honeycomb lattice have been synthesized, and the structure and magnetic properties were investigated through specific heat, magnetization and electrical transport measurements. The experimental results, along with theoretical explanation, established an Ising-like moment of the Tm$^{3+}$ ion with the Ising axis along the crystal c direction. The magnetic structure below the ordering temperature $T_N = 3$ K has been revealed by the powder neutron diffraction, and the Tm$^{3+}$ moments were found to be antiferromagnetically coupled with the nearest neighbours in the ab-plane. With fields along the c axis, the magnetic order was gradually suppressed with the critical field around $B_c \simeq 0.9$ T. At the meantime, strong spin fluctuations are induced by the field, that is evidenced by the broad peak in the magnetic susceptibility, the enhanced magnetic entropy and enhancement of the spin disorder scattering in the resistivity measurements, as the system is tuned through the critical point. The detailed spin dynamics remains unclear and further investigations with the inelastic neutron scattering techniques are needed, which may provide more determination information about the spin fluctuations and possible anisotropy of the exchange interactions in the 2D honeycomb lattice of the Tm$^{3+}$ Ising moments.

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A. Candini, G. C. Gazzadi, A. di Bona, M. Affronte, D. Ercolani, G. Biasiol, and L. Sorba, Hall Nano-Probes Fabricated by Focused Ion Beam, Nanotechnology 17, 2105 (2006).

http://www.mcphase.de; M. Rotter, J. Magn. Magn. Mater. 272-276, E481 (2004).

Y. Shen, C. Liu, Y. Qin, S. Shen, Y.-D. Li, R. Bewley, A. Schneiderwind, G. Chen, and J. Zhao, Intertwined Dipolar and Multipolar Order in the Triangular-Lattice Magnet TmMgGaO$_4$, Nat Commun 10, 4530 (2019).

C. Liu, C.-J. Huang, and G. Chen, Intrinsic Quantum Ising Model on a Triangular Lattice Magnet TmMgGaO$_4$, Phys. Rev. Research 2, 043013 (2020).

M. I. Aroyo, J. M. Perez-Mato, D. Orobengoa, E. Tasci, G. de la Flor, A. Kirov, Crystallography online: Bilbao Crystallographic Server, Bulg. Chem. Commun. 43(2) 183-197 (2011).

M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumov, S. Ivantchev, G. Madariaga, A. Kirov, and H. Wondratschek, Bilbao Crystallographic Server I: Databases and crystallographic computing programs, Z. Krist. 221, 1, 15-27 (2006).

M. I. Aroyo, A. Kirov, C. Capillas, J. M. Perez-Mato, and H. Wondratschek, Bilbao Crystallographic Server II: Representations of crystallographic point groups and space groups, Acta Cryst. A62, 115-128 (2006).

S. V. Gallego, E. S. Tasci, G. de la Flor, J. M. Perez-Mato, M. I. Aroyo, Magnetic symmetry in the Bilbao Crystallographic Server: a computer program to provide systematic absences of magnetic neutron diffraction, J. Appl. Cryst. 45 1236-1247 (2012).

J.M. Perez-Mato, S.V. Gallego, E.S. Tasci, L. Elcoro, G. de la Flor, and M.I. Aroyo, Symmetry-Based Computational Tools for Magnetic Crystallography, Annu. Rev. Mater. Res. (2015), 45:13.1-13.32.

L. S. Wu, S. E. Nikitin, Z. Wang, W. Zhu, C. D. Batista, A. M. Tsvelik, A. M. Samarai, D. A. Tennant, M. Brando, L. Vasilychev, M. Frontzkek, A. T. Savici, G. Sala, G. Ehlers, A. D. Christianson, M. D. Lumsden, and A. Podlesnyak, Tomonaga-Luttinger Liquid Behavior and Spinon Confinement in YbAlO$_3$, Nat Commun 10, 698 (2019).

L. S. Wu, S. E. Nikitin, M. Brando, L. Vasilychev, G. Ehlers, M. Frontzkek, A. T. Savici, G. Sala, A. D. Christianson, M. D. Lumsden, and A. Podlesnyak, Antiferromagnetic Ordering and Dipolar Interactions of YbAlO$_3$, Phys. Rev. B 99, 195117 (2019).