Magnetic structure and enhanced $T_N$ of the rare-earth intermetallic compound TbRhIn$_5$: Experiments and mean-field model


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In this work the physical properties of the intermetallic compound TbRhIn$_5$ were investigated by means of temperature-dependent magnetic susceptibility, electrical resistivity, heat-capacity, and resonant x-ray magnetic diffraction experiments. TbRhIn$_5$ is an intermetallic compound that orders antiferromagnetically at $T_N$=45.5 K, the highest ordering temperature among the existing RRhIn$_5$ (1-1-5, R=rare-earth) materials, which in contrast to what is expected from a de Gennes scaling along the RRhIn$_5$ series. The x-ray resonant diffraction data have allowed us to solve the magnetic structure of TbRhIn$_5$. Below $T_N$, we found a commensurate antiferromagnetic structure with a propagation vector $(1/2,0,1/2)$ and the Tb moments oriented along the c axis. Strong (over two orders of magnitude) dipolar enhancements of the magnetic Bragg peaks were observed at both Tb absorption edges $L_{II}$ and $L_{III}$, indicating a fairly high polarization of the Tb 5d levels. Using a mean-field model including an isotropic first-neighbor exchange interaction ($J_{R,R}$) and the tetragonal crystalline electrical field (CEF), we evaluate the influence of the CEF effects in the physical properties of TbRhIn$_5$. The results reported here seem to corroborate a general trend of CEF-driven effects on $T_N$ along the RRhIn$_5$ series.

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I. INTRODUCTION

The discovery of new series of structurally related compounds with novel physical behavior is an important approach to explore fundamental problems in the physics of highly correlated electron systems. Such problems include the interplay between superconductivity, magnetism, and heavy-fermion behavior in structurally related materials. Although the microscopic origin of this interplay remains a mystery, the search for new heavy-fermion superconductors (HFSs) is partially guided by the knowledge that certain structures favor the formation of this heavy electron ground state. Remarkable examples of amazing physical properties occurring in structurally related compounds are the series Ce$_m$MnIn$_{2m+1}$ (M=Co, Rh, or Ir, m = 1, 2), and their Pu-based analogs PuMGa$_5$. These materials grow in a tetragonal variant of the Cu$_2$Au-type structure and can be viewed as layers of a cubic cell (CeIn$_3$ or PuGa$_3$) stacked sequentially along the c axis with intervening layers of M(In, Ga)$_2$. The discovery of unconventional superconductivity (USC) in many of these compounds is an exciting opportunity to further explore the possibility of magnetically mediated superconductivity in strongly correlated electron systems and its relationship with dimensionality and crystal structures. For instance, systematic alloying studies in CeRh$_{1-x}$Ir$_x$In$_5$ (Refs. 12 and 13) and PuCo$_{1-x}$Rh$_x$Ga$_5$ (Ref. 9) (PuCoGa$_5$ possesses the highest superconducting transition temperature, $T_c=18$ K, among the pure Pu-based compounds) have revealed an intriguing linear dependence between $T_c$ and the ratio of the tetragonal lattice parameters $c/a$ at ambient pressure, indicating that the increasing of the quasi-two-dimensional (2D) character of their crystal structure may favor USC.

Like the high-$T_c$ and the organic superconductors, HFSs are believed to be magnetically mediated superconductors. Furthermore, in most cases, USC seems to occur at the vicinity of a magnetically ordered state and the spin fluctuations (SFs) associated with this magnetic phase may mediate the superconducting pair formation. More recently, a bridge connecting the HFSs and high-$T_c$ superconductors (HTSCs) has been proposed by NMR studies in PuCoGa$_5$. These studies have shown that superconductivity in this material is unconventional with d-wave symmetry and similar properties to those found in other HFSs and HTSCs, suggesting that these classes of complex USC may share the same pairing mechanism.

Focusing our attention now on the Ce-based HFSs, the magnetic properties of these materials are associated with their 4f electrons. Although these compounds display obvious heavy-fermion behavior, evidence for low-temperature 4f local moment behavior has also been found in this family. This apparent contradiction is directly related to an open question in condensed matter physics regarding the details of the crossover between quasilocalized 4f electron magnetic behavior at high $T$ to a renormalized heavy-electron state at lower temperatures. However, if certain structures favor USC mediated by magnetic fluctuations, it is an important first step to understand how layered structures can affect crystalline electric field (CEF) anisotropy, magnetic exchange and/or anisotropic transport properties (quasi-2D band structure). In this regard, detailed studies of the 4f electron magnetism along the series of rare-earth- and actinide-based 1-1-5 compounds may be very informative.

In the case of the Ce-based compounds, their Nd-, Sm-, and Gd-based structurally related magnetic materials have been studied in detail. It has been found that the magnetic properties of these non-Ce analogs mainly depend on the interplay between CEF effects and exchange magnetic interaction. For example, among the Nd-based compounds...
NdMn$_2$ and Nd$_2$Mn$_8$ analogs for $M=$Rh or Ir, a systematic relationship was found between the antiferromagnetic (AFM) ordering temperature $T_N$ and the low-$T$ CEF splitting. In addition, the magnetic properties of the tetragonal variants NdMn$_2$ and Nd$_2$Mn$_8$ are compared to that for cubic NdIn$_3$, $T_N$ is enhanced by a factor of 2.13,19,25 In contrast, the tetragonal CeRhIn$_5$ and Ce$_2$RhIn$_8$ present a $T_N$ a factor of 2 smaller than that for CeIn$_3$, whereas for the Gd-based tetragonal materials the low-temperature magnetic properties remain nearly unaltered compared to the GdIn$_3$.13,19,25 Finally, the resolved magnetic structures for some of these compounds have revealed that the rare-earth magnetic moments lie in the $ab$ plane for CeRhIn$_5$ and GdRhIn$_5$ compounds and point along the $c$ axis for NdRhIn$_5$, tetragonal materials.21–24

To further explore the trends in the evolution of the magnetic properties within the series, particularly for the RRhIn$_5$ compounds, we have investigated in greater detail25 the physical properties and solved the magnetic structure of TbRhIn$_5$. The enhanced $T_N$ of TbRhIn$_5$ compared to its cubic relatives and/or compared to its counterparts the RRhIn$_5$ series could be explained by the details of the tetragonal CEF of a given rare earth, as previously shown by theoretical calculation using a mean-field model including an isotropic first-neighbors exchange interaction ($J_{R,R}$) and the tetragonal CEF.26 Particularly for Tb$^{3+}$ ions, an enhancement of $T_N$ is more likely to occur when the Tb ordered moments are aligned along the $c$ axis. Using resonant x-ray magnetic diffraction (XRMS) experiments, we have resolved the magnetic structure of TbRhIn$_5$ and shown that in fact the Tb moments orient along the $c$ axis and form a commensurate antiferromagnetic structure with propagation vector $\tau=\left(\frac{1}{2},0,\frac{1}{2}\right)$. Using the same model of Ref. 26 we have tried to investigate the influence of the CEF effect on the macroscopic properties of TbRhIn$_5$. From simultaneous fits to the anisotropic magnetic and specific-heat data (with the constraint of having the easy axis along the $c$ direction) using this model, we extract a preliminary CEF scheme and a set of CEF parameters for TbRhIn$_5$.

Apart from the necessary confirmation of the CEF scheme of TbRhIn$_5$ with additional experiments [for instance by inelastic neutron scattering (INS)], the reported results seem to confirm the CEF-driven $T_N$ behavior and the direction of ordered moments observed in other members of the series. We discuss also the particular case where the rare-earth moments order out of the $c$ axis, for which $T_N$ can be reduced by tuning the CEF parameters. This fact represents an interesting frustration mechanism that may play some role in the origin of the relevant low-dimensional SFs in complex classes of materials such as the Ce$_m$Mn$_{3m+2}$ ($M=$Rh, Ir, and Co; $m=1,2$) HFSs.

II. EXPERIMENT

Single crystals of TbRhIn$_5$ with dimensions up to approximately 2 cm$^3$ were grown from In flux, as reported previously.3,5 Most of the crystals show column habit, with their long axis along the tetragonal $c$ axis. The tetragonal HoCoGa$_5$-type structure31 with cell parameters $a=4.595(4)$ Å and $c=7.418(4)$ Å were confirmed by x-ray powder diffraction and the crystal orientation was determined by the usual Laue method. Specific-heat measurements were performed in a Quantum Design physical properties measurement system (PPMS) small-mass calorimeter that employs a quasidiabatic thermal relaxation technique. Magnetization measurements were made in a quantum design dc superconducting quantum interference device and electrical resistivity was measured using the PPMS low-frequency ac resistance bridge and four-contact configuration. The samples used in the electrical resistivity were screened to be free of surface contamination by residual In flux.

XRMS measurements were carried out at the bending magnet beamline XRD2 of the Brazilian Synchrotron Light Source (LNLS), in Campinas, Brazil using a double-bounce Si(111) monochromator, with sagittal focusing.27 A Rh-coated mirror was used to vertically focus the beam and also to eliminate third- and higher-order harmonics in the incident beam. The bending magnet source delivers photon beams with a flux of $\sim 3 \times 10^{10}$ photons/s around 8 keV at 100 mA in a spot of area $\sim 0.6$ (vertical) x 2.0 mm$^2$ (horizontal) at the sample, with an energy resolution from the source of $\Delta E/E \sim 10^{-4}$. Our experiments were performed in the vertical scattering plane, i.e., perpendicular to the linear polarization of the incident photons ($\sigma$ polarization$^{28}$).

A platelet of TbRhIn$_5$, from the same batch as that used for macroscopic property measurements, was mechanically polished perpendicular to the $c$ axis ([001] flat surface) to eliminate surface contamination from the residual flux and to increase the reflectivity, which gives a mosaic spread characteristic by the full width at half maximum (FWHM) of $\sim 0.04^\circ$. The sample was cut parallel to the $ab$ plane to have the final shape of a long block with dimensions of $4 \times 3 \times 1$ mm$^3$ and to investigate reflections in the [h0l] zone axis. The size of the sample was chosen to ensure that the whole incident beam is intercepted by the $c$-axis surface for all angles of interest. The sample was mounted on the cold finger of a closed-cycle He cryostat (base temperature 11 K) with a cylindrical Be window.

III. RESULTS

The temperature dependence of the magnetic susceptibility measured for a magnetic field $H$=1 kOe applied parallel $\chi_0$ and perpendicular $\chi_{\perp}$ to the $c$ axis is presented in Fig. 1(a). Figure 1(b) shows the polycrystalline average of Fig. 1(a) data taken as $\chi_{pol}(T) = \chi_0 + 2\chi_{\perp}$. From a linear fit to the inverse of $\chi_{pol}(T)$ for $T > 140$ K using a Curie-Weiss law, we have obtained a Curie-Weiss temperature $\theta = -47(1)$ K and the Tb$^{3+}$ effective magnetic moment $\mu_{eff}=9.4(1)\mu_B$. As can be seen in Fig. 1(a) the magnetic susceptibility of TbRhIn$_5$ is higher for the field applied along the $c$ axis, in agreement to what was found for all other $R$ members except Gd.3,18,19 The ratio $\chi_0/\chi_{\perp} \sim 2.08$ taken at $T_N$ is mainly determined by the tetragonal CEF and it reflects the same order of magnetic anisotropy found for other members of these series.3,18,19 The solid lines in Fig. 1(a) are the best fits to the data using the mean-field model of Ref. 26.
The best fit yields a $J_{RR}=0.2$ meV ($J_{RR}$ is equal to $zK_{RKKY}$ in the notation of Ref. 26) for the exchange parameter and the CEF parameters $B_{20}=-1.4\times10^{-1}$ meV, $B_{40}=1.3\times10^{-2}$ meV, $B_{60}=-5.3\times10^{-3}$ meV, $B_{80}=0.21\times10^{-4}$ meV, and $B_{64}=1.5\times10^{-4}$ meV. The CEF level scheme obtained from the splitting of the Tb$^{3+}$ ($J=6$) multiplet in the tetragonal symmetry, given by the above parameters, is built up of three doublets (where the lowest energy level is represented by the $\Gamma_5^{(1)}$ doublet; see Table I and seven singlets with an overall splitting of roughly 310 K. The energies and wave functions of each particular CEF state are given in Table I.

It is important to point out that the obtained CEF scheme and the set of parameters need confirmation by further experiments such as INS. Particularly for low-symmetry systems like TbRhIn$_5$, a meticulous and systematic analysis of a large set of experiments including INS may be required to unambiguously obtain a CEF scheme and a unique set of CEF parameters.

As a preliminary analysis, our model with the set of parameters above could reproduce well the magnetic anisotropy and the peak of the magnetic susceptibility at $T_N\sim45.5$ K for both directions [Fig. 1(a)]. At lower $T$ an anisotropic Curie-like tail was found in the magnetic susceptibility data for all measured crystals. We could not reproduce simultaneously the high-$T$ anisotropy, the peak at $T_N$, and the low-$T$ tails for any set of parameters. Further experiments at lower $T$ are needed to establish the origin of this behavior.

Figure 2(a) shows the specific heat divided by temperature and the corresponding magnetic entropy [Fig. 2(b)] in the temperature range $0<T<150$ K for TbRhIn$_5$. To calculate the magnetic entropy, the phonon contribution was estimated from the nonmagnetic specific-heat data of YRhIn$_5$ and subtracted from the total specific heat of the magnetic compound. The recovery magnetic entropy at high $T$ is close to its expected values for $J=6$. An anomaly in the specific-heat data associated with the onset of AFM order can be seen at $T_N=45.5$ K in good agreement with the temperatures where the maximum in the magnetic susceptibility occurs (see Fig. 1). Again, the solid line in Fig. 2(a) represents the best fit to the data using our model for the same parameters.

### Table I. CEF states and associated energies $E_i$ and eigenfunctions $\Psi_i$ for Tb$^{3+}$ ion ($J=6$) in tetragonal symmetry according to results from the mean field-model.

<table>
<thead>
<tr>
<th>Label $\Gamma_i$</th>
<th>$E_i$ (K)</th>
<th>Eigenfunctions $\Psi_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_5^{(1)}$</td>
<td>0</td>
<td>$-0.99[\pm5]+0.042[\pm1]+0.132[\mp3]$</td>
</tr>
<tr>
<td>$\Gamma_3^{(2)}$</td>
<td>65</td>
<td>$-0.843(6)-6)+0.537(2)+2)$</td>
</tr>
<tr>
<td>$\Gamma_4^{(2)}$</td>
<td>84</td>
<td>$-0.983(6)-6)+0.18(2)+2)$</td>
</tr>
<tr>
<td>$\Gamma_1^{(1)}$</td>
<td>100</td>
<td>$0.724(4)+0.689(0)$</td>
</tr>
<tr>
<td>$\Gamma_5^{(2)}$</td>
<td>122</td>
<td>$-0.132[\pm5]-0.817[\pm1]-0.561[\mp3]$</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>137</td>
<td>$(-4)-4)$</td>
</tr>
<tr>
<td>$\Gamma_3^{(3)}$</td>
<td>155</td>
<td>$0.537(6)-6)+0.843(2)+2)$</td>
</tr>
<tr>
<td>$\Gamma_4^{(2)}$</td>
<td>179</td>
<td>$-0.689(4)+0.724(0)$</td>
</tr>
<tr>
<td>$\Gamma_5^{(3)}$</td>
<td>274</td>
<td>$-0.04[\pm5]+0.826[\pm1]-0.562[\mp3]$</td>
</tr>
<tr>
<td>$\Gamma_4^{(4)}$</td>
<td>310</td>
<td>$0.18(6)-6)+0.983(2)+2)$</td>
</tr>
</tbody>
</table>
used in the fit of the $\chi(T)$ data [the best set of parameters was obtained from simultaneous minimization process for both $\chi(T)$ and $C/T(T)$ data]. It is evident that a reasonable agreement between the experimental data and the fits is also obtained for the heat capacity data with the exception of the $T_N = T_{N1}$ temperature range where the contribution of magnetic fluctuations are important.

The temperature dependence of the electrical resistivity for TbRhIn$_5$ single crystals is plotted in Fig. 3. Among various measured crystals, the room temperature value of the resistivity ranges between 10 and 35 $\mu\Omega$ cm. At high temperature the data always showed a metallic behavior while, at low temperatures, a clear kink can be seen at the ordering temperature $T_N$.

The $c/a$ ratio and $T_N$ values for RRhIn$_5$ compounds are shown in Fig. 4. The solid line in Fig. 4(a) is the expected behavior for $T_N$ and $\theta$ according to the de Gennes factor $(g_f-1)^2/3(J+1)$ for the ground-state multiplet $J$ of each rare earth normalized by its value for GdRhIn$_5$. As for $R$=Ce and Nd,$^{19}$ $T_N$ of TbRhIn$_5$ does not follow the de Gennes scaling. Interestingly, $T_N$ for TbRhIn$_5$ is the highest among the existing RRhIn$_5$ members.

The microscopic low-temperature magnetism of TbRhIn$_5$ was further investigated by XRMX. For the sample orientation used in the experiments, with the zone axis [00l] parallel to the scattering plane, the resonant scattering cross section (the nonresonant scattering contribution was observed to be negligible) for the case of a dipolar resonance with a linear polarized incident beam perpendicular to the scattering plane may be written as$^{28,32}$

$$I \approx \sum_n \hat{u}_n \cdot \hat{k} e^{iQ \cdot r_n}$$

where $Q = k_f - k_i$, is the scattering vector, $\hat{k}_i$ is the direction of the scattered wave vector $k_i$, and $\hat{u}_n$ is the moment direction at the $n$th site. The proportionality symbol includes $Q$-independent resonant amplitudes, the Lorentz factor, arbitrary scale factors, and an angular correction factor for asymmetric reflections. The summation is over all the $n$th resonant ions in the magnetic unit cell and $r_n$ is the position of such an ion. Note that in the present geometry and in the absence of an in-plane $\pi$-polarized component of the incident beam, the dipolar resonant cross section terms are not sensitive to the component of the ordered moment perpendicular to the scattering plane (i.e., along the b axis).

Below $T_N = 46$ K, careful scans along the [h0l] direction revealed superstructure Bragg peaks of type $(\pm 2n+1,0,\pm 2n+1)$ ($n$, $m$ integers), appearing as a result of the strong resonant enhancements of the magnetic peaks for both Tb $L_{II}$ and $L_{III}$ edges, and the high magnetic moment per Tb$^{3+}$ ion of $\mu = 9.5 \mu_B$. In the low-temperature phase, magnetic peaks $(0,2n+1,0,2n+1)$ were also observed, revealing a twinned magnetic structure. The intensities of $(\pm 2n+1,0,\pm 2n+1)$ and $(0,2n+1,0,2n+1)$ were comparable, suggesting approximately equal domain population. Therefore, our magnetic cell is duplicated in the $a$ and $c$ directions when compared to the chemical one. Above $T_N$ only charge peaks consistent with the tetragonal HoCoGa$_5$-type structure were observed. The widths (FWHM) of magnetic peaks were the same as that for equivalent scans through a charge Bragg peak.

The magnetic structure of TbRhIn$_5$ was then resolved from the obtained modulation vector $\tau = (\frac{1}{2},0,\frac{1}{2})$ and the magnetic moment direction was established by comparing the observed intensities of some magnetic Bragg reflections with a model based on the resonant cross section of Eq. (1) (this method was first used in Ref. 33, where the reader can find more details about the correction factors entering the proportionality symbol). In Fig. 5, the integrated intensities of five magnetic reflections obtained at $T=20$ K are shown as solid squares. We used asymmetric reflections (Q vector out of the scattering plane) of the type $(0,2n+1,0,2n+1)$ in order to also analyze the $b$-axis component in the resonant cross section, which cannot be distinguished with Q vectors going into the scattering plane [i.e., with $(\pm 2n+1,0,\pm 2n+1)$ reflections]. Experimental reflections were taken at the maximum enhancement of the magnetic signal at the $L_{II}$ edge,
FIG. 5. Integrated intensities of five experimentally obtained magnetic reflections for TbRhIn₅ along with calculated intensities for a magnetic moment parallel to the c (solid line), a (dashed line), and b (dash-dotted line) axis. The reliability factor $R = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum I_{\text{obs}}$ is 4.4%.

$E=8253$ eV, and the data have been numerically integrated using Gaussian fit functions (solid squares in Fig. 5).

The comparison between the observed and calculated intensities has been made assuming the Tb³⁺ magnetic moment direction along all directions in the 3D space. The results for three possibilities are shown, the first one assuming the moments along the $c$ direction (solid line), the second with the moments aligned along the $a$ direction (dashed line), and the third one with the moments along the $b$ direction (dash-dotted line). As can be seen in Fig. 5 the model with the ordered moments $\hat{u}$ direction is the one in agreement with the observed data, as suggested by the susceptibility measurements in Fig. 1. A similar trend was also observed for NdRhIn₅ family compound in its low-temperature AFM phase with the moment locked in the $c$ axis. Given the experimental errors, the directions of the ordered moments is determined within $\pm 10^\circ$ of the $c$ direction.

In Fig. 6 the magnetic unit cell of TbRhIn₅ is shown according to results depicted in Fig. 5. A half magnetic cell is shown with moment directions at the Tb³⁺ ion crystallographic sites.

In order to use the resonant enhancement of the magnetic peaks, the primary beam energy was tuned to the $L_{II}$ and $L_{III}$ absorption edges of Tb³⁺ (tabulated as being 8252 and 7514 eV, respectively). In Figs. 7(a) and 7(b) we plot the scattered intensity of the $(1/2, 0, 1/2)$ magnetic Bragg peak as a function of the incident photon energy on tuning through the $L_{II}$ and $L_{III}$ edges, respectively. The data were corrected for absorption [coefficient $\mu(E)$ is shown with the solid line curve and the right side scale in Fig. 7] using the fluorescence emission. The inflection points of $\mu(E)$ curves were used to define the absorption edges. In both cases, the maximum resonant enhancement is observed $\sim 2$ eV above the edges, which is a signature of the electric dipole ($E1$) resonance involving electronic transitions $2p_{3/2} \rightarrow 5d$ and $2p_{3/2} \rightarrow 5d$. A remarkable enhancement of over two orders of magnitude for both edges has been obtained. From the fit to a Lorentzian-squared line profile, the width of resonance were found at both edges as being 6.2 and 6.4 eV for $L_{II}$ and $L_{III}$, respectively (corrected for energy resolution).

The relative strength $I(L_{II})/I(L_{III})$ of the resonant enhancements (the “branching ratio”) of the $E1$ resonances is $\sim 2.9$ which is in agreement with the theoretical expectations.

FIG. 6. The magnetic structure of TbRhIn₅ at 20 K. A half magnetic unit cell is shown. $\uparrow$ (↓) represents the directions “up” (“down”) of magnetic moments of Tb (depicted by gray filled circles) along the c axis.

FIG. 7. Energy dependence of the $(1/2, 0, 1/2)$ magnetic peak (open squares) through the Tb $L_{II}$ (a) and $L_{III}$ (b) edges. The open symbols are Gaussian fits to the elastic peak at each energy used in the scan. The data have been corrected for absorption. Solid line curve represents $\mu(E)$ obtained from the fluorescent yield (scale on the right). From the $\mu(E)$ inflection points we determine the absorption edge values (vertical dashed line) as being 8253 eV ($L_{II}$) and 7516 eV ($L_{III}$).
FIG. 8. Temperature dependence of the magnetic Bragg integrated intensities for (1/2, 0, 11/2) magnetic peak. The inset shows in detail the critical region around the transition at the Néel temperature for this compound. From a power-law fit to these data within the temperature range of approximately 3% below \( T_N \) we obtain \( T_N=45.56(2) \) K and a critical parameter \( \beta=0.35(2) \).

for branching ratios at the rare-earth L edges. This ratio is of interest since it relates to the underlying electronic and magnetic structures (see Refs. 35 and 36, and more recently, Ref. 37 and the references cited therein for more details). According to Ref. 35 in heavy rare-earth elements such as Tb, the \( E1 \) resonance at the \( L_{II} \) is \( \sim 2.5 \) times that of the \( L_{II} \) edge and Ref. 37 found a ratio of \( \sim 2 \). These expectations are in agreement with our observations. Intensity oscillations have been observed above the edges, and can be ascribed to magnetic diffraction anomalous fine structure oscillations \( ^{38} \) which are oscillations of the anomalous scattering factors associated with the interference of the photoelectron wave function with the surrounding atoms which cause a fine structure of oscillations in the energy line-shape spectrum.

The behavior of the ordered phase was measured as the temperature was raised at the \( L_{II} \) edge. The measurements of the integrated intensities were performed on the \( \{1/2,0,1\} \) satellite reflection. In Fig. 8 the data of longitudinal scans along this reflection are displayed as a function of the reduced temperature \( T/T_N \). As the temperature increases, the peak intensity gradually decreases and disappears above \( T_N \). This result, as well as the one obtained for the energy dependence described above, clearly confirms the magnetic nature of the observed peaks. Data were taken on two regimes: warming (filled circles in Fig. 8) and cooling (open circles). A fitting to the usual power-law expression \( \sim (1-T/T_N)^{2\beta} \) for a second-order phase transition (denoted by a solid line in the inset) within the temperature range of approximately 3% below \( T_N \) on the warming regime gives a magnetic transition temperature \( T_N=45.56(2) \) K and a critical order exponent \( \beta=0.35(2) \) for the Tb sublattice magnetization. This value of \( \beta \) is compatible with a three-dimensional Heisenberg system. No hysteresis was observed around the ordering temperature and the smooth decrease in intensity in the crossover to the paramagnetic phase is consistent with a second-order transition.

In Table II we summarize the experimental and CEF parameters obtained for TbRhIn\(_5\) in this work.

IV. DISCUSSION

As discussed in the Introduction, to follow the evolution of the 4f magnetism along the \( R_m\text{In}_3n+2 \) series is a crucial first step to achieve a deeper understanding of the complex physical properties of these materials. Early comparative studies of the magnetic properties in this family have shown that for the Ce-based materials where the magnetic ordered moments are not aligned along the \( c \) axis, \( T_N \) is suppressed to less than 0.5 of the CeIn\(_3\) value for CeRhIn\(_5\) where the Ce magnetic moments lie in the \( ab \) plane within the AFM state. On the other hand, for NdRhIn\(_5\), where the ordered moments point along the \( c \) axis, \( T_N \) is significantly enhanced when compared to that for the cubic NdIn\(_3\) parent compound. And last, for the Gd-based materials, where the CEF effects are small, the low-temperature magnetic properties remain nearly unaltered compared to those of GdIn\(_3\),\(^{13,19,21}\) suggesting that the low-temperature CEF scheme configuration plays a fundamental role in the observed trends.

Regarding the influence of a given CEF scheme in the AFM ordering temperature, it is reasonable to assume that if a system orders in a given direction and CEF parameters are modified making it more magnetically susceptible in some other direction, but without actually changing the order, the system may experiment some kind of magnetic frustration or the energy barrier between these states should diminish.\(^{26}\) Therefore, the ordering temperature should decrease as well. Inversely, if the system orders in a certain direction and CEF parameters change favoring even more this state, the ordering temperature should increase.

TbRhIn\(_5\) orders antiferromagnetically at \( T_N=45.5 \) K, which is an enhanced ordering temperature when compared to \( T_N \approx 32 \) K of TbIn\(_3\). As TbRhIn\(_5\) is more magnetically susceptible for a field applied along the \( c \) axis, according to the scenario above, the Tb moment must be ordered along the \( c \) axis to explain the enhanced \( T_N \) of TbRhIn\(_5\).\(^{26}\)

Taking advantage of the higher Q resolution available with x-ray scattering techniques and using the XRMS cross section to determine moment directions in magnetic compounds,\(^{28,33,39}\) we resolved the magnetic structure of TbRhIn\(_5\). Recently, this technique has also been successfully used to determine the magnetic structure of two Gd members of the \( R_m\text{In}_3n+2 \) \( (m=1,2; \ M=\text{Rh,Ir}; \ n=1) \) series.\(^{20,21}\)

| TABLE II. Experimental and CEF model parameters for TbRhIn\(_5\). |
|---|---|---|---|---|---|---|---|---|
| \( a \) (Å) | \( c \) (Å) | \( T_N \) (K) | J\(_{K,R} \) (meV) | \( T_{N,Rm\text{RhIn}_5} / T_{N,Rm\text{In}_3} \) | \( B_{20} \) (meV) | \( B_{40} \) (meV) | \( B_{44} \) (meV) | \( B_{60} \) (meV) |
| 4.595(4) | 7.418(4) | 45.5 | 0.2 | 1.39 | \(-1.4 \times 10^{-4}\) | \(1.3 \times 10^{-4}\) | \(-5.3 \times 10^{-3}\) | \(0.2 \times 10^{-4}\) | \(1.5 \times 10^{-4}\) |
As expected from the idea above, the solved magnetic structure of TbRhIn₅ reveals a commensurate AFM structure with propagation vector \( \frac{1}{2},0,\frac{1}{2} \) and the Tb moments oriented along the c axis (see Fig. 6). The direction of the ordered moments was established by comparing the observed intensities of five magnetic Bragg reflections (Fig. 5) with a model based on the resonant cross section for the case of dipolar resonance with a linear polarized incident beam perpendicular to the scattering plane [Eq. (1)]. The model considers the possible orientation of the moments along the three tetragonal axes. In Fig. 5 there is obvious agreement between experimental data and the model when the calculations were done assuming the moments along the c direction (solid line).

In addition, the mean-field model of Ref. 26 has shown that the enhancement of \( T_N \) for tetragonal compounds that orders axially is a general trend for tetragonal materials when the CEF parameters tend to increase the fluctuations along the c axis. Using this model we were able to fit our susceptibility and specific-heat data, reproducing all the main features of our data, including the prediction of AFM ordering along the c axis\(^{26} \) for the CEF and \( J_{R,K} \) parameters given in Table II. Although the CEF parameters of Table II may not be the unique set of this data, it is conclusive that the tetragonal CEF can cause the enhanced \( T_N \) of TbRhIn₅ since the Tb moments order along the c axis.

Therefore, the magnetic properties of the TbRhIn₅ compound are another experimental evidence of these general CEF-induced trends along \( R_m \text{In}_{3m+2} \) \((m=1,2; M=\text{Rh, Ir})\). As such, with the CEF effects being very important in determining \( T_N \), it is expected that the de Gennes scaling will fail to describe the behavior of \( T_N \) along the RRhIn₅ series (see Fig. 4).

It is important to note that the model of Ref. 26 has also predicted that, for \( J=5/2 \) and when the system spin is on the plane (for the Ce case), the Néel temperature approximately decreases when the CEF parameters increase fluctuations on the c axis, which is an effective measure of the system preference to be in the c direction. This prediction is consistent with the fact that the tetragonal CeRhIn₅ and Ce₂RhIn₄ present higher magnetic susceptibilities when the magnetic field is applied along the c axis, and \( T_N \) a factor of 2 smaller than that for CeIn₃. It is obvious that the hybridization and Kondo effects are very important in the case of the Ce-based materials, but it is interesting to note that this CEF-driven magnetic frustration mechanism combined with hybridization could create strong in-plane magnetic fluctuations that can mediate the quasi-2D unconventional superconductivity in these systems. It would be interesting to further test this model for other members of the \( R_m \text{In}_{3m+2} \) series that present a decrease of \( T_N \) for tetragonal compounds. Although the effect is only about 20\%, the tetragonal Sm-based compounds present smaller \( T_N \) values than their cubic relative SmIn₃. Therefore, according to the present model, the Sm-ordered moment for these materials should be aligned out of the c axis, most likely in the ab plane.

V. CONCLUSION

In conclusion, we have presented results of magnetic susceptibility, electrical resistivity, heat capacity, and x-ray magnetic diffraction experiments for antiferromagnet TbRhIn₅. The solved magnetic structure of TbRhIn₅ is commensurate with propagation vector \( \tau=\left(\frac{1}{2},0,\frac{1}{2}\right) \) and the Tb moments oriented along the c axis. The direction of the ordering Tb moments and the enhanced \( T_N \) of TbRhIn₅ compound is another experimental evidence of a more general CEF-induced trend along the \( R_m \text{In}_{3m+2} \) series \((m=1,2; M=\text{Rh, Ir})\). Using our mean-field model we evaluated the CEF effects on physical properties of TbRhIn₅ and proposed a possible CEF scheme and parameters for TbRhIn₅. Finally, based on the observed general CEF-induced \( T_N \) trend along the \( R_m \text{In}_{3m+2} \) series \((m=1,2; M=\text{Rh, Ir})\) we speculated that the particular case where the rare-earth moments ordered out of the c axis and the \( T_N \) can be reduced by tuning the CEF parameters could give rise to an interesting frustration mechanism that may be relevant to the physical properties of complex classes of materials such as the Ce₆m \text{In}_{3m+2} \((M=\text{Rh, Ir, and Co}; m=1,2) \) HFSs.

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