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Abstract
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Instability and evolution of the magnetic ground state in metallic perovskites GdRh$_3$C$_{1-x}$B$_x$

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We report investigations of the structural, magnetic, electrical transport, and thermal properties of five compositions of the metallic perovskite GdRh$_3$C$_{1-x}$B$_x$ (0.00 $\leq$ x $\leq$ 1.00). Our results show that all five compositions undergo magnetic ordering at low temperatures, but the nature of the ordered state is significantly different in the carbon- and the boron-rich compositions, where the former shows signatures of an amplitude-modulated magnetic structure and the latter exhibits evidence of an equal-moment incommensurate antiferromagnetic ordering. We also observe a remarkable field-dependent evolution of conduction carrier polarization in the compositionally disordered compounds. The outcomes indicate that this system is energetically situated in proximity to a magnetic instability where small variations in the control parameter(s), such as the lattice constant and/or electron density, lead to considerably different ground states.

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I. INTRODUCTION

Perovskite is one of the most well-studied crystal structure classes [1,2]. Materials crystallizing in this relatively simple structure exhibit many intriguing physical phenomena as well as application-oriented properties. Usually, when referring to a perovskite compound one means AB$_O$$_3$-type oxygen-containing material. However, there are several nonoxide perovskites that host a transition-metal ion in the place of oxygen at the face-center lattice sites of the cubic unit cell, and these are usually referred to as metallic perovskites. MgCNi$_3$ [3], RhFe$_2$N [4,5], Sc$_3$MC ($M = Al, Ga, In, Ti$) [6], Mn$_3$GaC [7–9], and RT$_3$X ($R = $ rare earth ion; $T = $ Pd, Rh; $X = $ B, C) [10–18] are some of the noted metallic perovskites that have been thoroughly investigated and several exciting properties such as superconductivity, giant magnetoresistance, anomalous thermal expansion, magnetocaloric effect, tunable valence behavior, and temperature-independent electrical resistivity have been observed. Interestingly, several binary RT$_3$ compounds related to the RT$_3$X perovskites also crystallize in the structurally related cubic AuCu$_3$ phase, where the body-center site remains vacant [19–23]. One such compound, GdPd$_3$, has recently been reported for its exciting oscillating magnetoresistance behavior that arises because of the extremely fragile magnetic structure of the material [24]. Binary GdRh$_3$, however, does not form in a melt-separable equilibrium phase [25], but the related GdRh$_3$B and GdRh$_3$C phases are reported to crystallize in an undistorted perovskite structure [16,18]. Preliminary results reported on GdRh$_3$X suggest considerably different properties of the boron- and the carbon-containing compounds [16].

We present in this paper an investigation of five compositions of GdRh$_3$C$_{1-x}$B$_x$ ($x = 0, 0.25, 0.50, 0.75, 1.00$) and find a systematic evolution of the properties that is apparently linked to the changes in the lattice parameter as well as the electron count of the system, both of which are altered when C is substituted by B. Our results indicate an evolution of the magnetic structure from an amplitude-modulated (AM) one in GdRh$_3$C to an equal-moment (EM) structure in GdRh$_3$B. This outcome, which is triggered by tweaking the relative compositions of small nonmagnetic metalloids B and C in a compound that hosts heavy rare-earth and transition-metal elements, suggests that these phases are formed near a magnetic tipping point where a small perturbation to the parameter(s) can destabilize the energy balance and lead to a considerably different ground states.

II. EXPERIMENTAL DETAILS

Samples were synthesized by arc-melting the stoichiometric amounts of highly pure (purity $\geq$ 99.9%) constituent elements from Alfa-Aesar in an inert atmosphere of argon. Postmelting, the samples were wrapped in Ta foils and annealed at 1000 °C for 240 h under vacuum. The samples had a metallic luster. Structural characterization of the samples was performed by refining temperature-dependent x-ray diffraction (XRD) data collected between 13 and 300 K using
a TTRAX-III powder diffractometer of Rigaku Inc., Japan which is equipped with a rotating-anode Cu x-ray source. The FullProf package [26] was used for Rietveld refinements of the powder XRD data collected at 15 temperatures on the five investigated compositions. Temperature- and magnetic-field-dependent magnetization $M$ measurements under zero-field-cooled conditions were carried out utilizing a Magnetic Properties Measurement System of Quantum Design, Inc., U.S.A. For these measurements, a small sample with a mass between 4.734 and 6.049 mg was secured inside a small transparent gel capsule with the help of a 1-cm² piece of Teflon tape to avoid sample movement during the measurement. The diamagnetic contribution of the sample holder, which was about four orders of magnitude smaller than the moment of each sample, was subtracted to obtain the magnetic signal of the sample. Heat capacity $C_p(T)$ data were collected using a Physical Properties Measurement System of Quantum Design, Inc., U.S.A. The masses of the samples used for the heat capacity measurements were between 5.308 and 11.133 mg. Electrical transport measurements were performed between the temperatures 2 and 300 K using a home-built multisample probe installed in a cryostat supplied by Oxford Inc., U.K. Bar-shaped samples with typical dimensions $1 \times 1 \times 4$ mm³ were used for the four-probe electrical resistivity measurements. In the cgs system of units for magnetism used in this paper, the Tesla (T) is a unit of convenience for the applied magnetic field, where $1 \, \text{T} = 10^4 \, \text{Oe}$.

### III. RESULTS

#### A. Crystal structure and lattice parameter

The room-temperature powder XRD data of GdRh₃C₁₋ₓBₓ ($x = 0, 0.25, 0.50, 0.75, \text{ and } 1$) show that all five investigated compositions crystallize in the cubic perovskite structure (space group: $Pm\bar{3}m$; No. 221) shown in Fig. 1(a). These simple cubic perovskite compounds are different from the vacancy-containing double perovskites that crystallize in a $T_1\text{Rh}_6\text{B}$-type structure (space group: $Fm\bar{3}m$; $Z = 4$) [27–29]. As shown in Supplemental Fig. S1 [30], the XRD data taken at 15 temperatures between $T = 13$ and $T = 300$ K demonstrate that the materials remain in a single phase at all temperatures within the aforementioned temperature range. Two small peaks that appear at $\approx 34^\circ$ and $\approx 41^\circ$ in the XRD pattern of GdRh₃B (Supplemental Figs. S1(e) and S1(j) [30]) have been identified as coming from binary GdRh₅ having the pattern of GdRh₃B (Supplemental Figs. S1(e) and S1(j) [30]) and therefore, it is expected to have a negligible effect on the occurrence of a phase transition at $\approx 100$ K, which is also supported by the $\rho(T)$ data in Supplemental Fig. S8 [30].

#### B. Magnetic properties

The magnetic susceptibilities $\chi \equiv M/H$ of the five GdRh₃C₁₋ₓBₓ compounds at low temperatures ($T \leq 30$ K) are shown in Fig. 2(a). The shapes and magnitudes of the $\chi(T)$ plots suggest ferromagnetic (FM) ordering in all five samples, but with considerably different magnetic ordering temperatures $T_M$ that range between $\sim 3$ and 10 K (Table I). The linear variation of the inverse susceptibility $\chi^{-1}$ with temperature for $T \gtrsim T_M$ indicates the presence of local magnetic moments in the materials that follow the Curie-Weiss law in the paramagnetic $T$ region [Fig. 2(b)]. The fitted values of the effective paramagnetic moment $\mu_{\text{eff}}$ and the Weiss temperature $\theta_p$ in the Curie-Weiss law are listed in Table I. The estimated value of $\mu_{\text{eff}}$ of GdRh₃C agrees with the expectation (7.94 $\mu_B$) for the spin $S = 7/2$ Gd$^{3+}$ ion with $g$-factor $g = 2$. However, the values of $\mu_{\text{eff}}$ in the remaining four compositions are slightly larger than expected, which apparently is due to partial

![FIG. 1. (a) Arrangement of Gd, Rh, and X atoms in the cubic unit cell of GdRh₃X ($X = B$ and C). Variation of the cubic unit cell parameter $a$ with the boron concentration $x$ is shown at temperatures (b) $T = 300$ K and (c) $T = 13$ K. (d) Temperature dependence of $a$ of the five GdRh₃C₁₋ₓBₓ compositions, where the $x$ is indicated next to the respective plots. Sizes of the error bars in (b)–(d) are smaller than the sizes of the symbols. Solid lines in (b)–(d) are guides to the eye.]
polarization of the conduction carriers [32–38]. The \( \theta_p \) varies almost linearly with the boron content [Fig. 2(c)]—a fact which shows that boron incorporation and the resultant lattice expansion manifest in a significant alteration of the strength of the resultant magnetic interaction in the compound. It also suggests that there are competing magnetic interactions present in these materials, and a minute tweaking of the parameters, such as the distance between the magnetic Gd\(^{3+} \) ions and/or the change in conduction carrier density induced by doping holes by replacing C with B, can alter their energy balance and could possibly lead to different magnetic ground states.

Figure 3(a) shows isothermal magnetization \( M \) versus magnetic field \( H \) data of the five GdRh\(_{3} \) \(_{1-x} \)B\(_{x} \) compositions measured at \( T = 2 \) K below their respective magnetic ordering temperatures (Table I). The \( M \) of the two end compositions, GdRh\(_{3} \)C and GdRh\(_{3} \)B, monotonically increases with increasing \( H \) and then saturates at high fields, exhibiting a behavior which is often observed in Gd\(^{3+} \) ferromagnets. While \( M(H) \) data of the two compounds are qualitatively similar, they are significantly different at low fields, where the former shows a slow saturation to \( \mu = 7 \mu_B \) but the latter attains this value, which is expected from the \( S = 7/2 \) Gd\(^{3+} \) ions, at the relatively lower field of \( \approx 0.5 \) T [Fig. 3(a)]. The \( M(H) \) data of the other three compositions, \( x = 0.25, 0.50 \), and \( 0.75 \), are similar, they are significantly different at low fields, where the former shows a slow saturation to \( \mu = 7 \mu_B \) but the latter attains this value, which is expected from the \( S = 7/2 \) Gd\(^{3+} \) ions, at the relatively lower field of \( \approx 0.5 \) T [Fig. 3(a)].

The magnetic ordering temperatures \( T_M, T_H, \) and \( T_R \) obtained from the \( \chi(T), C_p(T), \) and \( \rho(T) \) measurements, respectively, are listed in the column labeled by \( T^* \). The ratios \( f = \theta_p/\theta_R \) are listed in the last column.

### Table I. Parameters obtained from the analysis of powder x-ray diffraction \( I(2\theta) \), magnetic susceptibility \( \chi(T) \), magnetization \( M(H) \), heat capacity \( C_p(T) \), and electrical resistivity \( \rho(T) \) data of GdRh\(_{3} \)\(_{1-x} \)B\(_x \) (\( x = 0.00, 0.25, 0.50, 0.75, \) and \( 1.00 \)) and the nonmagnetic analog YRh\(_{3} \)B. The listed parameters are the lattice parameter \( a \), paramagnetic Weiss temperature \( \theta_p \), effective paramagnetic moment \( \mu_{\text{eff}} \), magnetic moment \( \mu_{50T} \) at \( H = 5.5 \) T, highest measured value of magnetic moment \( \mu_{\text{max}} \) for \( H \leq 5.5 \) T, Debye temperature \( \theta_D \), and Einstein temperature \( \theta_E \). The fractional contribution \( \alpha \) of the Einstein term to the \( C_p(T) \) is given in brackets below the respective value of the \( \theta_E \).

| Compound     | \( a \) (Å) | \( \theta_p \) (K) | \( \mu_{\text{eff}} \) (\( \mu_B \)) | \( \mu_{50T} \) (\( \mu_B/\text{f.u.} \)) | \( \mu_{\text{max}} \) (\( \mu_B/\text{f.u.} \)) | \( \theta_D \) (K) | \( \theta_E \) (K) | \( T^* \) | \( f \) |
|--------------|-------------|-------------------|-----------------------------|-------------------|-------------------|----------------|----------------|---------|-----|
| GdRh\(_{3} \)C | 13 K: 4.1343(1) | 1.3(7) | 7.95(5) | 7.01 | 7.01 | 522(21) | 158(3) | \( T_M = 3.3(2) \) | \( T_H = 3.3(1) \) | \( T_R = 3.3(5) \) | \( 0.4(2) \) |
|              | 300 K: 4.1421(1) |         |         |         |         |         |         | \[ \mu = 0.49(31) \] | \[ \mu = 0.49(31) \] | \[ \mu = 0.49(31) \] | \[ \theta_p/\theta_R \] |
| GdRh\(_{3} \)C\(_{0.75} \)B\(_{0.25} \) | 13 K: 4.1436(1) | 2.4(9) | 8.08(3) | 6.92 | 7.53 | 554(27) | 158(3) | \( T_M = 5.5(1) \) | \( T_H = 5.4(1) \) | \( T_R = 7.4(2) \) | \( 0.4(2) \) |
|              | 300 K: 4.1526(1) |         |         |         |         |         |         | \[ \mu = 0.51(31) \] | \[ \mu = 0.51(31) \] | \[ \mu = 0.51(31) \] | \[ \theta_p/\theta_R \] |
| GdRh\(_{3} \)C\(_{0.50} \)B\(_{0.50} \) | 13 K: 4.1480(7) | 6.7(9) | 8.00(6) | 6.42 | 7.08 | 526(18) | 154(3) | \( T_M = 9.0(2) \) | \( T_H = 9.7(1) \) | \( T_R = 10.6(1) \) | \( 0.7(1) \) |
|              | 300 K: 4.1568(2) |         |         |         |         |         |         | \[ \mu = 0.45(31) \] | \[ \mu = 0.45(31) \] | \[ \mu = 0.45(31) \] | \[ \theta_p/\theta_R \] |
| GdRh\(_{3} \)C\(_{0.25} \)B\(_{0.75} \) | 13 K: 4.1587(2) | 6.3(1) | 8.11(6) | 6.57 | 7.23 | 517(21) | 158(3) | \( T_M = 10.0(1) \) | \( T_H = 9.9(1) \) | \( T_R = 10.8(1) \) | \( 0.64(2) \) |
|              | 300 K: 4.1681(1) |         |         |         |         |         |         | \[ \mu = 0.49(31) \] | \[ \mu = 0.49(31) \] | \[ \mu = 0.49(31) \] | \[ \theta_p/\theta_R \] |
| GdRh\(_{3} \)B | 13 K: 4.1658(1) | 8.2(5) | 8.05(2) | 6.92 | 6.92 | 516(21) | 157(3) | \( T_M = 9.5(1) \) | \( T_H = 9.4(1) \) | \( T_R = 11.9(1) \) | \( 0.87(5) \) |
|              | 300 K: 4.1734(1) |         |         |         |         |         |         | \[ \mu = 0.48(31) \] | \[ \mu = 0.48(31) \] | \[ \mu = 0.48(31) \] | \[ \theta_p/\theta_R \] |
| YRh\(_{3} \)B | 300 K: 4.1647(2) |         |         |         |         |         | 551(12) | 171(2) | \[ \mu = 0.48(21) \] | \[ \mu = 0.48(21) \] | \[ \mu = 0.48(21) \] | \[ \theta_p/\theta_R \] |
0.50, and 0.75 are substantially different. The \( M \) in these three compositions first increases sharply with increasing \( H \), then shows a broad peak, and then starts decreasing with the further increase in \( H \). The maximum moment values \( \mu_{\text{max}} \) that these three compositions attain are significantly larger than possible solely from the Gd\(^{13}\) ions (Table I), indicating that a sizable field-dependent contribution to the measured moment is coming from polarization \( P \) of the conduction carriers [32–38]. The \( \mu_{\text{max}} \) is largest in GdRh\(_3\)C\(_{0.75}\)B\(_{0.25}\), where it attains a value of 7.53 \( \mu_B \) (Table I), suggesting that the \( P \) contributes up to 0.53 \( \mu_B \) to the observed moment in this composition in the explored range of applied fields (Fig. 3, inset). This value is in good agreement with the polarization \( 0.6 \pm 0.1 \mu_B \) reported in the literature for Gd metal [32–37]. The nonmonotonic behavior of the \( M(H) \) data suggests that the \( P \) is strongly field dependent in these three compounds. Furthermore, the \( P(H) \) plot shows a crossover from positive to negative values at the sample-dependent \( H_s \) (Fig. 3, inset), suggesting that along with the magnitude its orientation relative to the localized moments also evolves with \( H \), which is a remarkable result. Additionally, the fact that the field dependence of \( P \) occurs only in the compositions where either boron or carbon is partially substituted suggests that this phenomenon is apparently linked with the lattice disorder introduced by the substitution and the resultant modification of the local interactions. As expected in the paramagnetic state of localized moments, the \( M(H) \) plots are linear at \( T = 50 \) K [Fig. 3(b)]. The \( M(H) \) isotherms of the GdRh\(_3\)C\(_{1-x}\)B\(_x\) compounds at three temperatures are shown in Supplemental Fig. S4 [30].

### C. Heat capacity and magnetic entropy

The heat capacity \( C_p(T) \) data of the five GdRh\(_3\)C\(_{1-x}\)B\(_x\) compositions shown in the left panels of Fig. 4 demonstrate the occurrence of magnetic transitions at their respective ordering temperatures \( T_{\text{H}} \) (Table I), where the \( T_{\text{H}} \) values are the temperatures of the peaks in the \( C_p(T) \) data. The \( C_p(T) \) data shown in the right panels of Fig. 4 suggest that spin fluctuations persist up to \( \sim 10 \) and \( \sim 20 \) K in GdRh\(_3\)C and GdRh\(_3\)B, respectively. Spin fluctuations are also observed up to a sample-dependent temperature \( 10 \leq T \leq 20 \) K in the other three compositions. The high-temperature \( (T > T_{\text{H}}) \) \( C_p(T) \) data could not be fitted satisfactorily using solely the Debye model of acoustic phonons, as shown in Supplemental Fig. S5 [30], but the fit improved significantly by employing the single-frequency Einstein term [30] along with the Debye model [39] (Fig. 4, left panels). The estimated Debye temperature \( \Theta_D \), the Einstein temperature \( \Theta_E \), and the fractional contribution of the Einstein term are all listed in Table I. The low-temperature \( (T \leq 30 \) K) \( C_p(T) \) data of the GdRh\(_3\)C\(_{1-x}\)B\(_x\) compositions are shown along with the \( C_p(T) \) data of the nonmagnetic reference compound YRh\(_3\)B in the respective right panels in Fig. 4. The data for the boron-rich compositions \( (x = 0.50, 0.75, \text{and} 1.00) \) show a narrow peak centered at \( T_{\text{H}} \) and a shoulder at lower temperatures. This behavior is expected from an EM local moment system under the mean-field model [40–44]. However, the \( C_p(T) \) data on the carbon-rich compositions \( (x = 0.00 \text{ and} 0.25) \) exhibit a significantly different behavior in that they show a broad peak centered at their \( T_{\text{H}} \), which is qualitatively different from the \( \lambda \)-shaped peaks observed in the three boron-rich compositions. Such broad transitions have been reported in several Gd-based materials and are a characteristic signature of AM magnetic structures [43–47]. Molecular field theory predicts that the jump in \( C_{\text{mag}} \) for EM systems with spin \( S = 7/2 \) at the magnetic ordering temperature is \( \Delta C_{\text{mag}} = 21.14 \) J/mol K [44]. The observed \( \Delta C_{\text{mag}} \) is 16.9(3) and 11.5(5) J/mol K in the boron- and the carbon-rich compositions, respectively. The \( \Delta C_{\text{mag}} \) observed in the boron-rich compositions, which was about 20% smaller than expected, likely results from a broadening of the transition due to the presence of substantial short-ranged correlations that start building up above the respective \( T_{\text{H}} \) values (Fig. 4).

The magnetic contributions to the heat capacities estimated using \( C_{\text{mag}}(T) = C_p(T) - C_{\text{YRh}3\text{B}}(T) \) are shown in the left panels of Fig. 5. The \( C_{\text{mag}} \) below 1.8 K was extrapolated using \( C_{\text{AFM}} = BT^3 \), applicable for antiferromagnetic (AFM) spin waves [48], where \( B \) is a constant. The magnetic entropy \( S_{\text{mag}} \) of the boron-rich compositions \( (x = 0.50, 0.75, \text{and} 1.00) \),
FIG. 4. Left panels (a, c, e, g, i): Heat capacity \( C_p \) versus temperature \( T \) data of the five \( \text{GdRh}_3\text{C}_1-x\text{B}_x \) compositions. Solid red curves in the left column represent the fits of the \( C_p(T) \) data using the Debye–Einstein model as discussed in the text. Right panels (b, d, f, h, j): Low-temperature (\( T \leqslant 30 \text{ K} \)) \( C_p(T) \) data of the \( \text{GdRh}_3\text{C}_1-x\text{B}_x \) compositions are shown along with the \( C_p(T) \) data of the nonmagnetic analog compound \( \text{YRh}_3\text{B} \). The temperature axis of the \( C_p(T) \) data of \( \text{YRh}_3\text{B} \) was scaled to incorporate the difference in its molar mass compared to the \( \text{GdRh}_3\text{C}_1-x\text{B}_x \) compounds [24].

calculated using

\[
S_{\text{mag}}(T) = \int_0^T \frac{C_{\text{mag}}(T')}{T'} dT',
\]  

(1)
saturates to \( R \ln(2S+1) = R \ln 8 = 17.3 \text{ J/mol K} \) at around 10 K as expected for a \( S = 7/2 \) system (Fig. 5), where \( R \) is the molar gas constant.

However, as shown in Supplemental Fig. S6 [30], the \( S_{\text{mag}} \) of the carbon-rich compositions (\( x = 0.00 \) and 0.25) calculated using Eq. (1) appear to saturate at values which are significantly smaller than \( R \ln 8 \), suggesting a nonzero \( S_{\text{mag}} \) at \( T \approx 0 \text{ K} \) for these compositions. Therefore, we recalculated the \( S_{\text{mag}} \) for these two compositions using the expression

\[
S_{\text{mag}}(T) = R \ln 8 + \int_{30 \text{ K}}^T \frac{C_{\text{mag}}(T')}{T'} dT'.
\]  

(2)

As shown in Figs. 5(b) and 5(d), this explicitly gives the nonzero entropies extrapolated to \( T = 0 \). We find that the precise form of \( C_{\text{mag}}(T) \) extrapolated to \( T = 0 \) has little influence on the result. This observation indicates that not all the Gd spins order in these compositions and can at least partially explain the reduced heat capacity jump at the ordering temperature.
temperature. Thus, our $C_{\text{mag}}(T)$ and $S_{\text{mag}}(T)$ data collectively indicate that the magnetic ground state of the GdRh$_3$C$_{1-x}$B$_x$ compounds undergoes a notable transformation between $x = 0.25$ and $x = 0.50$.

### D. Electrical resistivity

The electrical resistivities $\rho$ of all five GdRh$_3$C$_{1-x}$B$_x$ compositions show metallic $T$ dependences at temperatures $T \gtrsim T_K$ (Fig. 6), where $T_K$ is the magnetic ordering temperature deduced from the $\rho(T)$ data. The high-temperature $\rho(T)$ data were fitted satisfactorily using the Bloch-Grüneisen model of electrical transport in metals (Supplemental Fig. S7 [30]). At low temperatures, the $\rho(T)$ data of the $x = 0.25$, 0.50, and 0.75 compositions exhibit well-defined peaks at their respective $T_B$ values (Table I), below which the $\rho(T)$ decreases sharply with a decrease in $T$ [Figs. 7(b)–7(d)]. The $\rho(T)$ of GdRh$_3$B shows a kink at $T_K$ and then an additional peak at $T_{R2}$ [Fig. 7(e)]. However, the low-$T$ $\rho(T)$ behavior of GdRh$_3$C is different; it exhibits a small, broad hump at its $T_R$ [Fig. 7(a)], then decreases sharply with a decrease in $T$. The sharp decrease in the $\rho(T)$ data observed in all five compositions below their respective $T_R$ values is due to the reduction in the spin disorder scattering in the magnetically ordered states.

To extract the magnetic contribution $\rho_{\text{mag}}$ contained in the observed $\rho(T)$ peaks of the GdRh$_3$C$_{1-x}$B$_x$ compositions, we subtracted the fitted Bloch-Grüneisen resistivity $\rho_{BG}$ from the experimental data (Fig. 7). The temperature variation of $\rho_{\text{mag}} = \rho - \rho_{BG}$ is shown in Figs. 8(b)–8(e) for $x = 0.25$, 0.50, 0.75, and 1.00, respectively. Because of the shallow hump observed in the $\rho(T)$ of GdRh$_3$C, it was not meaningful to do this analysis on this compound. Instead, we have plotted the thermal hysteresis data of GdRh$_3$C [Fig. 8(a)], which shows that the shallow peak disappears when the $\rho(T)$ data are taken while cooling the sample from above its magnetic ordering temperature. This suggests the presence of some kind of spin or domain blocking associated with the magnetic order in this compound. A similar observation was reported earlier in magnetic measurements of GdRh$_3$C [16]. The peaks observed in the $\rho(T)$ data of the $x = 0.25$, 0.50, 0.75, and 1.00 compositions are likely due to the opening of an AFM superzone pseudogap at the Fermi surface that occurs because of a magnetic structure which is incommensurate with the periodicity of the crystal structure [49–54]. To test this scenario, we fitted the $\rho_{\text{mag}}(T)$ data for $T_R \leq T \leq 30$ K using $\rho_{\text{mag}}(T) = A e^{\Delta/2k_B T}$, where $A$ is a constant and $2\Delta$ is the superzone band gap. We obtained reasonable fits for all four compositions. The fitted values of the parameters are listed in Supplemental Table S1 [30].

### IV. DISCUSSION

Our temperature-dependent XRD data and their analyses confirm that all five GdRh$_3$C$_{1-x}$B$_x$ compositions we studied are single phase and crystallize in the cubic perovskite structure. While the lattice parameter $a$ of four compositions with $x = 0.25, 0.50, 0.75$, and 1 show a positive thermal expansion between 13 and 300 K, the $a(T)$ of GdRh$_3$C exhibits an anomaly at $T \approx 100$ K. Since the temperature of the anomaly is quite high compared to the magnetic ordering temperature of the material, it is unlikely to be related to the magnetism of the compound. As electrical transport behavior of crystalline
materials closely correlates with the structural characteristics and can often detect small variations of them, we plotted the temperature variation of the temperature derivative of the resistivity $\rho(T)$ along with the $\alpha(T)$ of GdRh$_3$C in the same figure (Supplemental Fig. S8 [30]). Whereas $\alpha(T)$ exhibits a slope discontinuity at $\approx$ 100 K, $\rho(T)$ exhibits a discontinuity in its curvature at the same temperature, $T = 98(3)$ K. While the investigation of this transition is beyond the scope of this paper, the observed anomaly in $\alpha(T)$ is likely related to the energy balance between the bonding strengths and/or the elastic couplings and anharmonicity of the pair potential that leads to positive thermal expansion.

While the $\chi(T)$ and $M(H)$ data indicate FM ordering at low temperatures, the substantial evolution of $\theta_p$ in Fig. 2(e), which increases roughly six times in the boron-end composition compared to the carbon-end composition, suggests that competing magnetic interactions are present in the system, and their resultant strength varies significantly with changes in composition and lattice parameter. Additionally, the Gd spin is large, so molecular field theory is often useful to describe and fit the magnetic and thermal properties versus the applied magnetic field and temperature of Gd$^{3+}$-containing spin $S = 7/2$ compounds when these ions are crystallographically equivalent as in the present compounds [41]. For such compounds the ratio $f = \theta_p/T_{mag}$ can be instructive, where $\theta_p$ is the Weiss temperature in the Curie-Weiss law and $T_{mag}$ is the magnetic ordering temperature. For ferromagnets one expects $f = 1$, whereas for antiferromagnets one finds $f < 1$. A value between 0 and 1 can arise when competing FM and AFM interactions are both present between a spin and its neighbors such as in A-type antiferromagnets. As shown in the last column of Table I, for all the GdRh$_3$C$_{1-x}$B$_x$ compositions this ratio is $< 1$ within the error bars, except possibly for $x = 1$, indicating the presence of competing FM and AFM interactions and AFM ground states in these materials.

The slightly larger than expected value of $\mu_{eff}$ and the anomalous field dependence of $M$ observed in the $x = 0.25$, 0.50, and 0.75 compositions suggest that the conduction carriers not only are partially polarized but also are coupled in a field-dependent way with the Gd moments. As these compositions contain both boron and carbon, this remarkable phenomenon is apparently linked with the lattice disorder and the resultant alteration of the local interactions triggered by the substitution.

In this complex system, the $C_p(T)$ and $\rho(T)$ data provide substantial additional information on the nature of the underlying magnetic ground state. The shapes of the low-temperature $C_{mag}(T)$ plots confirm that the magnetic ground states are quite different in the boron- and the carbon-rich compositions. While the former exhibits a $\lambda$-shaped peak expected from the EM systems, the latter shows a broad peak with a reduced $\Delta C_{mag}(T)$ at the magnetic ordering temperature, a behavior which is reported for AM systems [43–47]. In Ref. [44], Blanco et al. estimate that $\Delta C_{mag}$ in AM systems is $2/3$ of the jump observed for the same in EM systems. Consistent with their estimation, we observed a jump of $\Delta C_{mag} = 16.6(3)$ J/mol K in the boron-rich compositions and $\Delta C_{mag} = 11.5(5)$ J/mol K in the carbon-rich compositions. Therefore, the shapes of the $C_{mag}(T)$ plots as well as the values of the $\Delta C_{mag}$ both collectively suggest that the underlying magnetic structure undergoes a transformation from AM type in $x = 0$ and 0.25 to EM type in $x = 0.50$, 0.75, and 1.00 compositions (Fig. 9). Furthermore, these results suggest that the GdRh$_3$C$_{1-x}$B$_x$ system is energetically positioned near a magnetic tipping point where a small change in the electron density, by 0.25 $e^-$/unit cell, induced by a change in composition can lead to a substantial alteration in the spin arrangements in their low-temperature magnetic structures.

The $S_{mag}(T)$ of boron-rich compositions ($x = 0.50, 0.75$, and 1.00) saturates at $Rhn8 = 17.3$ J/mol K, when the low-temperature ($T \lesssim 1.8$ K) $C_{mag}$ is extrapolated as $BT^3$ assuming AFM spin-wave behavior [Figs. 5(f), 5(h) and 5(j)]. However, if we consider a FM spin-wave dispersion and extrapolate the low-$T$ $C_{mag}$ as $BT^3/2$, then the $S_{mag}(T)$ of the same three compositions saturates to values which are considerably higher than Rhn8 (Supplemental Fig. S6 [30]). This shows that the AFM spin-wave description is a correct approximation for these three compositions. One can employ a more accurate expression given in Ref. [41] for the description of the low-temperature $C_{mag}$. However, since the simplified $BT^3$ provides a precise estimate at low temperatures, we have used it in our calculations. As the $\theta_T$ decreases with increasing carbon content, it seems more appropriate to use the same AFM spin-
wave formalism for extrapolation of the low-temperature $C_{\text{mag}}$ of the carbon-rich ($x = 0$ and 0.25) compositions. However, if we do that, then the $S_{\text{mag}}(T)$ saturates to values which are significantly smaller than Rh8 (Supplemental Fig. S6 [30]), suggesting that the AFM spin-wave approximation does not describe the magnetic excitations down to the lowest temperatures in the carbon-rich compositions that show signatures of AM magnetic behavior. Furthermore, even the FM spin-wave description does not account for the lost entropy of GdRh$_3$C (Supplemental Fig. S6 [30]). These observations further infer that not all the Gd spins are ordering at the respective $T_H$ values of the carbon-rich compositions. This behavior is typical of AM systems where the amplitude of the ordered magnetic moment varies in a periodic manner right below the magnetic ordering temperature and often evolves to an EM type structure at lower temperatures [44]. While neutron diffraction measurements are essential for determining the exact magnetic structure and its evolution below the magnetic ordering temperature, our $C_{\text{mag}}(T)$ and $S_{\text{mag}}(T)$ data together do provide indications that the underlying magnetic structures in boron-rich compositions ($x = 0.50, 0.75,$ and 1.00) are EM type, while the same in carbon-rich compositions ($x = 0$ and 0.25) are AM type (Fig. 9).

The GdRh$_3$C$_{1-x}$B$_x$ materials show a metallic behavior in the electrical transport measurements. The low-temperature $\rho(T)$ data for all the compositions show clear features, in terms of either the broad hump observed in the case of GdRh$_3$C or the well-defined peaks observed in the other four compositions. The observation of activated $T$ dependence $\rho_{\text{mag}}(T) = A e^\Delta/k_B T$ in the boron-rich compositions suggests that the underlying magnetic structure in these systems is an incommensurate AFM type (Fig. 8). The value of $\Delta$ goes down by a factor of about 3 in the carbon-rich composition $x = 0.25$ (Supplemental Table S1 [30]). This suggests that the superzone pseudogap starts closing with the increase in the carbon content, and the gap is fully closed with no indication of the activated behavior in GdRh$_3$C. These results confirm the conclusions achieved from the analysis of the $C_p(T)$ data and show that the magnetic ground states are significantly different in boron-rich compositions ($x = 0.50, 0.75,$ and 1.00) where the magnetic structure is EM type and in carbon-rich compositions ($x = 0.00$ and 0.25) which likely have an AM type magnetic structure.

Therefore, our results show that that while the magnetic measurements indicate an FM ordering in all five investigated compositions, the actual ground states are rather complicated and are decisively not a prototypical FM type. Competing interactions are definitely present in GdRh$_3$C$_{1-x}$B$_x$ and evolve with substitution. The interplay of the interactions within the localized Gd$^{+3}$ moments as well as between the local moments and the conduction carriers leads to a variety of outcomes such as field-dependent behavior of conduction carrier polarization, opening of the superzone pseudogap, and evolution of the ground state from AM type to EM type. If we consider only the two end compositions, then the magnetic ground states evolve from AM type in GdRh$_3$C to incommensurate EM type in GdRh$_3$B. It would be interesting to investigate whether this evolution is solely triggered by the increase in the lattice parameter and hence the distance between moment-bearing Gd$^{+3}$ ions or the change in the electron density introduced by doping holes in the system by replacing C with B also plays a role in this mechanism. In either case, this system, whose magnetism originates from 3-state Gd$^{+3}$ ions that do not have the added complexity of crystalline electric field effects or Kondo/heavy-fermion behaviors, presents an example of a scenario where the resultant magnetic ground state depends on a delicate balance of the parameters that are influenced by manipulating the relative content of small and nonmagnetic atoms.

V. CONCLUSION

The metallic perovskite materials GdRh$_3$C$_{1-x}$B$_x$ show intriguing properties where perturbation caused in the lattice as well as in the electron density by manipulation of the relative contents of the metalloids B and C manifests in a very significant transformation in the magnetic ground state—presumably AM type in GdRh$_3$C to incommensurate EM type in GdRh$_3$B. The observed noteworthy alteration in the ground state which is triggered by small nonmagnetic entities indicates that this system is positioned near a magnetic instability where a small alteration in the parameters leads to considerably different outcomes. Another remarkable observation is the field-dependent evolution of the conduction carrier polarization, which needs to be further explored. Observation of outstanding properties in the oxygen-based as well as in the nonoxide perovskites suggests that we must keep exploring new and unexplored members of this remarkable family.

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