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Spin-glass behavior and zero-field-cooled exchange bias in a Cr-based antiperovskite compound PdNCr₃

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We report the synthesis, structure, and magnetic and electrical/thermal transport properties of a Cr-based antiperovskite compound PdNCr₃, which crystallizes in MgCNi₃-type cubic structure (space group *Pm* $\bar{3}$ *m*, No. 221). Interestingly, the spin-glass (SG) behavior, which is confirmed by the corresponding characteristic parameters (the freezing temperature $T_0 = 61.4(2)$ K, the dynamical exponent $z\nu = 7.103(3)$, and the flipping time $\tau_0 = 2.714(2) \times 10^{-11}$ s), is observed in PdNCr₃. Furthermore, the value of the Sommerfeld–Wilson ratio ($R_W \sim 1.024(3)$) for PdNCr₃ is much smaller than those of cluster glass systems ($R_W > 100$) and Kondo cluster glass systems ($R_W = 20$ – 30), indicating that PdNCr₃ is a canonical SG system. Density functional theory calculation shows that the origin of SG in PdNCr₃ is attributed to the disordering located N vacancies, which is further confirmed by the measurement of sample PdN_{0.75}Cr₃ with more N deficiency. On the other hand, infrequently, the zero-field-cooled exchange bias (ZFC-EB) with an exchange bias field (H_E) of about 350 Oe is observed after zero-field cooling from an unmagnetized state in PdNCr₃. The values of H_E are found to depend strongly on temperature and measuring magnetic field. For PdNCr₃, the ferromagnetic unidirectional anisotropy, which is the origin of our ZFC-EB effect, is formed around the ferromagnetic–SG interface isothermally during the initial magnetization process below the blocking temperature. In addition, the training effect of ZFC-EB in PdNCr₃ is observed after the zero-field cooling process and has been explained well in terms of the spin configurational relaxation model.

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1. Introduction

Since the typical antiperovskite superconductor MgCNi₃ was found,¹ the antiperovskite compounds with a formula AXM₃ (A = Ga, Al, Sn, Zn, Cu, In, Ge *etc.*; X = C, N; M = Mn, Fe, Ni *etc.*) have been studied extensively due to their relatively simple structure and interesting properties, such as nearly zero temperature resistivity coefficient,^{2–4} giant magnetoresistance effect,^{5,6} giant barocaloric effect,⁷ phase separation,⁸ negative thermal expansion,⁹ magnetocaloric effect,¹⁰ spin-glass (SG) behavior,^{11–14} and magnetostriction.¹⁵ However, recent investigations of AXM₃ mainly focused on the Mn-based antiperovskite compounds (AXMn₃).^{2,3,4–11,13–15} According to the

previous theoretical investigations,^{16,17} the properties of antiperovskite compounds AXM₃ is mainly contributed by M-3d electrons in AXM₃.^{16,17} Compared to AXMn₃, AxCr₃, which has the most similar 3d electrons, might also possess some novel physical properties or new characteristics. Therefore, it will be very interesting and necessary to study the Cr-based antiperovskite compounds (AxCr₃). However, to date, and to the best of our knowledge, there have been few research studies on Cr-based antiperovskite compounds (AxCr₃).^{18,19}

As we know, the SG behavior is usually found in magnetic frustration and disorder systems.²⁰ Recently, the SG behavior has been found in Mn-based and Fe-based antiperovskite compounds such as in GaNMn₃, Cu_{0.7}Ga_{0.3}NMn₃, and SnCFe₃.^{11–14} However, to date, there has been no report about the SG behavior in Cr-based antiperovskite compound. In general, the exchange bias (EB) is easy to observe in a SG system. Especially, when a system consisting of the ferromagnetic (FM)–SG or FM–antiferromagnetic (AFM) interface is cooled with the magnetic field through the freezing temperature of the SG or the Néel temperature of AFM, EB is induced.²¹ Over the past 50 years, EB has been extensively investigated because of its application in ultrahigh-density magnetic recording, giant magnetoresistance, and spin valve devices.^{22,23}

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Two types of EB have been reported:²¹ on the one hand, if the EB is observed after field cooling (FC), we call it conventional EB (CEB); on the other hand, if the EB is obtained after zero-field cooling, we name it zero-field-cooled EB (ZFC-EB).^{21,24} The major investigations of EB are focused on the CEB and the study of ZFC-EB is less.^{21,24} Herein, in antiperovskite compounds, ZFC-EB is rarely found and its origin is unclear.^{11–14}

As a typical Cr-based antiperovskite compound, PdNCr₃ is little known except for the early studies focusing on synthesis processes and structural properties.¹⁹ In this paper, we successfully synthesized the Cr-based antiperovskite compound PdNCr₃ by a solid-state reaction method. And then, comprehensive characterization of PdNCr₃ was performed. Surprisingly, SG behavior and ZFC-EB were observed in PdNCr₃. Further evidence for SG behavior and ZFC-EB was supported by different experimental measurements and the density functional theory (DFT) calculations. Finally, the origin of SG and ZFC-EB in PdNCr₃ was elaborated in detail.

2. Experiment and calculation details

Polycrystalline samples of nominal PdNCr₃ and PdN_{0.75}Cr₃ were prepared by the conventional solid-state reaction. Powders of Pd (3 N, Alfa Aesar), Cr (3 N, Alfa Aesar), and CrN (3 N, Alfa Aesar) were mixed in the desired proportions, pressed into pellets (at a pressure of 25 MPa), sealed in evacuated quartz tubes ($\sim 10^{-3}$ Pa) and then annealed at 1073–1123 K for about 5–7 days. After quenching the tubes to room temperature, the products were pulverized, mixed, pressed into pellets, and annealed again at 1073–1123 K for about 6–8 days in order to obtain good homogeneity and crystallinity of our samples. X-ray powder diffraction (XRD) was performed using a Philips X'pert PRO X-ray diffractometer with Cu K_α radiation ($\lambda = 0.15406$ nm) at room temperature. The Rietveld refinement of XRD data was carried out using the Rietica software. The compositions of our samples were determined using an electron probe micro-analyzer (EPMA). Magnetic measurements were carried out on a quantum design superconducting quantum interference device magnetometer (SQUID-5T). For each zero-field-cooled (ZFC) measurement, the superconductor magnet of SQUID was demagnetized by oscillating fields at 300 K in order to remove the pinned magnetic flux. The electrical/thermal transport properties were characterized on a quantum design physical property measurement system (PPMS-9T). The electrical transport measurements were performed by a four-probe method to eliminate contact resistance. The measurement of specific heat was carried out by a heat-pulse relaxation method on PPMS-9T. The electronic structure was obtained from DFT in the generalized gradient approximation (GGA) according to Perdew, Burke, and Ernzerhof.²⁵ The ABINIT^{26–28} code with the projected augmented-wave (PAW)^{29,30} method was used. Electronic wave functions are expanded with plane waves up to an energy cutoff of 1200 eV. Brillouin zone sampling is performed on a Monkhorst-Pack (MP) mesh³¹ of $16 \times 16 \times 16$. The self-consistent calculations

were considered to be converged when the total energy of the system was stable within 2.7211×10^{-5} eV.

3. Results and discussion

3.1. Characterization of basic physical properties

Fig. 1(a) shows the Rietveld refinement of room-temperature powder XRD patterns of PdNCr₃. All the diffraction peaks could be indexed to the corresponding structure and space group ($Pm\bar{3}m$, No. 221), and there is no impurity in the sample. The related fitting parameter values (such as χ^2 , R_p and R_{wp}) are quite small as presented in Table 1, suggesting that our sample is relatively good in quality. At the same time, the refined lattice constant of PdNCr₃ is 3.8883(2) Å, which almost matches well with the values of the previous report (3.889 Å).¹⁹ The resulting parameters of the Rietveld refinement are summarized in Table 1. In addition, the inset of Fig. 1(a) displays the sketch map of the crystal structure for PdNCr₃, where the Cr atoms are located at the face-centered positions, the Pd atoms at the cubic corners, and the N atoms at the body-centered positions. Fig. 1(b) displays the XRD patterns of PdN_xCr₃ ($x = 1, 0.75, 0.5$). For the sample $x = 0.75$, there is no impurity. However, when $x = 0.5$, the Cr impurity marked by asterisk is observed.

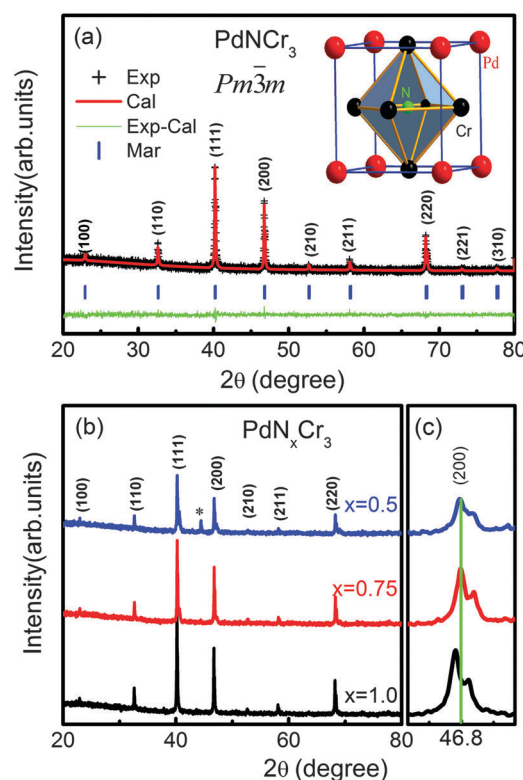


Fig. 1 (a) The Rietveld refined powder XRD patterns at room temperature for nominal PdNCr₃. The vertical marks (blue line) stand for the position of Bragg peaks, and the solid line (green line) at the bottom corresponding to the difference between experimental and calculated intensities. The inset shows the sketch of crystal structure for PdNCr₃. (b) The XRD patterns at room temperature for nominal PdN_xCr₃. (c) The enlargement of XRD patterns around the peak (200) for nominal PdN_xCr₃. The solid line is the guide to eyes.

Table 1 Crystallographic and refinement parameters obtained from the Rietveld refinement of powder XRD data of PdNCr₃

PdNCr ₃				
Structure		cubic		
Space group		<i>Pm</i> $\bar{3}$ <i>m</i>		
Formula unit		1		
Lattice constant (Å)		3.8883(2)		
<i>R</i> _P (%)		6.640		
<i>R</i> _{WP} (%)		5.366		
χ^2		1.462		
Atomic coordinates				
Atom	Wyckoff symbol	<i>x</i>	<i>y</i>	<i>z</i>
Pd	1a	0	0	0
N	1b	1/2	1/2	1/2
Cr	3c	1/2	1/2	0

Fig. 1(c) presents the enlargement of XRD patterns for PdN_xCr₃ (*x* = 1, 0.75, 0.5) around the (200) peak. It is necessary to point that a shoulder peak, which is induced by Cu K-Alpha 2 of X-ray diffractometer, is observed nearby the (200) peak. Compared with PdNCr₃, the (200) peak of samples *x* = 0.75 shifts to a high angle, suggesting that its lattice constant is contracted. In fact, the refined lattice parameter of PdN_{0.75}Cr₃ (*a* = 3.8862(2) Å), which is smaller than that of PdNCr₃ (*a* = 3.8883(2) Å), was obtained through the Rietveld refinement of XRD data. At the

same time, the value of Cr: Pd, measured by EPMA, is much close to 3 for both PdNCr₃ (Pd: Cr = 1:3.02) and PdN_{0.75}Cr₃ (Pd: Cr = 1:3.01). Here, it is well known that the N element is too light to determine its real content accurately using an EPMA or an Energy Dispersive Spectrometer. Therefore, the lattice contraction of PdN_{0.75}Cr₃ is mainly due to N deficiency. Namely, compared with PdNCr₃, PdN_{0.75}Cr₃ has more N deficiency.

In Fig. 2(a), we have presented the temperature dependent magnetization *M*(*T*) under ZFC and FC processes and inverse susceptibility χ^{-1} (*T*) (FC) curves of PdNCr₃ at a magnetic field of 1 kOe between 5 and 300 K. As shown in the *M*(*T*) curve of Fig. 2(a), two evident characters can be seen, namely, a weak irreversibility between *M*_{ZFC}(*T*) and *M*_{FC}(*T*) curves below *T*_{diff} = 72 K (defined by the temperature where *M*_{ZFC} = *M*_{FC}) and a sharp cusp in *M*_{ZFC}(*T*) curve around *T*_p = 48 K (defined by the maximum value of magnetization after ZFC process), which are indications of SG transition.¹² Fig. 2(b) shows the isothermal *M*(*H*) curves for PdNCr₃ at 5 and 300 K, and neither of them is saturated even up to *H* = 45 kOe. Especially, the room-temperature paramagnetic state is observed since the linear *M*(*H*) curve at 300 K. In order to get more information about the magnetism of PdNCr₃, we made a well fitted χ^{-1} (*T*) curve above 100 K by using the modified Curie-Weiss law:³²

$$\chi(T)^{-1} = \left(\frac{C}{T - \theta} + \chi_0 \right)^{-1}, \quad (1)$$

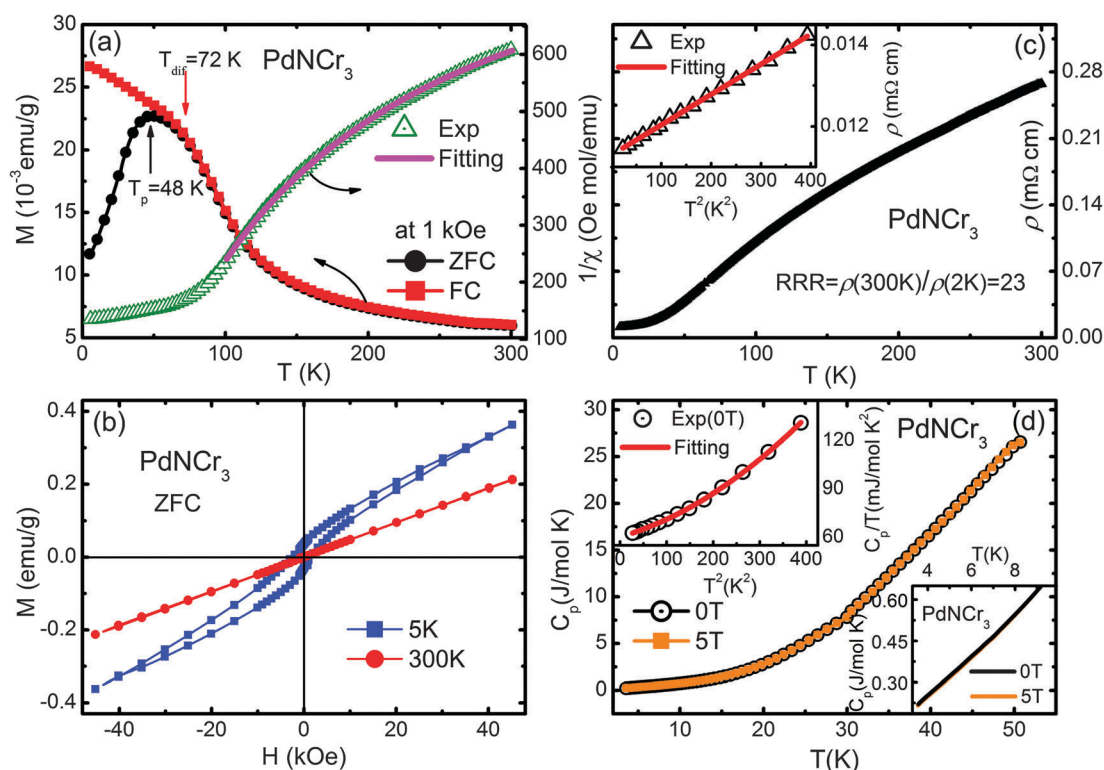


Fig. 2 (a) Temperature dependent magnetization *M*(*T*) curves under ZFC and FC processes and inverse susceptibility χ^{-1} (*T*) (FC) curves of nominal PdNCr₃ at a magnetic field of 1 kOe between 5 and 300 K. (b) *M*(*H*) curve at 5 and 300 K. (c) Temperature dependence of resistivity ρ(*T*) at zero magnetic field for nominal PdNCr₃. Inset presents the lower-*T* ρ(*T*) data plotted as ρ(*T*) vs. *T*². (d) Temperature dependent heat capacity *C_p*(*T*) at zero magnetic field and 5 T between 3.5 and 50 K for nominal PdNCr₃. Left inset displays the plot of *C_p*(*T*)/*T* vs. *T*² below 20 K and the solid line represents the linear fitting results according to eqn (3). Right inset reveals the enlargement of *C_p*(*T*) at lower temperatures.

Table 2 The parameters of magnetism, electrical transport, and specific heat in PdNCr₃ sample

	PdNCr ₃
χ_0 (10^{-3} emu mol ⁻¹)	1.03(3)
C (emu K mol ⁻¹)	0.1529(8)
θ (K)	51.2(3)
μ_{eff} (μ_B)	0.65(2)
ρ_0 ($\mu\Omega$ cm)	11.28(1)
A (10^{-3} $\mu\Omega$ cm K ⁻²)	7.5(1)
RRR	23.01(2)
γ (mJ mol ⁻¹ K ⁻²)	60.3(1)
β (mJ mol ⁻¹ K ⁻⁴)	0.084(2)
δ (10^{-6} mJ mol ⁻¹ K ⁻⁶)	2.53(5)
θ_D (K)	487.3(3)

where C is the Curie constant, θ stands for the Weiss temperature, and χ_0 is a temperature independent term. Correspondingly, we get the values of parameters as follows: $C = 0.153(2)$ emu K mol⁻¹, $\theta = 51.2(3)$ K, $\chi_0 = 1.03(3) \times 10^{-3}$ emu mol⁻¹. The positive Weiss temperature indicates the ferromagnetic (FM) exchange in this system. The effective magnetic moment per Cr atom, μ_{eff} is estimated to be $0.65(2) \mu_B$ from the relationship $\mu_{\text{eff}} = 2.83(C/\eta)^{0.5} \mu_B$ (where C is the Curie constant and η is the number of magnetic atoms in a unit cell and equal to 3 in the present case).³³

Fig. 2(c) displays the temperature dependence of resistivity $\rho(T)$ for PdNCr₃ at zero magnetic field between 2 and 350 K. Apparently, the magnitude of $\rho(T)$ increases basically with increasing temperature, indicating a good metallic behavior. As shown in the right inset of Fig. 2(c), the low- T resistivity is well fitted by the formula:³³

$$\rho = \rho_0 + AT^2, \quad (2)$$

where ρ_0 and A represent the residual resistivity and T^2 -term coefficient of the resistivity, respectively. This suggests a Fermi liquid behavior at low temperatures for PdNCr₃. Correspondingly, the fitting values of parameters $\rho_0 = 11.28(1) \mu\Omega$ cm and $A = 0.0075(2) \mu\Omega$ cm K⁻² are obtained. The low-temperature residual resistivity ρ_0 and the residual resistivity ratio (RRR), defined as $\text{RRR} = \rho(300 \text{ K})/\rho(2 \text{ K})$, are measures of sample quality such as in metals and alloys.³⁴ High ρ_0 values and small RRRs suggest sizable scattering from impurities, vacancies, or other defects.³⁴ Considering the polycrystalline nature of our sample, the small ρ_0 ($\sim 11.28 \mu\Omega$ cm) and relatively large RRR ($\sim 23.01(2)$) indicate a relatively good quality of PdNCr₃. Fig. 2(d) presents the low-temperature specific heat $C_P(T)$ curves with 0 T and 5 T. It can be found that both curves are almost overlapped in the whole temperature range and even in the enlargement of $C_P(T)$ curves at lower temperatures (to see the right illustration of Fig. 2(d)), suggesting tiny influence of spin fluctuation on specific heat for PdNCr₃. The left inset of Fig. 2(d) reveals the low-temperature (below 20 K) specific heat $C_P(T)$ of PdNCr₃ at 0 T plotted as $C_P(T)/T$ vs. T^2 , which can be well expressed by using the following equation:^{33,35}

$$C_P(T) = \gamma T + \beta T^3 + \delta T^5, \quad (3)$$

where γT describes the electronic contribution to the heat capacity and γ is the electron specific heat coefficient (Sommerfeld constant), βT^3 is the phonon contribution and β stands for phonon specific heat coefficient, and δT^5 reflects the deviation term. As a result, the fitted values of parameters γ , β , and δ are $60.3(1) \text{ mJ mol}^{-1} \text{ K}^{-2}$, $0.084(2) \text{ mJ mol}^{-1} \text{ K}^{-4}$, and $2.53(5) \times 10^{-6} \text{ mJ mol}^{-1} \text{ K}^{-6}$, respectively. The Debye temperature $\theta_D = \left(\frac{n \times 1.94 \times 10^6}{\beta} \right)^{1/3} = 487.3(3) \text{ K}$ (where n is the number of atoms in a unit cell, and here it is 5) is derived from the value of parameter β for PdNCr₃.³³

Finally, given the aforementioned experimental results the detailed parameters of magnetism, electrical transport, and low-temperature specific heat of PdNCr₃ are listed in Table 2.

3.2. Spin-glass behavior

In order to confirm and further illustrate the SG behavior, three methods of magnetic characterization including temperature dependent dc magnetization with different fields, frequency and field dependent ac susceptibility, and isothermal remanent magnetization are performed and described in the following text.

Fig. 3 shows the temperature dependence of dc magnetization $M(T)$ after ZFC and FC for PdNCr₃ at different magnetic fields. The magnetization increases with increasing magnetic field, while the T_p shifts to lower temperatures with increasing magnetic field, indicating the frozen SG state is gradually destroyed under large magnetic fields. These coincide well with other SG systems.^{11–14,20}

Fig. 4(a) presents the real part of ac susceptibility $\chi'(T)$ for PdNCr₃ as a function of temperature at an ac field of $H_{\text{ac}} = 3$ Oe with several fixed frequencies ($f = 1, 10, 100$, and 1000 Hz). It is found that $\chi'(T)$ exhibits a strongly frequency-dependent peak. As the frequency increases, the sharp peak shifts to higher temperatures, while the magnitude decreases, suggesting a characteristic feature of typical SG behavior and hence indicates a SG-type transition in PdNCr₃ with a freezing temperature $T_f \sim 64$ K.^{11–14,20,21} A criterion often used to compare the frequency dependence of freezing temperature T_f in

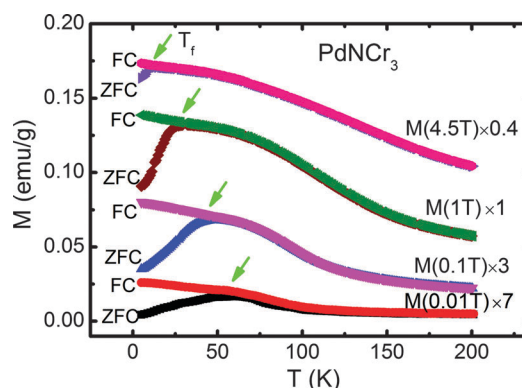


Fig. 3 Temperature dependent magnetization $M(T)$ curves under ZFC and FC processes with different magnetic fields up to 45 kOe.

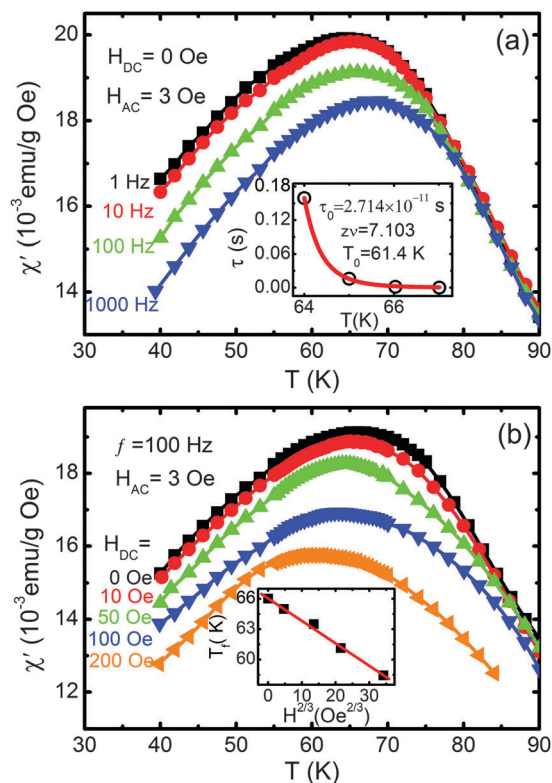


Fig. 4 (a) Temperature dependence of $\chi'(T)$ measured at several fixed frequencies for nominal PdNCr₃. Inset shows the best fit to eqn (5). (b) Temperature dependent $\chi'(T)$ at several fixed dc magnetic fields. Inset of (b): T_f is plotted as a function of $H_{dc}^{2/3}$.

different SG systems is to compare the relative shift in freezing temperature per decade of frequency:^{11–14,20,21}

$$\delta T_f = \frac{\Delta T_f}{T_f \Delta(\log_{10} f)}. \quad (4)$$

For PdNCr₃, we found $\delta T_f = 0.0156$, which is intermediate between those reported for the metallic SG systems (e.g., $\delta T_f = 0.005$ for CuMn alloy)³⁶ and those reported for noninteracting ideal superparamagnetic systems (e.g., $\delta T_f = 0.1$ for isolated particles theory).³⁷ At the same time, this value is close to those of SG systems with antiperovskite structure, such as GaNMn₃ ($\delta T_f = 0.037$),¹¹ SnCF₃ ($\delta T_f = 0.0165$),¹² and Cu_{0.7}Ga_{0.3}NMn₃ ($\delta T_f = 0.0127$),¹³ and those of other SG systems such as Cd_{0.6}Mn_{0.4}Te ($\delta T_f = 0.02$)³⁶ and Eu_{0.6}Sr_{0.4}S ($\delta T_f = 0.05$),³⁸ indicating a typical SG system for PdNCr₃. Generally, in the SG system, the relaxation time τ around transition temperature is described by the power law:^{11–13,39}

$$\tau = \tau_0 [T_f(f)/T_0 - 1]^{-z\nu}, \quad T_f > T_0, \quad (5)$$

where T_0 is the freezing temperature as the frequency tends to zero, τ_0 is the characteristic flipping time of single spin flip, τ is the relaxation time [defined as $\tau = 1/(2\pi f)$], $z\nu$ is the dynamical critical exponent, and T_f is the frequency dependent of the peak position in $\chi'(T)$. Then related parameters were obtained according to eqn (5). According to previous investigation for

Table 3 The values of δT_f fitted by eqn (4), relaxation time τ and $z\nu$ fitted by using eqn (5) for PdNCr₃ and other SG systems

Sample	δT_f	τ_0 (10^{-11} s)	$z\nu$	Ref.
PdNCr ₃	0.0156	2.71	7.103	This work
GaNm ₃	0.037	58.2	5.77	11
SnCF ₃	0.0165	2.42	9.441	12
Cu _{0.7} Ga _{0.3} NMn ₃	0.0127	0.127	10.2	13
Cd _{0.6} Mn _{0.4} Te	0.02	0.15	7.9	36

canonical SG behavior, $z\nu$ is between 4 and 13, and τ_0 is 10^{-10} – 10^{-13} s.⁴⁰ Here [inset of Fig. 4(a)], the parameters are: $T_0 = 61.4(2)$ K, $z\nu = 7.103(3)$, and $\tau_0 = 2.714(2) \times 10^{-11}$ s, indicating a typical SG behavior again. Besides, the values of δT_f fitted by eqn (4), relaxation time τ_0 , and $z\nu$ fitted by using eqn (5) for PdNCr₃ and other SG systems are summarized in Table 3.

Fig. 4(b) shows the real part of ac susceptibility $\chi'(T)$ with fixed ac magnetic field $H_{ac} = 3$ Oe and frequency $f = 100$ Hz at different extra dc magnetic fields H_{dc} (0–200 Oe) for PdNCr₃. Obviously, with increasing H_{dc} , the magnitude of peak decreases and the sharpness becomes rounded. Accordingly, the value of T_f shifts to lower temperatures as H_{dc} increases. It is well known that for ideal 3D-Heisenberg SG without any anisotropic effects, the weak irreversibility line related to the freezing of the transverse spin components is predicted to follow Gabay–Toulouse (GT)-like behavior where $T_f \propto H_{dc}^2$. Whereas, the strong irreversibility line related to the freezing of the longitudinal spin components is supposed to be DeAmeida–Thouless (AT)-like behavior where $T_f \propto H_{dc}^{2/3}$.⁴¹ As shown in the inset of Fig. 4(b), for PdNCr₃ the value of $T_f(H_{dc})$ exhibits AT-like behavior as expected for a 3D-Heisenberg SG. It is similar to the cases of other antiperovskite SG compounds (GaNm₃, SnCF₃, and Cu_{0.7}Ga_{0.3}NMn₃)^{11–13} and other SG compound Er_{0.4}Sr_{0.6}S.³⁸

Isothermal remanent magnetizations $M_{IRM}(t)$ were measured at different magnetic fields after the ZFC process from 300 to 5 K. It is worth noting that the sample was first zero-field cooled to the desired temperature, and then a magnetic field was applied for about 600 s. After switching off the magnetic field, the remanent magnetization was measured as a function of time. $M_{IRM}(t)$ decays so slowly that its value is nonzero even after several hours of decay, which is also a fingerprint of SG behavior. Fig. 5 presents the experimental data and fits them according to the formula:^{11–13}

$$M_{IRM}(t) = M_0 - \alpha \ln(t) \quad (6)$$

at different fields up to 10 kOe. As shown in the inset of Fig. 5, the fitting parameters M_0 and α as a function of magnetic field are plotted, and both values increase initially and then saturate, which has been observed in several different SG systems and can be ascribed to the existence of spin frustration.

Generally, the Kadowaki–Woods ratio (R_{KW}) (defined as $R_{KW} = A/\gamma^2$, where A is T^2 -term coefficient of the resistivity and γ stands for the Sommerfeld constant) and the Sommerfeld–Wilson ratio $R_W = (\pi^2 k_B^2 \chi_0)/(3\mu_B^2 \gamma)$ (where χ_0 is the temperature independent magnetic susceptibility, μ_B stands for the

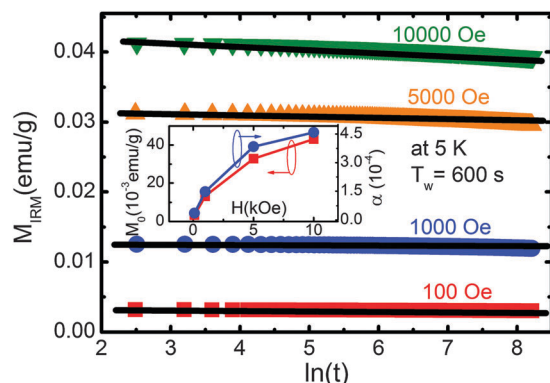


Fig. 5 Isothermal remanent magnetization (M_{IRM}) is plotted as a function of time t with H up to 10 kOe. The solid lines are fits to the experimental data according to the eqn (6). Inset shows the magnetic field dependence of the fitting parameters M_0 and α .

Bohr magneton, γ is the Sommerfeld constant, and k_B stands for the Boltzmann constant) are well-known measures of electron–electron correlation strength.³³ Recently, Anand *et al.* have reported a large Sommerfeld–Wilson ratio ($R_W \sim 247$) in a cluster SG system PrRhSn_3 .³⁹ An unusually high value of $R_W \sim 700$ is also reported by Z. Qu in a cluster SG system $(\text{Sr}_{1-x}\text{Ca}_x)_3\text{Ru}_2\text{O}_7$ for $x = 0.2$.⁴² Besides, $R_W \sim 20\text{--}30$ were observed in the Kondo cluster glass system $\text{GePd}_{1-x}\text{Rh}_x$ for $0.8 \leq x \leq 0.87$.⁴³ However, for a free electron gas system, R_W is only 1.³⁹ The observation of a large value of R_W suggests that the electronic interactions are significantly strong. It means that the magnitude of R_W can be a criterion for distinguishing different SG systems. As discussed above in PdNCr_3 , the values of parameters A , γ , and χ_0 are $0.0075(2) \mu\Omega \text{ cm K}^{-2}$, $60.3(1) \text{ mJ mol}^{-1} \text{ K}^{-2}$, and $1.03(3) \times 10^{-3} \text{ emu mol}^{-1}$, respectively. Accordingly, the value of $R_W = 1.024(3)$ is obtained, which is smaller than the strong correlation limit of 2 according to the Anderson model,⁴⁴ suggesting that PdNCr_3 is a weak electron–electron correlation system. At the same time, the calculated R_{KW} of PdNCr_3 is $2.06(2) \times 10^{-6} \mu\Omega \text{ cm (mJ mol}^{-1} \text{ K}^{-1})^{-2}$, which is smaller than the universal value of $a_0 = 1.0 \times 10^{-5} \mu\Omega \text{ cm (mJ mol}^{-1} \text{ K}^{-1})^{-2}$ for strong electron correlation systems,⁴⁵ indicating again that PdNCr_3 is a weak electron–electron correlation system. For PdNCr_3 , the value of R_W ($\sim 1.024(3)$) is much smaller than those of cluster glass systems (247 and 700) and Kondo cluster glass systems (20–30), indicating that PdNCr_3 is a canonical SG system.

In order to understand the magnetic ground state of PdNCr_3 , the DFT calculations were performed. As shown in

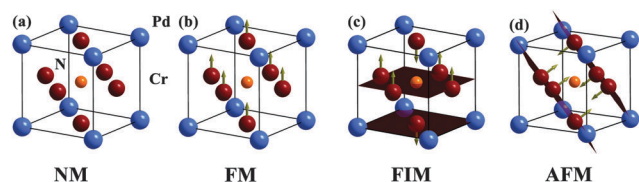


Fig. 6 The tested (a) NM, (b) FM, (c) FIM, and (d) AFM structures of PdNCr_3 . Yellow arrows in (b), (c), and (d) denote the magnetic moment of Cr atoms.

Table 4 The energy differences (ΔE) and magnetic moments per Cr atom (m) in different tested magnetic structures of stoichiometric PdNCr_3

	NM	FM	FIM	AFM
ΔE (meV f.u. ^{−1})	0	—	—	−6
m (μ_B per Cr)	—	0	0	1.468

Fig. 6, we tested four magnetic structures in PdNCr_3 including non-magnetic (NM) (Fig. 6(a)), ferromagnetic (FM) (Fig. 6(b)), ferrimagnetic (FIM) (Fig. 6(c)), and antiferromagnetic (AFM) (Fig. 6(d)) structures. In the tested FIM state, the magnetic moments in one horizontal plane are parallel, and are anti-parallel with those in the neighboring horizontal plane (Fig. 6(c)). In the tested AFM state the Cr-planes perpendicular to $[111]$ direction are antiferromagnetic (Fig. 6(d)), which is similar to the ground magnetic structure of GaCMn_3 .⁴⁶ The calculated energy differences and magnetic moments are shown in Table 4. It can be found that the tested AFM state has the lowest energy. Although the present calculations with only four magnetic structures are not enough to deduce the real magnetic structure in PdNCr_3 , it can still reflect that the AFM interaction is favored in this system. Fig. 7 displays the density of states (DOS) of PdNCr_3 with the tested AFM state. The 4d electrons of Pd mainly contribute to DOS between -6 eV and -2 eV. The DOS near Fermi energy (E_F) is predominately contributed by the 3d electrons of Cr. The large width of the Cr-3d bands implies the itinerant nature of the samples. The DOS at E_F ($N(E_F)$) is 6.51 states per eV, leading to the calculated electron specific heat coefficient $\gamma_{\text{cal}} = \frac{1}{3}k_B^2\pi^2N(E_F) = 15.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$. Such a value is much lower than that of our measured nominal PdNCr_3 ($\gamma_{\text{exp}} = 60.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$). The limited measuring temperature (only down to 3.5 K) could have some influence on the accuracy of the fitting for specific-heat measurement. And the N deficiency might have a chance to enhance $N(E_F)$ (see the discussion below). However, those factors are not enough to result in the large difference between the measured and the calculated γ . Hence, strong normalization should be considered. The almost overlapped curves of $C_P(T)$ with a magnetic field of 0 T and 5 T indicate that the spin fluctuation has little influence on specific heat. Therefore, the enhancement of γ should be attributed to electron–phonon coupling with the factor of

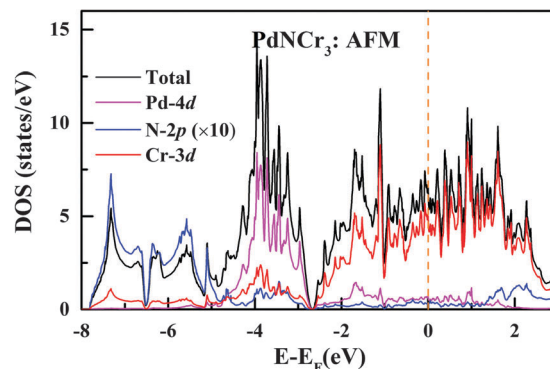


Fig. 7 DOS of PdNCr_3 with the tested AFM state.

$\frac{\gamma_{\text{exp}}}{\gamma_{\text{cal}}} = 1 + \lambda$, where λ is the electron–phonon coupling constant. In the present N deficient PdNCr_3 , a large λ with the value above 2 is expected. Similar strong renormalization is found in the isostructural compound MgCNi_3 . For example, the measured γ of MgCNi_3 is about $30 \text{ mJ mol}^{-1} \text{ K}^{-2}$,⁴⁷ while $N(E_F) \sim 5$ states per eV ($\gamma_{\text{cal}} \sim 11 \text{ mJ mol}^{-1} \text{ K}^{-2}$).⁴⁸ According to the BCS theory,⁴⁹ the higher $N(E_F)$ leads to a stronger electron–phonon coupling. Since our present sample has higher $N(E_F)$ than that of MgCNi_3 , the stronger renormalization from electron–phonon coupling is understandable.

SG behavior is usually observed as a system has the competition of FM and AFM. However, according to our calculation, the total energy of FM or FIM states is much higher and the magnetic moment of PdNCr_3 is converged to zero, which contradicts with the experimentally observed SG behavior and FM hysteresis (shown in Fig. 2(a) and (b)) in our nominal PdNCr_3 . Since it is hard to prepare a stoichiometric PdNCr_3 experimentally, we consider that the N deficiency of our nominal PdNCr_3 introduces the FM interaction, which is similar to the isostructural AlN_xMn_3 .⁵⁰ We theoretically investigated the N deficient samples $\text{PdN}_{0.75}\text{Cr}_3$, $\text{PdN}_{0.5}\text{Cr}_3$ and PdCr_3 with NM and FM states. The $\text{PdN}_{0.75}\text{Cr}_3$ and $\text{PdN}_{0.5}\text{Cr}_3$ were calculated using $2 \times 2 \times 1$ and $2 \times 1 \times 1$ supercells, respectively. The results show that the magnetic moment of PdCr_3 is converged to zero as well, while $\text{PdN}_{0.75}\text{Cr}_3$ and $\text{PdN}_{0.5}\text{Cr}_3$ show a small magnetic moment of $0.08 \mu_B \text{ f.u.}^{-1}$ and $0.23 \mu_B \text{ f.u.}^{-1}$, respectively.

This order of magnitude of the calculated values is in good agreement with that of the measured unsaturated magnetization ($\sim 0.02 \mu_B \text{ f.u.}^{-1}$) for our prepared nominal PdNCr_3 in 45 kOe magnetic field. This suggests that N vacancy exists in our nominal PdNCr_3 . The relation between N concentration and magnetic moment can be easily understood from the electronic structures. Fig. 8(a)–(c) show the density of states (DOS) of PdNCr_3 , $\text{PdN}_{0.5}\text{Cr}_3$, and PdCr_3 with the NM states. Since the 2p electrons of N hybridize strongly with Cr-3d electrons, the deficiency of N narrows the Cr-3d bands and changes the shapes of DOS. For PdNCr_3 , E_F locates at a valley of the DOS curve, leading to a small DOS at E_F ($N(E_F)$) of 6.21 states per eV. The E_F shifts to a peak of DOS for $\text{PdN}_{0.5}\text{Cr}_3$, which results in a large $N(E_F)$ about 8.20 states per eV. For PdCr_3 , E_F locates at a slope of DOS curve, and the $N(E_F)$ is about 5.24 states per eV. According to the Stoner criterion, a FM system must have $N(E_F)I > 1$ (here $N(E_F)$ is in the unit of states per eV per spin, and I is Stoner parameter, usually $I \approx 0.3$ for Cr-based antiperovskite compounds⁵¹). From Fig. 8(a)–(c), one can evaluate that the small N deficiency of our nominal PdNCr_3 will decrease E_F and largely enhance $N(E_F)$, resulting in a fulfillment of the Stoner criterion. Therefore, the FM interaction can be introduced by the N deficiency.

The SG behavior of our nominal PdNCr_3 can be understood by the analysis of the spin polarization of the Cr atoms around the N vacancy. In the $2 \times 1 \times 1$ supercell of $\text{PdN}_{0.5}\text{Cr}_3$, the six Cr atoms can be divided into different types: Cr_0 denotes the

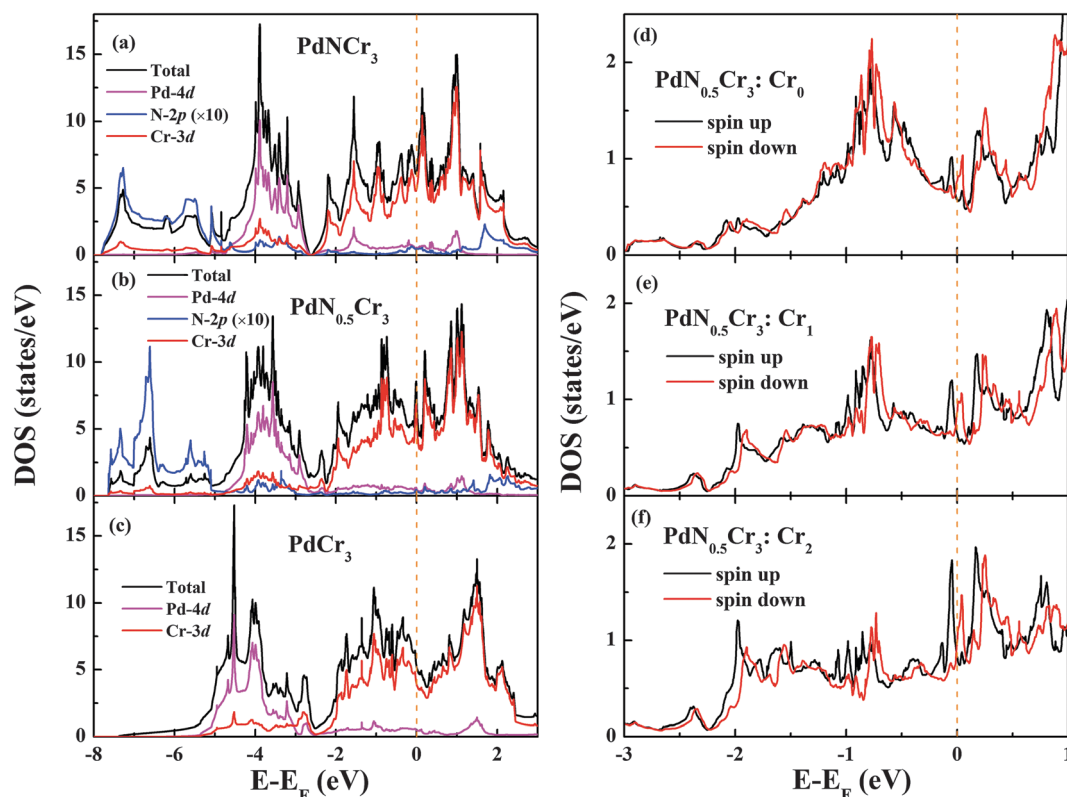


Fig. 8 Left panel: DOS of (a) PdNCr_3 , (b) $\text{PdN}_{0.5}\text{Cr}_3$, and (c) PdCr_3 with NM ground state. Right panel: spin polarized DOS of (d) Cr_0 , (e) Cr_1 , and (f) Cr_2 of $\text{PdN}_{0.5}\text{Cr}_3$.

two Cr atoms without N atom neighbor, Cr₁ denotes the two Cr atoms with only one neighboring N atom, and Cr₂ denotes the two Cr atoms with two neighboring N atoms. Our calculation shows that the magnetic moment of PdN_{0.5}Cr₃ is predominately contributed by Cr₂ atom. Fig. 8(d)–(f) show the spin-polarized projected DOS of Cr₀, Cr₁, and Cr₂ atoms, respectively. It can be found that the Cr₂ atom shows the largest difference between DOS of spin-up and spin-down electrons, while the Cr₀ atom shows the smallest difference between those. This indicates that the N vacancy strongly influences the magnetic behavior of its neighboring Cr atoms. In our polycrystalline sample, one can expect the randomly located N vacancies, which will lead to the randomly distributed magnetic moment. Therefore, together with the AFM background, SG behavior is observed. Similar SG behavior has been observed in antiperovskite compounds GaMnN₃ and SnCF₃, where the deviations of the stoichiometry are suggested.^{11,12}

In order to verify our analysis above, we prepared nominal PdN_{0.75}Cr₃ to induce more N defects intentionally. Fig. 9(a) shows the temperature dependence of dc magnetization $M(T)$ after ZFC and FC for nominal PdN_{0.75}Cr₃ at different magnetic fields. Apparently, the characteristics of the SG state such as the irreversibility between $M_{ZFC}(T)$ and $M_{FC}(T)$ curves and a sharp cusp in each $M_{ZFC}(T)$ curve appear. As shown in Fig. 9(b), T_p shifts to lower temperatures with increasing magnetic field, which is similar to the behavior of the $T_p(H)$ curve in nominal PdNCr₃ (see the inset of Fig. 9(b)). The only difference is the

value of T_p at a certain magnetic field for nominal PdN_{0.75}Cr₃ is higher than those of nominal PdNCr₃, suggesting that the SG state may be enhanced as the N deficiency increases. That is to say, the N content is closely related to the SG behavior in this system. Fig. 9(c) presents the isothermal $M(H)$ curves for nominal PdN_{0.75}Cr₃ at 5 and 300 K with a magnetic field up to 45 kOe. Both $M(H)$ curves appear nonlinear behavior at low magnetic field, indicating FM interaction exists in nominal PdN_{0.75}Cr₃ at these two temperatures. However, the magnetism of nominal PdNCr₃ at 300 K is paramagnetic. This difference means that the FM interaction is enhanced with the increasing N deficiency, which is in good agreement with our DFT calculations. Since the N defect seems to be unavoidable in the process of antiperovskite nitrides synthesis,^{11,14,52} SG behavior in a nominal PdNCr₃ system is robust.

3.3. Zero-field cooled exchange bias

It is well known that a spin-disordered interface is usually formed when a FM particle is embedded in a non-FM matrix.^{20,53,54} Considering the SG ground state in our sample PdNCr₃, the magnetic moments are long range disordered. However, the measured FM hysteresis indicates there must be some short range ordered moments distributed in the long range disordered matrix. Qualitatively, we can illustrate the SG behavior as the FM “domains” randomly embed in the non-FM or SG “matrix”. Based on the coupling between the FM “domains” and SG regions in SG PdNCr₃, the EB could be expected.

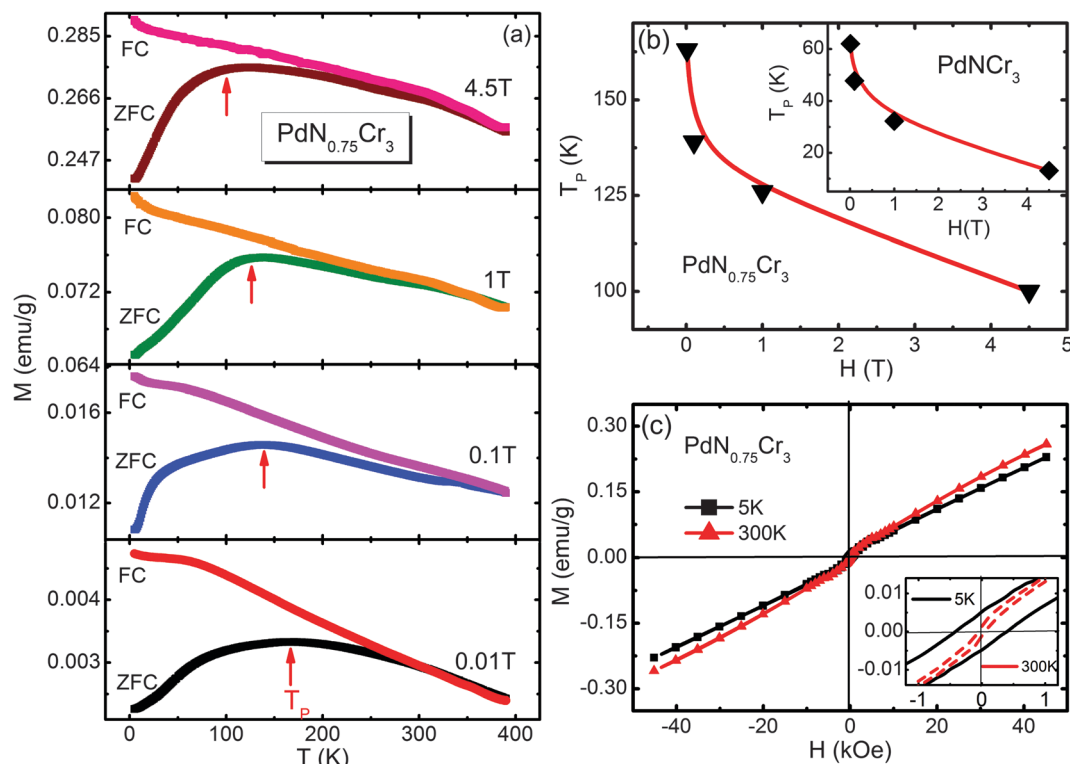


Fig. 9 (a) Temperature dependent magnetization $M(T)$ curves under ZFC and FC processes with different magnetic fields up to 45 kOe for nominal PdN_{0.75}Cr₃. (b) T_f as a function of magnetic field H for nominal PdN_{0.75}Cr₃. (c) $M(H)$ curves of nominal PdN_{0.75}Cr₃ at 5 and 300 K. Inset shows the enlargement of $M(H)$ curves around low magnetic fields.

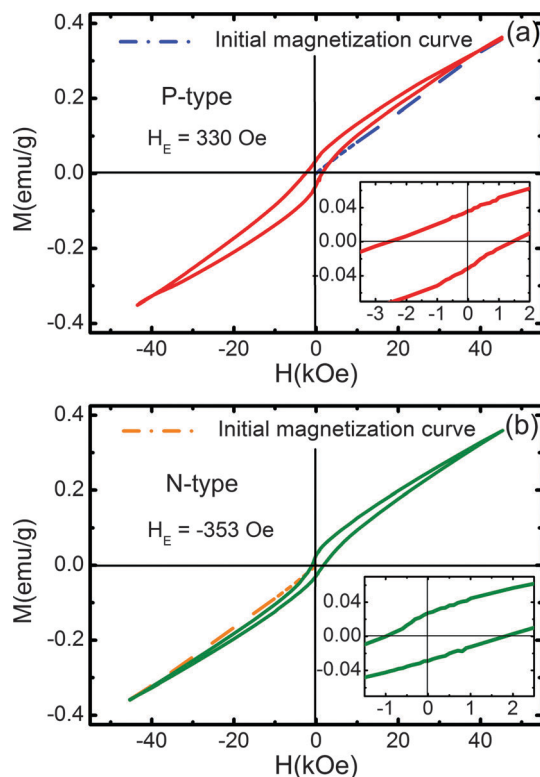


Fig. 10 $M(H)$ loops of nominal PdNCr_3 at 5 K after ZFC with $|H_{\text{max}}| = 45$ kOe from 300 K: (a) p-type, (b) n-type. The dashed lines are the initial magnetization curves. The insets show the larger scale at the low fields.

To confirm this argument, we have measured the hysteresis loops at 5 K, which is much lower than T_f , under ZFC and FC processes. It is worth noting that two measurement processes can be used to obtain a closed $M(H)$ loop after ZFC ($|+H_{\text{max}}| = |-H_{\text{max}}|$): (1) P-type, $0 \rightarrow (+H_{\text{max}}) \rightarrow 0 \rightarrow (-H_{\text{max}}) \rightarrow 0 \rightarrow (+H_{\text{max}})$, (2) N-type, $0 \rightarrow (-H_{\text{max}}) \rightarrow 0 \rightarrow (+H_{\text{max}}) \rightarrow 0 \rightarrow (-H_{\text{max}})$.²¹ In general, the same loop is expected for these two kinds of measurements except for the initial magnetization curve. However, for ZFC-EB they will be different, which have been reported previously.²¹ Fig. 10(a) presents the P-type $M(H)$ of PdNCr_3 at 5 K after ZFC from 300 K with maximum measurement field $H_{\text{max}} = (|+H_{\text{max}}| = |-H_{\text{max}}|) = 45$ kOe. Here, it is necessary to point that the ZFC and/or FC processes mentioned below are performed from 300 K. The dashed line shows the initial magnetization curve, which lies outside the major hysteresis loop. The magnetization at the starting point of the initial magnetization curve is zero, indicating that the

initial state at 5 K is an unmagnetized state. At the same time, the equal magnetization values in the highest positive and negative fields suggest that the shifted loop is not a nonsymmetrical minor hysteresis loop.²¹ We also measured the N-type $M(H)$ loop with opposite direction of the initial magnetization field after the ZFC process (see Fig. 10(b)), which shifts to the positive magnetic field axis. The insets of Fig. 10(a) and (b) reveal the enlargement of P-type and N-type $M(H)$ loops around low magnetic fields, respectively. Both P-type and N-type $M(H)$ loops shift to the opposite direction of the initial magnetic field axis, which cannot be expected from the effect of the remanent field of a superconductor magnet or remanent magnetization of the samples.²¹ The EB field (H_E) and coercive field (H_C) are defined as $H_E = -(H_{E-L} + H_{E-R})/2$ and $H_C = -(H_{E-L} - H_{E-R})/2$, respectively, where H_{E-L} and H_{E-R} are the left and right coercive fields, respectively.^{20,21} Correspondingly, we determine the H_E value of P-type loop to be 330 Oe and the N-type loop to be -353 Oe, respectively, which show a centrally symmetric image within the error of experimental measurements. These results indicate that the ZFC-EB in PdNCr_3 is intrinsic. In addition, the magnitude of H_E (~ 330 –353 Oe) in PdNCr_3 is intermediate when compared with those of other ZFC-EB systems such as $\text{La}_{0.25}\text{Y}_{0.25}\text{Sr}_{0.5}\text{MnO}_3$ ($H_E = 40$ Oe),²⁰ Ni-Mn-Ga ($H_E = 348$ Oe),⁵⁵ NiMnIn_{13} ($H_E = 1350$ Oe),²¹ and Mn_2PtGa ($H_E = 1700$ Oe).²⁴

Based on the model of non-percolating FM “domains” dispersed in the SG matrix, we argue that the ZFC-EB in PdNCr_3 is attributed to a FM unidirectional anisotropy formed at the interface between FM and SG during the initial magnetization process. In order to understand the formation of FM unidirectional anisotropy easily, a schematic diagram is plotted in Fig. 11. It is necessary to point that the CEB can be explained by the formation of FM unidirectional anisotropy at the interface between FM and SG phases upon FC process.⁵⁴ For the case of the ZFC process, after the sample is cooled to 5 K under zero magnetic field, non-percolating FM domains with disordered magnetization direction are frozen in the SG matrix (to see Fig. 11(a)). For the initial magnetization process at 5 K, as the magnetic field increases, the FM domains align along the direction of external field and may grow in size at the expense of SG to reduce the Zeeman energy of the spins at the FM/SG interface (to see Fig. 11(b)). Thus, the construction of the FM/SG interface in the interface spins of the FM and SG phases to minimize the free energy may result in the FM unidirectional anisotropy. However, the enlarged FM domains are metastable, and they will shrink by interface motion when the magnetic field is switched off or decreased. And then, this

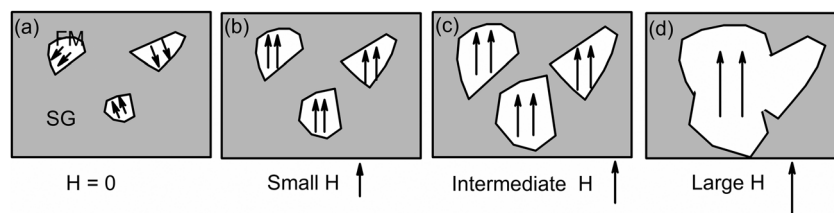


Fig. 11 (a–d) Simplified schematic diagrams of the evolution of the FM domains embedded in SG matrix under external magnetic field at 5 K.

will destroy the FM unidirectional anisotropy around the FM/SG interface. Oppositely, if the magnetic field continues to increase, FM domains grow continually and lead to the decrease of the distance between FM domains (see Fig. 11(c)). Finally, they may change from the non-percolating to percolating state (see Fig. 11(d)). As a result, a new stable FM-SG interface with unidirectional moment of FM is formed and may be pinned by the direct exchange interaction between the FM domains and hinder the decline of FM domains upon removing the magnetic field. This makes the FM unidirectional anisotropy reserved and correspondingly ZFC-EB appears at 5 K in PdNcr₃.⁵⁵

In order to further illustrate the ZFC-EB behavior in PdNcr₃, we performed some other magnetic measurements. Fig. 12(a) shows the $M(H)$ loops at 5 K under ZFC process with several different $H_{\max}$ (3–45 kOe). As displayed in the inset of Fig. 12(a), H_E increases with increasing $H_{\max}$. This behavior implies that with the increase of $H_{\max}$, the FM domains grow from non-percolating to partially percolating and to the fully percolating state, resulting in the increase of H_E . The measurements of $M(H)$ loops at 5 K after FC processes were performed (see Fig. 12(b)) and the H_E increases with increasing applied magnetic field (see the inset of Fig. 12(b)). The increase of H_E may be associated with the increase of the FM domain volume after the sample is cooled to 5 K under increasing magnetic field. Fig. 12(c) displays the $M(H)$ loops at different temperatures under the ZFC process and Fig. 12(d) presents the enlargement of Fig. 12(c) around low magnetic fields. As shown

in the inset of Fig. 12(c), the H_E decreases sharply with increasing temperature and disappears at the blocking temperature ($T_B \sim 45$ K). This behavior can be explained by the decreasing anisotropy interaction of the SG phase with the increase of temperature, which makes less and less SG hinder the FM domains rotation, and consequently H_E decreases. In a word, these above results can be understood in the model of FM domains embed in the SG matrix discussed above, which is similar to the EB effect of Ni-Mn-Ga alloys.⁵⁵

Generally, in the EB system, as the sample is continuously field cycled, a gradual decrease of the anisotropy interaction is commonly found, which is named the training effect.^{20,56,57} As a result, both H_{EB} and H_C decrease with increasing loop index number. For the present sample PdNcr₃, the consecutive hysteresis loops were measured continuously at 5 K after ZFC and FC processes. Fig. 13(a) and (b) show the expansion of the low magnetic field regions after ZFC and FC processes with index number n , respectively. In Fig. 13(a), the starting point of the initial magnetization curve is zero, suggesting that the initial state at 5 K is an unmagnetized state. As the index number n increases, the left coercive field H_{E-L} shifts to right while the right coercive field H_{E-R} moves to left. On the other hand, as shown in Fig. 13(b), the initial magnetization is not zero, which is consistent with the FC ($H = 45$ kOe) process. From Fig. 13(b), it is obvious that both H_{E-L} and H_{E-R} shift to right with increasing n , which is similar with the training effect of other CEB systems.²⁰ Fig. 13(c) and (d) present the training

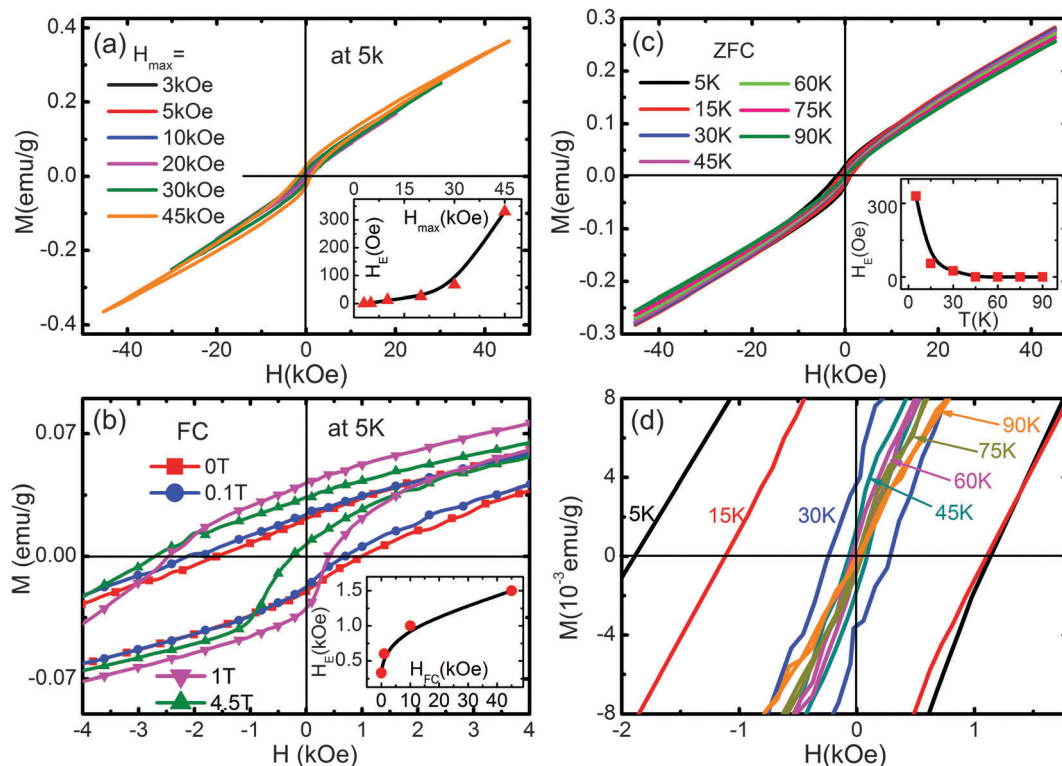


Fig. 12 (a) $M(H)$ loops at 5 K after ZFC with several different $H_{\max}$ from 300 K. The inset presents $H_{\max}$ dependence of H_E . (b) $M(H)$ loops at 5 K after FC with several different H_{FC} from 300 K; the inset shows H_{FC} dependent H_E . (c) $M(H)$ loops after ZFC from 300 K with several different temperatures. The inset displays temperature dependent H_E . (d) The larger scale of (c) at the low fields.

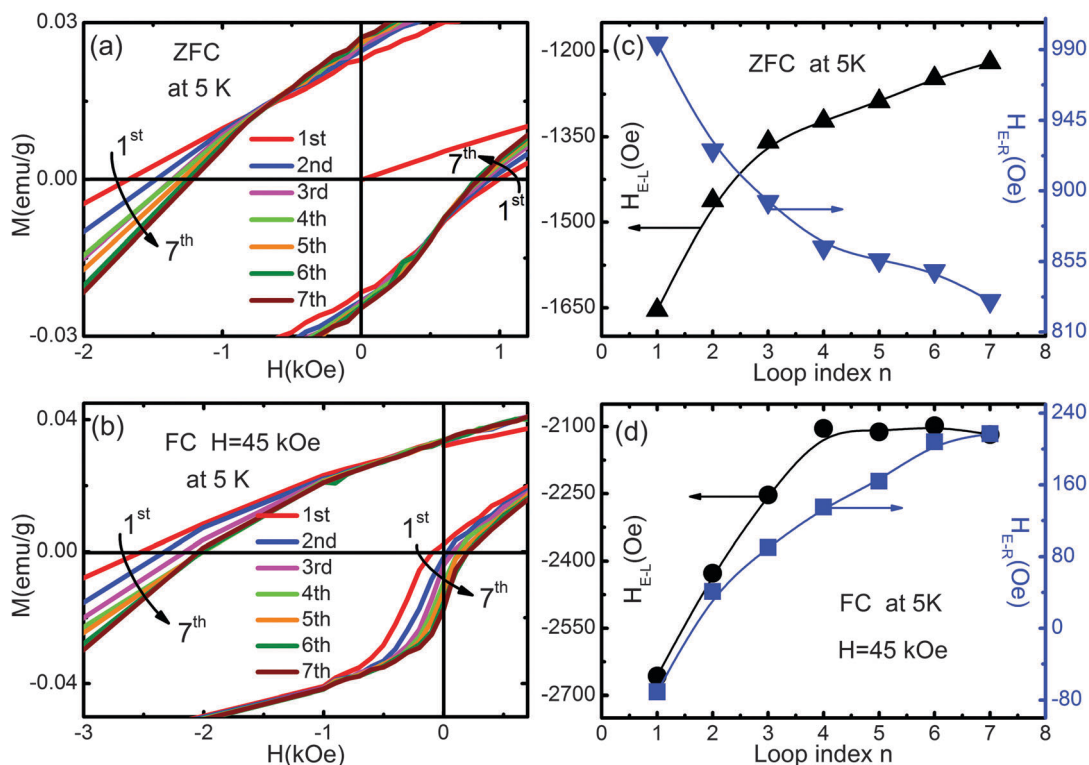


Fig. 13 (a, b) The enlarged view of the central region of the hysteresis loops after ZFC and FC ($H_{FC} = 45$ kOe) processes, respectively, showing training effect of exchange bias at 5 K. (c, d) The number of field cycles (n) dependence of right and left coercive field at 5 K after ZFC and FC ($H_{FC} = 45$ kOe), respectively.

effect on the H_{E-L} and H_{E-R} individually after ZFC and FC processes, respectively. Obviously, the H_{E-L} and H_{E-R} show different behavior after different cooling modes. According to the data of Fig. 13(c) and (d), we obtained the H_E and H_C as a function of loop index n for ZFC and FC processes, which are plotted in Fig. 14(a) and (b), respectively. For the ZFC process, as shown in Fig. 14(a), both H_E and H_C decrease with increasing n , indicating that the training effect is present in PdNCr₃. However, for the FC process (see Fig. 14(b)), the H_E decreases monotonously while the H_C decreases first and then ($n > 4$) increases with increasing n , which indicates that the training effect is inappropriate after the FC process. The training effect confirms another evidence for the existence of ZFC-EB in PdNCr₃, namely, the ZFC-EB of PdNCr₃ is intrinsic.

Furthermore, it is often found experimentally that the relationship between H_E and loop index n can be expressed by a simple power law:^{20,57}

$$H_E - H_{E\infty} = \frac{\kappa}{\sqrt{n}} \quad (7)$$

Here, $H_{E\infty}$ is the exchange bias field in the limit of infinite loops and κ is the sample-dependent constant. Fig. 14(c) shows the best fitted curve of the experimental data (H_E data for $n > 1$) after the ZFC process with eqn (7). The fitted curve shows satisfactory agreement with the experimental data and the corresponding fitting parameters $H_{E\infty} = 114$ Oe and $\kappa = 216$ Oe are obtained. However, as shown in the inset of Fig. 14(c), the

experimental data after the FC process deviate from the fitted line according to eqn (7), indicating that the training effect is inappropriate after the FC process again. Namely, the EB of PdNCr₃ is not a CEB, but a ZFC-EB. Although the power-law decay of EB has been observed widely, its origin still remains unexplained. Recently, Binek *et al.* considered the training effect in FM/AFM heterostructures in the framework of nonequilibrium thermodynamics.⁵⁷ It was proposed that consecutively cycled hysteresis loops of the FM layer could cause the spin configurational relaxation of the AFM interface magnetization toward equilibrium and the corresponding formula can be obtained describing loop index n dependent H_E as follows:⁵⁷

$$H_E(n+1) - H_{E\infty} = -\gamma_H [H_E(n) - H_{E\infty}]^3, \quad (8)$$

where γ_H is a sample-dependent constant and $H_{E\infty}$ is the exchange bias field in the limit of infinite loops. As displayed in Fig. 14(d), our experimental data [$H_E(n)$ for $n = 1-6$] after the ZFC process were well fitted according to eqn (8), and the fitting parameters $\gamma_H = 3.4(2) \times 10^{-6}$ Oe⁻² and $H_{E\infty} = 67.5(4)$ Oe were obtained. The training effect can be explained in terms of the demagnetization of the non-FM surface region.^{58,59} As the FM domain switches back and forth under the influence of the applied field, a relaxation of the surface spin configuration toward the equilibrium is induced due to the surface drag of the exchange interaction. This is particularly relevant for the SG phase observed in the present system PdNCr₃ of our investigation, since when the applied field consecutively cycles, some of

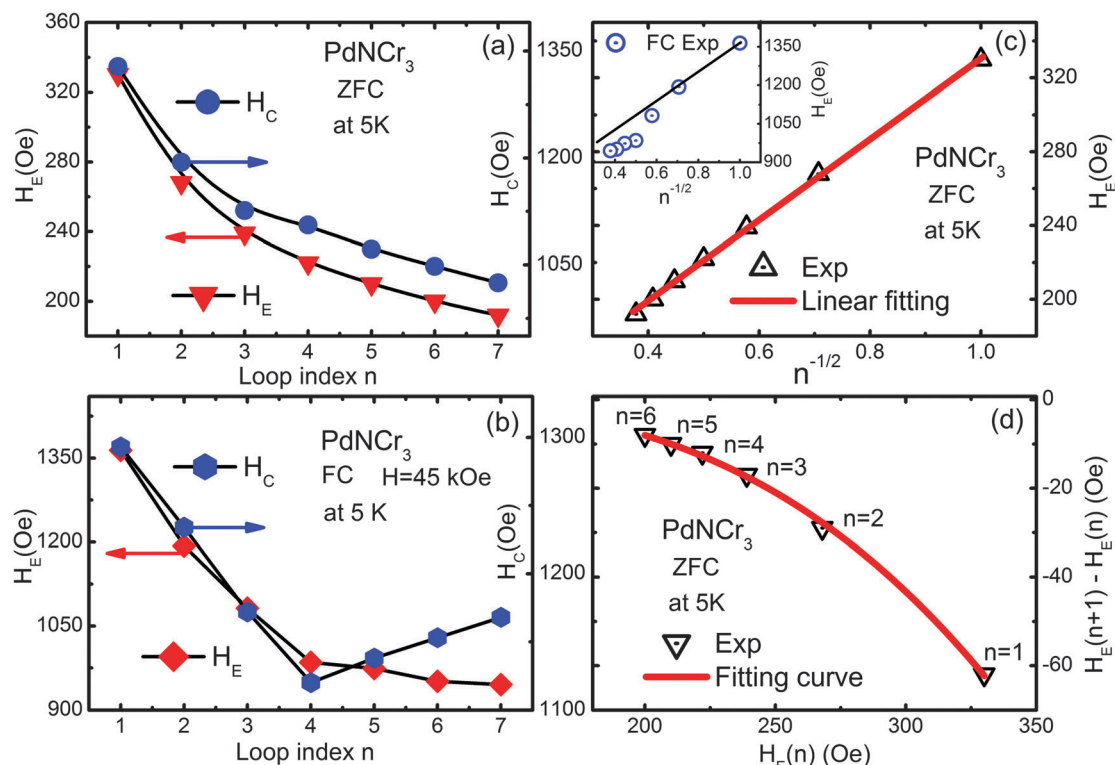


Fig. 14 (a, b) The number of field cycles (n) dependent H_E and H_C at 5 K after ZFC and FC ($H_{FC} = 45$ kOe) processes, respectively. (c) The plot of H_E vs. $n^{-1/2}$ at 5 K for ZFC process and the solid line represents the linear fitting results according to eqn (7). Inset shows the plot of H_E vs. $n^{-1/2}$ at 5 K for FC process. The solid line is a guide for eyes. (d) The plot of H_E vs. $H_E(n+1) - H_E(n)$ at 5 K for ZFC process and the solid line represents the fitting results according to eqn (8).

the frozen SG spins along the initial magnetization field direction may change their directions and fall into other metastable configurations, which would decrease the strength of exchange coupling at the FM/SG interfaces. Therefore, the observed training effect in PdNCr_3 can be interpreted well with the spin configurational relaxation model [eqn (8)].

4. Conclusions

In summary, the synthesis, structure, and magnetic and electrical/thermal transport properties of the anti-perovskite compound PdNCr_3 have been investigated systematically. Exhilaratingly, SG and ZFC-EB were observed in PdNCr_3 . In order to further illustrate the SG, comprehensive magnetic measurements, such as temperature dependent dc magnetization with different fields, frequency and field dependent ac susceptibility, and isothermal remanent magnetization, were performed. The corresponding characteristic parameters ($\delta T_f = 0.0156$, $T_0 = 61.4(2)$ K, $z\nu = 7.103(3)$, and $\tau_0 = 2.714(2) \times 10^{-11}$ s) and the magnetic relaxation effects indicate the nature of SG in PdNCr_3 . Furthermore, the value of $R_W \sim 1.024(3)$ is much smaller than those of cluster glass systems ($R_W > 100$) and Kondo cluster glass systems ($R_W = 20\text{--}30$), suggesting that PdNCr_3 is a canonical SG system. DFT calculation shows that the origin of SG of our nominal PdNCr_3 is attributed to the

disordering located N vacancies, which is confirmed by the further measurement of sample $\text{PdN}_{0.75}\text{Cr}_3$ with more N deficiency. On the other hand, a large ZFC-EB ($H_E \sim 350$ Oe) at 5 K is observed after zero-field cooling from an unmagnetized state. The values of H_E in PdNCr_3 are found to depend strongly on temperature and measuring field. Based on the above result that the FM “domains” randomly embed in the SG “matrix”, the magnetic unidirectional anisotropy, which is the origin of the ZFC-EB, is formed around the FM/SG interface isothermally below the blocking temperature in PdNCr_3 . In addition, the training effect of PdNCr_3 is observed after the ZFC process and has been explained in terms of the spin configurational relaxation model.

Acknowledgements

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References

- 1 T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky,

- K. Inumara, H. W. Zandbergen, N. P. Ong and R. J. Cava, *Nature*, 2001, **411**, 54.
- 2 E. O. Chi, W. S. Kim and N. H. Hur, *Solid State Commun.*, 2001, **120**, 307.
- 3 L. Ding, C. Wang, L. H. Chu, J. Yan, Y. Y. Na, Q. Z. Huang and X. L. Chen, *Appl. Phys. Lett.*, 2011, **101**, 251905.
- 4 S. Lin, B. S. Wang, J. C. Lin, Y. N. Huang, W. J. Lu, B. C. Zhao, P. Tong, W. H. Song and Y. P. Sun, *Appl. Phys. Lett.*, 2012, **101**, 011908.
- 5 B. S. Wang, P. Tong, Y. P. Sun, L. J. Li, W. Tang, W. J. Lu, X. B. Zhu, Z. R. Yang and W. H. Song, *Appl. Phys. Lett.*, 2009, **95**, 222509.
- 6 K. Kamishima, T. Goto, H. Nakagawa, N. Miura, M. Ohashi, N. Mori, T. Sasaki and T. Kanomata, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **63**, 024426.
- 7 D. Matsunami, A. Fujita, K. Takenaka and M. Kano, *Nat. Mater.*, 2015, **14**, 73–78.
- 8 Y. Sun, C. Wang, Q. Z. Huang, Y. F. Guo, L. H. Chu, M. Arai and K. Yamaura, *Inorg. Chem.*, 2012, **51**, 7232–7236.
- 9 K. Takenaka and H. Takagi, *Appl. Phys. Lett.*, 2005, **87**, 261902.
- 10 J. Yan, Y. Sun, H. Wu, Q. Z. Huang, C. Wang, Z. X. Shi, S. H. Deng, K. W. Shi, H. Q. Lu and L. H. Chu, *Acta Mater.*, 2014, **74**, 58–65.
- 11 B. Song, J. K. Jian, H. Q. Bao, M. Lei, H. Li, G. Wang, Y. P. Xu and X. L. Chen, *Appl. Phys. Lett.*, 2008, **92**, 192511.
- 12 B. S. Wang, P. Tong, Y. P. Sun, X. B. Zhu, Z. R. Yang, W. H. Song and J. M. Dai, *Appl. Phys. Lett.*, 2010, **97**, 042508.
- 13 X. H. Zhang, Q. Yuan, J. C. Han, J. G. Zhao, J. K. Jian, Z. H. Zhang and B. Song, *Appl. Phys. Lett.*, 2013, **103**, 022405.
- 14 S. Dhar, O. Brandt, A. Trampert, K. J. Friedland, Y. J. Sun and K. H. Ploog, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **67**, 165205.
- 15 K. Asano, K. Koyama and K. Takenaka, *Appl. Phys. Lett.*, 2008, **92**, 161909.
- 16 F. Grandjean and A. Gerard, *J. Phys. F: Met. Phys.*, 1976, **6**, 451.
- 17 A. L. Ivanovskii, R. F. Sabiryanov and A. N. Skazkin, *Phys. Solid State*, 1998, **40**, 1516.
- 18 H. M. Tütüncü and Ga. P. Srivastava, *J. Appl. Phys.*, 2012, **112**, 093914; D. F. Shao, W. J. Lu, S. Lin, P. Tong and Y. P. Sun, *Adv. Condens. Matter Phys.*, 2013, **2013**, 136274; B. Wiendlocha, J. Tobola, S. Kaprzyk and D. Fruchart, *J. Alloys Compd.*, 2007, **442**, 289.
- 19 M. Nardin, G. Lorthioir, M. Barberon, R. Madar, E. Fruchart and R. Fruchart, *C. R. Acad. Sci.*, 1972, **274C**, 378.
- 20 S. Karmakar, S. Taran, E. Bose, B. K. Chaudhuri, C. P. Sun, C. L. Huang and H. D. Yang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 144409.
- 21 B. M. Wang, Y. Liu, P. Ren, B. Xia, K. B. Ruan, J. B. Yi, J. Ding, X. G. Li and L. Wang, *Phys. Rev. Lett.*, 2011, **106**, 077203.
- 22 J. Nogúes and I. K. Schuller, *J. Magn. Magn. Mater.*, 1999, **192**, 203.
- 23 J. Nogúes, *et al.*, *Phys. Rep.*, 2005, **422**, 65.
- 24 A. K. Nayak, M. Nicklas, S. Chadov, C. Shekhar, Y. Skourski, J. Winterlik and C. Felser, *Phys. Rev. Lett.*, 2013, **110**, 127204.
- 25 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 26 X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J.-Y. Raty and D. C. Allan, *Comput. Mater. Sci.*, 2002, **25**, 478.
- 27 X. Gonze, *Z. Kristallogr.*, 2005, **220**, 558.
- 28 X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Cote, T. Deutsch, L. Genovese, P. Ghosez, M. Giantomassi, S. Goedecker, D. R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. J. T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. J. Verstraete, G. Zerah and J. W. Zwanziger, *Comput. Phys. Commun.*, 2009, **180**, 2582.
- 29 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.
- 30 M. Torrent, F. Jollet, F. Bottin, G. Zerah and X. Gonze, *Comput. Mater. Sci.*, 2008, **42**, 337.
- 31 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Solid State*, 1976, **13**, 5188.
- 32 Z. Liu, T. Waki, Y. Tabata and H. Nakamura, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **89**, 054435.
- 33 P. Tong, Y. P. Sun, X. B. Zhu and W. H. Song, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 245106.
- 34 T. H. Scabarozzi, S. Amini, P. Finkel, O. D. Leaffer, J. E. Spanier, M. W. Barsoum, M. Drulis, H. Drulis, W. M. Tambussi, J. D. Hettinger and S. E. Lofland, *J. Appl. Phys.*, 2008, **104**, 033502.
- 35 R. J. Goetsch, V. K. Anand, A. Pandey and D. C. Johnston, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 054517.
- 36 A. Mauger, J. Ferré, A. Ayadi and P. Nordblad, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 9022.
- 37 J. L. Dormann, L. Bessais and D. Fiorani, *J. Phys. C: Solid State Phys.*, 1988, **21**, 2015.
- 38 N. Bontemps, J. Rajchenbach, R. V. Chamberlin and R. Orbach, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1984, **30**, 6514.
- 39 V. K. Anand, D. T. Adroja and A. D. Hillier, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 014418.
- 40 J. A. Mydosh, *Spin Glasses: An Experimental Introduction*, Taylor & Francis, London, 1993.
- 41 M. Gabay and G. Toulouse, *Phys. Rev. Lett.*, 1981, **47**, 201.
- 42 Z. Qu, L. Spinu, H. Yuan, V. Dobrosavljevic, W. Bao, J. W. Lynn, M. Nicklas, J. Peng, T. Liu, D. Fobes, E. Flesch and Z. Q. Mao, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 180407(R).
- 43 T. Westerkamp, M. Deppe, R. Kuchler, M. Brando, C. Geibel, P. Gegenwart, A. P. Pikul and F. Steglich, *Phys. Rev. Lett.*, 2009, **102**, 206404.
- 44 K. G. Wilson, *Rev. Mod. Phys.*, 1975, **47**, 773.
- 45 K. Kadowaki and S. B. Woods, *Solid State Commun.*, 1986, **58**, 507.

- 46 D. Fruchart and E. F. Bertaut, *J. Phys. Soc. Jpn.*, 1978, **44**, 781.
- 47 A. Wälte, G. Fuchs, K.-H. Müller, A. Handstein, K. Nenkov, V. N. Narozhnyi, S.-L. Drechsler, S. Shulga, L. Schultz and H. Rosner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 174503.
- 48 D. J. Singh and I. I. Mazin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **64**, 140507(R).
- 49 L. N. Cooper, *Phys. Rev.*, 1956, **104**, 1189; J. Bardeen, L. N. Cooper and J. R. Schrieffer, *Phys. Rev.*, 1957, **106**, 162; J. Bardeen, L. N. Cooper and J. R. Schrieffer, *Phys. Rev.*, 1957, **108**, 1175.
- 50 D. F. Shao, W. J. Lu, J. C. Lin, P. Tong, H. B. Jian and Y. P. Sun, *J. Appl. Phys.*, 2013, **113**, 023905.
- 51 D. F. Shao, W. J. Lu, P. Tong, S. Lin, J. C. Lin and Y. P. Sun, *J. Phys. Soc. Jpn.*, 2014, **83**, 054704.
- 52 J. C. Lin, B. S. Wang, P. Tong, W. J. Lu, L. Zhang, X. B. Zhu, Z. R. Yang, W. H. Song, J. M. Dai and Y. P. Sun, *Appl. Phys. Lett.*, 2011, **98**, 092507.
- 53 D. Niebieskikwiat and M. B. Salamon, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 174422.
- 54 M. Ali, P. Adie, C. H. Marrows, D. Greig, B. J. Hickey and R. L. Stamps, *Nat. Mater.*, 2007, **6**, 70.
- 55 Z. D. Han, B. Qian, D. H. Wang, P. Zhang, X. F. Jiang, C. L. Zhang and Y. W. Du, *Appl. Phys. Lett.*, 2013, **103**, 172403.
- 56 Y. K. Tang, Y. Sun and Z. H. Cheng, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 012409.
- 57 Ch. Binek, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 014421.
- 58 J. Keller, P. Miltényi, B. Beschoten, G. Güntherodt, U. Nowak and K. D. Usadel, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **66**, 014431.
- 59 M. Hennion, F. Moussa, G. Biotteau, J. Rodríguez-Carvajal, L. Pinsard and A. Revcolevschi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **61**, 9513.