



Synthesis and characterization of antiperovskite nitrides $\text{GaNCr}_{3-x}\text{Mn}_x$



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ABSTRACT

The effects of Mn-doping on the crystal structure, magnetic and electrical/thermal transport properties of $\text{GaNCr}_{3-x}\text{Mn}_x$ ($0 \leq x \leq 1.5$) have been investigated systematically. As a result, the lattice constant and the residual resistivity increase, while the residual resistivity ratio, electron thermal conductivity, and room-temperature carrier concentration decrease with increasing Mn-doping level. The ground state of parent compound GaNCr_3 is nonmagnetic, interestingly, the ferrimagnetism and antiferromagnetism are observed in Mn-doped samples $\text{GaNCr}_{3-x}\text{Mn}_x$. Correspondingly, around the antiferromagnetic transition of $\text{GaNCr}_{3-x}\text{Mn}_x$ the correlation effect is studied. Furthermore, the analysis of thermal conductivity data suggests that the electron thermal conductivity plays a major role in total thermal conductivity of GaNCr_3 at low temperatures, while the phonon thermal conductivity is dominant for Mn-doped GaNCr_3 in the whole temperature of 5–330 K. The positive values of Seebeck coefficient and Hall coefficient indicate that the nature of charge carrier is hole-type in $\text{GaNCr}_{3-x}\text{Mn}_x$.

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1. Introduction

Since the first antiperovskite superconductor MgCNi_3 was reported in 2001 [1], the antiperovskite structural compounds AXM_3 ($A = \text{Ga, Al, Sn, Zn, Cu, In, Ge, etc.}; X = \text{C, N}; M = \text{Mn, Fe, Ni, etc.}$) have been studied extensively in the last decade and plenty of interesting physical properties and potential functionalities such as superconductivity [2–4], strong electron–electron correlation [5,6], magnetic frustration [7], giant magnetoresistance [8–10], magnetocaloric effect [11–13], negative thermal expansion [14–16], magnetostriction [17], and nearly zero temperature coefficient of resistivity have been observed [18–20]. Especially, recent investigations of AXM_3 are mainly focused on the Mn-, Fe-, and Ni-based antiperovskite compounds [1–20].

Up to now, there is still no detailed experimental research on Cr-based antiperovskite compounds (AXCr_3) except for a few theoretical reports [21–23]. For example, in 2007, the Cr-based antiperovskite nitrides GaNCr_3 and RhNCr_3 were suggested as potential candidates for MgCNi_3 -like superconductor by using the Korringa–Kohn–Rostoker method [23]. Furthermore, Shao et al. investigated the Cr-based

antiperovskite carbides AlCCr_3 and GaCCr_3 based on the density functional theory and found that the band structures of above-mentioned samples were very similar to the superconducting MgCNi_3 , suggesting a possible superconductive behavior in AlCCr_3 and GaCCr_3 [22]. Hitherto, there is no report about successful synthesis of AlCCr_3 and GaCCr_3 [24]. Although we have tried to synthesize, however, the MAX phase compounds Cr_2AC ($A = \text{Al, Ga}$) [25,26] and surplus Cr were obtained instead of antiperovskite carbides AlCCr_3 and GaCCr_3 . Subsequently, we focus on the synthesis of antiperovskite nitrides GaNCr_3 and RhNCr_3 . As to the synthesis of RhNCr_3 , no experimental research has been reported so far. More than a decade ago, the antiperovskite GaNCr_3 phase was obtained but accompanied by some impurities such as GaN , Ga_3Cr , and Cr_2GaN [27,28]. Furthermore, the physical properties of GaNCr_3 are poorly known except for the low-temperature specific heat reported previously [29].

Based on the investigations of Mn- and Fe-based antiperovskite compounds AXM_3 ($M = \text{Mn, Fe}; X = \text{C, N}$), the chemical doping at M site can effectively manipulate the basic physical properties [10,30–32]. For instance, in $\text{GaMn}_{3-x}\text{Ni}_x$, $\text{SnMn}_{3-x}\text{Fe}_x$, $\text{CuNMn}_{3-x}\text{Co}_x$, and $\text{GaFe}_{3-x}\text{Cr}_x$, the chemical doping can affect the magnetic and electrical properties and so on [10,30–32]. Meanwhile, GaNMn_3 has been extensively investigated in last several decades and abundant physical properties were reported [33–35]. Therefore, the Mn-doping is expected to influence the physical properties of Cr-based antiperovskite compounds $\text{GaNCr}_{3-x}\text{Mn}_x$.

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In this work, high-quality polycrystalline samples for antiperovskite nitrides $\text{GaNCr}_{3-x}\text{Mn}_x$ ($0 \leq x \leq 1.5$) were synthesized and their structural, magnetic, electrical/thermal transport properties were reported. With increasing the Mn-doping level x , the lattice increases monotonously and, correspondingly, the magnetic, electrical/thermal transport properties display an interesting and regular behavior. In addition, no superconductivity was detected above 2 K in any samples investigated.

2. Experimental details

Polycrystalline samples of $\text{GaNCr}_{3-x}\text{Mn}_x$ ($x=0, 0.1, 0.3, 0.5, 1.0$, and 1.5) were prepared by the direct solid-state reaction [27,28]. Powders of Ga (5N, Alfa-Aesar), Mn (4N, Alfa-Aesar), Cr (3N, Alfa-Aesar), and self-made CrN 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 973–1073 K for about 7 days. After quenching the tubes to room temperature, the products were pulverized, mixed, pressed into pellets, and annealed again at 1073–1173 K for about 8 days in order to obtain the homogeneous samples. X-ray powder diffraction (XRD) was performed using a Philips X'pert PRO X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=0.15406$ nm) at room temperature. Magnetic measurements were performed on a Quantum Design superconducting quantum interference device magnetometer (SQUID-5T). The electrical/thermal transport properties were measured on a Quantum Design physical property measurement system (PPMS-9T). The electrical transport measurements were carried out by a four-probe method to eliminate contact resistance. The measurement of specific heat was performed by a heat-pulse relaxation method on PPMS-9T. The Hall coefficient (R_H) was measured by an AC method at room temperature by reversing the direction of a magnetic field of 5T on PPMS-9T.

3. Results and discussion

3.1. Structural properties

Fig. 1(a) shows the Rietveld refinement of the room-temperature powder XRD pattern of GaNCr_3 . All the diffraction peaks could be indexed to the cubic antiperovskite structure (space group: $Pm\bar{3}m$). The related fitting parameters values (such as χ^2 , R_p and R_{wp}) are considerable low as presented, suggesting a good antiperovskite nitride GaNCr_3 is obtained. Fig. 1(b) displays the sketch map of the crystal structure for GaNCr_3 . The refined lattice parameter (a) obtained by using the Rietveld refinement technique is 0.3879 nm, which matches well with the previous report (~ 0.3876 nm) [24]. Fig. 1(c) reveals the room-temperature XRD patterns for $\text{GaNCr}_{3-x}\text{Mn}_x$ ($0 \leq x \leq 1.5$). Obviously, all the samples are single phase with a cubic antiperovskite structure. The Rietveld refinements were performed for all the samples and the detailed refined lattice parameters of $\text{GaNCr}_{3-x}\text{Mn}_x$ ($x=0, 0.5, 1.0$, and 1.5) are listed in Table 1. As shown in Fig. 1(d), the refined lattice constant increases with increasing x . These results can be easily understood, when considering the lattice parameters of GaNCr_3 (~ 0.3876 nm) and GaNMn_3 (~ 0.3903 nm) [24,35].

3.2. Magnetic properties

Our experimental results reveal that GaNCr_3 is nonmagnetic, which is consistent with the previous report [23]. Fig. 2(a)–(c) shows the temperature dependent magnetization $M(T)$ curves for the selected samples $\text{GaNCr}_{3-x}\text{Mn}_x$ with $x=0.5, 1.0$, and 1.5 at a magnetic field of 1 kOe under both zero-field-cooled (ZFC) and field-cooled (FC) processes between 5 and 380 K, respectively. As shown in Fig. 2(a), with the increase of temperature, an abrupt decrease of magnetization appears around 42 K, meaning the occurrence of a

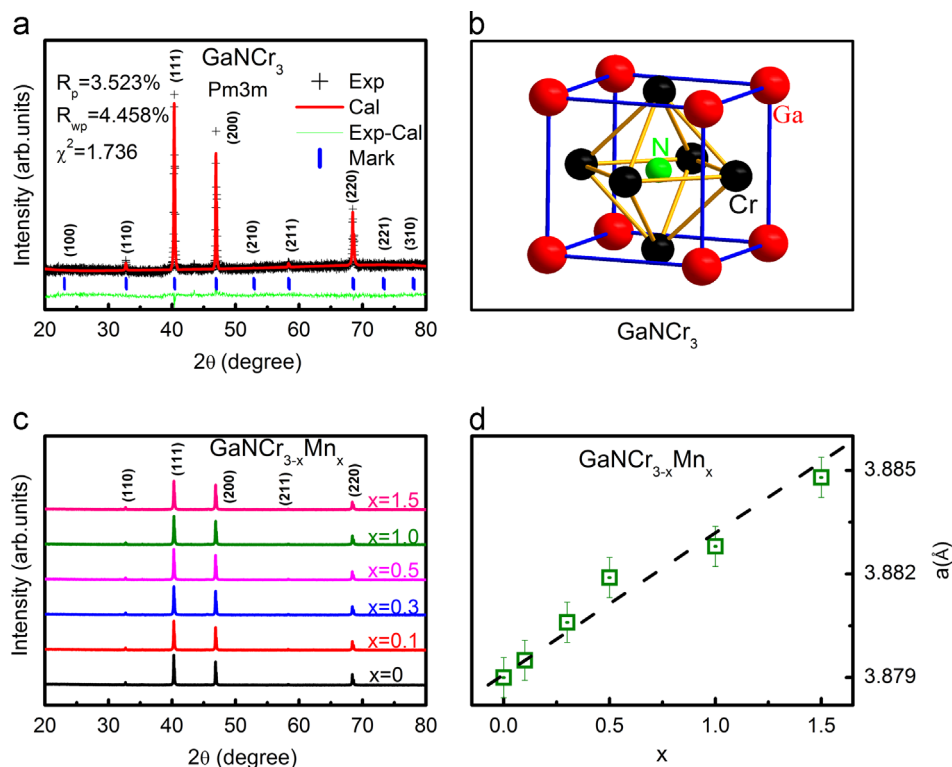


Fig. 1. (a) The Rietveld refined powder XRD patterns for GaNCr_3 , the vertical marks (vertical lines) indicate the position of Bragg peaks, and the solid line (thin solid line) at the bottom corresponding to the difference between observed and calculated intensities; (b) the crystal structure of GaNCr_3 ; (c) room-temperature X-ray powder diffraction for all the samples $\text{GaNCr}_{3-x}\text{Mn}_x$ ($0 \leq x \leq 1.5$); (d) the refined lattice constant a as a function of doping level x ; the dashed line is guide to the eyes.

magnetic transition. The inset of Fig. 2(a) shows the isothermal magnetization curves $M(H)$ at 5 K, from which we can find that the ground state of $\text{GaNCr}_{2.5}\text{Mn}_{0.5}$ is ferrimagnetic (FIM). That is to say, the magnetic transition in $M(T)$ curves of Fig. 2(a) is a FIM-paramagnetic (PM) phase transition. Similarly, for GaNCr_2Mn , there also exists a FIM-PM magnetic transition around 42 K based on the $M(T)$ curves of Fig. 2(b) and the $M(H)$ at 5 K in the upper inset of Fig. 2(b). Moreover, considering the $M(H)$ at 90 K in the upper inset of Fig. 2(b) and the enlarged $M(T)$ curves in the under inset of Fig. 2(b), an antiferromagnetic (AFM)-PM transition is observed at 118 K for GaNCr_2Mn . For $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$, as shown in Fig. 2(c), an evident AFM-PM transition around 158 K is found in $M(T)$ curves. In order to further verify the AFM-PM transition, the isothermal magnetization curves $M(H)$ at 5 and 90 K are measured, which are shown in the upper inset of Fig. 2(c). The $M(H)$ curve at 90 K increases in an essentially linear fashion with magnetic field, suggesting an AFM state at 90 K. Correspondingly, the AFM-PM transition at 158 K in $M(T)$ curve of Fig. 2(c) is confirmed. However, the $M(H)$ curve at 5 K

Table 1

The Lattice constant (a), Curie constant (C), Weiss temperature (θ), residual resistivity (ρ_0), residual resistivity ratio (RRR), Sommerfeld constant (γ), phonon specific heat coefficient (β), deviations term coefficient (δ), Debye temperature (θ_D), and carrier concentration at 300 K ($n_{300\text{ K}}$) of $\text{GaNCr}_{3-x}\text{Mn}_x$.

$\text{GaNCr}_{3-x}\text{Mn}_x$	$x=0$	$x=0.5$	$x=1.0$	$x=1.5$
a (Å)	3.879	3.882	3.883	3.885
C (emu K/mol)	–	2.7924	2.7265	2.6247
θ (K)	–	–715	–514	–409
ρ_0 (mΩ cm)	0.008	0.091	0.145	0.221
RRR	19.6	3.62	1.51	1.37
γ (mJ/mol K ²)	38.75	84.17	64.65	58.20
β (mJ/mol K ⁴)	0.075	0.104	0.123	0.084
δ (10^{-4} mJ/mol K ⁶)	2.48	1.88	1.64	2.42
θ_D (K)	507	453	430	489
$n_{300\text{ K}}$ ($10^{21}/\text{cm}^3$)	5.68	2.71	2.01	1.09

appears a tiny anomaly (nonlinearity) around low magnetic field in the under inset of Fig. 2(c), meaning that there may exist a weak ferromagnetism at the ground state of $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$. The upturn (below 42 K) in $M(T)$ curve of Fig. 2(c) may be attributed to the above mentioned weak ferromagnetism. Fig. 2(d) displays the temperature dependence of the inverse of magnetic susceptibility curve $\chi^{-1}(T)$ for $\text{GaNCr}_{3-x}\text{Mn}_x$, where the corresponding magnetic transitions (FIM-PM, AFM-PM) can be observed clearly. For each selected samples $\text{GaNCr}_{3-x}\text{Mn}_x$ ($x=0.5, 1.0, 1.5$), the magnetic transition around 42 K is always there. However, the ferrimagnetism becomes weak for $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$ based on the magnitude of $\chi^{-1}(T)$ below 42 K in Fig. 2(d). As Mn doping level x increases, another magnetic transition (AFM-PM) appears in GaNCr_2Mn (~ 118 K) and $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$ (~ 158 K). It seems that the antiferromagnetism mentioned above is enhanced with a further increase of Mn-doping. Between $T=280$ and 380 K, the $\chi^{-1}(T)$ curve of $\text{GaNCr}_{3-x}\text{Mn}_x$ is proportional to the temperature manifesting a modified Curie-Weiss behavior $\chi^{-1} = [C/(T-\theta)] + \chi_0(1-AT^2)^{-1}$, where $C/(T-\theta)$ is the contribution of Curie-Weiss, parameters C and θ is the Curie constant and Weiss temperature; χ_0 is Pauli-paramagnetic susceptibility, $\chi_0 AT^2$ is the correction term [6]. Correspondingly, the Weiss temperature (θ) and Curie constant (C) of $\text{GaNCr}_{3-x}\text{Mn}_x$ were obtained and summarized in Table 1. As shown in Table 1, all the Weiss temperatures, which increase with the increasing x , are negative. This suggests an AFM interaction in the ground state of Mn-doped GaNCr_3 .

According to the previous theoretical studies, in antiperovskite structural compound AXM_3 , the density of states (DOS) at the Fermi level E_F [$N(E_F)$] is mainly contributed from M -3d electrons [23,36,37]. Similarly, in GaNCr_3 , the $N(E_F)$ is dominated by Cr-3d electrons [23]. At the same time, the calculations of band structure indicate that the position of E_F is located at the right hand of a sharp peak and the analysis of $N(E_F)$ shows that GaNCr_3 is very close to ferromagnetic (FM) instability [23]. On the one hand, as the lattice constant increases with increasing Mn-doping level x , the E_F position shifts to the lower energy boundary (namely,

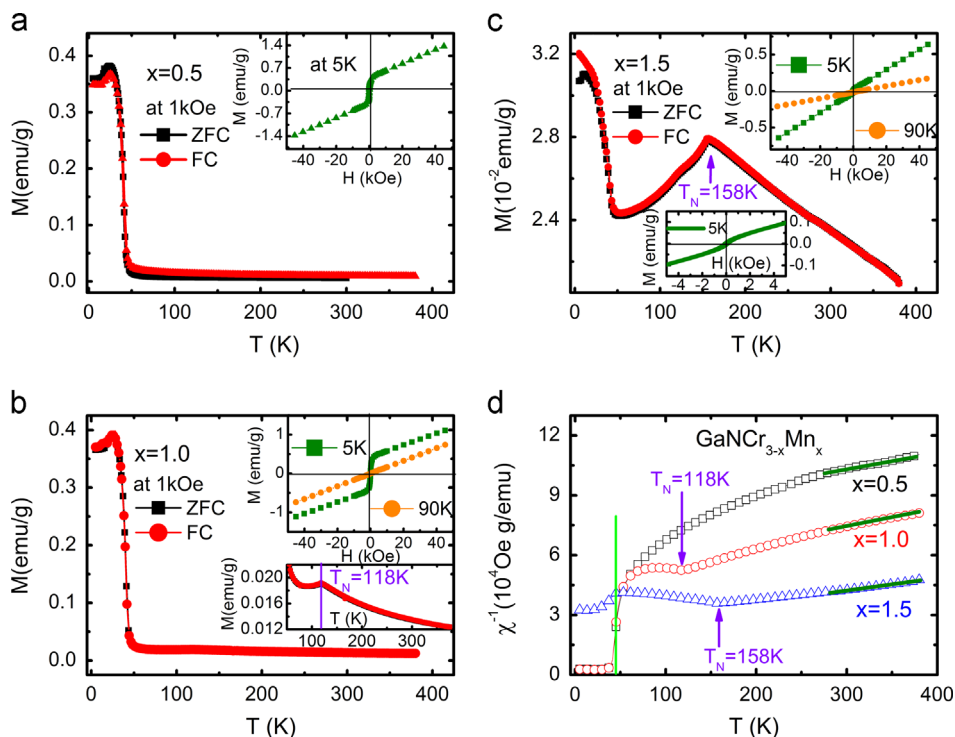


Fig. 2. Temperature dependent magnetization $M(T)$ curves at 1 kOe under ZFC/FC processes for $\text{GaNCr}_{3-x}\text{Mn}_x$ ($0 \leq x \leq 1.5$): (a) $x=0.5$; (b) $x=1.0$; (c) $x=1.5$. The insets of (a) show the isotherm magnetization $M(H)$ curves at 5 K. The upper and under insets of (b) display the $M(H)$ curves at 5 and 90 K and the enlargement of $M(T)$ between 50 and 380 K, respectively. For (c), the upper inset presents the $M(H)$ curves at 5 and 90 K and the under inset reveals the enlargement of $M(H)$ curve at 5 K between 5 and -5 kOe. (d) Temperature dependence of the inverse of magnetic susceptibility curve $\chi^{-1}(T)$ for $\text{GaNCr}_{3-x}\text{Mn}_x$. Solid lines are fitting results according to the Curie-Weiss law.

moving towards a sharp peak of DOS), which may increase the value of $N(E_F)$ in $\text{GaNCr}_{3-x}\text{Mn}_x$. Correspondingly, a FM stability is achieved in Mn-doped samples $\text{GaNCr}_{3-x}\text{Mn}_x$, such as the appearance of FIM ground state in $\text{GaNCr}_{2.5}\text{Mn}_{0.5}$, GaNCr_2Mn , and $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$. On the other hand, in the GaNMn_3 , the ground state is AFM, which is resulted from the AFM interaction of the nearest-neighbor Mn atoms [33,38]. As the Mn-doping level x increases in $\text{GaNCr}_{3-x}\text{Mn}_x$, the AFM interaction may be strengthened and a weak AFM-PM is obtained at 118 K in GaNCr_2Mn . With further increasing x , the enhanced AFM interaction results in the shift of AFM-PM transition to high temperature (~ 158 K) and the weakening of FIM ground state in $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$. In a word, the evolution of magnetism in $\text{GaNCr}_{3-x}\text{Mn}_x$ is mainly attributed to the competition between FM and AFM interactions with increasing Mn-doping level x .

3.3. Electrical transport properties and correlation effect

Fig. 3(a) displays the temperature dependence of resistivity $\rho(T)$ for $\text{GaNCr}_{3-x}\text{Mn}_x$ with $x=0, 0.5, 1.0$, and 1.5 at zero magnetic field between 2 and 350 K. Apparently, for each sample, the magnitude of $\rho(T)$ of $\text{GaNCr}_{3-x}\text{Mn}_x$ increases basically with increasing temperature, indicating a good metallic behavior of $\text{GaNCr}_{3-x}\text{Mn}_x$. At the same time, the magnitude of $\rho(T)$ increases with increasing x , which may be attributed to the lattice disorder resulting from the difference of atom size between Cr and Mn. However, the predicted superconductivity does not appear upon cooling down to 2 K for GaNCr_3 [23]. It is interesting to test the superconductivity of GaNCr_3 at lower temperatures.

In order to understand the evolution of resistivity of $\text{GaNCr}_{3-x}\text{Mn}_x$ more clearly, the normalized resistivity $\rho(T)/\rho(350\text{ K})$ was plotted in Fig. 3(b), where a kink around corresponding T_N of GaNCr_2Mn and $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$ is observed. Generally, the low-temperature residual resistivity (ρ_0) and residual resistivity ratio (RRR), defined as $\text{RRR} = \rho(300\text{ K})/\rho(5\text{ K})$, are measures of sample quality [39]. High ρ_0 values and small RRRs suggest sizable scattering from impurities, vacancies, or other defects. As shown in Fig. 3(a), ρ_0 increases with Mn-doping level x in $\text{GaNCr}_{3-x}\text{Mn}_x$. Moreover, the RRR decreases with

increasing x , which is plotted in inset of Fig. 3(b). Especially, GaNCr_3 has the smallest ρ_0 of 0.008 m Ω cm and the largest RRR of 19.6, indicating a good quality of the sample. All these results can be understood as follows: as the Mn-doping level x increases, more and more Mn atoms enter into the site of Cr. Given the sizes of both Cr and Mn atoms are different, resulting in an increase of lattice disorder and other defects. As a result, the magnitude of resistivity increases, while the RRR decreases with increasing x . In addition, the detailed values of ρ_0 and RRR for $\text{GaNCr}_{3-x}\text{Mn}_x$ are listed in Table 1.

The temperature dependent resistivity $\rho(T)$ of GaNCr_3 at zero magnetic field between 2 and 350 K is replotted in Fig. 3(c). As shown in the left inset of Fig. 3(c), the low-temperature resistivity is well fitted by the formula $\rho = \rho_0 + AT^2$ (ρ_0 and A represent the residual resistivity and T^2 -term coefficient of the resistivity, respectively) up to about 70 K, indicating a Fermi liquid behavior for GaNCr_3 at low temperatures. That is to say, the electron–electron scatterings are dominant at low temperatures [40]. However, at the elevated temperature (70–250 K), $\rho(T)$ increases basically linearly with increasing the temperature (see the right inset of Fig. 3(c)), indicating that the contributions of electron–phonon scattering have exceeded those of the electron–electron scattering. This behavior can be simply understood as follows: with increasing the temperature, the number of phonon increases quickly, leading to the enhancement of the electron–phonon scattering [13].

Fig. 3(d) displays the temperature dependence of resistivity $\rho(T)$ at zero magnetic field and 5 T between 2 and 350 K for GaNCr_2Mn and $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$. Obviously, the $\rho(T)$ curves at different magnetic fields of 0 T and 5 T are overlapped, even around the T_N , demonstrating that the resistivity $\rho(T)$ of series samples $\text{GaNCr}_{3-x}\text{Mn}_x$ is weakly magnetic field-dependent.

For the purpose of the study of correlation effect between magnetism and resistivity for GaNCr_2Mn , the $\rho(T)$ and $M(T)$ curves are plotted in one picture, which are shown in Fig. 4(a). Obviously, there appears a kink in $\rho(T)$ curve around the AFM-PM transition of 118 K. Furthermore, we also measured the specific heat of GaNCr_2Mn around the AFM-PM transition, which is plotted in Fig. 4(b). A sharp peak of $C_p(T)$ ($T_p = 116$ K) is observed around the

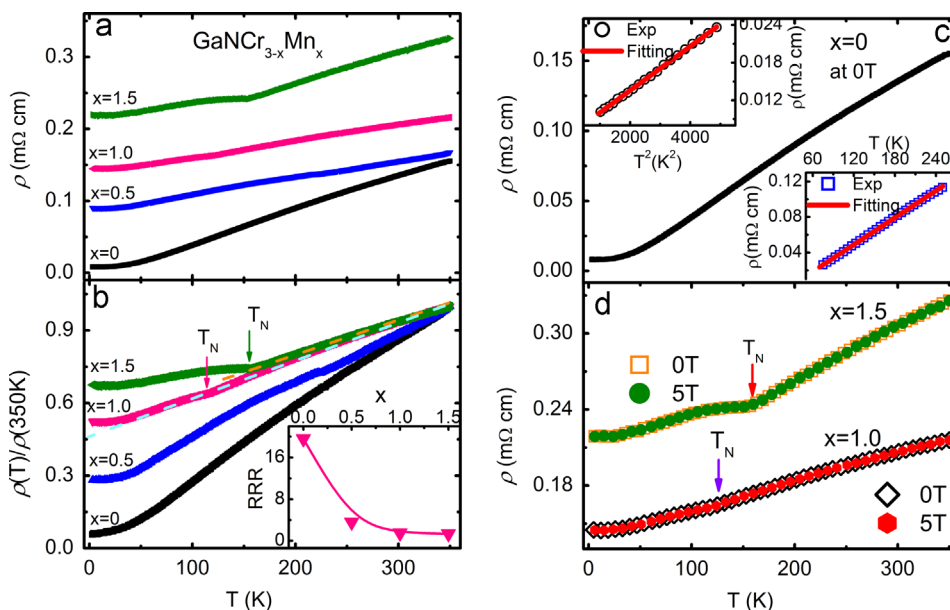


Fig. 3. (a) Temperature dependent resistivity $\rho(T)$ at zero field for $\text{GaNCr}_{3-x}\text{Mn}_x$ ($0 \leq x \leq 1.5$); (b) T -dependent normalized resistivity $\rho(T)/\rho(350\text{ K})$ for $\text{GaNCr}_{3-x}\text{Mn}_x$. The dashed line is guide to the eye. The inset shows the RRR as a function of Mn-doping level x ; (c) temperature dependent resistivity $\rho(T)$ at zero field for GaNCr_3 ; Left inset: lower- T $\rho(T)$ data plotted as $\rho(T)$ vs. T^2 ; Right inset: linear fits of $\rho(T)$ data for all GaNCr_3 at the range of 70–250 K; solid lines are fitting results for both cases; (d) temperature dependent resistivity $\rho(T)$ at zero field and 5 T for selected samples $\text{GaNCr}_{3-x}\text{Mn}_x$ with $x=1.0$ and 1.5 .

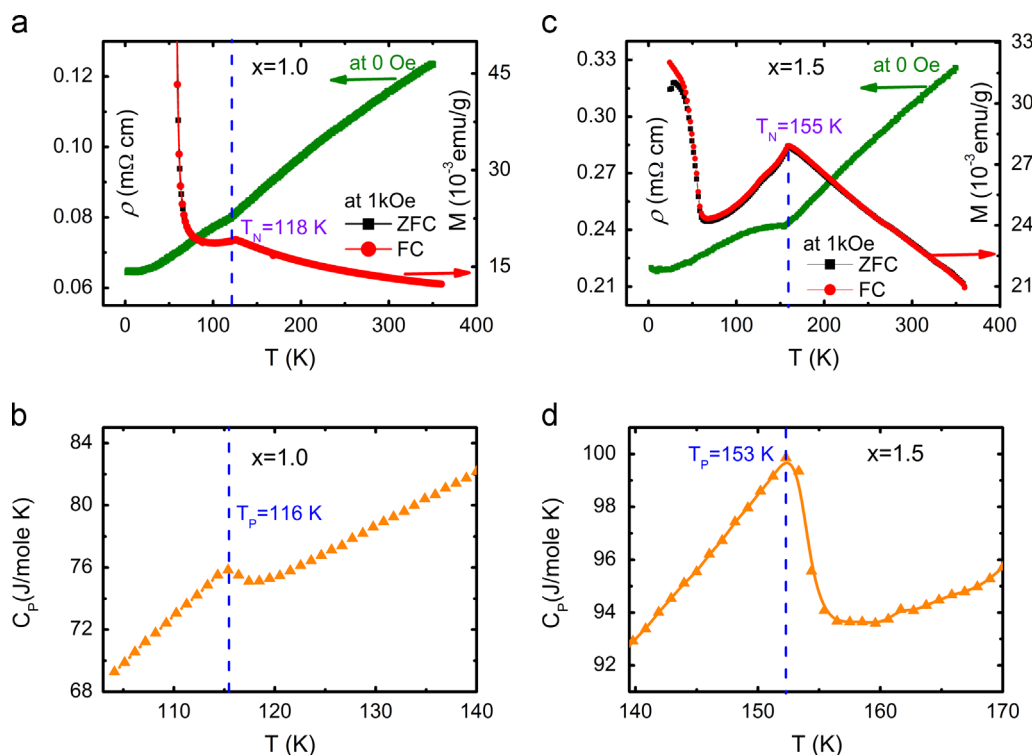


Fig. 4. (a) Temperature dependent magnetization $M(T)$ and resistivity $\rho(T)$ for GaNCr_2Mn ; (b) T -dependent specific heat $C_p(T)$ between 100 and 140 K; (c) temperature dependent $M(T)$ and resistivity $\rho(T)$ for $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$; (d) T -dependent specific heat $C_p(T)$ between 140 and 170 K. The dashed line is guide to the eyes.

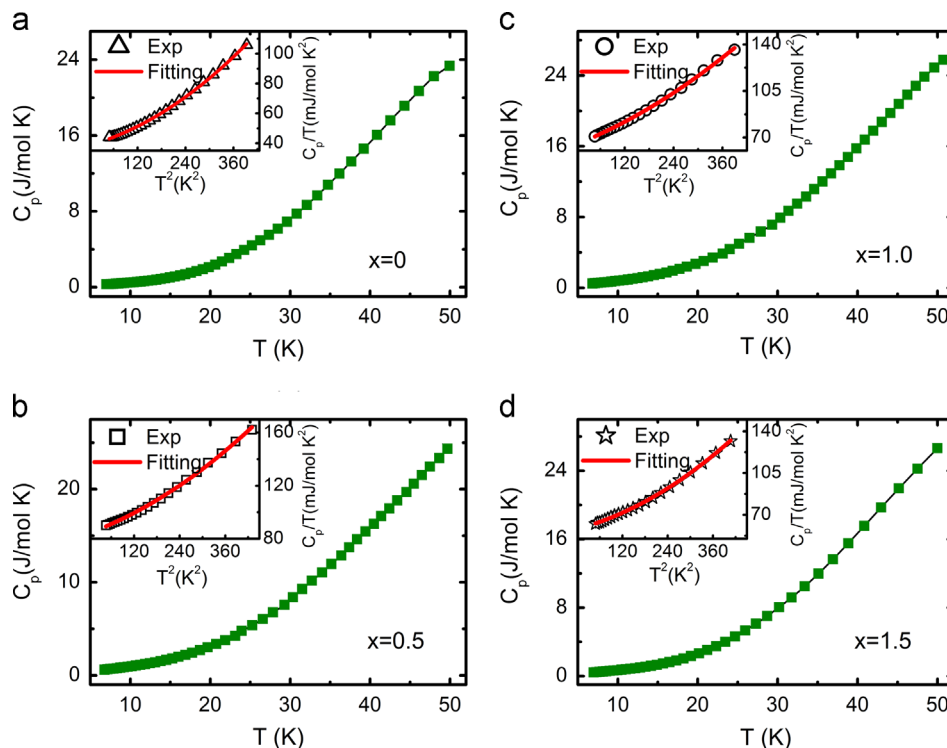


Fig. 5. Temperature dependent specific heat $C_p(T)$ at zero field between 7 and 50 K for $\text{GaNCr}_{3-x}\text{Mn}_x$: (a) $x=0$; (b) $x=0.5$; (c) $x=1.0$; (d) $x=1.5$. The inset shows the plot of $C_p(T)/T$ vs. T^2 below 20 K and the solid line represents the fitting results according to Eq. (1).

corresponding AFM-PM magnetic transition ($T_N=118$ K) for GaNCr_2Mn . Analogously, Fig. 4(c) and (d) reveals the similar phenomenon for $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$. All these results suggest that the correlation effect among magnetism, resistivity, and specific heat is likely to be a bulk effect for GaNCr_2Mn and $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$.

3.4. Low-temperature specific heat study

Fig. 5(a)–(d) shows the specific heat $C_p(T)$ for $\text{GaNCr}_{3-x}\text{Mn}_x$ measured between 6.7 and 50 K at zero field. As shown in each inset of Fig. 5(a)–(d), the data below 20 K is plotted as $C_p(T)/T$ vs. T^2

which can be well expressed by using the following equation [5,6]:

$$C_P(T)/T = \gamma + \beta T^2 + \delta T^4 \quad (1)$$

where γ (Sommerfeld constant) is the electronic contribution, β is the phonon contribution, and δ reflects the deviation term. The fitted values of parameters γ , β , and δ for $\text{GaNCr}_{3-x}\text{Mn}_x$ are collected in Table 1. Especially, the fitted values of parameters γ ,

β , and δ for GaNCr_3 are 38.75 mJ/mol K², 0.075 mJ/mol K⁴, and 2.48×10^{-4} mJ/mol K⁶, respectively. Accordingly, the Debye temperature $\theta_D = (n \times 1.94 \times 10^6 / \beta)^{1/3} = 507$ K of GaNCr_3 (where n is the number of atoms in a unit cell) is derived from the value of coefficient β [5,6]. In addition, the calculated Debye temperatures of $\text{GaNCr}_{3-x}\text{Mn}_x$ are also listed in Table 1.

3.5. Thermodynamic properties

Fig. 6(a) presents the temperature dependent thermal conductivity $\kappa(T)$ for $\text{GaNCr}_{3-x}\text{Mn}_x$ at zero field (5–330 K). Obviously, a broadened peak can be seen around 50 K for GaNCr_3 and 100 K for $\text{GaNCr}_{3-x}\text{Mn}_x$ with $x=0.5, 1.0$, and 1.5 . In general, the total thermal conductivity can be expressed as a sum of lattice (κ_L) and electronic (κ_e) terms, i.e., $\kappa(T) = \kappa_L(T) + \kappa_e(T)$. The electronic thermal conductivity κ_e can be estimated based on the Wiedemann–Franz (WF) law [$\kappa_e \rho / T = L_0$, where $L_0 = 2.45 \times 10^{-8}$ W Ω K⁻² is the Lorentz number] and the value of κ_L was obtained in terms of $\kappa(T) - \kappa_e(T)$. Previous experimental investigations have approved that the WF law is a universal formula for many materials (including simple metals, strongly electron-correlated compounds, and low-dimensional systems) [41,42]. Here, for $\text{GaNCr}_{3-x}\text{Mn}_x$, the values of κ_L and κ_e were separated and plotted as a function of temperature in Fig. 7(a)–(d), respectively. For GaNCr_3 , the value of κ_e is larger than that of κ_L below 260 K, while above 260 K it is just contrary. Therefore, the peak of $\kappa(T)$ around 50 K is suggested to mainly result from the contribution of $\kappa_e(T)$. However, for $\text{GaNCr}_{3-x}\text{Mn}_x$ ($x=0.5, 1.0$, and 1.5), the value of κ_L is larger than that of κ_e in the whole investigated temperature range (5–330 K), indicating that the total $\kappa(T)$ mainly originates from the contribution of κ_L . Accordingly, the broadened peak of $\kappa(T)$ around 100 K for $\text{GaNCr}_{3-x}\text{Mn}_x$ with $x=0.5, 1.0$, and 1.5 can be attributed to T -dependent value of κ_L . Here, this abnormal peak is a typical feature for the reduction of thermal scattering at low temperatures owing to the enhancement of

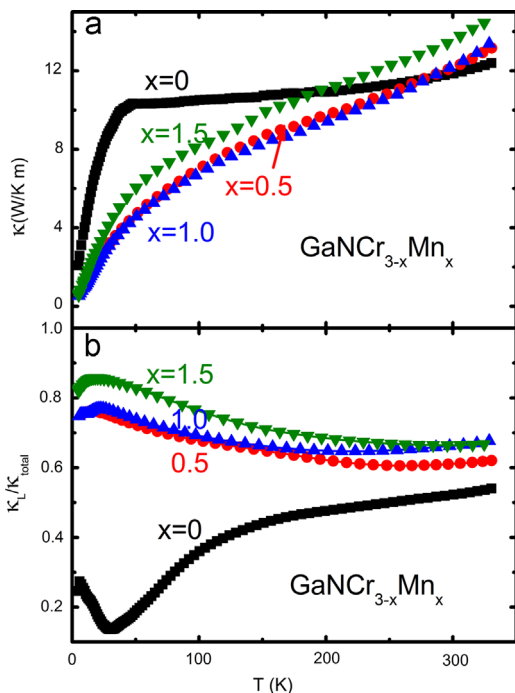


Fig. 6. (a) Temperature dependent thermal conductivity $\kappa(T)$ for $\text{GaNCr}_{3-x}\text{Mn}_x$ and (b) $\kappa_L/\kappa_{\text{total}}$ (T) curve for $\text{GaNCr}_{3-x}\text{Mn}_x$.

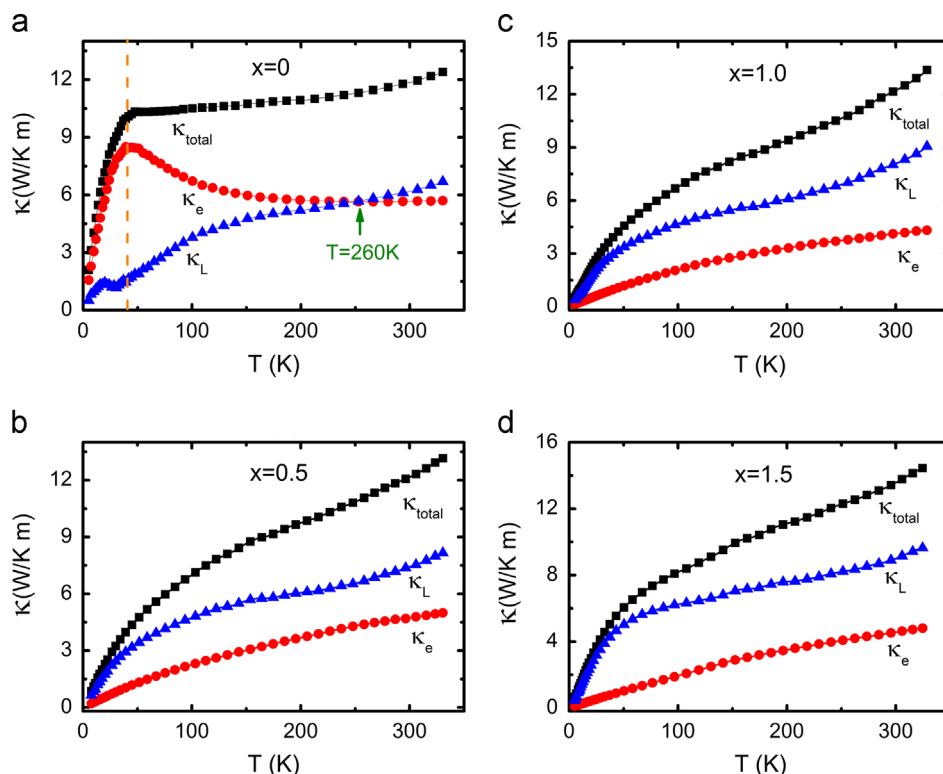


Fig. 7. (a) Temperature dependent thermal conductivity κ_{total} , electronic thermal conductivity κ_e , lattice thermal conductivity κ_L for $\text{GaNCr}_{3-x}\text{Mn}_x$: (a) $x=0$; the dashed line is guide to the eyes; (b) $x=0.5$; (c) $x=1.0$; (d) $x=1.5$.

phonon freezing with decreasing the temperature [43]. Fig. 6 (b) displays the temperature dependent $\kappa_L/\kappa_{\text{total}}$ (T) for $\text{GaNCr}_{3-x}\text{Mn}_x$. In the whole investigated temperature range (5–330 K), the magnitude of $\kappa_L/\kappa_{\text{total}}$ increases with increasing x . That is to say, the electron thermal conductivity κ_e decreases with Mn doping level x , which may be attributed to the increase of resistivity with increasing x as shown in Fig. 3(a). Given the WF law $\kappa_e\rho/T = L_0$, at a certain temperature, the increase of resistivity ρ can lead to the decrease of κ_e .

The temperature dependent Seebeck coefficient $\alpha(T)$ was also measured at zero field (5–300 K) and plotted in Fig. 8(a). Usually, in single-band model, the sign of $\alpha(T)$ could reflect the type of carriers reasonably. In whole range of temperature (5–300 K), the positive value of $\alpha(T)$ in $\text{GaNCr}_{3-x}\text{Mn}_x$ indicates that the hole-type carriers are dominant [43,44], which is much different from those of Mn-based antiperovskite compounds (eg., GaCMn_3 , SnCMn_3) where the main carriers are electron-type [7,43]. In order to further confirm the above result, we obtained the Hall coefficient (R_H) at room temperature (to see Fig. 8(b)) by measuring the magnetic field dependent Hall resistivity $\rho_{xy}(T)$ for $\text{GaNCr}_{3-x}\text{Mn}_x$. The positive R_H of $\text{GaNCr}_{3-x}\text{Mn}_x$ is consistent with the results of $\alpha(T)$. For all the samples, $\text{GaNCr}_{3-x}\text{Mn}_x$, the value of $\alpha(T)$ increases with increasing temperature at first, then decreases gradually after reaching a broad peak. Similar behavior has been observed in many Heusler alloys (eg., Ni_2MnGa) where such a broad peak at elevated temperatures is attributed to the existence of a pseudo-gap in the electronic density of state [45]. However, no evident abnormality occurs in $\rho(T)$ curve as mentioned above. Therefore, the existence of the broad peak may be closely related with the phonon scatterings [43]. In addition, using the formula of $n = 1/|eR_H|$ (e is the charge of electron), the room-temperature carrier concentrations ($n_{300\text{ K}}$) for $\text{GaNCr}_{3-x}\text{Mn}_x$ are obtained and plotted in Fig. 8(b). Apparently, the $n_{300\text{ K}}$ decreases with increasing x , which is consistent with the results of $\rho(T)$ at 300 K. Correspondingly, the detailed values of $n_{300\text{ K}}$ are listed in Table 1.

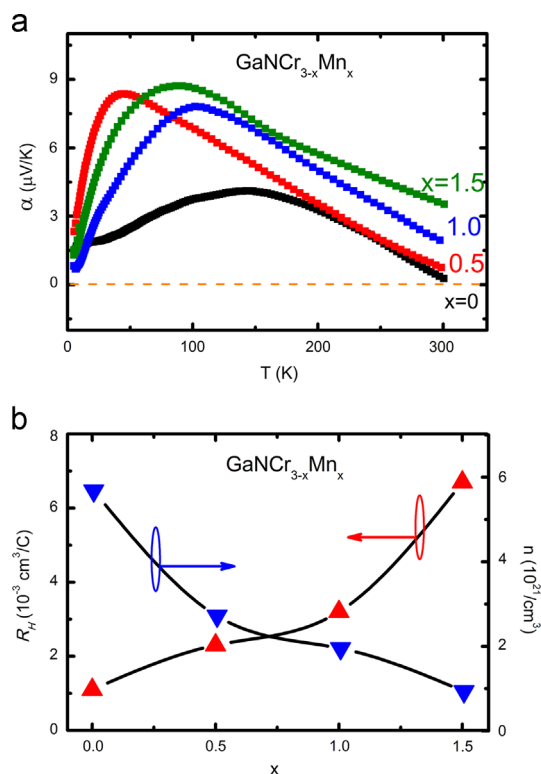


Fig. 8. (a) Temperature dependent Seebeck coefficient $\alpha(T)$ at zero field in a temperature range of 5–300 K for $\text{GaNCr}_{3-x}\text{Mn}_x$. The dashed line is guide to the eye; (b) room-temperature R_H and carrier concentration for $\text{GaNCr}_{3-x}\text{Mn}_x$.

4. Conclusion

In summary, we have synthesized a high quality polycrystalline GaNCr_3 and found that there is no superconductivity by measuring the resistivity down to 2 K. At the same time, the effects of Mn-doping on the crystal structure, magnetic and electrical/thermal transport properties of $\text{GaNCr}_{3-x}\text{Mn}_x$ ($0 \leq x \leq 1.5$) have been investigated systematically. As a result, the lattice constant a and ρ_0 increase, while the RRR, κ_e , and $n_{300\text{ K}}$ decrease with the increasing Mn-doping level x . Interestingly, there is a nonmagnetic ground state for parent compound GaNCr_3 , however, the ferromagnetism and antiferromagnetism are observed in Mn-doped samples. Correspondingly, around the AFM-PM transition of GaNCr_2Mn and $\text{GaNCr}_{1.5}\text{Mn}_{1.5}$ the correlation effect is obtained among magnetism, resistivity, and specific heat. Furthermore, the low-temperature specific heat and thermal conductivity of $\text{GaNCr}_{3-x}\text{Mn}_x$ ($x=0, 0.5, 1.0$, and 1.5) are investigated in detail, and it is found that the electron thermal conductivity κ_e plays a major role in total thermal conductivity κ_{total} of GaNCr_3 at low temperatures, while the phonon thermal conductivity κ_L is dominant in the whole temperature of 5–330 K for Mn-doped GaNCr_3 . In addition, the positive value of $\alpha(T)$ and R_H in $\text{GaNCr}_{3-x}\text{Mn}_x$ indicate the charge carriers are hole-type.

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