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Abstract

Perovskite-type Nd_{1-x}La_xCrO₃ ($0 \leq x \leq 1.0$) polycrystalline samples were synthesized using solid state reaction. Structural studies indicate that the lattice parameters, metal–oxygen bond lengths, and angles of Nd_{1-x}La_xCrO₃ strongly depend on the La content. Two magnetic transition temperatures, Cr³⁺ antiferromagnetic ordering temperature (T_N) and the spin reorientation phase transition temperature (T_{SRPT}), have been observed in the M - T curves. The increase in T_N and decrease in T_{SRPT} with increasing x value can be explained by the change in the magnetic interactions due to La doping. The heat capacity of Nd_{1-x}La_xCrO₃ measured from 2 to 300 K reveals that the lattice, electronic, and magnetic contributions to heat capacity can be well interpreted quantitatively using the Debye and Schottky models. The splitting energy of the Cr³⁺ $3d_{2g}$ orbital and the Nd³⁺ ground state have been calculated by fitting to the Schottky anomaly at very low temperature. The Cr–Nd interaction is suppressed gradually by La doping, which is verified by the calculation of the mean-field interaction parameter. This doping dependence provides directed evidence of TM – RE magnetic interactions in perovskite compounds, in agreement with the proposed model.

Keywords

Structure, magnetic, thermal, properties, Nd_{1-x}La_xCrO₃

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Structure, magnetic, and thermal properties of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0 \leq x \leq 1.0$)

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Perovskite-type $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0 \leq x \leq 1.0$) polycrystalline samples were synthesized using solid state reaction. Structural studies indicate that the lattice parameters, metal–oxygen bond lengths, and angles of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ strongly depend on the La content. Two magnetic transition temperatures, Cr^{3+} antiferromagnetic ordering temperature (T_N) and the spin reorientation phase transition temperature (T_{SRPT}), have been observed in the M - T curves. The increase in T_N and decrease in T_{SRPT} with increasing x value can be explained by the change in the magnetic interactions due to La doping. The heat capacity of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ measured from 2 to 300 K reveals that the lattice, electronic, and magnetic contributions to heat capacity can be well interpreted quantitatively using the Debye and Schottky models. The splitting energy of the Cr^{3+} $3d_{2g}$ orbital and the Nd^{3+} ground state have been calculated by fitting to the Schottky anomaly at very low temperature. The Cr–Nd interaction is suppressed gradually by La doping, which is verified by the calculation of the mean-field interaction parameter. This doping dependence provides directed evidence of TM – RE magnetic interactions in perovskite compounds, in agreement with the proposed model. © 2010 American Institute of Physics. [doi:10.1063/1.3505800]

I. INTRODUCTION

Rare-earth (RE) transition-metal (TM) oxide compounds with perovskite ABO_3 structure have been attracting renewed attention in connection with the discovery of high critical temperature (T_c) superconductivity, colossal magnetoresistance, and multiferroicity. Recently, $RE\text{MnO}_3$ compounds have been studied extensively due to their interesting strong coupling between the lattice, charge, and spin, which leads to colossal magnetoresistance.^{1–3} Moreover, novel multiferroicity, that is, the coupling of electric polarization and magnetism, has been observed in some $RE\text{FeO}_3$ and $RE\text{MnO}_3$ compounds.^{4,5} The structural, electrical, and magnetic properties of $RE\text{CrO}_3$ compounds have been studied as well. Based on the dependence of their resistivity on temperature and polarization, DyCrO_3 , HoCrO_3 , YbCrO_3 , and LuCrO_3 (Refs. 6–10) were predicted to show ferroelectric ordering due to distorted CrO_6 polyhedra. LaCrO_3 has been found to be highly conductive at high temperature, which would be useful in fuel cells.^{11,12}

As one of the typical $RE\text{CrO}_3$ compounds, NdCrO_3 crystallizes in an orthorhombic structure with space group $Pnma$. The Nd^{3+} ions are located in the spaces between CrO_6 octahedra. Magnetic ordering of Cr^{3+} ions was observed at the Néel temperature, $T_N = 219 \pm 1$ K. The magnetic structure is antiferromagnetic (AFM) with net moment from the canted spin arrangement, whereby Cr^{3+} ions are antiferromagnetically coupled to the nearest Cr^{3+} ions.¹³ The magnetic ordering of Cr undergoes a spin reorientation phase transition ($SRPT$) at a characteristic temperature, $T_{SRPT} = 35.1$ K. A neutron diffraction study has shown that the Nd–Cr interaction is able to polarize the Nd sublattice at temperatures be-

low T_{SRPT} .¹⁴ Nd^{3+} single-ion anisotropy was found to play an important role in the low-temperature magnetic properties, which results in a Schottky anomaly. The splitting of the Nd^{3+} ground doublet in NdCrO_3 was calculated to be $\Delta E/k_B = 25.9$ at 34 K, where ΔE is the split in energy and k_B is Boltzmann's constant, by optical spectroscopy measurements. However, very few studies of doping effects on NdCrO_3 have been conducted that focus on the magnetic and thermal properties.

Generally, substitutions on RE or TM sites in $RE\text{TMO}_3$ compounds will result in alterations to the crystal field, and consequently, the interactions between RE and TM ions and their electron configurations will be changed. Thus, the substitution of magnetic RE^{3+} ions provides a direct approach to study the interactions and electron configurations in $RE\text{TMO}_3$ compounds. The strengths of TM – TM , RE – TM , and RE – RE interactions in $RE\text{TMO}_3$ were found to observe a descending order, which depends on the electron configuration, the bonding strength, the bond lengths, and the bond angles. Unlike the electron configuration of Nd^{3+} ions ($4f^3$), the outermost shell of La^{3+} ions is fully occupied in the configuration $5s^2p^6$. Moreover, the radius of the La^{3+} ion is 1.061 Å, which is greater than that of the Nd^{3+} ion (0.995 Å). The crystal structure and electrical properties of La doped NdCrO_3 have been studied by neutron diffraction.^{15,16} However, to the best of our knowledge, the magnetic and thermal properties of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ have not been reported. Doping La into NdCrO_3 provides a good system to study the effects of nonmagnetic dopants on the structural, magnetic, and thermal properties of $RE\text{CrO}_3$ compounds, and is expected to provide direct evidence of interactions among the magnetic cations.

In the present work, a detailed and systematic study of the structural, magnetic, and thermal properties of

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$\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0.0 \leq x \leq 1.0$) has been carried out. The main goal of this paper is to provide comprehensive information on the influence of nonmagnetic dopants on the structural, magnetic, crystal field, and thermal properties of NdCrO_3 . Structural study indicates that the lattice parameters, and the Cr–O bond lengths and angles vary along with the doping level of La^{3+} . Detailed measurements of the magnetic properties reveal that the Cr–Cr interaction is enhanced by La^{3+} doping. The observed weak ferromagnetic moment is possible due to canting of the antiferromagnetically ordered Cr^{3+} moments. The electron configurations of Cr^{3+} and Nd^{3+} have been investigated by Curie–Weiss fittings. Heat capacity measurements ($x=0.0, 0.5$, and 1.0) are reported for this system for the first time, and they show clear features for the transitions at T_N and T_{SRPT} (from separation of different contributions to heat capacity). The low temperature Schottky anomalies are also discussed in detail. The Nd–Cr interaction is found to be depressed by La doping.

II. EXPERIMENTAL

$\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0 \leq x \leq 1.0$) powder samples were prepared by a solid state reaction of ternary oxides from Nd_2O_3 , La_2O_3 , and Cr_2O_3 . The purity of all chemicals, obtained from Sigma-Aldrich, was 99.99%. Stoichiometric quantities of oxides were weighed and mixed in an agate mortar, followed by pressing at 200 MPa into pellets 15 mm in diameter. Samples were then sintered at 1100 °C for 12 h. The products were then crushed, ground, pressed into pellets, and sintered again at 1300 °C for 12 h, followed by slow cooling in air at a rate of 5 °C/min.

The crystal structures of the samples were examined by x-ray diffraction (XRD; GBC MMA), using Cu $K\alpha$ radiation at $\lambda=1.54056$ Å. XRD Rietveld refinement calculations were conducted via the RIETICA software package (version 1.7.7). Raman scattering measurements with shifts ranging from 100 to 2000 cm^{-1} were performed with a Raman spectrometer (HR320; HORIBA Jobin Yvon) at room temperature. An Ar^+ laser with a wavelength of 632.8 nm was used for excitation of the Raman signals. The magnetic measurements were carried out using a 14 T physical properties measurement system (14 T PPMS; Quantum Design) equipped with a vibrating sample magnetometer (VSM) over a wide temperature range from 10 to 300 K and in magnetic fields up to 5 T. The heat capacity was measured using a thermal relaxation technique with the 14 T PPMS over a temperature range from 2 to 300 K.

III. RESULTS AND DISCUSSION

A. Structural properties

All compounds of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ were synthesized as well-crystallized single-phase powders (Fig. 1). All the diffraction peaks can be indexed well with an orthorhombic perovskite structure by Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 88-0695. Rietveld refinement was carried out to calculate the lattice parameters, bond lengths, and bond angles. The calculation results are shown in Table I. The lattice parameters a , b , and c , as well as the Cr–O bond lengths from refinement results, are plotted in

FIG. 1. (Color online) Measured and calculated XRD patterns for selected samples ($x=0.0$ and 1.0). All the samples are indexed well by JCPDS Card No. 88-0695. The dashed lines are experimental data, while the solid lines are the calculation results. The vertical bars indicate the peak positions that are calculated by refinement, and the bottom solid lines indicate the differences between experimental and calculation results.

Fig. 2. Cr–O (1) is the bond along the c direction while Cr–O (2) and Cr–O (3) are the bonds in the ab plane. Lattice parameter a is reduced, while b and c are increased as the La doping level rises. Overall, the lattice expands as a result of La substitution. The Cr–O bond lengths and angles also vary sequentially with the different doping levels. The La doping leads to increased Cr–O (1) bond lengths but decreased Cr–O (2) and Cr–O (3) bond lengths, and increased Cr–O–Cr (along the c direction) bond angles up to nearly 180° (for $x \geq 0.5$). The ionic radii, r , of La^{3+} and Nd^{3+} are 1.061 Å and 0.995 Å, respectively. Thus the increase in the unit cell with La doping can be attributed to the different sizes of the La^{3+} and Nd^{3+} ions. The Goldschmidt tolerance factor, t , is given by $t=(r_A+r_O)/[\sqrt{2}(r_B+r_O)]$ for ABO_3 compounds.¹⁷ The value of t for $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ samples increases from 0.882 to 0.907 as the value of x increase from 0 to 1, indicating that the crystal structure becomes less distorted from that of ideal perovskite as a result of La doping.

B. Raman spectra

Considering the relatively weak oxygen contribution to the structure factors in XRD analysis, Raman spectroscopy was carried out to search for possible disorder effects in the

TABLE I. XRD Rietveld refinement calculation results for $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0 \leq x \leq 1.0$).

Atom	Position	x	y	z	B
$x=0.0$, $a=5.480(1)$ Å, $b=7.699(5)$ Å, $c=5.425(6)$ Å, $\alpha=\beta=\gamma=90^\circ$, $R_{\text{WP}}=13.2\%$, $R_p=9.1\%$					
Nd	4 (c)	0.042(4)	0.25	0.004(5)	0.6
Cr	4 (b)	0	0	0.5	0.6
O (1)	4 (c)	0.479(5)	0.25	0.086(7)	0.6
O (2)	8 (d)	0.295(5)	0.042(9)	-0.239(6)	0.6
$x=0.2$, $a=5.476(1)$ Å, $b=7.715(3)$ Å, $c=5.438(8)$ Å, $\alpha=\beta=\gamma=90^\circ$, $R_{\text{WP}}=14.1\%$, $R_p=10.3\%$					
Nd	4 (c)	0.038(9)	0.25	0.003(7)	0.6
La	4 (c)	0.038(9)	0.25	0.003(7)	0.6
Cr	4 (b)	0	0	0.5	0.6
O (1)	4 (c)	0.481(1)	0.25	0.085(1)	0.6
O (2)	8 (d)	0.288(3)	0.041(0)	-0.234(1)	0.6
$x=0.5$, $a=5.475(9)$ Å, $b=7.737(1)$ Å, $c=5.465(3)$ Å, $\alpha=\beta=\gamma=90^\circ$, $R_{\text{WP}}=10.7\%$, $R_p=7.4\%$					
Nd	4 (c)	0.032(5)	0.25	0.002(1)	0.6
La	4 (c)	0.032(5)	0.25	0.002(1)	0.6
Cr	4 (b)	0	0	0.5	0.6
O (1)	4 (c)	0.485(2)	0.25	0.081(6)	0.6
O (2)	8 (d)	0.287(9)	0.039(5)	-0.233(5)	0.6
$x=0.8$, $a=5.476(9)$ Å, $b=7.751(5)$ Å, $c=5.499(6)$ Å, $\alpha=\beta=\gamma=90^\circ$, $R_{\text{WP}}=10.2\%$, $R_p=7.1\%$					
Nd	4 (c)	0.029(2)	0.25	0.001(3)	0.6
La	4 (c)	0.029(2)	0.25	0.001(3)	0.6
Cr	4 (b)	0	0	0.5	0.6
O (1)	4 (c)	0.485(1)	0.25	0.074(1)	0.6
O (2)	8 (d)	0.278(1)	0.039(7)	-0.227(6)	0.6
$x=1.0$, $a=5.478(6)$ Å, $b=7.757(3)$ Å, $c=5.514(7)$ Å, $\alpha=\beta=\gamma=90^\circ$, $R_{\text{WP}}=12.6\%$, $R_p=8.5\%$					
La	4 (c)	0.024(1)	0.25	0.000(9)	0.6
Cr	4 (b)	0	0	0.5	0.6
O (1)	4 (c)	0.489(9)	0.25	0.071(5)	0.6
O (2)	8 (d)	0.273(2)	0.038(2)	-0.221(7)	0.6

light anion sublattice. Raman spectroscopy analysis of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0 \leq x \leq 1.0$) was performed in a wavenumber range from 100 to 2000 cm^{-1} , with special attention to the vibrational bands that are most affected by oxygen motion. Figure 3 shows the Raman spectra of orthorhombic phase samples as obtained with $xx(A_g)$, $yy(A_g)$, $zz(A_g)$, $x'x'(A_g + B_g)$, $xz(B_{2g})$, and $yx'(B_{1g} + B_{3g})$ scattering configurations at room temperature. The irreducible representation of the Raman modes for the perovskite orthorhombic $Pnma$ structure at the center of the Brillouin zone is given by:¹⁸

$$\Gamma = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}. \quad (1)$$

Equation (1) shows that there are 24 Raman-active modes. There are four equivalent Cr^{3+} ions within the unit cell occupying sites with inversion symmetry. Hence, the Raman spectra originate from optical modes wherein the chromium cations remain stationary.¹⁹ In order to identify the Raman shift peaks for different La doped samples, the $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ Raman spectra were fitted in the range of 100–800 cm^{-1} by a Gaussian fitting method.²⁰ Seven vibration modes have been identified (four A_g , two B_{2g} , and one B_{3g}), which are indexed in Fig. 3(a). The main atomic motions according to the seven modes are ascribed to the O–Cr–O rotation and bending [$A_g(2)$], RE–O(1) stretching

[$B_{2g}(7)$], CrO_6 bending [$B_{2g}(5)$], CrO_6 breathing [$A_g(5)$], CrO_6 stretching [$A_g(4)$], CrO_6 rotation [$A_g(3)$], and O^{2-} in-plane-antistretching [$B_{3g}(2)$], respectively.²¹ The wavenumbers (cm^{-1}) of these vibration modes identified in the Raman spectra were plotted as a function of x value for the $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ samples, as shown in Fig. 3(b). Most of the Raman modes above 100 cm^{-1} show a frequency decrease with increasing La doping level in $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$. Similar observations have been reported for some other perovskite compounds.^{22–25} Features of the $B_{2g}(7)$, $A_g(4)$, and $A_g(3)$ modes are associated with the vibration of oxygen ions. Their frequencies decrease with increasing La content, because of the increase in the RE–O and Cr–O force constants. The replacement of Nd^{3+} by La^{3+} leads to a slight distortion of the crystal structure from the ideal perovskite structure and thus results in decreases in the wavenumbers of the $B_{2g}(5)$ and $A_g(5)$ modes with increasing x value. Only the $A_g(2)$ and $B_{3g}(2)$ vibration modes shift to higher wavenumbers with doping, which can be explained by a two-phonon model.^{26,27}

C. Magnetic properties

The magnetic susceptibility, χ , as a function of temperature T from 10 to 300 K in magnetic field of $H=1000$ Oe is

FIG. 2. Structural parameters as determined from Rietveld refinement of XRD data for $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0.0 \leq x \leq 1.0$): (a) lattice parameters as a function of x value; (b) the Cr-O bond length as a function of doping level in the samples: Cr-O (1) is the bond along the c direction while Cr-O (2)/(3) are the bonds in the ab plane.

plotted in Fig. 4(a). Doping La into NdCrO_3 reduces the magnitude of χ below the transition temperature and has a strong effect on χ - T behavior below the magnetic ordering temperature. With falling temperature, the first magnetic ordering was observed at $T_N = 219.6$ K for undoped NdCrO_3 , which is attributed to the Cr^{3+} spin ordering.²⁸ It is found that T_N increases linearly from 219.6 K for pure NdCrO_3 to 291.3 K for LaCrO_3 . In $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$, the Cr^{3+} ions are predominantly ordered antiferromagnetically with a small canting angle, which results in a net moment starting to appear below T_N . For the samples with $x \geq 0.5$ at temperatures below T_N , χ continuously increases as the temperature is decreased. For samples with $x < 0.5$, the χ - T curve shows an obvious drop below T_N , giving a cusp at $T \approx 180$ K. Because the magnitude of χ is small and increases with decreasing temperature, the Cr^{3+} spins align with high magnetic anisotropy below T_N in the samples with $x \geq 0.5$, whereas the system is less anisotropic when $x < 0.5$. Between T_N and T_{SRPT} , the Cr^{3+} moments are predominantly ordered antiferromagnetically and parallel to the c axis with a small canting angle, which results in a net moment along the a axis. The Cr sublattice undergoes a long-range cooperative ordering transition, as evidenced by a wide λ -shaped peak at T_N that can be observed in the χ - T measurements. Since La doping results in a larger unit cell volume, shorter in-plane Cr-O bond lengths,

FIG. 3. Effect of La doping on the Raman spectra of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0.0 \leq x \leq 1.0$) at room temperature: (a) Raman spectra for samples with different doping levels. Seven vibration modes have been identified in the spectra. (b) Raman shift as a function of doping level for vibration modes in the samples.

and a nearly straight Cr-O-Cr (out-of-plane) bond, the Cr-Cr AFM ordering is enhanced, resulting in decreasing χ and increasing T_N in doped samples. A second transition was observed at $T_{SRPT} = 37.6$ K in the sample with $x = 0.0$. It was found that T_{SRPT} is depressed in the doped samples and disappears in the pure LaCrO_3 sample within the measurement temperature range, as shown in the Fig. 4(a) inset. The magnetic susceptibility decreases in a corresponding way to the increasing value of x . In NdCrO_3 , the high- T Γ_2 (F_x, C_y, G_z) configuration of the Cr spin ordering system discontinuously changes into the low- T Γ_1 (A_x, G_y, C_z) configuration at T_{SRPT} . Since it has been verified that the Cr spin system is unaffected by the Cr-RE interaction,²³ the only possible explanation for the decreased T_{SRPT} is a distorted crystal structure. Above T_{SRPT} , the Nd^{3+} ions are polarized by the Cr-Nd exchange. The extremely strong Cr-Nd coupling has been reported to be greater than the corresponding coupling in the other RECrO_3 compounds.^{23,28} Because the total angular momentum is $J = 0$ for La^{3+} ions, the La doping can reduce the magnetic contribution of Nd^{3+} to the total magnetization. Therefore, decreased χ was observed in the doped samples.

A Curie-Weiss law fitting of $1/\chi$ versus T above T_N from 300 to 350 K was carried out to calculate the electron

FIG. 4. (Color online) Magnetic properties of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($x=0.0, 0.1, 0.2, 0.3$, and 0.4) samples: (a) magnetic susceptibility as a function of temperature (field cooled measurement) over the temperature range from 10 to 300 K in a magnetic field of 1000 Oe, with the inset showing the variation in the magnetic transition temperatures with x ; (b) magnetization as a function of field up to 5 T at 10 K.

configurations of magnetic ions. Generally, the Curie constant of the samples can be expressed as a function of the effective magnetic moment as follows:

$$C = \frac{N\mu_{\text{eff}}^2}{3k_B}, \quad (2)$$

where C is the Curie constant, N is the number of magnetic molecules, μ_{eff} is the effective magnetic moment, and k_B is the Boltzmann constant. For the pure LaCrO_3 sample, only Cr^{3+} carries magnetic moment and only one transition temperature (T_N) has been observed. Therefore, the magnetic properties are dominated by the interaction of Cr^{3+} ions. The total effective magnetic moments in LaCrO_3 were calculated to be $\sim 3.213 \mu_B/\text{Cr}^{3+}$, where μ_B is the Bohr magneton. The Cr^{3+} ions in LaCrO_3 have three localized $3d$ -electrons, which leads to a total possible spin quantum number S with values $1/2$ and $3/2$. The possible μ_{eff} are $3.873 \mu_B/\text{Cr}^{3+}$ for the high spin state (HS), and $1.732 \mu_B/\text{Cr}^{3+}$ for the low spin state, respectively. By comparing with calculated results from linear fitting of $1/\chi$ - T curves, Cr^{3+} was found in HS in LaCrO_3 . Since magnetic moment in the other $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ samples ($0 \leq x \leq 0.9$) has contributions from both Cr^{3+} and Nd^{3+} ions,

the spin state of Nd^{3+} ions can be obtained by subtracting the contribution of Cr^{3+} ions from the Curie-Weiss fitting results. It is found that the net moment carried by RE^{3+} ions is from $\sim 2.038 \mu_B$ for $x=0.9$ to $\sim 2.7 \mu_B$ for $x=0.0$. Therefore, the decreasing magnetic moment of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ with doping should be ascribed to substitution by nonmagnetic La^{3+} ions and straightened neighboring CrO_6 octahedra. The interaction between Nd and Cr will also be influenced by doping as a result (to be discussed in more detail later). The magnetization, M , as a function of magnetic field H up to 5 T at 10 K and room temperature is plotted in Fig. 4(b). Doping La into NdCrO_3 depresses the magnitude of M at 10 K. M is composed of two components in $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ samples. The first is characterized by linear behavior in the H - T curve and is comparable to what is observed in pure LaCrO_3 at 10 K; the second is a small ferromagnetic component that saturates at a magnetic field of about 4 T. This result is consistent with the χ - T measurement. At room temperature, all the samples show typical paramagnetic behavior.

D. Heat capacity

The temperature dependence ($2 \text{ K} < T < 300 \text{ K}$) of the heat capacity, C_p , measured without magnetic field is shown in Fig. 5 for the $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($x=0.0, 0.5$, and 1.0) samples. The overall shape of $C_p(T)$ is generally consistent with the results of prior work on pure NdCrO_3 .^{28,29} The C_p of all the samples in the high temperature (high- T) range follows the Dulong-Petit law, that is, the high- T limiting value is consistent with the classical value of $3R$ per atomic site in the formula unit, where R is the molar gas constant. The most notable $C_p(T)$ feature at high- T is the clear λ -shape anomalous peak at T_N for all the samples. Note that the temperature range for the C_p - T curves is well below the orthorhombic to rhombohedral phase transition observed at $T \approx 533 \text{ K}$ for undoped LaCrO_3 .³⁰ Jumps in the heat capacity are evident for a long-range cooperative ordering transition. The λ -peak shifts to higher temperatures as the doping level increases. The peak position corresponds to the ordering temperature T_N . Because the high- T Γ_2 (F_x, C_y, G_z) configuration discontinuously changes into the low- T Γ_1 (A_x, G_y, C_z) configuration at T_{SRPT} ,¹³ an apparent spin reorientation phase transition is also observed at T_{SRPT} in the heat capacity curves, as shown in Fig. 5(b)–5(d). The low temperature (low- T) region ($2 \text{ K} < T < 20 \text{ K}$) is shown in more detail in the upper inset of Fig. 5. A clearly rounded peak with a maximum at $T_{\text{max}} = 10 \pm 3 \text{ K}$ is predominant in the doped samples because of the Schottky anomaly, the heat capacity anomaly at very low temperature due to energy splitting.^{31,32} The T_{max} decreases as the x value increases. This indicates that both the systematic shift in the λ -peak position at high- T and the decrease in the Schottky anomaly at low- T are due to the nonmagnetic La doping effect.

Figure 6 shows a magnified view of the $200 \text{ K} < T < 300 \text{ K}$ region for $x=0.0, 0.5$, and 1.0 , illustrating that the C_p anomaly shifts to higher temperatures as x increases. The anomaly at the ordering temperature apparently exhibits a well-defined T_N in magnetometry (see below). A smooth

FIG. 5. (Color online) (a) Temperature dependence of heat capacity ($2 \text{ K} < T < 300 \text{ K}$) of selected samples with $x=0.0, 0.5$, and 1.0 . The inset is a magnified view of C_p at low temperature. (b)–(d) are the temperature dependences of the magnetic and thermal properties for the samples with $x=0.0, 0.5$, and 1.0 from 2 K to 300 K , respectively.

background has been extracted from all the curves using a third-order polynomial fitting (excluding the region around T_N) in order to extract the excess magnetic heat capacity, $\Delta C_p(T)$, as shown in Fig. 6(b). The magnitude of $\Delta C_p(T)$ is found to be almost the same for all the samples. The anomaly appears when a characteristic λ -shape peak is associated

with a conventional second-order paramagnetic to AFM phase transition. The magnetic entropy, S_{Mag} , associated with the AFM ordering transition can be calculated from this plot,³³

$$S_{Mag} = \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT, \quad (3)$$

where T_1 and T_2 define a temperature range around T_N , e.g., $T_N \pm 25 \text{ K}$. The calculated S_{Mag} are 0.457 , 0.484 , and $0.304 \text{ J mol}^{-1} \text{ K}^{-1}$ for samples with $x=0.0$, $x=0.5$, and $x=1.0$, respectively. The calculated S_{Mag} (e.g., $1.28 \text{ J mol}^{-1} \text{ K}^{-1}$ for NdCrO_3) is well below the expected full spin entropy,

$$S_{Mag} = R \ln(2S + 1), \quad (4)$$

where S is the spin of Cr^{3+} ions in the samples, and R is the molar gas constant.

The low- T region ($2 \text{ K} < T < 20 \text{ K}$) is shown in more detail in Fig. 7. In order to quantify the contributions to C_p , the data are fitted by $C_p(T) = \gamma T + \beta T^3 + C_p^{Mag}(T)$, where the γT term describes the electronic contribution, the βT^3 term describes the lattice contribution, and $C_p^{Mag}(T)$ is the extracted magnetic contribution to C_p . The electronic contribution, γ , is given in a free-electron model by $\gamma = \pi^2 k_B^2 N(E_F)/3$, where $N(E_F)$ is the density of states at the Fermi level, and the lattice contribution, β , is given in the

FIG. 6. (Color online) (a) Expanded view of the heat capacity as a function of temperature for $x=0.0, 0.5$, and 1.0 samples in the high- T range. (b) Excess magnetic heat capacity extracted from heat capacity by subtracting a smooth background as described in the text.

FIG. 7. (Color online) Thermal properties for selected samples ($x=0.0, 0.5, 1.0$) below 20 K: (a) heat capacity as function of temperature (open symbols). The solid line is the nonmagnetic contribution to C_p . (b) Temperature dependence of the nonmagnetic heat capacity plotted as C_p/T vs T^2 . The solid lines are fits to $C_p(T) = \gamma T + \beta T^3$. (c) Schottky anomaly of the samples extracted by subtracting electronic and lattice contributions from the heat capacity. (d)–(f) are the fits to the Schottky anomaly from a modified Schottky model at low temperature for $x=0.1, 0.5$, and 0.0 , respectively. The open circles in the plots show the experimental results.

Debye model by $\beta = 234Nk_B/\Theta_D^3$, where N is the number of ions/mole and Θ_D is the Debye temperature. The nonmagnetic (electronic+lattice) contributions are fitted from 2 to 45 K (excluding the region of the Schottky anomaly) using $C_p = \gamma T + \beta T^3$, as indicated by the solid line in Fig. 7(a). The fitting results are plotted as C_p/T versus T^2 [Fig. 7(b)] in

order to examine each contribution to the specific heat. The parameter γ extracted from the fitting is quite small, which indicates the existence of a very small amount of free electrons. The Debye temperatures Θ_D , estimated by the term β , are 436 K, 473 K, and 544 K for the $x=0.0, 0.5$, and 1.0 samples, respectively. The overall magnitude (380–600 K) of

the Θ_D is the typical for ABO₃ type perovskite oxides.^{34–36} The magnetic contribution $C_P^{Mag}(T)$, therefore, can be evaluated by subtracting the nonmagnetic contribution [solid line in Fig. 7(a)] from C_P . The temperature dependence (2 K < T < 20 K) of the magnetic contribution $C_P^{Mag}(T)$ is plotted in Fig. 7(c). It demonstrates that the magnetic contribution $C_P^{Mag}(T)$ decreases as the x value increases. This can be understood through the fact that nonmagnetic La³⁺ substitution reduces the total magnetic contribution to the Nd_{1-x}La_xCrO₃ system. To separate the Nd³⁺ and Cr³⁺ contributions to $C_P^{Mag}(T)$ at low- T is a complicated task. Note that for $x = 1.0$ (LaCrO₃), only Cr³⁺ ions carry magnetic moment. The Schottky anomaly at low- T therefore can only be attributed to Cr³⁺ ions. $C_P^{Mag}(T)$, therefore, can be fitted by a modified Schottky form:²⁹

$$C_P^{Mag}(T) = \left(\frac{n}{N_{Cr}} \right) R \left(\frac{\Delta E}{k_B T} \right)^2 \frac{u_0}{v_1} \frac{\exp(\Delta E/k_B T)}{\left[1 + \left(\frac{u_0}{v_1} \right) \exp(\Delta E/k_B T) \right]^2}, \quad (5)$$

where n/N_{Cr} is the fraction of Cr sites contributing to C_P , R is the molar gas constant, ΔE is the energy level splitting, and u_0/v_1 is the degeneracy ratio of ground state splitting. The equation indicates that the C_P - T curve at very low temperature is not symmetric, falling off rapidly on the low-temperature side and slowly on the high-temperature side. The equation also predicts a peak in the vicinity of the characteristic temperature $\Delta E/k_B T$. Figure 7(d) shows the temperature dependence of the magnetic heat capacity for the $x = 1.0$ sample. With the exception of the tail at $T > 20$ K, this model provides a good fit (as shown by the solid line in Fig. 7(d), with $u_0/v_1 = 1/2$, $\Delta E = 1.2$ meV). The value of n/N_{Cr} is found to 0.14%. Based on this very small n/N_{Cr} value, we conclude that a small amount of Cr³⁺ ions in the sample are trapped in finite spin states, even at low temperature. This Schottky anomaly has also been reported for the other perovskite oxides.^{37–40} The possible reason is that the defects (e.g., O²⁻ point defects⁴¹) cause the unpaired electrons of Cr³⁺ ions to be stabilized in a finite spin state. In the samples with $x < 1.0$, Nd³⁺ ions provide a magnetic contribution to $C_P^{Mag}(T)$, which can be obtained after subtraction of the Cr³⁺ contribution. Considering that all the Nd³⁺ ions contribute to the anomaly and $u_0/v_1 = 1$ for the Nd³⁺ ground state splitting, the Schottky form can be applied to fit the contribution of Nd³⁺ ions:

$$C_P^{Mag}(T) = N_{Nd} k_B \left(\frac{\Delta E}{k_B T} \right)^2 \frac{\exp(\Delta E/k_B T)}{[1 + \exp(\Delta E/k_B T)]^2}, \quad (6)$$

where N_{Nd} is the number of Nd³⁺ ions. The results of fitting for the $x = 0.5$ and $x = 0.0$ samples are plotted in Figs. 7(e) and 7(f), respectively. The T_{max} is found to be 11.2 K and 7.9 K in the sample with $x = 0.0$ and 0.5, respectively. Calculated $\Delta E/k_B$ for Nd³⁺ ions in this work gives a value of the energy splitting of ~ 27 K, in excellent agreement with neutron inelastic experiments (~ 28 K).²⁸ The energy splitting $\Delta E/k_B$ is reduced in the La doped samples, which is attributed to the weaker Cr-RE interactions. The splitting of the Cr³⁺ 3d orbital and the Nd³⁺ ground state in Nd_{1-x}La_xCrO₃ are shown

FIG. 8. (a) Cr³⁺ 3d and (b) Nd³⁺ ground state splitting schemes of Nd_{1-x}La_xCrO₃.

in Fig. 8. We propose that these doped La³⁺ ions dilute the concentration of magnetic Nd³⁺ ions, which is associated with the reduction in Cr-Nd interactions. Well-fitted plotting for low- T total $C_P^{Mag}(T)$ therefore can be performed by collecting the magnetic contributions from both Cr³⁺ and Nd³⁺, as shown in Figs. 7(d)–7(f).

In order to understand the doping effect on the Cr-Nd interaction, the Zeeman splitting of the ground doublet of Nd³⁺ can be expressed as

$$\Delta E = 2(-\mu_{Nd} H_{Nd-Cr} + J_{Nd} \eta), \quad (7)$$

where μ_{Nd} is the effective moment of Nd³⁺, H_{Nd-Cr} is the effective exchange field, J_{Nd} is the exchange constant of the Nd-Nd interaction, and η is a dimensionless mean-field parameter describing the magnetically induced order of Nd in the Γ_1 mode. Because of its relatively small value, as confirmed by neutron diffraction,⁴² η can be neglected at T_{SRPT} . In addition, H_{Nd-Cr} can be treated as a temperature independent parameter, due to the fact that the Cr sublattice is fully locked at very low temperature. Thus, the effective exchange field can be obtained as 89.6 kOe for the $x = 0.0$ and 81.8 kOe for the $x = 0.5$ samples from the Curie-Weiss and Schottky anomaly fittings. Therefore the Nd-Cr mean-field interaction parameters can be calculated from $n_{Nd-Cr} = H_{Nd-Cr}/\mu_{Cr}$ as 27.89 kOe/ μ_B and 25.46 kOe/ μ_B for $x = 0.0$ and $x = 0.5$, respectively.

IV. CONCLUSION

This work has verified the strong influence of La doping on the physical properties of NdCrO₃. Comparison of the structure of pure phase material and Nd_{1-x}La_xCrO₃ shows that the expanded lattice volume is a result of La substitution. Cr-O-Cr bond lengths and angles varied sequentially according to the doping level, which was confirmed by XRD and Raman studies. The increasing T_N and decreasing T_{SRPT} from La doping can be attributed to the enhanced Cr-Cr magnetic exchange interaction and depressed Nd³⁺-Cr³⁺ coupling, respectively. Two components of magnetization (antiferro- and ferro-) in magnetic field were observed in Nd_{1-x}La_xCrO₃, which is ascribed to canted antiferromagnetic ordering of Cr³⁺. The electron configuration of both Cr³⁺ and Nd³⁺ were found to be HS state by the Curie-Weiss fitting. The heat capacity study revealed that the Debye temperature for the samples was increased by La doping. The lattice, electronic, and magnetic contributions to heat capacity have been quantified. The low- T Schottky anomaly indicates increasing energy level splitting of Cr³⁺ and Nd³⁺ from doping. The Cr-Nd interaction is also depressed by La doping, which was confirmed by calculation of mean-field interaction parameters.

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