Magnetic, thermal, and electrical properties of $La_{1-x}Ca_xCrO_3$ ($0 \le x \le 0.5$)

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A broad range of measurements of $La_{1-x}Ca_xCrO_3$ ($0 \le x \le 0.5$) are presented. $LaCrO_3$ is an insulating antiferromagnet with Néel temperature $T_N = 293$ K. Substitution of Ca^{2+} for La^{3+} decreases T_N with a slope of -210 K/x; this is more rapid than that of Sr substitution ($dT_N/dx = -90$ K/x) reported by [Tezuka *et al.*]. Solid State Chem. **141**, 404 (1998)]. Since Sr doping affects the Cr-O-Cr bond angles more severely, it is suggested that Ca doping provides a reliable measure of the influence of *d*-orbital vacancies on T_N . Ca doping induces a small ferromagnetic moment that rises rapidly at small doping and falls with *x* above x=0.05. At x=0.40, the ferromagnetic moment vanishes, but returns at x=0.50. In addition, the electrical resistivity at x=0.40 is significantly larger than at x=0.30 and 0.50. These observations near x=0.4 may signify a change in the spin structure associated with the magnetic lattice and coupling between the charge carriers and magnetism. Heat capacity measurements on x=0 and 0.20 reveal no discernible electronic term and Debye temperatures near 700 K. Comparisons are made with perovskite manganese oxides.

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I. INTRODUCTION

Transition metal oxides exhibit a wide range of interesting electrical and magnetic properties. In recent years, manganese oxides have been studied extensively because of strong coupling among the charge, lattice, and spin degrees of freedom that leads to colossal magnetoresistance.¹ Similar behavior has been observed in some cobalt oxides which exhibit a well-known low-spin to high-spin transition.² The electrical, magnetic, and structural properties of Cr oxides have been reported in a number of publications. LaCrO₃ is antiferromagnetic^{3,4} below 290 K. It is a poor electrical conductor at room temperature, but its high conductivity at high temperature as well as its ability to withstand high temperatures has made it useful as an interconnect between fuel cells and as a material for heating elements.⁴

A limited number of doping studies of LaCrO₃, focusing on the electrical and magnetic properties, have been conducted whereby divalent ions such as Sr or Ca are substituted for trivalent La. Sakai et al.³ investigated doping levels up to 75% Ca and a number of oxygen concentrations. They reported the crystal structure over a wide range of temperature (12 K $\leq T \leq$ 1300 K), revealing an orthorhombic to rhombohedral phase transition at about 600 K for La_{0.80}Ca_{0.20}CrO₃. In addition, they reported the antiferromagnetic structure as G type for a number of Ca concentrations and conducted some magnetic susceptibility measurements. More recently, Tezuka et al. published⁴ an investigation of the magnetic and structural properties of $La_{1-x}Sr_xCrO_3$ with $0 \le x \le 0.25$. They also found an orthorhombic to rhombohedral phase transition for 0 and 5% Sr doping at 526 K and 413 K, respectively. Furthermore, they were able to establish the antiferromagnetic structure associated with both of these phases for x=0.15 as G type. The dc electrical transport of $La_{1-x}Sr_xCrO_3$ ($0 \le x \le 0.40$) is thermally activated in the range 300 K $\leq T \leq 2000$ K with activation energies between 0.11 and 0.19 eV and temperature-dependent behavior consistent with conduction by small polarons.^{5,6} The Seebeck coefficients are essentially temperature independent, revealing that the carrier mobility is thermally activated. The ac electrical transport shows a significant frequency dependence between 50 Hz and 20 kHz, consistent with conduction by small polarons.⁵

LaCrO₃ is an interesting compound to compare to CaMnO₃, the end member of the colossal magnetoresistance system La(Ca)MnO₃. Both transition metal ions in these compounds have three electrons in the 3d shell, which leads to total spin S=3/2. The antiferromagnetic structure is G type in both, whereby each Mn⁴⁺ and Cr³⁺ ion is antiferromagnetically coupled to its neighbor. This structure is predicted by considerations of covalency by Goodenough,¹³ arguments which should be valid for Cr and Mn transition metal compounds. Structural transitions, such as the orthorhombic to rhombohedral phase transition observed^{3,4} in La_{0.80}Ca_{0.20}CrO₃ are also observed in manganese oxides.⁷ Furthermore, the electrical transport of manganese oxides is polaronic in nature as well.8 A major difference between these two systems is the observation of ferromagnetism in the manganese oxides, which occurs over a rather broad range of doping and dopants.¹ This can be attributed to the mixture of Mn³⁺ and Mn⁴⁺ ions which leads to double exchange.^{9–11} In the case of LaCrO₃, doping of 4 + ions forLa³⁺ would be required for double exchange to occur; this would lead to filled t_{2g} levels and finite electron occupancy in the e_g levels. As of this date, no such experiments have been reported to our knowledge.

In the present paper, the structural, magnetic, thermal, and electrical properties of $La_{1-x}Ca_xCrO_3$ are investigated. The main goal of this paper is to expand our knowledge of these compounds and provide more information about the influence of doping on the antiferromagnetism and weak ferromagnetic moment. Detailed measurements of the magnetic properties reveal that the weak ferromagnetic moment is likely due to canting of the antiferromagnetically ordered Cr moments. Recent research on the manganese oxides, also revealing a weak ferromagnetic moment, is discussed in re-

lation to these observations. Our heat capacity measurements (x=0 and 0.20), the first reported for this system, reveal clear features at the antiferromagnetic transition temperatures and Debye temperatures near 700 K. The electrical resistivity decreases with Ca doping until x=0.4, where an anomalous increase occurs; this appears to correlate with the absence of the weak ferromagnetic moment and may indicate a change in the antiferromagnetic spin structure and coupling of the charge carriers to the magnetism.

II. EXPERIMENT

Ten polycrystalline samples of $La_{1-r}Ca_rCrO_3$ ($0 \le x$ ≤ 0.5) were synthesized using standard solid-state reaction. Stoichiometric quantities of La₂O₃ (dried at 550 °C), CaCO₃, and Cr₂O₃ were weighed and mixed for 10 min in an agate mortar followed by reaction in an alumina crucible at 1300 °C overnight. The samples were then reground for 5 min, placed in the crucible, and reacted at 1450 °C for 20 h. This last step was repeated once with reaction to temperatures of 1500 °C for $0 \le x \le 0.3$ and 1450 °C for samples with $x \ge 0.40$. Finally, the samples were pressed into pellets and reacted at the same temperatures as in the previous reaction for 20 h followed by slow cooling in air at a rate of 1.5 °C/min. All samples were investigated with powder x-ray diffraction and found to exhibit only the perovskite phase typical to these compounds and no secondary impurity phases. The x-ray data were refined using the program suite GSAS and the space group *Pnma*.¹² We were unable to investigate the oxygen content of the prepared samples, but note that this has been studied in the past with deviation from 3 close to zero.³

The samples range in color from light green (x=0), to dark brown (x=0.05 and 0.10), to black ($x \ge 0.15$). LaCrO₃ never forms a good hard sintered sample, remaining with the consistency of a pressed powder even after reaction at 1500 °C. Samples with a small amount of Ca sinter very well, forming strong hard pellets. Thus, the addition of Ca has a significant effect on the sinterability of this compound.

Measurements were conducted using a Quantum Design Physical Properties Measurement System (PPMS). This unit has a vibrating-sample magnetometry option that operates at 40 Hz. In measuring the magnetization M versus T, samples are cooled in a field from 400 K at a rate of 0.8 K/min; data are acquired in the temperature sweep mode. M versus magnetic field H data were acquired at sweep rates of 100 Oe/s either after zero-field cooling or ramping the magnet to zero field in an oscillatory mode whereby the field is gradually nullified by a series of oscillations about zero field with successively reduced amplitude. Electrical resistivity was measured using a four-probe dc technique. The heat capacity was measured using a thermal relaxation technique.

III. RESULTS AND DISCUSSION

The lattice parameters obtained from Rietveld refinement are plotted in Fig. 1 and listed in Table I. Overall, the lattice shrinks as a result of Ca substitution by 4.5% for the doping range studied. All three lattice parameters are reduced in



FIG. 1. Lattice parameters as determined from Rietveld refinement of powder x-ray diffraction data for $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$. The parameters *a*, *b*, and *c* are represented by the solid squares, open squares, and solid circles, respectively. Uncertainties in the refined values are smaller than the size of the data points.

magnitude with *x*, and the overall orthorhombic distortion is reduced as well. The lattice parameters *a*, $b/\sqrt{2}$, and *c* differ by, at most, 0.3% from one another at x=0.5. The ionic radii of eight-coordinated La³⁺ and Ca²⁺ are 1.16 Å and 1.12 Å, respectively, a difference of about 3.5%.¹⁴ Using these radii, the difference in volume of the ions is calculated and found to be approximately 10%. Thus, the differing unit cell volumes of LaCrO₃ and La_{0.5}Ca_{0.5}CrO₃ can easily be attributed to the differing volumes of the La and Ca ions. The Goldschmidt tolerance factor is given by $t=(r_A+r_x)/[\sqrt{2}(r_B+r_x)]$ for *ABX*₃ compounds.^{15,16} Generally a purely cubic structure forms for t=1. LaCrO₃ and CaCrO₃ have values of t=0.903 and 0.889, respectively, which indicates that they should have crystal structures slightly distorted from cubic, as observed.

The magnetization M versus temperature T in magnetic field H=2000 Oe is plotted in Fig. 2 for selected specimens. These data were collected by cooling the samples in constant magnetic field from 400 K. Ca doping depresses the magnetic transition T_N in a manner that is more severe than that observed for Sr doping.⁴ This comparison is illustrated in Fig. 3 where T_N versus x is plotted for $La_{1-x}Ca_xCrO_3$ (open symbols) and $La_{1-x}Sr_xCrO_3$ (solid symbols).¹⁷ For $La_{1-x}Ca_xCrO_3$, T_N is depressed at a rate near x=0 of $dT_N/dx = -210 \text{ K/x}$ as determined by fitting a second-degree polynomial to T_N versus x and taking the linear coefficient as the slope¹⁷ in the limit $x \approx 0$. This is significantly stronger than $dT_N/dx = -90 \text{ K/x}$ observed for $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$. This can be understood through structural considerations. Although Ca and Sr are isovalent in this compound, Sr²⁺ has an ionic radius¹⁴ of 1.26 Å, which corresponds to an ionic volume about 26% larger than La³⁺. Thus, substitution of Sr would lead to a slightly larger unit cell volume and Cr-O-Cr bond angles nearer to 180°. Since straightening of the bond angle generally enhances the magnetic exchange interaction,¹⁸ we assert that this is the mechanism through which Sr substitution leads to higher values of T_N than Ca substitution. These arguments are consistent with the reduction of T_N observed

TABLE I. Room temperature lattice parameters, magnetic saturation moments,^a electrical resistivity at 300 K, and activation energies of $La_{1-x}Ca_xCrO_3$.

x	a (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$V(Å^3)$	M_{sat} (5 K) (μ_B /Cr ion)	ho (300 K) (m Ω cm)	E_g (meV)
0	5.4798(2)	7.7598(3)	5.5157(2)	234.54(2)	0	3.1×10^{6}	1160
0.05	5.4710(3)	7.7445(4)	5.5035(3)	233.18(2)	0.013	3000	84.4
0.10	5.4629(3)	7.7319(5)	5.4943(3)	232.07(3)	0.011	973	89.9
0.15	5.4577(3)	7.7225(5)	5.4878(3)	231.30(3)	0.011	805	91.7
0.20	5.4511(2)	7.7121(3)	5.4770(2)	230.25(2)	0.005	747	94.9
0.25	5.4392(3)	7.6944(4)	5.4638(3)	228.67(2)	0.003	910	99.0
0.30	5.4309(3)	7.6821(4)	5.4523(3)	227.48(2)	0.002	779	101
0.40	5.4207(3)	7.6635(4)	5.4359(3)	225.82(2)	0	20071 ^b	150
0.50	5.4073(3)	7.6421(4)	5.4199(2)	223.97(2)	0.012	1203	129

 ${}^{a}M_{sat}$ is determined as the intercept of two linear lines drawn through the low- and high-field regions of the M versus H curves.

^bA second x=0.4 sample displayed ρ (300 K)= 3.4×10^6 m Ω cm and $E_g=219$ meV. The difference between this value and the ρ (300 K) value in the table is likely the result of small compositional and density variations between the two samples.

upon replacement of La^{3+} by smaller rare earth ions.¹⁹ It is important to note that the average Cr-O-Cr bond angle is about 160°, according to powder neutron diffraction data on LaCrO₃; also, a 30% substitution of Ca for La increases the angle by only³ about 1°. As a result, since Ca substitution has a rather small effect on the bond angle important for magnetic exchange, we believe that the majority of the herein observed depression of T_N results from the doped-hole concentration which increases with *x*. Thus the La_{1-x}Ca_xCrO₃ system provides a better measure of the influence of *d*-orbital electron vacancies on T_N than the La_{1-x}Sr_xCrO₃ system.

Doping Ca into LaCrO₃ enhances the magnitude of M below the magnetic transition and has a strong effect on the temperature dependence of M in the antiferromagnetic state. We investigated the behavior of M on H in some detail in order to better understand this effect. Some example data are illustrated in Fig. 4 for La_{0.85}Ca_{0.15}CrO₃ where M versus H is

shown at a number of temperatures above and below T_N . At T=5 K, M is composed of two components. The first is linear in H and comparable in magnitude to that observed in LaCrO₃ at 5 K (plotted at the center of the upper left panel) and in the paramagnetic state of $La_{0.85}Ca_{0.15}CrO_3$ (lower right panel, data at 300 K); the second is a small ferromagnetic component that saturates at a magnetic field of about 30 kOe. The ferromagnetic component shrinks in magnitude with increasing temperature, vanishing above the Néel temperature of 255.4 K. As a function of x, the ferromagnetic component increases rapidly at low doping, followed by a decrease. This behavior is illustrated in the data for the saturation moment M_{sat} versus x which are tabulated in Table I; M_{sat} is determined as the intercept of two linear lines drawn through the low- and high-field regions of the M versus Hcurves. Such a rapid increase in M_{sat} is also observed²¹ for small doping concentrations of La in CaMnO₃, although in



FIG. 2. Magnetization versus temperature at 2000 Oe for $La_{1-x}Ca_xMnO_3$ with x=0, 0.10, 0.15, 0.30, and 0.50.



FIG. 3. Néel temperature T_N plotted versus x for La_{1-x}Ca_xCrO₃ (open circles) and La_{1-x}Sr_xCrO₃ [solid circles, data from Tezuka *et al.* (Ref. 4)].



FIG. 4. Magnetization *M* versus magnetic field *H* at a number of temperatures for La_{0.85}Ca_{0.15}CrO₃ with T_N =255.4 K. In the *T*=5 K panel (upper left) *M* versus *H* is shown for LaCrO₃ at 5 K. The same scale is used in all six panels.

the La(Ca)CrO₃ system the saturation moment is far smaller. In fact, the saturation moment at 5 K for x=0.15 is $0.011 \mu_B$ /Cr ion which is under 1% of full ferromagnetic saturation.

Although the values of M_{sat} are very small, we observe in Figs. 4 and 5 extremely large coercive fields for this system. For example, the coercive field at 5 K is about 13 kOe for x=0.15 and 19 kOe for x=0.30. The observation of large coercive fields reveals that a substantial magnetic field is required to orient the magnetic domains along the direction of the applied field. The large coercive field may be associated with the microstructure of the specimens.²⁰ It would probably not be present if the ferromagnetic component were due to impurities. Careful inspection of the data in Fig. 5 indicates that the magnetic moment at 60 kOe for 5 K is slightly smaller than the moment at 20 K in the same field; this would not be the case if the ferromagnetic moment were due simply to an impurity phase. Furthermore, the values of M_{sat} (5 K) in Table I illustrate a decrease with x in the region $0.05 \le x \le 0.40$, also suggesting that the observed ferromagnetic moment is not due to an impurity phase. Thus, we believe the observed ferromagnetic component to be intrinsic and the result of a minor amount of canting of the antiferromagnetic moments. It should be stressed that the magnitude of the canting is very small since the average Cr magnetic moment for x=0.15 should be $2.85\mu_B/Cr$ ion. An average canting angle for this sample of 0.22° at 5 K is estimated



FIG. 5. Magnetization *M* versus magnetic field *H* at a number of temperatures for $La_{0.70}Ca_{0.30}CrO_3$ with $T_N=208.9$ K. The same scale is used in all six panels.

based on M_{sat} (5 K)=0.011 μ_B /Cr ion and simple vector analysis. Such canting, or noncollinear ferromagnetism is common in perovskite compounds^{11,21} and has been reported³ from neutron powder diffraction for La(Ca)CrO₃. An interesting observation is the absence of a ferromagnetic moment at 5 K for *x*=0.40; this coincides with a large increase in the electrical resistivity which may indicate a change in the spin arrangement associated with the antiferromagnetic order (see discussion of electrical resistivity below). It is of value to note that in many measurements we observed a spontaneous magnetic moment nearly as large as M_{sat} after zero-field cooling. Our suspicion is that this is an effect caused by strain induced on the sample from the sample holder.²²

Heat capacity at constant pressure C_P was measured for LaCrO₃ and La_{0.80}Ca_{0.20}CrO₃. These data are presented in Fig. 6. The curve for La_{0.80}Ca_{0.20}CrO₃ is shifted downward for clarity. At the highest temperatures, $C_P \approx 12.4R$, where *R* is the gas constant. The classical Dulong-Petit result for a system containing five atoms would be 15*R*, although the light atoms might reduce this slightly.²⁴ Below 240 K the two curves lie on top of one another except for a weak feature at 150 K in La_{0.80}Ca_{0.20}CrO₃ which could be due to a small amount of Ca-rich phase or an experimental artifact. Note that this feature is well below the orthorhombic to rhombohedral phase transition³ observed at ≈ 650 K. Jumps in the heat capacity are evident at the magnetic phase transitions. By drawing straight lines through the data above and



FIG. 6. Heat capacity at constant pressure C_P plotted versus temperature for LaCrO₃ and La_{0.80}Ca_{0.20}CrO₃ in zero magnetic field. The curve for La_{0.80}Ca_{0.20}CrO₃ is shifted downward by 10 J/mol K for clarity.

below the transition and assuming the standard steplike feature for a second-order phase transition, we extract the jumps $\Delta C = 8.2 \pm 0.2$ and 5.0 ± 0.2 J/mol K for x = 0 and 0.20, respectively. We fit the data to an equation of the form C_P $=\gamma T + \beta T^3$ in the region 2 K $\leq T \leq 30$ K. Inclusion of an additional term proportional to T^2 , to account for magnetic spin waves, did not improve the fit quality.²³ It was therefore omitted. The parameter γ extracted from the fits was zero within our uncertainty; this can be understood through electrical transport measurements^{5,6} (see below) which indicate the existence of few, free electrical carriers. The term β was identical for both samples with a value of 0.175(1) mJ/mol K (Ref. 4). For antiferromagnetic samples, β is due to both the lattice contribution and an antiferromagnetic contribution.^{23,25} As a result, it is difficult to separate the two. However, we can estimate the Debye temperature Θ_D using the Debye curve²⁶ which suggests that at 350 K we are close to $0.5\Theta_D$ or $\Theta_D \approx 700$ K. This is significantly larger than values estimated for perovskite manganese oxides, which may be related to the significantly higher melting temperature of the chromium oxides. Plots of C_P/T were made in order to calculate the total entropy change ΔS from 2 K to 300 K. Values of $\Delta S = 106.46$ and 106.27 J/mol K were found for x=0 and 0.20, respectively.

The dc electrical resistivity ρ was measured in the temperature range $100 \le T \le 400$ K. Example data for x=0.2 and 0.3 are presented in Fig. 7 as $\ln \rho$ versus 1000/T and values of ρ (300 K) are presented in Table I. No features are apparent in the region near T_N for any of the samples, suggesting weak coupling between the charge carriers and the magnetism. It is interesting to note that ρ (300 K) falls with x until 0.40 where a sharp increase is observed followed by a drop at x=0.50; a second sample of x=0.40 also showed a large value of ρ (300 K) relative to the neighboring compositions. This value of x coincides as well with a loss of the ferromagnetic moment M_{sat} , suggesting that the magnetism and electrical conduction both exhibit unusual behavior at x=0.40; such behavior could result from a change in the spin arrange-



FIG. 7. Electrical resistivity versus inverse temperature for $La_{0.80}Ca_{0.20}CrO_3$ and $La_{0.70}Ca_{0.30}CrO_3$ in zero magnetic field.

ment associated with the antiferromagnetic order and coupling between the charge carriers and magnetic moments. Doping-induced changes in the spin arrangement of the magnetic lattice are well known in systems such as²⁷ $La_{1-x}Ca_{x}MnO_{3}$. The $\rho(T)$ data were also plotted as $ln(\rho/T)$ versus 1/T in order to investigate the possibility that they would obey the equation $\rho(T) = AT \exp(W_B/k_BT)$ representing electrical conduction by small polarons.²⁸ In this equation, W_B is the polaron binding energy, k_B is the Boltzmann constant, and A is a constant. However, these plots did not yield straight-line behavior. We note though that prior reports on $La_{1-r}Sr_rCrO_3$ illustrate that the electrical resistivity obeys the expected polaronic behavior⁶ in the range 300 K $\leq T$ ≤ 2000 K. To provide an energy gap E_{g} that gives a measure of the thermal excitation needed for conduction, we fit the data to $\rho(T) = B \exp(E_{\rho}/k_B T)$; in this equation B is a constant. The data were fitted in the temperature range 300 K $\leq T$ $\leq 400 \text{ K}$; straight-line behavior was observed in this narrow temperature range and the obtained energy gaps are presented in Table I. The values are in the same range as those reported⁶ for $La_{1-r}Sr_rCrO_3$. Obviously, both models mentioned above do not provide adequate descriptions of our data through the entire temperature range of our measurements. Another model, the variable-range hopping model, was also applied by Webb, Sayer, and Mansingh.⁵ They showed that the electrical resistivity data for $La_{1-r}Sr_rCrO_3$ obey the variable-range hopping behavior $\left[\ln(1/\rho)\right]$ versus $T^{-1/4}$ linear] in the narrow range 100 K $\leq T \leq 200$ K, but noted that this functional behavior is erroneous upon further inspection and that it is generally valid at lower temperatures. We believe that electrical resistivity data on single crystals or high-quality thin films are necessary to fully investigate the electrical conduction properties of this system. For this reason, the results presented herein are simply a guide to the general behavior and are certainly influenced by grain boundary effects due to the polycrystalline nature of the samples.

IV. CONCLUSIONS

This study reveals a strong influence of Ca doping on the physical properties of $LaCrO_3$. The system exhibits a change

in mechanical properties with small concentrations of x; the Ca-doped samples sinter better and are significantly harder. A color change is also noted with LaCrO₃ changing from green to black for $x \ge 0.15$. A strong suppression of T_N results from substitution of Ca²⁺ for La³⁺. Since Ca substitution has a small effect on the Cr-O-Cr bond angles, it is argued that the depression of T_N can be attributed to nonstructural effects—namely, the substitution of holes on Cr³⁺ sites. A very small ferromagnetic moment is observed with a large coercivity. The magnetic data suggest that this ferromagnetism is intrinsic and probably the result of canted antiferromagnetic moments. This assertion agrees with results from the analysis of neutron powder diffraction data.³ An interesting change in the electrical and magnetic properties occurs at x=0.40 which may signify a change in the spin structure associated with the magnetic lattice and a new type of antiferromagnetic order. In fact, at x=0.30 neutron diffraction measurements reveal that the G-type magnetic structure exhibits canting toward the A-type magnetic structure³ (sheet ferromagnetism). It would be interesting to conduct neutron powder diffraction on samples in this range of x to investigate if the transition to A-type order takes place at x=0.40. The heat capacity data for two specimens reveal distinct features at the magnetic transitions and large Debye temperatures in the neighborhood of 700 K.

While $LaCrO_3$ is in itself interesting, it is intriguing to compare it to $CaMnO_3$ given the recent interest in manga-

nese oxides. Both compounds have three electrons in the 3dshell and thus have fully occupied t_{2g} levels which lead to the G-type antiferromagnetic structure. Small doping levels of electrons into CaMnO₃, by substitution of under 5% La for Ca, provide electrons in the e_g levels which lead to local ferromagnetic exchange via the double-exchange mechanism^{21,29} and the formation of ferromagnetic clusters approximately 10 Å in diameter. La doping levels above 10% lead to the C-type antiferromagnetic structure.²⁹ Doping of holes into LaCrO₃ also leads to a small ferromagnetic moment, albeit significantly weaker than the moment observed in CaMnO₃. The larger mobility of the e_g electrons, their importance for the double-exchange mechanism, and the narrow-band nature⁶ of the holes with t_{2g} symmetry can probably be invoked to explain these differences. Further studies of the Cr oxides, especially into the magnetic structure at Ca doping levels beyond x=0.30, would be of interest. In addition, doping of LaCrO3 with electrons could lead to occupied e_g levels and ferromagnetic exchange, which would be important to investigate considering the physical behavior of the perovskite manganese oxides.

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