

## Anomalous Electronic State in $\text{CaCrO}_3$ and $\text{SrCrO}_3$

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Comprehensive measurements of electrical transport properties under pressure, thermal conductivity, magnetic susceptibility, and room-temperature compressibility have been used to characterize  $\text{SrCrO}_3$  and  $\text{CaCrO}_3$  perovskites synthesized under high pressure. Comparison with other narrow-band perovskite oxides suggests that their anomalous physical properties are correlated with bond-length instabilities caused by the crossover from localized to itinerant electronic behavior.

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First-row transition-metal oxides with the perovskite or a perovskite-related structure allow a study of the transition from localized to itinerant electronic behavior in states of  $3d$ -orbital parentage by isovalent or heterovalent substitution of the large  $A$  cation. Complete crossover has been monitored in the mixed-valent  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  superconductive system and the  $\text{La}_{1-x}(\text{Ca}, \text{Sr})_x\text{MnO}_3$  system exhibiting a colossal magnetoresistance. Access to the electronic state at crossover in a single-valent system, however, is always plagued by structural instabilities. High pressure has proven to be very useful, and critical in some cases, for studying physical properties in the narrow-band perovskites exhibiting structural instabilities. The  $\text{RNiO}_3$  family is now a well-studied system showing the complete evolution from a paramagnetic metal to a magnetic insulator [1]. The insulator phase below an insulator-metal transition temperature  $T_{\text{IM}}$  does not have globally ionic Ni-O bonding; this bonding segregates into ordered ionic and covalent bonds. It is important to note that the difference between the more ionic Ni-O bond and the more covalent Ni-O bond decreases with increasing size of the rare-earth ion [1,2]. Therefore, it becomes increasingly difficult to resolve the difference between these two kinds of Ni-O bond, and an intermediate Ni-O bond length is stabilized as the itinerant electronic state is approached.  $\text{SrCrO}_3$  and  $\text{CaCrO}_3$  offer the opportunity to study the structural and physical properties in a phase having a Cr-O bond length other than its regular ionic bond length given in the literature. Moreover, comparison between the  $\text{ACr}^{4+}\text{O}_3$  and the  $\text{RNiO}_3$  family can reveal the difference between  $\pi$ -bonding electrons and the  $\sigma$ -bonding electrons at the crossover. The  $\text{ACr}^{4+}\text{O}_3$  compounds were initially studied some three decades ago [3–5]. These preliminary studies reported a  $T_{\text{N}} \approx 90$  K in antiferromagnetic  $\text{CaCrO}_3$  and no long-range magnetic order in  $\text{SrCrO}_3$ . Further study of these materials has been inhibited by the need to prepare them under high oxygen pressure. In this Letter, we report a comprehensive characterization of  $\text{SrCrO}_3$  and  $\text{CaCrO}_3$  polycrystalline samples synthesized under high pressure by resolving the crystal structure and by measuring electrical transport properties, thermal conductivity, magnetic sus-

ceptibility, and the equation of state (EOS). We demonstrate remarkable bonding instabilities in these compounds by their glassy thermal conductivity, pressure-induced bond softening, and insulator-metal transition.

High-pressure synthesis was carried out as described previously [4] except that commercial high-purity (3N) CaO, SrO, and  $\text{CrO}_2$  were used as the starting materials. As-made pellets of high-pressure products include about 5% impurity phases as initially checked by powder x-ray diffraction. Powder samples of the high-purity perovskite phase, as shown by the x-ray powder diffraction in Fig. 1, can be obtained by washing the high-pressure sample with dilute acid. The high-purity powder was pressed into a pellet for the magnetic measurements whereas as-made pellets of the high-pressure products were cut with a diamond saw into rectangular bars for the transport measurements. X-ray diffraction data were collected with  $0.02^\circ$  and 15 s/step. Diffraction data were refined with the cubic  $Pm\bar{3}m$  space group in  $\text{SrCrO}_3$  and the orthorhombic  $Pbnm$  in  $\text{CaCrO}_3$  by using Rietveld analysis (Fullprof program) [6]; the analysis gives lattice parameters  $a = 3.81982(3)$  Å for  $\text{SrCrO}_3$  and  $a = 5.2886(1)$  Å,  $b = 5.3172(2)$  Å, and  $c = 7.4844(1)$  Å for  $\text{CaCrO}_3$ . Other relevant structural parameters are listed inside Fig. 1. These lattice parameters match those in the literature [3–5] to the third decimal place. The comparisons of lattice parameters and the Seebeck coefficient with that from Ref. [5] confirm that we have precisely the same compounds as the samples made before in which the oxygen stoichiometry was determined chemically [3,4]. Moreover, the occupied density from the Rietveld analysis also indicates that the compounds are close to chemical stoichiometry. The magnetization measurements were performed on a SQUID magnetometer (Quantum Design), and all other measurements of transport properties were carried out on home-made setups. The x-ray diffraction under high pressure was carried out on a diamond-anvil cell (DAC) as described previously [7]. A small amount of  $\text{CaF}_2$  powder was mixed with the sample as the pressure manometer [8]. The measurement of resistance under pressure was also made in a DAC with MgO as the pressure medium.

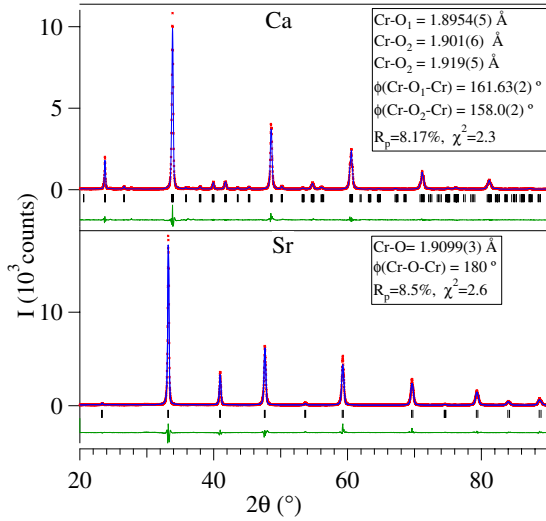


FIG. 1 (color online). X-ray powder diffraction pattern for  $\text{SrCrO}_3$  and  $\text{CaCrO}_3$  with  $\text{Cu } K\alpha$  radiation. Fitting patterns from the Rietveld analysis are also superimposed in the figure. Results from the Rietveld analysis are listed inside the figure.

Although the inverse magnetic susceptibility  $\chi^{-1}(T)$  of  $\text{SrCrO}_3$  in Fig. 2(a) shows a quite remarkable temperature dependence, fitting to the Curie-Weiss law gives a  $\mu_{\text{eff}} \approx 8.3\mu_B$ , which is significantly higher than the expected value for two localized  $t_2$  electrons on a  $\text{Cr}^{4+}$  ion. Such a failure of the Curie-Weiss law is typical of a nonlocalized electronic state in  $\text{SrCrO}_3$ . On the other hand, in comparison with other strongly correlated metallic perovskites such as  $\text{LaNiO}_3$  and  $\text{LaCuO}_3$ , the magnitude of  $\chi(300\text{ K})$  is nearly double that of  $\text{LaNiO}_3$  and an order of magnitude higher than that of  $\text{LaCuO}_3$ . Moreover, the  $\chi^{-1}(T)$  curves of  $\text{LaNiO}_3$  and  $\text{LaCuO}_3$ , shown in Fig. 2(a), are much less temperature dependent than the  $\chi^{-1}(T)$  of  $\text{SrCrO}_3$ . This finding shows the presence of a considerable volume fraction of strong-correlation fluctuations [9] in  $\text{SrCrO}_3$ . Measurement in 100 Oe, plotted in the inset of Fig. 2(a), shows a clear separation between the field-cooled (FC) and zero-field-cooled (ZFC) susceptibility of  $\text{SrCrO}_3$ , which may signal the existence of some short-range ordering although no  $T_N$  is discernible. The weak temperature dependence and semiconductorlike  $\rho(T)$ , solid line of Fig. 2(b), may represent either grain-boundary scattering in this polycrystalline sample or an exotic electronic conduction. The very small Seebeck coefficient  $\alpha$ , which is related to the bulk property, indicates a high carrier density. However, the  $\alpha(T)$  curve of  $\text{SrCrO}_3$  does not behave like that of a metal as was found in  $\text{LaNiO}_3$  ( $n$ -type) and  $\text{LaCuO}_3$  ( $p$ -type). A minimum of  $\alpha(T)$  occurring near 160 K is at too high a temperature for the phonon-drag effect; this temperature corresponds roughly to the deviation from a linear relationship in  $\chi^{-1}(T)$  and the onset temperature where the thermal conductivity  $\kappa(T)$  of Fig. 2(c) starts to decrease. The glassy  $\kappa(T)$  of  $\text{SrCrO}_3$  is in sharp contrast to the thermal conductivity found in the

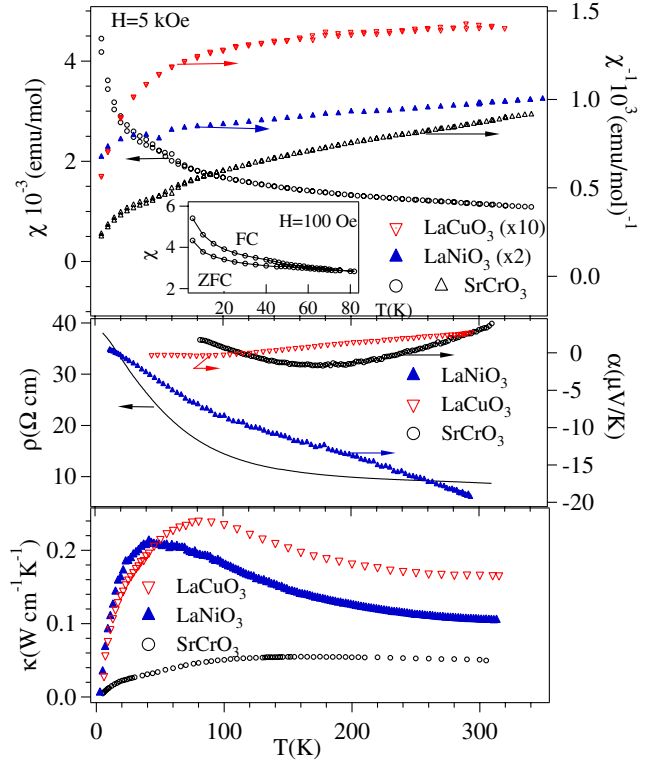


FIG. 2 (color online). Temperature dependences of the magnetization, resistivity, thermoelectric power, and thermal conductivity of  $\text{SrCrO}_3$ ,  $\text{LaNiO}_3$ , and  $\text{LaCuO}_3$ .

other strongly correlated metals  $\text{LaNiO}_3$  and  $\text{LaCuO}_3$ . The electronic conduction contributes to the heat transfer in these metallic compounds. The phononlike  $\kappa(T)$  of the lattice contribution can be derived by using the electrical conductivity via the Wiedemann-Franz law [10]. Up to this point,  $\text{SrCrO}_3$  behaves like neither a paramagnetic metal nor a magnetic insulator. A reduced and glassy  $\kappa(T)$  signals some remarkable bond-length fluctuations.

The  $\chi^{-1}(T)$  of  $\text{CaCrO}_3$  in Fig. 3(a) shows a much steeper temperature dependence than  $\text{SrCrO}_3$ . A  $\mu_{\text{eff}} \approx 3.7\mu_B$  obtained by fitting  $\chi^{-1}(T)$  to the Curie-Weiss law is not too far from the localized-electron spin-only value. The magnetic transition at  $T_N \approx 90\text{ K}$  also matches that reported previously [4]. However, not observed in the early experiments is a large splitting of the ZFC and FC  $\chi(T)$  curves. The extremely small and nonlinear magnetization  $M(H)$  are indicative of a canted spin structure below  $T_N$  and a large magnetocrystalline anisotropy. However, a drop of  $\kappa(T)$  in Fig. 3(b) on cooling below  $T_N \approx 90\text{ K}$  is opposite to what happens in most magnetic insulators and in the hexagonal  $\text{RMnO}_3$  compounds where the phonons are restored below  $T_N$  [11]. The overall suppression of  $\kappa(T)$  in  $\text{CaCrO}_3$  appears to be related to bond-length fluctuations that are not associated with spin fluctuations. Moreover, short-range magnetic order must induce some orbital fluctuations at temperatures well above 90 K in order to account for a gradual decline of  $\kappa(T)$  with decreasing

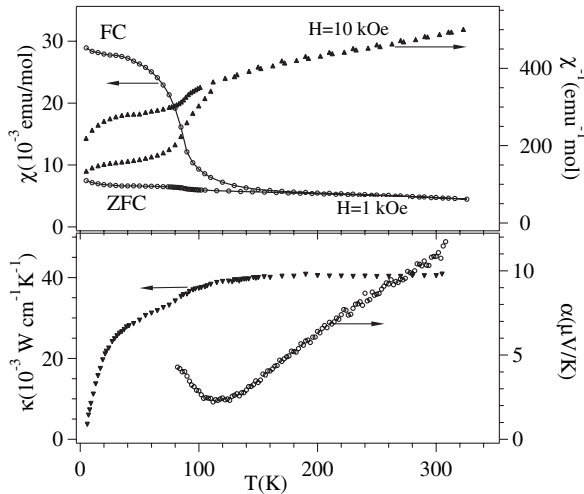


FIG. 3. The same as Fig. 2 (without resistivity) for  $\text{CaCrO}_3$ . Inset: magnetization to 5.5 T at 5 K.

temperature below 160 K where the FC and ZFC  $\chi(T)$  curves diverge above  $T_N$ .

A physically sound solution to these anomalous physical properties must rely on the study of their crystal structure. The structure simulation obtained by using the software SPUDS [12] provides a guideline to the structure with ionic bonds [13]. Results from the Rietveld analysis as listed in Fig. 1 show a significantly shorter Cr-O bond length by a  $\Delta r \approx 0.05 \text{ \AA}$  in both  $\text{CaCrO}_3$  and  $\text{SrCrO}_3$  than the ionic Cr-O bond length  $1.96 \text{ \AA}$  calculated by SPUDS. A nearly identical bond-length reduction  $\Delta r \approx 0.042 \text{ \AA}$  from the ionic bond to the intermediate Ni-O bonding state at the crossover from localized to itinerant electronic behavior has been seen in  $\text{RNiO}_3$  [1]. On the other hand, a further reduction by a  $\Delta r \geq 0.06 \text{ \AA}$  from the ionic Ni-O bond length is needed in order for  $\text{RNiO}_3$  to be metallic. Comparison with the  $\text{RNiO}_3$  family motivates structural studies under chemical and hydrostatic pressure. We have chosen to study  $\text{SrCrO}_3$  and  $\text{CaCrO}_3$  under pressure. Fitting the  $V$ - $P$  curve of Fig. 4 to the Birch-Murnaghan equation gives a bulk modulus  $B_0 = 178 \pm 5 \text{ GPa}$  for  $P < 4 \text{ GPa}$ , which falls in line with the  $B_0$  for a broad range of  $A^{2+}B^{4+}O_3$  perovskite oxides [14]. At  $P > 4 \text{ GPa}$ ,  $\text{SrCrO}_3$  remains a cubic perovskite, but the structure becomes much more compressible by showing a much reduced  $B_0 = 144 \pm 2 \text{ GPa}$ . A similarly low bulk modulus in perovskite oxides has only been seen in two other cases so far: (a)  $B_0 = 122\text{--}150 \text{ GPa}$  for  $\text{LaCoO}_3$  where pressure induces a spin-state transition [15,16] and (b)  $B_0 = 144 \text{ GPa}$  for  $\text{Nd}_{0.5}\text{Sm}_{0.5}\text{NiO}_3$  where pressure induces a transition from an insulator to a metallic phase [7]. Both cases show that the perovskite becomes much more compressible where a pressure-induced electronic-state transition is involved. Interestingly, the inset of Fig. 4 shows that  $\text{SrCrO}_3$  becomes “soft” where the difference between the ionic Cr-O bond from SPUDS and the Cr-O bond under

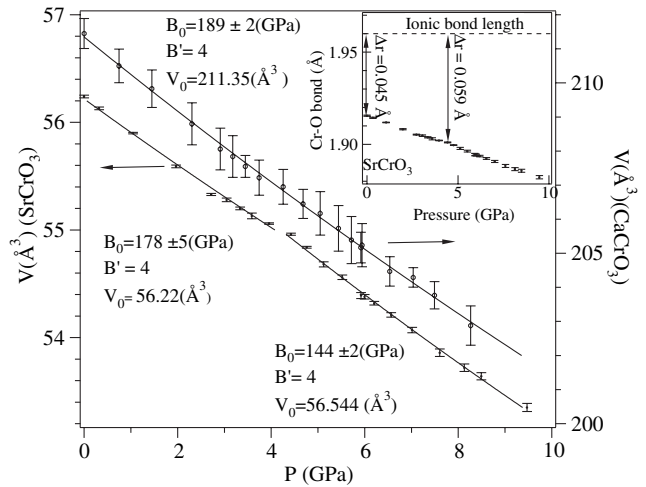


FIG. 4. Pressure dependence of the volume for  $\text{SrCrO}_3$  and  $\text{CaCrO}_3$ . Inset: the pressure dependence of the Cr-O bond length for  $\text{SrCrO}_3$ ; see the text for details.

pressure reaches a  $\Delta r \approx 0.059 \text{ \AA}$ , which matches almost perfectly to the bond-length reduction from the ionic to the metallic bond in  $\text{RNiO}_3$ . In order to confirm the origin of the bond softening near 4 GPa, we have performed the measurement of resistance under pressure to 24 GPa shown in Fig. 5. In this  $\ln R$  versus  $P$  plot, it is clear that  $R$  changes against  $P$  more dramatically at low pressure than at higher pressures. This change, however, is still not solid proof for an electronic-state transition to a metallic phase near 4 GPa since grain-boundary resistance is also lowered dramatically at relatively low pressures. As plotted in the inset of Fig. 5, metallic conductivity becomes clearly visible at 10 GPa. The insulator-metal transition temperature  $T_{\text{IM}}$  where  $R(T)$  shows a minimum, decreases under even higher pressure. It requires a measurement of  $R(T)$  at  $T > 300 \text{ K}$  in order to locate precisely this shallow minimum of  $R(T)$  where  $T_{\text{IM}}$  is near room temperature. However, extrapolation of the  $T_{\text{IM}}(P)$  curve to lower pressure, see inset of Fig. 5, would locate a  $T_{\text{IM}} \approx 300 \text{ K}$  near 5 GPa. This result not only confirms that the bond softening near 4 GPa found in the structural study under pressure is due to the electronic transition to a metallic phase, but it also proves unambiguously that  $\text{SrCrO}_3$  is a paramagnetic insulator with bond-length instabilities at ambient pressure.

Results of Rietveld analysis provide important additional structural features for characterizing the bonding in  $\text{SrCrO}_3$  and  $\text{CaCrO}_3$ :

(1) *A stretched Cr-O bond in  $\text{SrCrO}_3$ .*—A tolerance factor  $t < 1$  in a perovskite  $\text{AMO}_3$  places the A-O bond under tensile stress and the M-O bond under a compressive stress. This mismatch is released by a cooperative octahedral-site rotation, and the M-O bond length remains nearly a constant for  $t < 1$  as long as there is no electronic transition [1]. However, the perovskite structure finds no way to relieve an M-O bond under tension for  $t > 1$ . The M-O bond length in the metastable high-pressure phase is

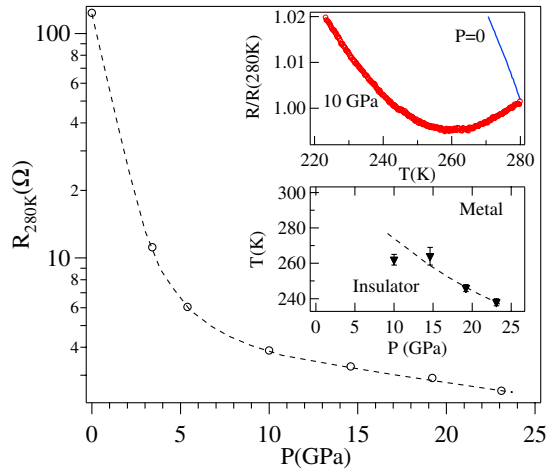


FIG. 5 (color online). Pressure dependence of the resistance at 280 K. Inset (a) temperature dependence of the renormalized resistance at different pressures; inset (b) pressure dependence of the metal-insulator transition temperature.

stretched due to the compressive stress on the too long equilibrium A-O bond length. As listed inside Fig. 1, the average bond length  $\langle \text{Cr-O} \rangle = 1.905 \text{ \AA}$  in  $\text{CaCrO}_3$  is slightly smaller than the  $\langle \text{Cr-O} \rangle = 1.9099 \text{ \AA}$  in  $\text{SrCrO}_3$ , which suggests that the Cr-O bond in  $\text{SrCrO}_3$  is stretched due to a tolerance factor  $t > 1$ .

(2) *Sensitivity of the electronic bandwidth to the Cr-O-Cr bond angle.*—The bandwidth  $W$  in the perovskite structure can be calculated for  $\sigma$ -bonding electrons via the formula [17]  $W \approx \cos[(180^\circ - \phi)/2]/d_{\text{Cr-O}}^{3.5}$ . By using the structural parameters listed inside of Fig. 1, we obtained a  $W = 0.10386$  (arb. unit) for  $\text{SrCrO}_3$  versus  $W = 0.10306$  for  $\text{CaCrO}_3$ . This tiny difference in the calculated bandwidth is insufficient to justify the transition from the paramagnetic, insulating phase of  $\text{SrCrO}_3$  to the antiferromagnetic insulating phase of  $\text{CaCrO}_3$ . Some other factor such as the competition for the  $\text{O}:2p_\pi$  electron between the A-O bond and Cr-O bonds should be taken into account.

(3) *A Jahn-Teller distortion of the  $\text{Cr}^{4+}$ -ion site.*— $\text{Cr}^{4+}:t_2^2$  is a Jahn-Teller ion like the  $\text{V}^{3+}$  ion. The  $J$ - $T$  distortion is suppressed in the cubic  $\text{SrCrO}_3$ . In  $\text{CaCrO}_3$ , however, the Rietveld analysis gives three different Cr-O bond lengths. The difference between the longest and the shortest Cr-O bond is comparable to that found in  $\text{YVO}_3$  at room temperature. Although the bond length splitting in a  $\text{MO}_{6/2}$  octahedron depends on the octahedral rotation angle in the orthorhombic perovskites [18], the relatively large bond length splitting at  $160^\circ$  rotation angle in  $\text{CaCrO}_3$  suggests that the  $J$ - $T$  distortion may take place for the intermediate bond length between the typical ionic bond length and the metallic bond length.

In conclusion, the perovskite insulators  $\text{SrCrO}_3$  and  $\text{CaCrO}_3$  provide a unique example of the approach to crossover from localized to itinerant electronic behavior

from the localized-electron side as the lattice instabilities do not manifest themselves as a phase segregation. We have demonstrated that the Cr-O bond length in these compounds is different from the ionic bond on the one side and a covalent (or metallic) bond on the other. The bonding instability in this phase leads to a significant degree of bond-length fluctuations that suppress the phonon thermal conductivity and are responsible for anomalous transport and magnetic properties. The bonding instability has been further confirmed by the pressure-induced bond softening where the electronic transition to the metallic phase takes place in  $\text{SrCrO}_3$ . Replacing Sr by Ca gives a negligible change of the bandwidth, but it may induce the  $J$ - $T$  distortion of the  $\text{Cr}^{4+}$  sites in  $\text{CaCrO}_3$ . Narrowing of the  $\pi^*$  bandwidth appears to be dominated by a greater competition for the  $\text{O}-2p_\pi$  electrons between the Ca-O bond versus Cr-O bond.

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