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Bond-length fluctuations and the spin-state transition in $L\mathrm{CoO}_3$ ($L=\mathrm{La}$, Pr, and Nd)

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The temperature dependence of thermal conductivity, $\kappa(T)$, and magnetic susceptibility, $\chi(T)$, have been measured on single crystals of $L\mathrm{CoO}_3$ ($L=\mathrm{La}$, Pr, Nd) grown by the floating-zone method. The susceptibility measurement shows a progressive stabilization of the low-spin (LS) state of Co(III) with decreasing size of the L^{3+} ion, and the population of excited intermediate-spin (IS) or high-spin (HS) state Co(III) ions begins to increase at 200 K and 300 K for PrCoO_3 and NdCoO_3 compared with 35 K in LaCoO_3. The low-temperature Curie-Weiss paramagnetic susceptibility of $L\mathrm{CoO}_3$ is an intrinsic property arising from surface cobalt and, possibly, a LS ground state bearing some IS character caused by the virtual excitation to the IS state. The transition from a LS to a IS/HS state introduces bond-length fluctuations that suppress the phonon contribution to $\kappa(T)$ below 300 K. The suppressed $\kappa(T)$ could be further reduced by dynamic Jahn-Teller distortions associated with the IS/HS species. A smooth transition in $\rho(T)$ and $\alpha(T)$ and a nearly temperature independent $\alpha(T)\approx 20\ \mu\mathrm{V/K}$ above 600 K do not support a thermally induced, homogeneous Mott-Hubbard transition model for the high-temperature transition of LaCoO_3 from an insulating to a conductive state. A two-phase process is proposed for the interval $300\ \mathrm{K}<T<700\ \mathrm{K}$ with a conductive phase growing in a matrix of IS states with localized e electrons that are stabilized by Jahn-Teller distortions that may be dynamic.

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INTRODUCTION

The thermally driven spin-state transition in the perovskite LaCoO_3 has intrigued one of us since the 1950s.[1] Goodenough originally proposed that, in lieu of an intermediate spin (IS) t^5e^1 state that could undergo a disproportionation reaction $2t^5e^1=t^5e^0+t^5e^2$, the system would find it energetically more favorable to stabilize high-spin (HS) t^4e^2 states where the nearest neighbors can be in the low-spin (LS) t^6e^0 state; such an ordered configuration could achieve the extra covalent bonding in a LS CoO_6 site without costing the energy U required to create Co(IV) and Co(II) ions. A neutron-diffraction study has indeed shown that the Co remains Co(III) to higher temperatures.[2] However, the paramagnetic susceptibility $\chi(T)$ showed that below 35 K the cobalt are all predominantly in their LS state and the higher spin states are thermally excited above 35 K. Goodenough[3] had also argued that the observed ferromagnetic saturation moment of $1.5\mu_B$ in metallic $\mathrm{La}_{0.5}\mathrm{Ca}_{0.5}\mathrm{CoO}_3$ is due to stabilization of the IS state by a transformation of localized σ bonding e states into an itinerant electron σ^* band. These ideas were applied to LaCoO_3 and to the system $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{CoO}_3$.[1] The model assumed the HS/LS ratio approached unity at 300 K; and between room temperature and a smooth transition to the more conductive phase near 500 K HS-rich regions with itinerant σ^* electrons of e-orbital parentage would form, the volume fraction of the conductive HS-rich phase growing to beyond its percolation threshold in an insulator matrix of ordered HS and LS Co(III).

In 1995, Potze *et al.*[4] revived interest in a LS-IS-HS three-spin-state model for LaCoO_3. In the three-spin-state scenario, Co(III) ions are thermally activated to the IS state from LS state around 100 K, and then from the IS state to a mixed state of IS and HS around 500 K. LDA+U (Ref. 5) and Hartree-Fock[6] calculations derived that the IS state is energetically favorable compared with the HS state at low temperatures. With an IS electronic configuration of t^5e^1, a Jahn-Teller distortion is expected because of the orbital degeneracy of the e_g state. Yamaguchi *et al.*[7] observed a phonon-mode change in their Raman spectra during the spin-state transition of LaCoO_3 which signaled local lattice distortions typical of Jahn-Teller distortions that remove an e-orbital degeneracy. A subsequent pair density function (PDF) analysis of pulsed neutron data by Louca *et al.*[8] confirmed the presence of local lattice deformations. These findings provide convincing evidence for stabilization of an IS state with localized e electrons by dynamic, local Jahn-Teller site distortions. The LS-IS-HS model has also been successful to fit the magnetic susceptibility, thermal expansion, specific heat, and elastic modulus of LaCoO_3.[9–11]

Since the spin-state transition from LS to a higher spin state, either IS or HS, is associated with an electronic transfer from a t orbital to an e orbital, bond-length fluctuations are expected to be associated with the thermally excited spin-state transitions. Bond-length fluctuations have been shown to suppress the phonon contribution to the thermal conductivity.[12] Therefore, thermal conductivity becomes a natural probe of spin-state transitions. The present study was undertaken to determine whether bond-length fluctuations associated with IS/LS (or HS/LS) fluctuations and/or dynamic, local Jahn-Teller distortions at IS Co(III) suppress the phonon contribution to the thermal conductivity. Since long-range orbital ordering does not suppress thermal conductivity in LaMnO_3,[13] the data would also provide an independent check on whether a long-range, static orbital ordering at IS Co(III) occurs below room temperature. As far as we know, the dynamic lattice response to the spin state transition has not been reported. The results show that phononic thermal conductivity is suppressed in the temperature range of thermal excitation to a higher Co(III) spin state for three $L\mathrm{CoO}_3$ single crystals ($L=$La, Pr, and Nd). No evidence was found of a static, long-range orbital ordering.

EXPERIMENT

Single crystals of $L\mathrm{CoO}_3$ ($L=$La, Pr, and Nd) were grown by the traveling solvent floating zone (TSFZ) method. The precusors were made by the Pechini method with $\mathrm{La(NO_3)_3 \cdot 6H_2O}$, $\mathrm{Co(NO_3)_2 \cdot 6H_2O}$, precalcined $\mathrm{Pr_6O_{11}}$ and $\mathrm{Nd_2O_3}$ as raw materials. The content of crystal water in $\mathrm{La(NO_3)_3 \cdot 6H_2O}$ and $\mathrm{Co(NO_3)_2 \cdot 6H_2O}$ was determined by TGA before weighing. $\mathrm{Pr_6O_{11}}$ and $\mathrm{Nd_2O_3}$ were dissolved in nitric acid before mixing with cobalt nitrate solution. The precusors were dried at 200 °C and then decomposed at 500 °C. The obtained black powders were then pressed into pellets and sintered at 1000 °C for 24 h in air with intermediate grinding. The resulting powder was hydrostatically pressed into a rod with a size of 5-mm diameter by 80 mm and sintered at 1150 °C for 15 h in air. Single crystals were grown in an NEC Image furnace equipped with two halogen lamps. The growth rate was kept constant at 1.5 mm/h in a 3 atm oxygen atmosphere. High oxygen pressure is necessary to keep the melting zone stable and to get the perovskite phase. The feed and seed rods were rotated in opposite directions at the speed of 30 rpm during the crystal growth to homogenize the melting zone. Black, shining single crystals were obtained with a typical size of 4–6-mm diam by 5-mm length.

A small piece from the ingot was ground into fine powders for the determination of the lattice parameters by x-ray powder diffraction with Si powder as internal standard. Thermoelectric power was measured in air in the temperature interval $100\,\mathrm{K}<T<800\,\mathrm{K}$ with a homemade device. Magnetic susceptibility data were obtained with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) in the temperature range $5\,\mathrm{K}<T<400\,\mathrm{K}$. Fine copper wire was used as sample holder; it has a magnetic response as small as 10^{-7} emu. Thermal conductivity was measured between 4 and 330 K by a steady-state heat-flow technique with a systematic error less than 20%. The systematic error mainly comes from the uncertainty in measurement of the sample size and the distance between the thermocouples.

RESULTS AND DISCUSSION

All three compositions are single phase as determined by x-ray powder diffraction. As-grown $\mathrm{LaCoO_3}$ is a slightly distorted perovskite that could be indexed with rhombohedral ($R\bar{3}c$) structure while $\mathrm{PrCoO_3}$ and $\mathrm{NdCoO_3}$ are orthorhombically distorted ($Pbnm$) at room temperature. Lattice parameters at 300 K are consistent with previous reports.[14] The thermoelectric power curves $\alpha(T)$ of single crystals of $\mathrm{PrCoO_3}$ and $\mathrm{NdCoO_3}$ are shown in Fig. 1. The $\alpha(T)$ of polycrystalline $\mathrm{LaCoO_3}$ from Ref. 1 is also shown for comparison. Below 100 K, $\alpha(T)$ is not measurable because of the high resistance of the samples. The step at 300 K is due to a change in the measurement apparatus. The high value of α below 300 K ($>550\ \mu$V/K) implies a near stoichiometric oxygen content of 3.002; $\alpha(T)$ decreases more dramatically with increasing temperature in the interval $300\,\mathrm{K}<T<600\,\mathrm{K}$ and reaches a small, positive, and nearly temperature-independent value of $\sim 20\ \mu$V/K at $T>600$ K.

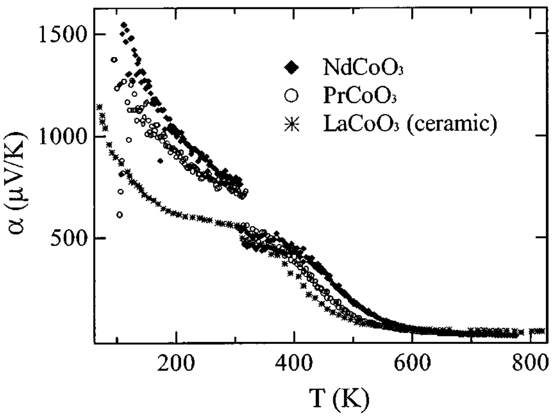

FIG. 1. Temperature dependence of the thermoelectric power α in single-crystal $\mathrm{PrCoO_3}$ and $\mathrm{NdCoO_3}$. The $\alpha(T)$ of polycrystalline $\mathrm{LaCoO_3}$ after Señarís-Rodríguez is from Ref. 1. The step at room temperature is due to a change in measurement apparatus.

The magnetic susceptibility of our $\mathrm{LaCoO_3}$ crystal (Fig. 2) agrees very well with previous studies.[7] The susceptibility shows an abrupt increase with increasing temperature in the interval $35\,\mathrm{K}<T<100\,\mathrm{K}$ and then roughly exhibits a Curie-Weiss behavior at temperatures above 120 K. The sharp increase beginning at 35 K corresponds to the population increase of higher-spin-state Co ions, either IS or HS. The sharp minimum at 35 K and the Curie-Weiss–like behavior at temperatures below 35 K have previously been attributed to impurities[7] or to localized spins associated with the surface and/or lattice defects.[1] However, a nearly identical low-temperature behavior of $\chi(T)$ has been found by all investigators on both polycrystalline and single-crystal samples,

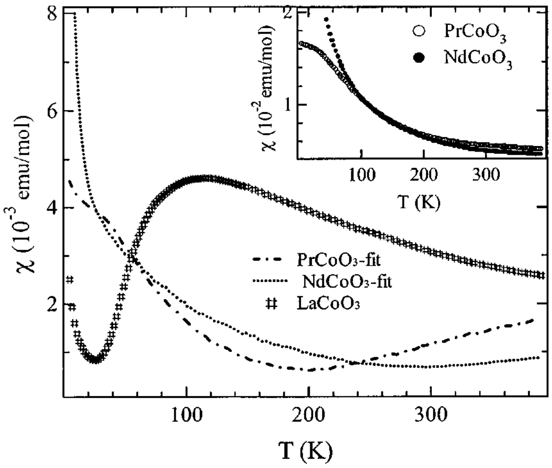

FIG. 2. Temperature dependence of the molar magnetic susceptibility of single-crystal $L\mathrm{CoO}_3$ ($L=$La, Pr, and Nd) measured at 500 Oe. Contributions from magnetic Pr^{3+} and Nd^{3+} were subtracted. Inset: Measured magnetic susceptibility before the subtraction for $\mathrm{PrCoO_3}$ and $\mathrm{NdCoO_3}$.

and a similar behavior occurs at relatively higher temperatures in the CoO_3 array of the $PrCoO_3$ and $NdCoO_3$ samples (see below), which suggests that this may be an intrinsic phenomenon in these cobaltates.

The measured susceptibilities of $PrCoO_3$ and $NdCoO_3$ are dominated by the signal from the magnetic L^{3+} ions as shown in the inset of Fig. 2. To obtain the susceptibility variation associated with the spin-state transition in the CoO_3 array, we subtracted the polynomial fit of the $\chi(T)$ curve for $L\mathrm{AlO}_3$ compounds from the $\chi(T)$ of the corresponding $L\mathrm{CoO}_3$. The core electron diamagnetism of Al and the van Vleck paramagnetism are negligible compared with the susceptibility of the CoO_3 array. This method appeared to be successful in the study of $L\mathrm{NiO}_3$ perovskites.[15] Subtraction of the L^{3+} contribution to $\chi(T)$ gave the curve for the CoO_3 array of Fig. 2. It shows a minimum at 200 and 300 K for $PrCoO_3$ and $NdCoO_3$, respectively. Below these temperatures, $\chi(T)$ for the CoO_3 array shows roughly a Curie-Weiss-like behavior as does $LaCoO_3$ below 35 K. The LS state has been reported to be stabilized by substitution of a smaller rare earth for La in $LaCoO_3$ up to the temperature $T \approx 500$ K where the transition from an insulating to a conductive state takes place.[16] Substitution of a smaller L^{3+} ion for La^{3+} increases the chemical pressure on the Co-O bonds, an effect that is reflected in the change from rhombohedral to orthorhombic symmetry of the lattice; this pressure stabilizes the LS configuration as does hydrostatic pressure.[17] Therefore, the systematic shift to higher temperatures in the minimum of $\chi(T)$ as the radius of the L^{3+} ion decreases is interpreted to reflect stabilization of the LS state to higher temperatures; the minimum in $\chi(T)$ would be an upper limit for the onset temperature of excitations to higher-spin states. The temperatures defined by the minimum in $\chi(T)$ are similar to the onset temperatures defined by infrared spectroscopy.[18]

The susceptibility of a system with a nonmagnetic ground state and a magnetic excited state can be described in units of emu/mol by Van Vleck's $kT \sim \Delta H$ formula[9]

$$\chi(T)=\frac{N_A g^2 \mu_B^2 \nu S(S+1)(2S+1)e^{(-\Delta H/T)}}{3k_B T[1+\nu(2S+1)e^{(-\Delta H/T)}]}, \tag{1}$$

where N_A is the Avogadro number, μ_B is the Bohr magneton, and k_B is the Boltzmann constant; ΔH is the energy splitting of the two states, S and ν are the total spin and the orbital degeneracy of the excited states, and g is the spectroscopic splitting factor. Although this calculation assumes the enthalpy ΔH is independent of temperature and does not include excitation to the HS state, the susceptibility of $LaCoO_3$ could be fit well below room temperature with an orbitally nondegenerate IS state as the excited state after subtracting the low temperature Curie-Weiss-like contribution. Our fit for $LaCoO_3$ gives a ΔH of 180 K, in agreement with a previous report.[9] A similar fitting with Eq. (1) shows ΔH increases significantly to 1095 K and 2750 K for $PrCoO_3$ and $NdCoO_3$, respectively. In an attempt to fit $\chi(T)$ with a LS/HS scenario, we could not get a reasonable fitting with a fixed g equal to 2. Instead, g values of 0.93, 1.43, and 3.72 are necessary to improve the fitting for $LaCoO_3$, $PrCoO_3$, and $NdCoO_3$, respectively. From this point of view, our data appear to support excitation from the LS to the IS state.

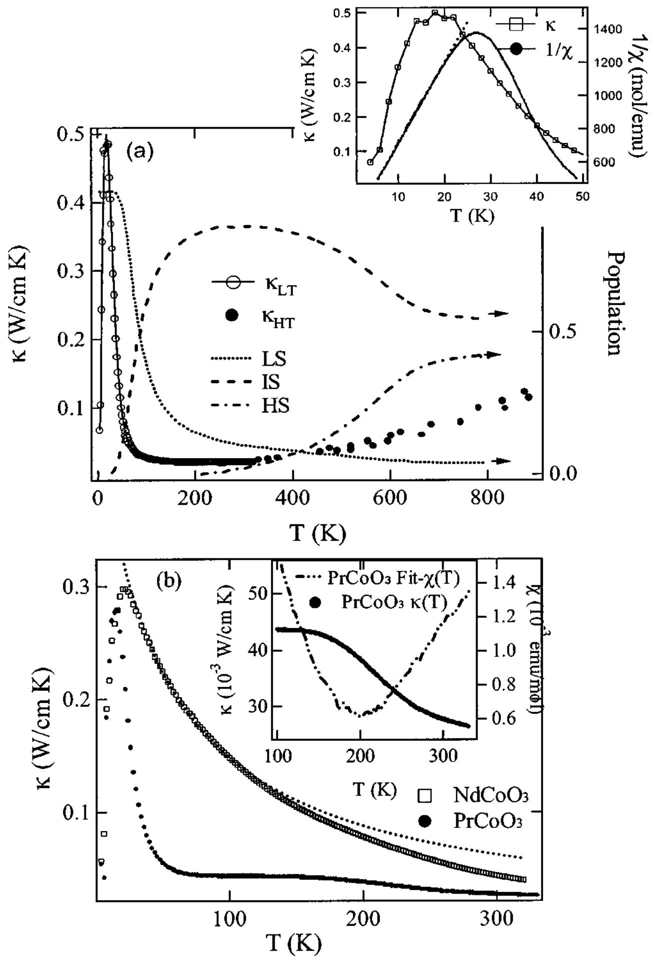

FIG. 3. (a) Temperature dependence of thermal conductivity $\kappa(T)$ and populations of Co(III) ions in different spin states for $LaCoO_3$. The high-temperature thermal conductivity (κ_{HT}) after Pillai and George is from Ref. 19 measured on a polycrystalline sample. The populations of Co(III) ions in different spin states after Asai are from Ref. 2. Inset: An enlarged representation of $\kappa(T)$ and magnetic susceptibility $\chi(T)$ in the vicinity of the spin-state transition in $LaCoO_3$. The dashed line highlights the deviation of $1/\chi(T)$ associated with spin-state transition. (b) Temperature dependence of $\kappa(T)$ in single-crystal $PrCoO_3$ and $NdCoO_3$. The dashed line is the fitted $\kappa(T)$ of $NdCoO_3$ according to a $1/T$ law. Inset: An enlarged representation of $\kappa(T)$ and $\chi(T)$ in the vicinity of the spin-state transition in $PrCoO_3$.

The temperature dependence of the thermal conductivity, $\kappa(T)$, of $LaCoO_3$ is shown in Fig. 3(a). The thermal conductivity above 400 K is from Pillai and George.[19] The $\kappa(T)$ curve shows a large, sharp peak around 20 K; it drops sharply with increasing temperature to a quite low, nearly temperature independent value up to room temperature. It is reported to increase gradually with temperature above 300 K.[19] Obviously, the thermal conductivity decay above 20 K does not obey a $1/T$ law; the lattice component of the thermal conductivity is strongly suppressed above 35 K where the higher spin states are becoming thermally excited.

In a crystal, heat may be carried by electrons, phonons, and magnons. The electrical resistivity of $L\mathrm{CoO}_3$ has been well characterized with an insulating behavior below ~ 500 K,[20] so the electronic contribution to $\kappa(T)$ can be neglected below room temperature. The magnetic contribution is also negligible in a 3D paramagnetic phase. Therefore, the high $\kappa(T)$ setting in below 35 K reflects the phonon contribution. The high value of $\kappa(T)$ at 20 K indicates that phonons are well established in this temperature range. The temperature dependence of $\kappa(T)$ correlates with the population variation of Co(III) ions in different spin states. In the LS-IS-HS model, the populations of different spin states have been estimated based on a neutron-diffraction experiment as shown in Fig. 3(a).[2] The sharp suppression of $\kappa(T)$ on heating above 35 K coincides with the appearance of the IS state and $\kappa(T)$ becomes almost temperature independent at a low value when the population of the IS state is over 50% at about 80 K. In the Goodenough model, the quick decay of $\kappa(T)$ above 35 K begins with the appearance of the HS state, and $\kappa(T)$ is almost temperature independent in the temperature range where the dynamic, short-range-ordered LS:HS state dominates. The inset of Fig. 3(a) clearly demonstrates the suppression of $\kappa(T)$ and the variation of $\chi(T)$ with temperature due to the spin-state transition. The $\kappa(T)$ data do not resolve whether the higher spin states initially excited are high-spin (HS) coordinated by LS nearest neighbors or IS states stabilized by local Jahn-Teller distortions. But no matter which model is correct, we can conclude that the transition from the LS to the IS/HS state suppresses phononic thermal conductivity.

The $\kappa(T)$ suppression due to the spin-state transition could also be demonstrated in PrCoO_3 and NdCoO_3 [Fig. 3(b)]. Our susceptibility measurement of PrCoO_3 suggests $T\Delta S \approx \Delta H$ around 200 K, where ΔS is the entropy change of IS/HS state. The $\kappa(T)$ curve around this temperature, as shown in the inset, unambiguously illustrates the thermal conductivity response to the spin-state transition. The $\kappa(T)$ curve begins to drop near 140 K, which is somewhat lower than the temperature T_{min} where $\chi(T)$ shows a minimum. The $\kappa(T)$ curve of PrCoO_3 approaches a value similar to that of LaCoO_3 near room temperature. A smooth change of $\kappa(T)$ near 200 K reflects the spin-state transition. The sharp drop of $\kappa(T)$ with increasing temperature below 50 K in PrCoO_3 has an origin other than the spin-state transition of the CoO_3 array. The phonon contribution to $\kappa(T)$ of NdCoO_3 is retained to higher temperatures. $\kappa(T)$ begins to be suppressed and deviate from the $1/T$ law above 150 K whereas its magnetic susceptibility shows a broad minimum near 300 K. The minimum in $\chi(T)$ occurs where $T\Delta S \approx \Delta H$ and is shifted further to higher temperatures as ΔH increases than is the onset of the transition to the IS state. Therefore, the temperature difference between the minimum in $\chi(T)$ and the onset of the suppression of $\kappa(T)$ increases with ΔH. Comparison of the $\kappa(T)$ and $\chi(T)$ data for LaCoO_3, PrCoO_3, and NdCoO_3 shows that $\kappa(T)$ is a more sensitive probe of the onset of the spin-state transition than is $\chi(T)$ for the CoO_3 array; the low-temperature paramagnetism obscures this onset in the $\chi(T)$ data of LaCoO_3, but not in the $\chi(T)$ of PrCoO_3 and NdCoO_3.

The spin-state transition from LS to either IS or HS involves the electron transfer from a t orbital to an e orbital. This transition will bring in an ionic size change of the octahedral-site Co(III) ion. The ionic radius of LS Co(III) was fitted to be 0.545 Å, while IS and HS Co(III) have larger radii with values of 0.56 and 0.61 Å, respectively.[10] A thermally driven transition of the spin state will produce a random distribution of variable bond lengths, which in turn suppresses the phononic thermal conductivity.

Since both IS and HS Co(III) are Jahn-Teller ions in an octahedral site, the suppressed $\kappa(T)$ due to the mixture of LS/IS (or HS) would be further reduced if the Jahn-Teller deformations associated with the IS/HS states are dynamic. On the other hand, a modest restoration of $\kappa(T)$ is expected in a temperature range where the concentration of IS Co(III) is high enough for static, cooperative Jahn-Teller distortions as is seen in LaMnO_3.[21]

The space group $R\bar{3}c$ of the rhombohedral LaCoO_3 is not compatible with a cooperative Jahn-Teller distortion. A recent observation[22] of a lowering of the symmetry of LaCoO_3 from $R\bar{3}c$ to the subgroup I2/a accommodates a long-range-ordered Jahn-Teller distortion as well as octahedral-site rotations about a cubic [111] axis. The parameter Δ to describe the bond length variation in the $\mathrm{MO}_{6/2}$ octahedra due to the orbital ordering is defined as

$$\Delta = \frac{1}{6}\sum_{n=1}^{6}\left(\frac{d_n}{\langle d\rangle}-1\right)^2 .$$

A $\Delta = 3.5\times 10^{-5}$ for GdFeO_3 represents a typical value for the distortion of an $\mathrm{MO}_{6/2}$ octahedral site due to rotations alone in the orthorhombic $Pbnm$ space group.[23] In LaCoO_3, Maris *et al.*[22] found three unequal Co-O bond lengths in the temperature interval $90\ \mathrm{K} < T < 300\ \mathrm{K}$ with calculated Δ values up to 6×10^{-4}, which would appear to point to a static Jahn-Teller ordering in LaCoO_3 in the interval $90\ \mathrm{K} < T < 300\ \mathrm{K}$. However, the suppression of $\kappa(T)$ over the whole temperature range $35\ \mathrm{K} \leqslant T \leqslant 330\ \mathrm{K}$ suggests that if the orbitals of the IS Co(III) are statically ordered, then a minority LS Co(III) phase or a conductive Co(III): $t^5\sigma^{*1}$ phase must coexist with the orbitally ordered Co(III): t^5e^1 phase.

Suppression of $\kappa(T)$ by a dynamic Jahn-Teller distortion has also been demonstrated in $\mathrm{LaMn}_{1-x}\mathrm{Ga}_x\mathrm{O}_3$.[21] The substitution of nonmagnetic Ga(III) ions dilutes the cooperative Jahn-Teller distortion and therefore results in orbital fluctuations at the Jahn-Teller Mn(III) ions. The volume of orbital fluctuations persisting below T_N increases with x and progressively suppresses $\kappa(T)$. In the cobaltates, the nonmagnetic LS Co(III) ions may play a similar role as does Ga(III) in $\mathrm{LaGaMnO}_3$. Both the magnitude and the temperature dependence of $\kappa(T)$ for LaCoO_3 in the temperature interval $80\ \mathrm{K} < T < 330\ \mathrm{K}$ are similar to those for $\mathrm{LaMn}_{1-x}\mathrm{Ga}_x\mathrm{O}_3$ with $x \geqslant 0.35$.

The $\kappa(T)$ of PrCoO_3 below 100 K resembles that of LaCoO_3 with a sharper suppression of $\kappa(T)$ than the $1/T$ decay found in NdCoO_3. An almost temperature-independent value of 4.5 W cm/K in the interval $80\ \mathrm{K} < T < 140\ \mathrm{K}$ is about 2 W cm/K larger than that of LaCoO_3 and that of $PrCoO_3$ at 330 K, which implies that some other fluctuations suppressing $\kappa(T)$ in $PrCoO_3$ below 140 K are distinguishable from the spin-state transition. We note that the strong energy overlap of the outer-lying $4f$ orbital of Pr^{3+} with neighboring oxygen $2p$ levels of $PrBa_2Cu_3O_{7-\delta}$ results in a characteristically mixed or fluctuating valence situation reminiscent of heavy-fermion systems.[24]

Optical-conductivity spectra, resistivity, and Hall coefficient measurements have suggested that the high-temperature transition from an insulating to a conductive state in $LaCoO_3$ should be viewed as a thermally induced, homogeneous Mott-Hubbard transition. However, an $\alpha(T) \approx 20\,\mu V/K$ that is nearly temperature-independent above 600 K seems not to support a homogeneous metallic phase above 600 K. Moreover, a homogeneous transition should be first order,[25] so the smooth transition in $\rho(T)$ and $\alpha(T)$ in the range $350\,K < T < 600\,K$ is more characteristic of a mixed phase transition in which the volume fraction of the more conductive phase grows to beyond percolation at the transition. Such a phase transition is characterized by bad-metal behavior in the conductive phase with an elevated thermoelectric power.

An abnormally large thermal expansion of $LaCoO_3$ in the intervals $35\,K < T < 200\,K$ and $400\,K < T < 700\,K$ signals that the excitation to higher spin states occurs in a two-step process. In the LS-HS model, excitation to a HS/LS ratio approaching unity occurs below 300 K and the excitation of additional HS Co(III) to create an IS phase with σ^* electrons occurs above 300 K. In the LS-IS-HS model, IS Co(III) are excited below 300 K and HS Co(III) are excited at higher temperatures, which is in agreement with the analysis of the paramagnetic susceptibility data. However, with this latter scenario, the $\kappa(T)$ data can only support the suggestion that the transition to a conductive state above 600 K is due to an orbital order-disorder transition if the transition involves a two-phase process in the interval $300\,K < T < 700\,K$ as originally proposed by Goodenough;[1] but the matrix in which a conductive phase grows is a matrix of IS states with localized e electrons that are stabilized by Jahn-Teller site distortions.

Since Sr substitution in $La_{1-x}Sr_xCoO_3$ creates an IS $t^5\sigma^{*1-x}$ state, it is logical to identify the conductive phase above 500 K with a phase in which mobile charge carriers occupy a σ^* band. Although a contraction of the equilibrium M-O bond is normally found on passing from a localized to an itinerant electronic state,[25] in $LaCoO_3$ the conductive phase is HS-rich and therefore has the larger lattice parameter. This phase is to be distinguished from the $La_{1-x}Sr_xCoO_{3-\delta}$ IS phase.

The final point is to find the origin of the Curie-Weiss-like magnetic susceptibility below the low-temperature transition to the LS state. The minimum of $\chi(T)$ for $LaCoO_3$ at 35 K varies in magnitude in different reports, and single crystals show a smaller minimum than ceramic samples. The $\chi(T)$ below 35 K has been postulated to signal the population of impurities, oxygen nonstoichiometry, or Co(II) associated with reconstructed surfaces. An impurity amount $< 1\%$ has been obtained by Zobel *et al.*[9] by fitting $\chi(T)$ with $\chi = p/T + \chi_0$ and assuming a large spin cluster with $S = 10$. The fit of our $LaCoO_3$ $\chi(T)$ data with the above equation gives an even lower impurity concentration than that reported by Zobel *et al.* However, the fit of $\chi(T)$ for $PrCoO_3$ and $NdCoO_3$ gives larger p values, which could be seen from the temperature dependence of the fitted $\chi(T)$. But we have no reason to believe that there are more impurities in $PrCoO_3$ and $NdCoO_3$. An intrinsic, homogeneous moment giving a small μ_{eff} and a Weiss constant θ near zero could arise because the LS and IS states have an energy separation $\Delta H > kT$ that is small enough to admit the introduction of virtual excitation to the IS state.

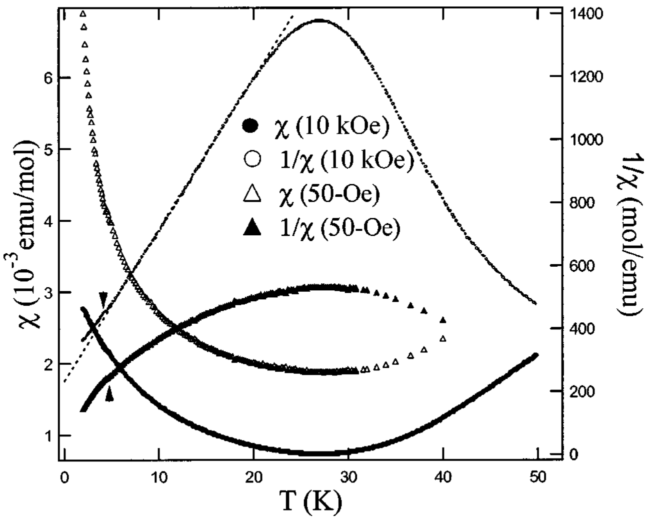

FIG. 4. The temperature dependence of magnetic susceptibility $\chi(T)$ and $1/\chi(T)$ of $LaCoO_3$ single crystal measured at 10 kOe and 50 Oe in the temperature interval $2\,K < T < 50\,K$. The arrows indicate the slope change of $1/\chi(T)$ at 4.5 K. The dashed line is a guide of the slope change of $1/\chi$ (10 kOe) curve.

A preliminary investigation has revealed the presence of two contributions to the low temperature $\chi(T)$, an intrinsic paramagnetic component that we have fit with the Curie-Weiss law, and a ferromagnetic component from surface cobalt with a $T_c \approx 85\,K$ that increases in magnitude with the surface to volume ratio of the sample.[26] Figure 4 shows the temperature dependence of $\chi(T)$ and $1/\chi(T)$ for $LaCoO_3$ measured at 10 kOe and 50 Oe in the interval $2\,K < T < 50\,K$. $\chi(T)$ is smaller at 10 kOe than at 50 Oe since the ferromagnetic component saturates at low temperatures, and a linear behavior of $1/\chi(T)$ below 25 K is shown. At 50 Oe, the magnetization of the ferromagnetic component remains temperature dependent below 25 K, which causes the nonlinear behavior of $1/\chi(T)$. It is obvious that $1/\chi(T)$ measured at 10 kOe does not cross the origin, which indicates a nonzero Weiss constant. This fact implies that the paramagnetic component in low temperature $\chi(T)$ cannot be from isolated impurities. The other important feature in Fig. 4 is the slope change of $1/\chi(T)$ at about 4.5 K (arrows), which may indicate a structural transformation.

CONCLUSIONS

We have confirmed that the thermal conductivity is a sensitive probe of bond-length fluctuations by using it to study the spin-state transition in three single-crystal perovskite cobaltates $L\mathrm{CoO}_3$ with $L=\mathrm{La}$, Pr, Nd. Analysis of our data in conjunction with transport data and paramagnetic susceptibility leads us to the following conclusions: (1) the phononic thermal conductivity is suppressed at temperatures where the transition from LS to IS/HS state takes place. (2) the low-temperature Curie-Weiss paramagnetic susceptibility is an intrinsic property arising from surface cobalt and, possibly, a LS ground state bearing some IS character caused by virtual excitation to the IS state; $\chi(T)$ of LaCoO_3 shows a slope change which could indicate a structural transformation at 4.5 K; (3) the smooth insulator-metal transition near 500 K reflects the coexistence of a conductive phase that grows to beyond percolation in an IS localized-electron matrix.

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