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Evidence for a low-spin to intermediate-spin state transition in $LaCoO_3$

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We present measurements of the magnetic susceptibility and of the thermal expansion of a $LaCoO_3$ single crystal. Both quantities show a strongly anomalous temperature dependence. Our data are consistently described in terms of a spin-state transition of the Co^{3+} ions with increasing temperature from a low-spin ground state ($t_{2g}^6e_g^0$) to an intermediate-spin state ($t_{2g}^5e_g^1$) without (100–500 K) and with (>500 K) orbital degeneracy. We attribute the lack of orbital degeneracy up to 500 K to (probably local) Jahn-Teller distortions of the CoO_6 octahedra. A strong reduction or disappearance of the Jahn-Teller distortions seems to arise from the insulator-to-metal transition around 500 K.

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Transition-metal oxides have fascinating physical properties as, e.g., high-temperature superconductivity in the cuprates or colossal magnetoresistance in the manganites. Their properties are often governed by a complex interplay of charge, magnetic, structural, and orbital degrees of freedom. Moreover, for a given oxidation state some transition metals display different spin states as is the case in various cobalt oxides. Quite recently a class of layered cobalt compounds with the chemical composition $RE\mathrm{BaCo_2O_{5+\delta}}$ (RE = rare earth) has attracted considerable interest. These compounds show a broad variety of ordering phenomena and other transitions, e.g. (antiferro- and/or ferro-) magnetic order, charge and/or orbital order, metal-insulator transitions, or spin-state transitions.[1–9] For $TlSr_2CoO_5$ it has been proposed that a metal-insulator transition is driven by a spin disproportionation, which consists of an alternating ordering of Co^{3+} ions in an intermediate-spin state (IS: $t_{2g}^5e_g^1$; S = 1) and in a high-spin state (HS: $t_{2g}^4e_g^2$; S = 2).[10,11]

The occurrence of Co^{3+} in different spin states is known since the 1950s from $LaCoO_3$,[12,13] which transforms with increasing temperature from a nonmagnetic insulator to a paramagnetic insulator around 100 K and shows an insulator-to-metal transition around 500 K. But even for this rather simple pseudocubic perovskite, the nature of these transitions is still unclear. The ground state is usually attributed to the low-spin configuration (LS: $t_{2g}^6e_g^0$; S = 0) and the paramagnetic behavior above 100 K to the thermal population of an excited state. However, the question whether the excited state has to be identified with the HS or the IS state is subject of controversial discussions. Early publications often assume a LS/HS scenario.[14–16] In order to explain the insulating nature up to 500 K, an ordering of LS and HS Co^{3+} ions has been proposed which vanishes at the insulator-to-metal transition.[17,18] Yet the presence of a HS configuration below 400 K has been questioned on the basis of x-ray absorption and photoemission experiments.[19] Alternative descriptions of $LaCoO_3$ favoring a LS/IS scenario[20–24] are mainly based on the results of LDA+U calculations,[25] which propose that due to a strong hybridization between Co-$e_g$levels and O-2p levels the IS state is lower in energy than the HS state. Within this scenario the occurrence of orbital order and its melting have been proposed in order to explain the insulating nature below 500 K and the insulator-to-metal transition, respectively.[25] Up to now there is no experimental evidence, neither for an orbitally ordered state, nor for a HS/LS superstructure.

In this paper we present a study of the thermal expansion α and of the magnetic susceptibility χ of a $LaCoO_3$ single crystal. The combined analysis of α and χ gives clear evidence for a thermal population of the IS state *without* orbital degeneracy. The lack of orbital degeneracy could arise from orbital order as proposed in Ref. 25 or it can be interpreted as a consequence of Jahn-Teller (JT) distortions of the CoO_6 octahedra with Co^{3+} in the JT-active IS state. Above 600 K, our $\chi(T)$ analysis suggests the presence of the IS state *with* orbital degeneracy, which may arise from a suppression or strong reduction of the JT distortion due to the insulator-to-metal transition.

The crystal used in this study was cut from a large single crystal ($l \simeq 8$ cm; $\phi \simeq 6$ mm) grown by the floating-zone technique in an image furnace. The crystal is strongly twinned as usual for distorted perovskites. The magnetization has been measured by a superconducting quantum interference device (SQUID) magnetometer in the temperature range from 2 K up to 300 K in an applied field of 50 mT and by a Faraday balance in the temperature range from 200 K up to 1000 K in a field of 1 T. A high-resolution measurement of the linear thermal expansion $\alpha = 1/L\,\partial L/\partial T$ has been performed using a capacitance dilatometer from 4 to 180 K.

The magnetic susceptibility of our $LaCoO_3$ crystal (Fig. 1) agrees well with that found in previous studies.[13,15,16,21] The maximum around 100 K signals the spin-state transition of the Co^{3+} ions. For higher temperatures $\chi(T)$ shows (i) a Curie-like decrease up to about 500 K, (ii) a temperature-independent plateau between 500 and 600 K, and (iii) again a Curie-like decrease above 600 K. The increase of $\chi(T)$ below 30 K arises most probably from a Curie contribution due to magnetic impurities and/or oxygen nonstoichiometry. In order to obtain the Curie susceptibility χ^C of Co^{3+} we

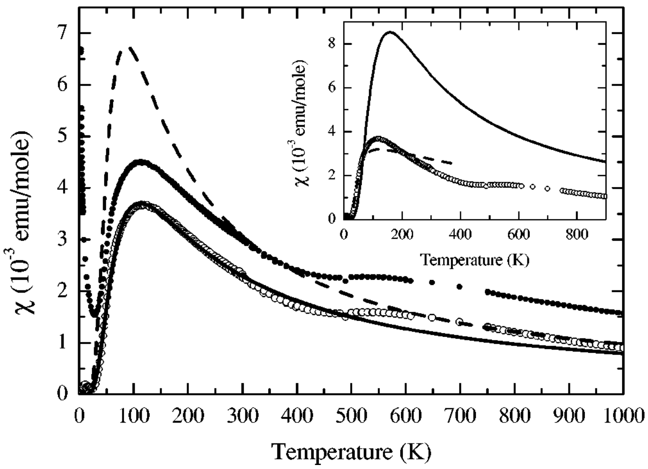

FIG. 1. Total (●) and Curie susceptibility χ^C(○) of $LaCoO_3$. The solid line is a fit of $\chi^C(T)$ up to 400 K for a LS/IS scenario with $S=1$, $\Delta \simeq 180$ K, $g \simeq 2.1$, and $\nu=1$ in Eq. (1). The dashed line is calculated by increasing the orbital degeneracy to $\nu=3$ and leaving all other parameters fixed. The inset shows calculations of $\chi^C(T)$ for a LS/HS scenario (see text).

subtract a term $(P/T+\chi_0)$ from the raw data. Here P/T represents the impurity contribution and $\chi_0=\chi_{\mathrm{dia}}+\chi_{\mathrm{vV}}$, the sum of the diamagnetic contribution of the core electrons and of the paramagnetic van Vleck susceptibility of Co^{3+}. A fit of the low-temperature data gives $P=0.02$ emuK/mole and $\chi_0=6.5\times10^{-4}$ emu/mole. The magnitude of P allows us to estimate an impurity content of less than 1%.[26] Our value of χ_0 is close to those observed, e.g., in Ref. 15 in $LaCoO_3$ or in $ZnCo_2O_4$ with Co^{3+} in the LS state.[27]

The susceptibility of a system with a nonmagnetic ground state and a magnetic excited state reads

$$\chi^C(T)=\frac{N_{\mathrm{A}}g^2\mu_{\mathrm{B}}^2}{3k_{\mathrm{B}}T}\,\frac{\nu S(S+1)(2S+1)e^{-\Delta/T}}{1+\nu(2S+1)e^{-\Delta/T}}. \tag{1}$$

Here N_{A} is the Avogadro number, μ_{B} the Bohr magneton, and k_{B} the Boltzmann constant, Δ denotes the energy splitting of the two states, g is the Landé factor, S the spin, and ν the orbital degeneracy of the excited state. For simplicity we consider a purely ionic model for $LaCoO_3$ and the spin-only values for the magnetic moments, where the ground state of Co^{3+} is the LS state with S=0 and the electronic configuration $t_{2g}^6e_g^0$. The excited state is either the IS (S=1 and $t_{2g}^5e_g^1$) or the HS (S=2 and $t_{2g}^4e_g^2$) state. In the HS (IS) state the $t_{2g}^{\downarrow}$($t_{2g}^{\downarrow}$and $e_g^{\uparrow}$) levels are only partially filled. Therefore the HS state consists of 3 orbital states, which are degenerate in a cubic crystal field leading to $\nu=3$. The IS state contains 6 orbital states but even in a cubic field these states are split into two orbital triplets separated by an energy of about 1 eV due to the Coulomb interaction within the 3d shell.[28] Thus, an orbital degeneracy $\nu=3$ is expected for the IS state, too. The orbital degeneracy is lifted by lower symmetries and the crystal symmetry of $LaCoO_3$ is only rhombohedral. It is, however, unclear whether this can be observed in $\chi^C(T)$. First, the rhombohedral distortion of $LaCoO_3$ is very small. Second, the crystal field of the Co^{3+} levels is mainly determined by the surrounding O^{2-} ions and it is not clear whether the CoO_6 octahedra are distorted, i.e., whether the local symmetry of the Co^{3+} ions is less than cubic. From neutron scattering only one Co-O distance is reported,[29] whereas optical data give evidence for different Co-O distances.[23] This question is further discussed below. Our *combined* analysis of χ and α will allow an unambiguous decision as to which of the four scenarios, LS/IS or LS/HS with or without orbital degeneracy, yields the appropriate description of the spin-state transition of $LaCoO_3$.

The inset of Fig. 1 shows an attempt to describe $\chi^C(T)$ within a LS/HS scenario. Note that Eq. (1) has only Δ as a free parameter (the g-factor may be varied only to some extent). In order to reproduce the strong increase of χ^C below 100 K one has to use an energy splitting $\Delta \simeq 290$ K but in this case the calculated $\chi^C(T)$ for $T>100$ K is much larger than the experimental data (solid line in the inset of Fig. 1). In this calculation we have set $g=2$ and $\nu=1$. Assuming an orbital degeneracy $\nu=3$ of the HS state even increases the discrepancy between experimental and calculated data. There are some possibilities to improve the description within a LS/HS scenario. One is to use $g \simeq 1.1$ (and $\Delta \simeq 190$ K) but such a small g-factor is very unlikely.[30] Another one is to introduce an antiferromagnetic nearest-neighbor coupling J_{AF} as has been done in Ref. 16. On a mean field level this leads to

$$\chi^{MF}(T)=\frac{\chi^C(T)}{1+k_{\mathrm{B}}/N_{\mathrm{A}}g^2\mu_{\mathrm{B}}^2zJ_{\mathrm{AF}}\chi^C(T)}, \tag{2}$$

where $\chi^C(T)$ is given by Eq. (1) and z is the number of nearest neighbors. A fit according to Eq. (2) for $T\leqslant 400$ K is shown by the dashed line in the inset of Fig. 1. By setting $g=2$, $\nu=1$, and $z=6$, we obtain $\Delta \simeq 220$ K and $J_{\mathrm{AF}} \simeq 56$ K (a fit for $\nu=3$ yields $\Delta \simeq 270$ K and $J_{\mathrm{AF}} \simeq 62$ K). Such a strong *antiferromagnetic* coupling is, however, in clear contradiction to neutron scattering experiments which give evidence for a weak *ferromagnetic* coupling.[14] From these arguments we conclude that a LS/HS scenario does not give a consistent description of the magnetic properties of $LaCoO_3$ up to about 500 K.

In contrast to the LS/HS scenario, a good description is found for $\chi^C(T)$ within a LS/IS scenario. This is shown by the solid line in the main panel of Fig. 1. By setting $\nu=1$ the fit yields $\Delta \simeq 180$ K and a reasonable $g \simeq 2.1$. When an orbital degeneracy $\nu=3$ of the IS state is assumed, the quality of the fit becomes worse (not shown in Fig. 1). Thus, the fit of $\chi^C(T)$ favors an orbitally nondegenerate IS state below 500 K. Orbital degeneracy might become important above 600 K as indicated by the dashed line in Fig. 1, which is obtained by "switching on" the orbital degeneracy (setting $\nu=3$) and leaving the other parameters unchanged ($\Delta \simeq 180$ K and $g \simeq 2.1$). Obviously, the dashed line is quite close to the experimental $\chi^C(T)$ for $T>600$ K.

In Fig. 2 we show the linear thermal expansion of $LaCoO_3$and of $La_{0.82}Sr_{0.18}CoO_3$. Our high-resolution data confirm previous results obtained by neutron diffraction[14] but allow a more detailed analysis. Whereas α of

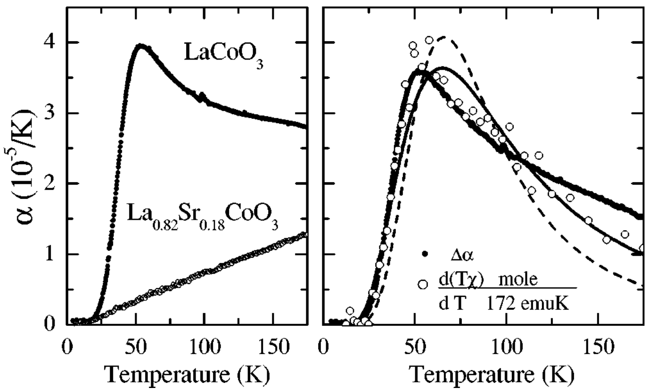

FIG. 2. Left: Thermal expansion of pure (●) and of Sr-doped $LaCoO_3$(○). Right: Anomalous thermal expansion $\Delta\alpha$ (●) of $LaCoO_3$ obtained by subtracting α of $La_{0.82}Sr_{0.18}CoO_3$. The lines are fits of $\Delta\alpha$ for a LS/IS scenario without ($S=\nu=1$; solid line) and for a LS/HS scenario with orbital degeneracy [$S=2$, $\nu=3$; dashed line; see Eq. (3)]. The open symbols (○) show $\partial(T\chi^C(T))/\partial T$ scaled on $\Delta\alpha$, i.e., there is a scaling relation $C\Delta\alpha(T)=\partial(T\chi^C(T))/\partial T$ with $C=172$ emuK/mole.

$La_{0.82}Sr_{0.18}CoO_3$ shows a weak monotonous increase with temperature as expected for ordinary solids, the thermal expansion of $LaCoO_3$ is highly unusual: It is rather large and has a pronounced maximum around 50 K. In view of the spin-state transition that occurs in $LaCoO_3$ (but not in $La_{0.82}Sr_{0.18}CoO_3$) a straightforward interpretation of the anomalous behavior of α can be given. In the LS state of Co^{3+} all electrons occupy t_{2g} levels whereas in the IS and HS state e_g levels are also occupied. Since the e_g states are oriented towards the surrounding negative O^{2-} ions, a population of Co^{3+} in the IS (or HS) state causes an additional widening of the lattice. Simply speaking, the ionic radius of Co^{3+} depends on its spin state and increases with increasing number of electrons in the e_g states ($r^{HS}_{Co^{3+}}>r^{IS}_{Co^{3+}}>r^{LS}_{Co^{3+}}$).

Note that it is not possible to detect a sharp anomaly of α at a characteristic temperature in agreement with specific heat data which also do not show such an anomaly.[31] That means, the spin-state transition in $LaCoO_3$ is not a phase transition in the thermodynamic sense. This justifies the description of the spin-state transition by a thermal population of an excited magnetic state from the LS state which remains the state of the lowest energy [as assumed in Eq. (1)]. The (additional) relative length change due to the spin-state transition is proportional to the thermal population of the excited state, and the anomalous thermal expansions given by its temperature derivative, i.e.,

$$\Delta\alpha(T)=d\frac{\Delta\nu(2S+1)e^{-\Delta/T}}{T^2(1+\nu(2S+1)e^{-\Delta/T})^2}. \tag{3}$$

The product $\nu(2S+1)$ is the total degeneracy of the excited IS (HS) state and d is determined by the different Co–O bond lengths for Co^{3+} in the IS (HS) and in the LS state, respectively.

The anomalous thermal expansion $\Delta\alpha$ of $LaCoO_3$ shown in the right panel of Fig. 2 is obtained by subtracting α of $La_{0.82}Sr_{0.18}CoO_3$ from the raw data. With respect to $\Delta\alpha$ the different scenarios only differ by the total degeneracy $\nu(2S+1)$, which amounts to 3 and 5 for the IS and HS state without, and 9 and 15 for the IS and HS state with orbital degeneracy, respectively. In Fig. 2 we only show the fits for a LS/IS scenario without [$\nu(2S+1)=3$; solid line] and for a LS/HS scenario with orbital degeneracy [$\nu(2S+1)=15$; dashed line]. The two other fits are lying between the solid and the dashed curve. The fit for $\nu(2S+1)=3$ gives the best description of the experimental $\Delta\alpha(T)$ and yields $\Delta\simeq185$ K in good agreement with $\Delta\simeq180$ K from the fit of χ^C. The deviations above 50 K may arise from the uncertainty in background determination and/or a temperature dependence of Δ. Depending on the model the values of d vary between 0.66% and 0.38% (see Table I). They are much smaller than the difference of the Co–O bond lengths of 3% obtained from the sums of the tabulated ionic radii[32] of O^{2-} and Co^{3+} in the LS and the HS state (1.89 Å and 1.95 Å), respectively, giving further evidence against a LS/HS and for a LS/IS scenario in $LaCoO_3$, because the Co–O bond length of the IS state is expected to lie between those of the LS and the HS state of Co^{3+}.

TABLE I. Parameters d and Δ of the fits of the anomalous thermal expansion $\Delta\alpha$ of $LaCoO_3$ (see Fig. 2) obtained for a LS/IS and for a LS/HS scenario with ($\nu=3$) and without ($\nu=1$) orbital degeneracy of the excited IS (HS) state. The respective scaling factors C of Eq. (4) are given in the last row. Experimentally we find $C^{exp}=172$ emuK/mole.

	LS/IS: $S=1$		LS/HS: $S=2$	
	$\nu=1$	$\nu=3$	$\nu=1$	$\nu=3$
d (%)	0.66	0.44	0.55	0.38
Δ (K)	185	265	205	256
C(emuK/mole)	167	84	601	290

The separate fits of both $\chi^C(T)$ and $\Delta\alpha(T)$ already favor a LS/IS scenario without orbital degeneracy but much more convincingly this conclusion is obtained by a scaling behavior between both quantities. From Eqs. (1) and (3) a straightforward calculation yields

$$C\Delta\alpha(T)=\frac{\partial[T\chi^C(T)]}{\partial T} \tag{4}$$

with $C=N_Ag^2\mu_B^2/3k_BS(S+1)/\nu d$. As shown in Fig. 2 this scaling behavior is well fulfilled by the experimental data. The scaling unambiguously reveals that the anomalous thermal expansion of $LaCoO_3$ arises from the spin-state transition. Moreover, the scaling factor $C^{exp}=172$ emuK/mole agrees almost perfectly with $C=167$ emuK/mole expected for a LS/IS scenario without orbital degeneracy (see Table I). In contrast, the other three scenarios yield strongly different scaling factors ranging from 84 to 601 emuK/mole. Thus, our data clearly exclude descriptions within a LS/IS scenario with orbital degeneracy[21,22] and also within a LS/HS scenario with or without orbital degeneracy.[14–17]

Within an ionic picture the LS/IS scenario in LaCoO$_3$ is surprising. The energies of the different spin states of Co^{3+} are determined by the balance of the Hund's rule coupling of parallel spins and the crystal-field splitting Δ_{CF} between the t_{2g} and the e_g levels. The ground state is either the HS (small Δ_{CF}) or the LS (large Δ_{CF}) but never the IS state. Moreover, the IS is expected to lie at least about 1 eV above the ground state.[28] In order to explain the much smaller value observed experimentally ($\Delta \simeq 185\ \mathrm{K} \simeq 0.016\ \mathrm{eV}$) the energy of the IS state has to be lowered relative to the LS and HS states. This can arise from a hybridization between the Co-e_g and the O-$2p$ levels as has been found in LDA+U band-structure calculations.[25] We note that an additional stabilization of the IS state can arise from a JT distortion. The IS state is strongly JT-active because of the partially filled e_g level. The HS state is only weakly JT-active since the gain of JT energy is much less in a partially filled t_{2g} level, and the LS is not JT-active at all. Thus, a JT distortion favors the IS state and it easily explains the lifting of the orbital degeneracy. Remarkably, this picture can also account for the behavior of χ^C above 500 K. Due to the insulator-to-metal transition there are delocalized charge carriers. The corresponding charge fluctuations usually suppress (or weaken) the JT distortions. Then an orbital degeneracy of 3 has to appear above 500 K as suggested by our $\chi^C(T)$ analysis. In addition, an increase of the energy gap Δ may be expected because of the loss of JT energy. However, the analysis of $\chi^C(T)$ above 600 K does not allow us to determine a high-temperature value of Δ with sufficient accuracy. This latter point deserves further clarification.

In summary, our combined study of the magnetic susceptibility and the thermal expansion shows that the spin-state transition in LaCoO$_3$ is consistently described by a thermal population of the intermediate-spin state. The intermediate-spin state has no orbital degeneracy up to about 500 K. This may arise from (local) Jahn-Teller distortions of the CoO$_6$ octahedra. We analyzed our data within a simple ionic model of LaCoO$_3$ but we stress that the experimentally observed scaling between $\Delta\alpha$ and $\partial(\chi T)/\partial T$ is model-independent and may serve as a sensitive test of more sophisticated models.

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