Spin-State Transition in $LaCoO_3$: Direct Neutron Spectroscopic Evidence of Excited Magnetic States

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A gradual spin-state transition occurs in $LaCoO_3$ around $T \sim 80$–120 K, whose detailed nature remains controversial. We studied this transition by means of inelastic neutron scattering and found that with increasing temperature an excitation at $\sim$0.6 meV appears, whose intensity increases with temperature, following the bulk magnetization. Within a model including crystal-field interaction and spin-orbit coupling, we interpret this excitation as originating from a transition between thermally excited states located about 120 K above the ground state. We further discuss the nature of the magnetic excited state in terms of intermediate-spin ($t_{2g}^5 e_g^1$, $S = 1$) versus high-spin ($t_{2g}^4 e_g^2$, $S = 2$) states. Since the g factor obtained from the field dependence of the inelastic neutron scattering is $g \sim 3$, the second interpretation is definitely favored.

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Because of its rich and, in many respects, puzzling properties, $LaCoO_3$ keeps attracting attention and remains a controversial topic. It is known that the ground state is nonmagnetic, corresponding to a low-spin (LS) state of Co^{3+} ions (t_{2g}^6, $S = 0$). However, with increasing temperature (as well as with La $\rightarrow$ Sr substitution), first a crossover into a magnetic, but still insulating, state appears at about 80–120 K, followed by another crossover into a ''bad metallic'' magnetic state at $T \sim 400$–600 K. The original interpretation of the low-temperature crossover was done in terms of thermally induced population of the low-lying high-spin (HS) state [1]; this process is furthermore favored by thermal expansion, since the HS Co^{3+} has a much larger radius ($\sim$0.61 Å) than the LS state ($\sim$0.545 Å). Later, especially after LDA + U band structure calculations became available [2], another interpretation was put forward: Within this scenario, the first crossover at $\sim$100 K would be due to a transition into an intermediate-spin (IS) state. This interpretation was accepted in many papers [3–5]. None of these studies, however, gave a definite proof that the first thermally excited state is indeed the IS one. Very recent measurements indicate that it could still be the HS state [6–9]. This interpretation was also used in Ref. [10], where the indications for the dynamic ordering of HS and LS states [11] are presented.

Also, theoretically, the situation is not clear: Hartree-Fock calculations showed that the HS state or the HS-LS ordered state is more stable than the IS state [12], in contrast to LDA + U calculations [2]. Thereby, model calculations on a CoO_6 cluster explicitly including the Co-O hybridization showed that it is difficult to stabilize an IS ground state [13].

With this controversy in mind, we undertook a neutron scattering study of $LaCoO_3$ at different temperatures with the goal of identifying the energy level of the thermally excited state of Co^{3+}. We discovered that a rather unusual feature in the spectrum appears with increasing temperature in the form of a thermally induced relatively sharp inelastic peak at an energy transfer of $\sim$0.6 meV. The intensity of this peak strongly increases with T following the behavior of the magnetic susceptibility $\chi(T)$, suggesting that the inelastic scattering occurs between thermally populated magnetic states. The position and the temperature dependence of the intensity of this peak also coincide with the excitations observed by ESR [6]. By analyzing the features of this novel excitation, and combining it with model calculations, we discuss the two possible scenarios mentioned above and conclude that the excitation of the HS state is much more plausible.

Polycrystalline $LaCoO_3$ was prepared by standard sintered techniques using La_2O_3 and Co_3O_4 of a minimum purity of 99.99%. The respective amounts of starting reagents were mixed and calcinated at temperatures 1000–1200 °C during at least 100 h in air, with several intermediate grindings. The sample was checked by x-ray diffraction and found to be single phase within experimental accuracy. The space group $R\bar{3}c$ and lattice parameters of $a = 5.4433(1)$ Å and $c = 13.0932(4)$ Å are in agreement with previously published data [1,14,15]. The inelastic neutron scattering (INS) measurements were performed on the time-of-flight spectrometer FOCUS [16] installed at the spallation neutron source SINQ at Paul Scherrer Institut, Villigen, Switzerland. Zero-field experiments were carried out in the temperature interval of 1.5–100 K using a conventional helium cryostat. The data were col-

lected using incoming neutron energies of 3.5 and 20 meV, giving an energy resolution at the elastic position (full width at half maximum) of 0.1 and 1.6 meV, respectively. The triple-axis spectrometer TASP with final neutron energy 4.7 meV was used for the measurements in an external magnetic field up to $H = 6$ T.

The high-resolution low-energy-transfer inelastic spectra for a few selected temperatures are shown in Fig. 1. There are no excitations in the energy window $E < 1.5$ meV for temperatures $T < 30$ K. A single inelastic peak at an energy transfer $\delta E = 0.61 \pm 0.05$ meV was found at intermediate temperatures starting from $T \sim 30$ K. This feature is apparently intrinsic and not related to surface properties: We obtained practically the same results on a single crystal, although with poorer statistics due to the small size (6 g) of our single-crystalline sample. A strong broadening of the transition was observed with increasing temperature. Note that the spectra obtained from a nonmagnetic reference compound $LaAlO_3$ remain structureless at all temperatures. The high-energy-transfer spectra observed for $LaCoO_3$ exhibit several broad inelastic peaks at about 10, 14, and 22 meV (not shown). However, all of these peaks exhibit a clear increase of their intensity with scattering vector and temperature. Therefore, we conclude that they are due to phonon scattering, in agreement with previously published data [4]. No evidence for other magnetic excitations was observed in the $LaCoO_3$ spectra within the available energy window. We cannot completely exclude that the peaks at about 10, 14, and 22 meV are of mixed spin-state phonon character: The expected phonon–spin-state interaction can be rather strong, as the ionic radii of the HS (or IS) and LS states are very different.

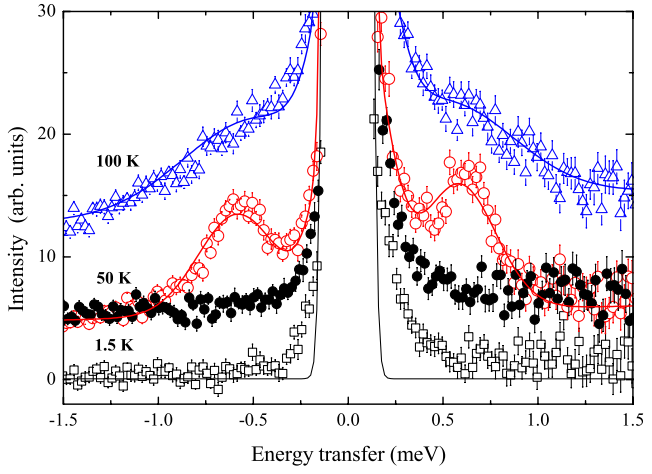

FIG. 1 (color online). Temperature evolution of the INS profiles measured in $LaCoO_3$. The solid circles correspond to the $LaAlO_3$ nonmagnetic reference compound at $T = 50$ K. The lines are the result of least-squares fits using Gaussian functions to describe the line shape of the transition. For clarity, an offset has been added to the various curves.

For noninteracting ions, the thermal neutron cross section for the transition $|\Gamma_i\rangle \rightarrow |\Gamma_j\rangle$ is given in the dipole approximation by [17]

$$\frac{d^2\sigma}{d\Omega d\omega} \sim \frac{1}{Z} \exp\left(-\frac{E_i}{k_B T}\right) F^2(\mathbf{Q}) |\langle \Gamma_j | M_\perp | \Gamma_i \rangle|^2 \times \delta(E_i - E_j \pm \hbar\omega). \quad (1)$$

Here $F^2(\mathbf{Q})$ is the magnetic form factor, $M_\perp$ is the component of $2S + L$ perpendicular to the scattering vector $\mathbf{Q}$, and Z is the partition function. It follows from Eq. (1) that the energy gap $\Delta E = E_i - E_0$ between the ground state and the excited state can be deduced either directly from the position of the corresponding inelastic peak (in the case of nonzero matrix element $|\langle \Gamma_0 | M_\perp | \Gamma_i \rangle|$) or from the temperature dependence of the transition between two excited levels $\delta E = E_j - E_i$, which is governed by Boltzmann statistics. Note that the direct transition ΔE out of the ground state was observed neither in the previous INS experiments [4,18] nor in our current measurements, most likely due to selection rules ($\Delta S = 0, \pm 1$) as will be discussed below. In order to determine the energy of the excited state, we apply the least-squares fitting procedure to the temperature dependence of the integrated intensity I of the INS signal as shown in Fig. 2. The position of the excited states turns out to be 10.3 ± 1 meV, which coincides well with the results obtained from ESR (12 meV, Ref. [6]). Our estimation is based on a temperature-independent level splitting scheme, within the temperature interval of 0–80 K. However, we cannot exclude a variation of the position of the excited states due to thermal expansion of the unit cell or due to coupling of the larger thermally excited magnetic (HS or IS) Co ion with the neighboring LS ions [19,20]. A level crossing of the ground and excited states as suggested from the LDA + U calculations [2] can be excluded, since this would result in a nonmonotonic temperature behavior of I around

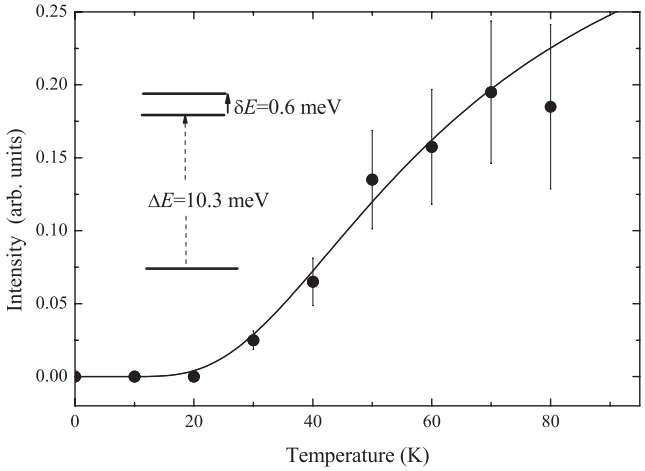

FIG. 2. Observed (circles) and fitted (solid line) temperature dependence of the integral intensity of the INS peak at 0.6 meV. The resulting level scheme is shown in the inset.

$T < 80$ K, which was not observed in our experiment. Furthermore, the position of the peak at $\delta E = 0.6$ meV is unaltered, suggesting that the trigonal crystal field (CF) remains nearly constant in this temperature range.

The observed magnetic INS, which was obtained as the difference of the intensities at 50 and 5 K, is shown in Fig. 3. A clear shift of the transition to the higher energy $\sim$1.5 meV was observed in magnetic field $H = 6$ T compared to the zero-field spectrum, thus firmly establishing its magnetic origin. Note that we cannot detect the second excitation at $\sim$0.3 meV in $H = 6$ T (transition between the other component of the Zeeman-split doublet to a singlet one $|-1\rangle \rightarrow |0\rangle$) due to the overlap with the high intensity elastic line. The intensity of the magnetic excitation $|0\rangle \rightarrow |+1\rangle$ at 1.5 meV (6 T) is reduced roughly by a factor of 2 with respect to that of the excitations $|0\rangle \rightarrow |\pm 1\rangle$ at 0.6 meV (0 T). The change in energy of this peak from 0.6 to about 1.5 meV in a magnetic field of 6 T is in good agreement with the g factor measured from ESR experiments [6], i.e., $g \sim 3$.

There are two possible origins of this excited state: either HS or IS states of Co^{3+}. The HS state with $S = 2$ has, in a cubic CF, the occupation $t_{2g}^4 e_g^2$; i.e., it has a half filled shell of $t_{2g}^3 e_g^2$, say, with spins up, and one extra spin-down electron on a triple-degenerate t_{2g} level, which can be described by an effective orbital moment $\tilde{L} = 1$ [21]. The total multiplicity of this state is $(2S + 1)(2\tilde{L} + 1) = 15$. Spin-orbit coupling splits this state into the lowest-lying triplet $\tilde{J} = S - \tilde{L} = 1$; next is a quintet $\tilde{J} = 2$; and the highest-lying state has $\tilde{J} = 3$. If the system is strongly distorted, there will be a ground-state orbital singlet and a higher excited orbital doublet. In the left panel in Fig. 4, we show the energy-level diagram for the high-spin state as a function of trigonal distortion. This energy-level diagram has been calculated for a CoO_6^{9-} cluster, including full multiplet theory, spin-orbit coupling, and Co-O hybridization. The fine-tuned parameters have been provided by a recent soft-x-ray absorption and magnetic circular dichroism study [20]. The calculations have been done with the use of the program XTLS8 [22]. For the HS, there are two places in the energy-level diagram where an excitation of 0.6 meV can happen. If the trigonal crystal field is relatively small, the $\tilde{J} = 1$ triplet will be split by this crystal field. On the other hand, if it is rather large, the orbital singlet with $S = 2$ will be split due to spin-orbit coupling. In both cases, the splitting is governed by second-order effects and the resulting splitting is much smaller than the perturbing interaction. The scenario of a small crystal field with respect to the spin-orbit coupling has been discussed in quite detail recently [7]. The scenario of a large crystal field with respect to the spin-orbit coupling is equivalent to a spin-only scenario.

One should also consider what would be the situation if the first excited state is an IS Co^{3+}, which follows from LDA + U theoretical calculations [2] and which was used to interpret a number of experimental data [3–5]. This case is actually much more interesting and more difficult to treat theoretically. First, due to a strong attraction of the e_g electron and t_{2g} hole, the lowest states are $(x^2 - y^2)^1 \times (\underline{xy})^1$ and two others obtained from it by permutation of x, y, z (for details, see [13]). Therefore, the total orbital degeneracy of the IS state in a cubic CF is 3 and not 6 $(3t_{2g} \times 2e_g)$ as one could have expected. We can thus again describe these states by the effective orbital triplet $\tilde{L} = 1$. The resulting $(2\tilde{L} + 1)(2S + 1) = 9$ states are split by the spin-orbit coupling into multiplets $\tilde{J} = 2, 1, 0$, the quintet $\tilde{J} = 2$ being the lowest state. Strong enough distortions, or orbital ordering, modify the energy-level scheme as shown in the right panel in Fig. 4. If the distortions are larger than the spin-orbit coupling constant, the ground state becomes an orbital singlet, split due to second-order spin-orbit interactions into two levels that could very well be 0.6 meV apart from each other. In cubic symmetry, the $\tilde{J} = 2$ quintet originating from the IS state

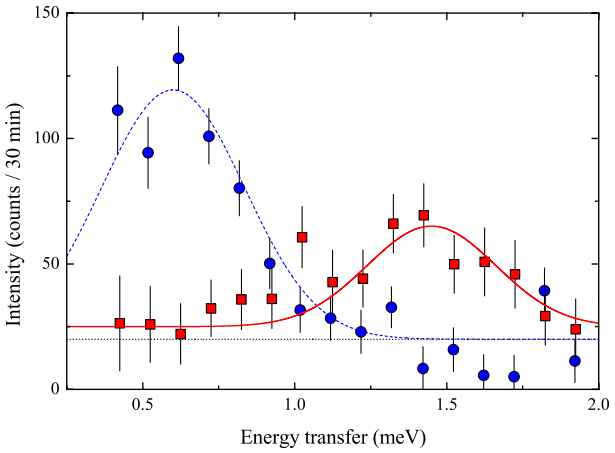

FIG. 3 (color online). The magnetic inelastic scattering at $T = 50$ K in 0 (circles) and 6 T (boxes) applied field.

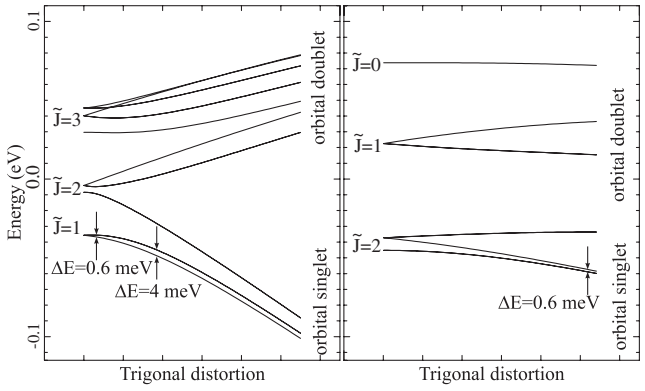

FIG. 4. Schematic diagram of the excitation spectrum of high-spin (left) and intermediate-spin (right) Co^{3+} as a function of trigonal distortion (see text). The $\tilde{J} = 1$ state in the left panel is split by trigonal distortion into a lower singlet and an upper doublet. Similarly, the $\tilde{J} = 2$ state in the right panel is split into a doublet, a singlet, and a doublet.

is, however, also split due to second-order interactions, into a lowest nonmagnetic doublet and an excited magnetic triplet. This splitting seems to be somewhat larger than the measured value of 0.6 meV.

From a comparison of the magnetic susceptibility with the anomalous expansion coefficient of $LaCoO_3$, Zobel *et al.* [5] concluded that the total degeneracy of the first magnetic excited state is 3. This leaves only two possibilities open. The first magnetic excited state in $LaCoO_3$ can be a HS state with a small noncubic crystal field, or it can be an IS state with a large noncubic crystal field or orbital ordering. There is one striking difference between these scenarios: This is the predicted g factor. The HS state with a small noncubic distortion is a spin-orbit triplet with a g factor of about 3.5 [7,21], whereas the IS with a strong noncubic distortion is a spin triplet with a g factor of about 2.0. ESR measurements found a g factor of 3.35–3.55 [6], supporting the HS state; this also agrees with our results since we obtained $g \sim 3$ (see Fig. 3). This conclusion is also strongly supported by the recent study of $LaCoO_3$ by x-ray absorption and x-ray magnetic circular dichroism [20]; cf. [23].

An HS state can also explain the absence of the direct observation of the excited magnetic state in INS: Because of selection rules ($\Delta S = 0, \pm 1$), an excitation from the LS state ($S = 0$) to the HS state ($S = 2$) is not allowed (which would not be the case for an IS scenario). Hereby one should notice that, due to spin-orbit coupling, spin is not a good quantum number, but since the spin-orbit coupling is small compared to the multiplet splitting, the admixture of $S = 1$ states and, consequently, the intensity of such ''forbidden'' transitions should be small, too.

To summarize, we observe a novel inelastic excitation in $LaCoO_3$ which is due to a thermally excited magnetic state of Co^{3+} ions. This confirms the presence of a thermally induced spin-state transition (or rather crossover) at $T \sim 100$ K from the LS Co^{3+} to a magnetic HS or IS state. We discuss both possibilities theoretically and show that one can explain both our and other results (thermodynamic, ESR) in the framework of a HS spin-orbit triplet as a first excited state, with the g factor $\sim$3–3.5, weakly split by small distortions from the cubic symmetry. Another possibility would be the IS state with orbital ordering or strong noncubic crystal fields, which, however, seems to be ruled out because it would lead to the wrong value of the g factor $\sim$2 instead. Thus, we conclude that the spin-state transition in $LaCoO_3$ is that from the low- to the high-spin state.

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[23] In a recent Letter, Phelan *et al.* [24], which appeared after the submission of our Letter, the authors obtained similar experimental results but interpreted them using the IS picture. They based this interpretation on two arguments: that the excited state is a triplet [5] and that there appear ferromagnetic correlations between magnetic states. But, as we have shown above, when one takes into account spin-orbit interaction, it is the HS state which is a triplet, the IS state being a quintet instead. Ferromagnetic correlations can probably be explained in the picture of oxygen holes (cf. [25]) which should be very important in this system with a small charge transfer gap.
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