Spin State Transition in $LaCoO_3$ Studied Using Soft X-ray Absorption Spectroscopy and Magnetic Circular Dichroism

M. W. Haverkort,[1] Z. Hu,[1] J. C. Cezar,[2] T. Burnus,[1] H. Hartmann,[1] M. Reuther,[1] C. Zobel,[1] T. Lorenz,[1] A. Tanaka,[3] N. B. Brookes,[2] H. H. Hsieh,[4,5] H.-J. Lin,[5] C. T. Chen,[5] and L. H. Tjeng[1]

[1]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany*
[2]*European Synchrotron Radiation Facility, Boîte Postale 220, 38043 Grenoble Cédex, France*
[3]*Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan*
[4]*Chung Cheng Institute of Technology, National Defense University, Taoyuan 335, Taiwan*
[5]*National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 30076, Taiwan*
(Received 19 January 2006; published 26 October 2006)

Using soft x-ray absorption spectroscopy and magnetic circular dichroism at the Co-$L_{2,3}$ edge, we reveal that the spin state transition in $LaCoO_3$ can be well described by a low-spin ground state and a triply degenerate high-spin first excited state. From the temperature dependence of the spectral line shapes, we find that $LaCoO_3$ at finite temperatures is an inhomogeneous mixed-spin state system. It is crucial that the magnetic circular dichroism signal in the paramagnetic state carries a large orbital momentum. This directly shows that the currently accepted low- or intermediate-spin picture is at variance. Parameters derived from these spectroscopies fully explain existing magnetic susceptibility, electron spin resonance, and inelastic neutron data.

DOI: 10.1103/PhysRevLett.97.176405 PACS numbers: 71.20.−b, 71.28.+d, 71.70.Ch, 78.70.Dm

$LaCoO_3$ shows a gradual nonmagnetic to magnetic transition with temperature, which was interpreted originally four decades ago as a gradual population of high-spin (HS, $t_{2g}^4 e_g^2$, $S = 2$) excited states starting from a low-spin (LS, t_{2g}^6, $S = 0$) ground state [1–8]. This interpretation continued to be the starting point for experiments carried out up to roughly the first half of the 1990s [9–12]. All this changed with the theoretical work in 1996 by Korotin *et al.*, who proposed on the basis of local density approximation + Hubbard U (LDA + U) band structure calculations, that the excited states are of the intermediate-spin (IS, $t_{2g}^5 e_g^1$, $S = 1$) type [13]. Since then many more studies have been carried out on $LaCoO_3$ with the majority of them [14–27] claiming to have proven the presence of this IS mechanism. In fact, this LDA+U work is so influential [28] that it forms the basis of most explanations for the fascinating properties of the recently synthesized layered cobaltate materials, which show giant magnetoresistance as well as metal-insulator and magnetic transitions with various forms of charge, orbital, and spin ordering [29,30].

In this Letter, we critically reexamine the spin state issue in $LaCoO_3$. There have been several attempts made since 1996 in order to revive the LS-HS scenario [31–35], but these were overwhelmed by the above-mentioned flurry of studies claiming the IS mechanism [14–27]. Moreover, a new investigation using inelastic neutron scattering (INS) has recently appeared in Ref. [36], again making the claim that the spin state transition involves the IS states. Here, we used soft x-ray absorption spectroscopy (XAS) and magnetic circular dichroism (MCD) at the Co-$L_{2,3}$ edge, and we revealed that the spin state transition in $LaCoO_3$ can be well described by a LS ground state and a triply degenerate HS excited state, and that an inhomogeneous mixed-spin state system is formed. Parameters derived from these spectroscopies fully explain existing magnetic susceptibility and electron spin resonance (ESR) data and provide support for an alternative interpretation of the INS [37]. Consequently, the spin state issue for the new class of the layered cobaltates needs to be reinvestigated [29,30].

Single crystals of $LaCoO_3$ have been grown by the traveling floating-zone method in an image furnace. The magnetic susceptibility was measured using a Quantum Design vibrating sample magnetometer (VSM), reproducing the data reported earlier [19]. The Co-$L_{2,3}$ XAS measurements were performed at the Dragon beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan with an energy resolution of 0.3 eV. The MCD spectra were collected at the ID08 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble with a resolution of 0.25 eV and a degree of circular polarization close to 100% in a magnetic field of 6 Tesla. Clean sample areas were obtained by cleaving the crystals *in situ* in chambers with base pressures in the low 10^{-10} mbar range. The Co $L_{2,3}$ spectra were recorded using the total electron yield method (TEY). O-*K* XAS spectra were collected by both the TEY and the bulk sensitive fluorescence yield (FY) methods, and the close similarity of the spectra taken with these two methods verifies that the TEY spectra are representative for the bulk material. A CoO single crystal is measured *simultaneously* in a separate chamber to obtain relative energy referencing with better than a few meV accuracy, sufficient to extract reliable MCD spectra.

Figure 1 shows the set of Co-$L_{2,3}$ XAS spectra of $LaCoO_3$ taken for a wide range of temperatures. The set is at first sight similar to the one reported earlier [38], but it is in fact essentially different in details. First of all, our set

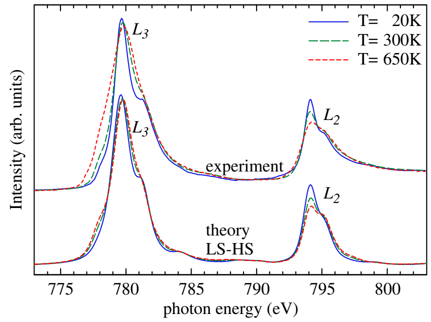

FIG. 1 (color online). Experimental Co-$L_{2,3}$ XAS spectra taken from $LaCoO_3$ at various temperatures between 20 and 650 K, together with the corresponding theoretical isotropic spectra calculated using a CoO_6 cluster in the LS-HS scenario. For clarity, only the 20, 300, and 650 K spectra are shown.

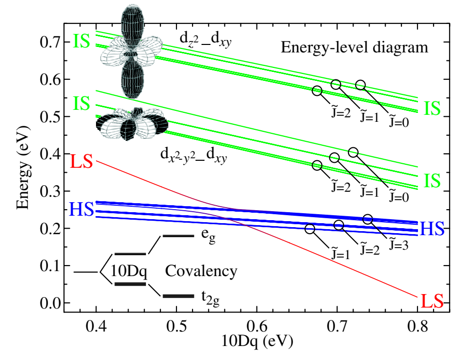

FIG. 2 (color online). Energy level diagram of a CoO_6 cluster [43] as a function of the ionic part of the crystal field splitting $10Dq$.

includes a low temperature (20 K) spectrum representative for the LS state, and second, our spectra do not show a pronounced shoulder at 777 eV photon energy which is characteristic for the presence of Co^{2+} impurities [39]. The extended temperature range and especially the purity of the probed samples provide the required sensitivity for the spin state related spectral changes.

The spectra are dominated by the Co $2p$ core-hole, spin-orbit coupling which splits the spectrum roughly into two parts, namely, the L_3 ($h\nu \approx 780$ eV) and L_2 ($h\nu \approx 796$ eV) white lines regions. The line shape of the spectrum depends strongly on the multiplet structure given by the Co $3d$-$3d$ and $2p$-$3d$ Coulomb and exchange interactions, as well as by the local crystal fields and the hybridization with the O $2p$ ligands. Unique to soft x-ray absorption is that the dipole selection rules are very effective in determining which of the $2p^5 3d^{n+1}$ final states can be reached and with what intensity, starting from a particular $2p^6 3d^n$ initial state ($n = 6$ for Co^{3+}) [40,41]. This makes the technique extremely sensitive to the symmetry of the initial state, e.g., the spin state of the Co^{3+} [30].

Utilizing this sensitivity, we first simulate the spectrum of a Co^{3+} ion in the LS state using the successful configuration interaction cluster model that includes the full atomic multiplet theory and the hybridization with the O $2p$ ligands [40–42]. The CoO_6 cluster is taken to have the octahedral symmetry, and the parameters are the same as the ones which successfully reproduce the spectrum of LS $EuCoO_3$ [30,43]. The result with the ionic part of the crystal field splitting set at $10Dq = 0.7$ eV is shown in Fig. 1 and fits well the experimental spectrum at 20 K.

Next we analyze the spectra for the paramagnetic phase. We use the same cluster, keeping the O_h' symmetry, and calculate the total energy level diagram as a function of $10Dq$, see Fig. 2. We find that the ground state of the cluster is either LS or HS (and never IS) with a crossover at about $10Dq = 0.58$ eV [44]. We are able to obtain good simulations for the spectra at all temperatures, see Fig. 1, provided that they are made from an incoherent sum of the above-mentioned LS cluster spectrum calculated with $10Dq = 0.7$ eV and a HS cluster spectrum calculated with $10Dq = 0.5$ eV. It is not possible to fit the entire temperature range using one cluster with one particular temperature-independent $10Dq$ value for which the ground state is LS-like and the excited states HS-like. Moreover, each of these two $10Dq$ values have to be sufficiently far away from the LS-HS crossover point to ensure a large enough energy separation between the LS and HS so that the two do not mix due to the spin-orbit interaction. Otherwise, the calculated low temperature spectrum, for instance, will disagree with the experimental one. All this indicates that $LaCoO_3$ at finite temperatures is an inhomogeneous mixed-spin state system.

The temperature dependence has been fitted by taking different ratios of LS and HS states contributing to the spectra. The extracted HS percentage as a function of temperature is shown in Fig. 3(a). The corresponding effective activation energy is plotted in Fig. 3(b). It increases with temperature and varies between 20 meV at 20 K to 80 meV at 650 K, supporting a recent theoretical analysis of the thermodynamics [35]. Here we would like to point out that these numbers are of the order $k_B T$ and reflect total energy differences which include lattice relaxations [35] as sketched in the inset of Fig. 3(b). Without these relaxations, we have for the LS state ($10Dq = 0.7$ eV) an energy difference of at least 50 meV between the LS and the HS as shown in Fig. 2. In such a frozen lattice, the energy difference is larger than $k_B T$. It is also so large that the ground state is indeed highly pure LS as revealed by the 20 K spectrum.

To check the validity of our analysis, we calculate the magnetic susceptibility using the CoO_6 cluster and the HS occupation numbers from Fig. 3 as derived from the XAS data. The results are plotted in Fig. 3(c) (triangles) together with the magnetic susceptibility as measured by the VSM (solid line). We can observe clearly a very good agreement: the magnitude and its temperature dependence are well reproduced. This provides another support that the spin state transition is inhomogeneous and involves lattice relaxations. A homogeneous LS-HS model, on the other hand, would produce a much too high susceptibility if it is

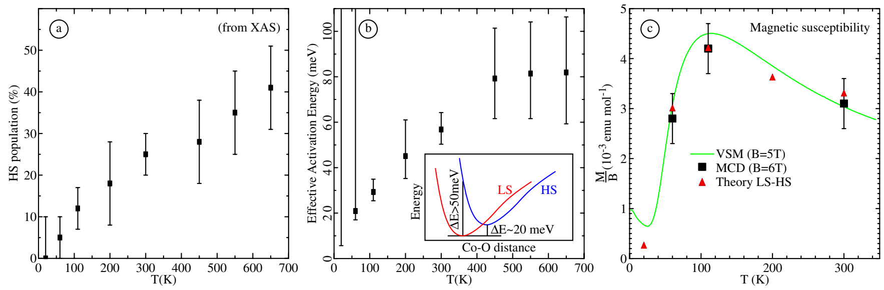

FIG. 3 (color online). (a) HS population from XAS data. (b) Corresponding effective activation energy between the LS and the lowest HS state. The inset sketches the role of lattice relaxations. (c) Magnetic susceptibility measured by VSM (solid line), calculated from the cluster (triangles) using the HS population of Fig. 3(a), and extracted from MCD data (squares) of Fig. 4.

to peak at 110 K [11,12,14,19]. In addition, it is crucial to realize that the Van Vleck contribution to the magnetic susceptibility strongly depends on the intermixing between the LS and HS states. It is precisely this aspect which also sets the condition that the energy separation between the LS and HS states in the cluster should be larger than 50 meV; otherwise, the calculated Van Vleck contribution would already exceed the experimentally determined total magnetic susceptibility at low temperatures. This in fact is a restatement of the above-mentioned observation that the low temperature spectrum is highly pure LS.

To further verify the direct link between the spectroscopic and the VSM magnetic susceptibility data, we carried out MCD experiments on $LaCoO_3$ at 60, 110, and 300 K, i.e., in the paramagnetic phase, using a 6 Tesla magnet. Figure 4 shows XAS spectra taken with circularly polarized soft-x rays with the photon spin parallel and antiparallel aligned to the magnetic field. The difference in the spectra using these two alignments is only of the order of 1%, but can nevertheless be measured reliably due to the good signal to noise ratio, stability of the beam, and the accurate photon energy referencing. The difference curves are drawn in the middle of Fig. 4 with a magnification of 25 times. Hereby, we have subtracted a small signal due to the presence of about 1.5% Co^{2+} impurities. We also plotted the simulated MCD spectra from the cluster model within the LS-HS scenario, and we can clearly observe a very satisfying agreement with the experiment. Alternatively, using the MCD sum-rules developed by Thole and Carra *et al.* [45,46], we can extract directly the orbital (L_z) and spin ($2S_z$) contributions to the induced moments without the need to do detailed modeling [47]. This result normalized to the applied magnetic field is plotted in Fig. 3(c), and we can immediately observe the close agreement with the VSM data.

An important aspect that emerges directly from the MCD experiments is the presence of a very large induced orbital moment: we find that $L_z/S_z \approx 0.5$. This means that the spin-orbit coupling (SOC) must be considered in evaluating the degeneracies of the different levels, as is done for the energy level diagram in Fig. 2. Let us discuss the consequences for the HS state. We see that the 15-fold degenerate (3-fold orbital and 5-fold spin) HS state is split by the SOC. A t_{2g} electron has a pseudo orbital momentum of $\tilde{L} = 1$ [48], which couples with the spin to a pseudo total momentum of $\tilde{J} = 1$, 2 or 3. The $\tilde{J} = 1$ triplet is the lowest in energy, and we find from our cluster that this state has $L_z = 0.6$ and $S_z = 1.3$, in good agreement with the experimental $L_z/S_z \approx 0.5$. Realizing that this state is a triplet with a spin momentum (S_z) so close to 1, it is no wonder that many studies incorrectly interpreted this state as an IS state. Its expectation value for the spin [$\langle S^2 \rangle = S(S+1)$] is however very close to 6, and the formal occupation numbers of the d_{z^2} and the $d_{x^2-y^2}$ orbitals are both equal to 1. This state is clearly a HS state and should not be confused with an IS state. We find a g-factor of 3.2, in good agreement with the values found from ESR [32,34] and INS data [37].

We have shown so far that the spin state transition in $LaCoO_3$ is in very good agreement with a LS-HS picture. The question now remains if it could also be explained within a LS-IS scenario. For that, we first have to look at what the IS actually is. The IS state has one hole in the t_{2g}

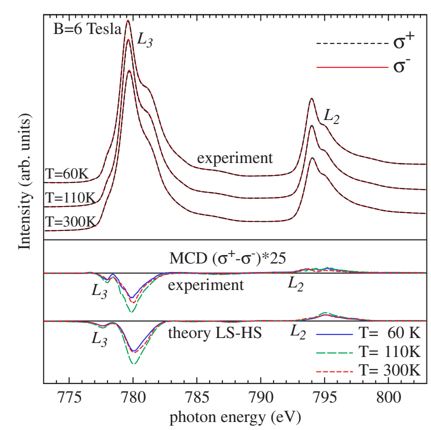

FIG. 4 (color online). Top curves: experimental Co-$L_{2,3}$ XAS spectra taken from $LaCoO_3$ at 60, 110, and 300 K using circularly polarized x rays with the photon spin aligned parallel (dotted line, σ^+) and antiparallel (solid line, σ^-) to the 6 Tesla magnetic field. Middle curves: experimental MCD spectra. Bottom curves: theoretical MCD spectra calculated in the LS-HS scenario.

shell and one electron in the e_g shell. Because of the strong orbital dependent Coulomb interactions, the strong-Jahn-Teller states of the type $d_{z^2}\underline{d}_{xy}$ and their x, y, z-cyclic permutations have much higher energies than the weak-Jahn-Teller $d_{x^2-y^2}\underline{d}_{xy}$ plus cyclic permutations. Here the underline denotes a hole. See Fig. 2. These weak-Jahn-Teller states indeed form the basis for the orbital ordering scheme as proposed for the IS scenario by Korotin *et al.* [13]. However, these real-space states do not carry a large orbital momentum and are therefore not compatible with the values observed in the MCD measurements. Likewise, the strong Jahn-Teller-like local distortions in the IS state proposed by Maris *et al.* [24] would lead to a quenching of the orbital momentum. We therefore can conclude that the IS scenarios proposed so far have to be rejected on the basis of our MCD results. Moreover, an IS state would lead in general to a much larger Van Vleck magnetism than a HS state. This is related to the fact that the LS state couples directly to the IS via the SOC, while the HS is not. To comply with the measured low temperature magnetic susceptibility, the energy difference between the LS and IS has to be 150 meV at least, making it more difficult to find a mechanism by which the maximum of the susceptibility occurs at 110 K. Finally, within the LS-IS scenario, we were not able to find simulations which match the experimental XAS and MCD spectra.

To summarize, we provide unique spectroscopic evidence that the spin state transition in $LaCoO_3$ can be well described by a LS ground state and a triply degenerate HS excited state, and that an inhomogeneous mixed-spin state system is formed. The large orbital momentum revealed by the MCD measurements invalidates existing LS-IS scenarios. A consistent picture has now been achieved which also explains available magnetic susceptibility, ESR and INS data.

We would like to thank Lucie Hamdan for her skillful technical and organizational assistance in preparing the experiments. The research in Cologne is supported by the Deutsche Forschungsgemeinschaft through SFB 608.

[1] R. R. Heikes, R. C. Miller, and R. Mazelsky, Physica (Amsterdam) **30**, 1600 (1964).
[2] G. Blasse, J. Appl. Phys. **36**, 879 (1965).
[3] C. S. Naiman *et al.*, J. Appl. Phys. **36**, 1044 (1965).
[4] G. H. Jonker, J. Appl. Phys. **37**, 1424 (1966).
[5] J. B. Goodenough and P. M. Raccah, Jpn. J. Appl. Phys., Suppl. **36**, 1031 (1965).
[6] P. M. Raccah and J. B. Goodenough, Phys. Rev. **155**, 932 (1967).
[7] J. B. Goodenough, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford, 1971), Vol. 5.
[8] V. G. Bhide, D. S. Rajoria, G. Rama Rao, and C. N. R. Rao, Phys. Rev. B **6**, 1021 (1972).
[9] K. Asai *et al.*, Phys. Rev. B **50**, 3025 (1994).
[10] M. Itoh, I. Natori, S. Kubota, and K. Motoya, J. Phys. Soc. Jpn. **63**, 1486 (1994).
[11] M. Itoh, M. Sugahara, I. Natori, and K. Motoya, J. Phys. Soc. Jpn. **64**, 3967 (1995).
[12] S. Yamaguchi, Y. Okimoto, H. Taniguchi, and Y. Tokura, Phys. Rev. B **53**, R2926 (1996).
[13] M. A. Korotin *et al.*, Phys. Rev. B **54**, 5309 (1996).
[14] T. Saitoh *et al.*, Phys. Rev. B **55**, 4257 (1997); **56**, 1290 (1997).
[15] S. Stølen *et al.*, Phys. Rev. B **55**, 14 103 (1997).
[16] K. Asai *et al.*, J. Phys. Soc. Jpn. **67**, 290 (1998).
[17] J. Okamoto *et al.*, Phys. Rev. B **62**, 4455 (2000).
[18] P. Ravindran *et al.*, J. Appl. Phys. **91**, 291 (2002).
[19] C. Zobel *et al.*, Phys. Rev. B **66**, 020402(R) (2002).
[20] P. G. Radaelli and S.-W. Cheong, Phys. Rev. B **66**, 094408 (2002).
[21] T. Vogt, J. A. Hriljac, N. C. Hyatt, and P. Woodward, Phys. Rev. B **67**, 140401(R) (2003).
[22] I. A. Nekrasov, S. V. Streltsov, M. A. Korotin, and V. I. Anisimov, Phys. Rev. B **68**, 235113 (2003).
[23] D. Louca and J. L. Sarrao, Phys. Rev. Lett. **91**, 155501 (2003).
[24] G. Maris *et al.*, Phys. Rev. B **67**, 224423 (2003).
[25] A. Ishikawa, J. Nohara, and S. Sugai, Phys. Rev. Lett. **93**, 136401 (2004).
[26] M. Magnuson *et al.*, Europhys. Lett. **68**, 289 (2004).
[27] K. Knizek, P. Novak, and Z. Jirak, Phys. Rev. B **71**, 054420 (2005).
[28] The Korotin Phys. Rev. B 1996 paper has at present already been cited more than 170 times.
[29] See List of References in Hu *et al.*.
[30] Z. Hu *et al.*, Phys. Rev. Lett. **92**, 207402 (2004).
[31] M. Zhuang, W. Zhang, and N. Ming, Phys. Rev. B **57**, 10 705 (1998).
[32] S. Noguchi *et al.*, Phys. Rev. B **66**, 094404 (2002).
[33] T. Kyômen, Y. Asaka, and M. Itoh, Phys. Rev. B **67**, 144424 (2003).
[34] Z. Ropka and R. J. Radwanski, Phys. Rev. B **67**, 172401 (2003).
[35] T. Kyômen, Y. Asaka, and M. Itoh, Phys. Rev. B **71**, 024418 (2005).
[36] D. Phelan *et al.*, Phys. Rev. Lett. **96**, 027201 (2006).
[37] Z. Podlesnyak *et al.* (to be published).
[38] M. Abbate *et al.*, Phys. Rev. B **47**, 16 124 (1993).
[39] S. I. Csiszar *et al.*, Phys. Rev. Lett. **95**, 187205 (2005).
[40] See review by F. M. F. de Groot, J. Electron Spectrosc. Relat. Phenom. **67**, 529 (1994).
[41] See review in the Theo Thole Memorial Issue, edited by A. P. Hitchcock, G. E. McGuire, and J. J. Pireaux, J. Electron Spectrosc. Relat. Phenom. **86**, 1 (1997).
[42] A. Tanaka and T. Jo, J. Phys. Soc. Jpn. **63**, 2788 (1994).
[43] CoO_6 cluster parameters [eV]: $\Delta = 2.0$, $pd\sigma = -1.7$, $U_{dd} = 5.5$, Slater integrals 80% of Hartree Fock values.
[44] In a pure ionic model, the LS-HS crossover occurs at $10Dq \approx 2.2$ eV.
[45] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, Phys. Rev. Lett. **68**, 1943 (1992).
[46] P. Carra, B. T. Thole, M. Altarelli, and X. Wang, Phys. Rev. Lett. **70**, 694 (1993).
[47] The sum-rules give numbers for L_z and $S_z + \frac{7}{2}T_z$; $T_z = 0$ for the HS state as justified from cluster calculations; the number of $3d$ holes is about 3.5.
[48] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).