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Spin-state-driven metal-insulator transition in (La,Sr)CoO$_3$ under high-pressure

R. Lengsdorf,[1] J.-P. Rueff,[2,3] G. Vankó,[4,5] T. Lorenz,[1] L. H. Tjeng,[1] and M. M. Abd-Elmeguid[1]
[1]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, 50937 Köln, Germany*
[2]*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, Boîte Postale 48, 91192 Gif-sur-Yvette Cedex, France*
[3]*Laboratoire de Chimie Physique-Matière et Rayonnement (UMR 7614), Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[4]*European Synchrotron Radiation Facility, Boîte Postale 220, F-38043, Grenoble Cedex 9, France*
[5]*KFKI Research Institute for Particle and Nuclear Physics, P. O. Box 49, H-1525 Budapest, Hungary*

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Using Co $K\beta$ x-ray emission spectroscopy (XES) we have investigated the effect of pressure on the Co spin state of a single crystal of metallic, ferromagnetic La$_{0.82}$Sr$_{0.18}$CoO$_3$. The analysis of the XES spectra up to 14.4 GPa at 300 and 34 K clearly shows a gradual pressure-induced spin-state transition from a high- or intermediate-spin to a low-spin state. These results provide microscopic evidence that the recently observed pressure-induced metal-insulator transition in (La,Sr)CoO$_3$ is driven by a simultaneous spin-state transition. We further show that under high pressures the low-spin state is relatively stable against temperature, in contrast to that in the LaCoO$_3$ case. This is attributed to an enhancement of the crystal field splitting at high pressures.

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Long-standing issues associated with perovskite-type strongly correlated oxides such as RMO_3, R and M being a trivalent rare earth and a $3d$ transition metal, respectively, are the microscopic origin of the metal-insulator (MI) transition and the nature of the ground state. This is related to the fact that in this class of materials the MI transition is driven by an interplay between charge, orbital, and spin degrees of freedom and can be induced by varying the carrier concentration, temperature, magnetic field, and external pressure.[1] An exemplary series for this interplay and its impact on the magnetic and electronic properties is La$_{1-x}$Sr$_x$CoO$_3$ ($0 \leqslant x \leqslant 0.5$). The ground state of the undoped insulating LaCoO$_3$ is nonmagnetic with the Co^{3+} in the low-spin (LS) configuration ($t_{2g}^6 e_g^0$, $S=0$). However, upon increasing temperature ($T \approx 100$ K), the system undergoes a transition to a magnetic state, which has been attributed to the thermal excitation of the LS state to either the high-spin (HS, $t_{2g}^4 e_g^2$, $S=2$), e.g, Refs. 2–4 or the intermediate-spin (IS, $t_{2g}^5 e_g^1$, $S=1$) state, e.g., Refs. 5–9 At higher temperatures around 500 K the system undergoes an insulator-metal transition.[10] The controversy about the nature of the spin-state transition at ≈ 100 K has been solved very recently by soft x-ray absorption and magnetic circular dichroism experiments on LaCoO$_3$:[11] the spin-state transition in LaCoO$_3$ can be well described by an inhomogeneous mixture of a LS ground state and a triply degenerate HS state. The formation of such a HS state has also been suggested by very recent inelastic neutron scattering measurements on LaCoO$_3$.[12] Likewise, doping the system with Sr^{2+}, which formally creates Co^{4+} ions, induces a change of the Co^{3+} spin state that dramatically affects the magnetic and transport properties of the system: the ground state becomes ferromagnetic for $x \geqslant 0.18$, with a simultaneous transition from the insulating to a metallic state.[13–17] In the metallic region, the ferromagnetic coupling is attributed to double exchange between Co^{3+} and Co^{4+} ions.[15,18] However, the nature of the spin states and their relationship to the MI transition is far from being clear.

To obtain a deeper insight into the correlation between the spin and charge degrees of freedom in this system, we recently investigated the effect of external pressure on conducting ferromagnetic ($T_C = 157$ K) La$_{0.82}$Sr$_{0.18}$CoO$_3$ located near the boundary of the MI transition.[19] Here, we observed a quite unusual effect: a transition from the metallic to an insulating state and a decrease of T_C with increasing pressure, while the lattice structure remains unchanged. The temperature dependence of the electrical resistivity (ρ) clearly showed an insulating behavior, where the magnitude of ρ dramatically increases by about four orders of magnitude at 5.7 GPa and 4.2 K.[19] These results are opposite to those found in related systems. For example, La$_{1-x}$Sr$_x$MnO$_3$ (Ref. 20) becomes metallic under high pressure, which is usually expected because reducing the lattice constant with increasing pressure causes a broadening of the effective bandwidth. To understand the origin of the observed pressure-induced MI transition in this system, we also have investigated the effect of pressure on the Co magnetic moment in La$_{0.82}$Sr$_{0.18}$CoO$_3$ by magnetization measurements at 1 GPa.[19] The analysis of the data revealed a small reduction of the magnetic moment of about 5%, which may indicate a change of the Co spin state from magnetic HS or IS to a nonmagnetic LS state. However, magnetization as a macroscopic technique does not allow direct detection of the Co spin state and its pressure dependence on a microscopic level. Moreover, it is applicable only in a very small pressure range and thus is not adequate to explore possible changes of the Co magnetic moment in an extended pressure range, where the resistivity changes dramatically. Thus, it remains an open question whether the Co spin state transforms to a LS state under high pressure, causing the unusual pressure-induced MI transition in (La,Sr)CoO$_3$.

In this paper, we present an investigation of the pressure effect on the Co spin state of single crystals of La$_{0.82}$Sr$_{0.18}$CoO$_3$ up to 14.4 GPa and at different temperatures (300 and 34 K) using $K\beta$ x-ray emission spectroscopy (XES), a technique whose sensitivity to the spin state and its changes with pressure has been well demonstrated in many transition metal oxide materials.[21–23] Our experimental results provide microscopic evidence for a gradual HS or IS to LS transition with increasing pressure, and clearly indicate that the observed pressure-induced MI transition in $La_{0.82}Sr_{0.18}CoO_3$ is driven by a simultaneous spin-state transition.

Single crystals of $La_{0.82}Sr_{0.18}CoO_3$ were grown by the traveling zone method under oxygen pressure of 5 bar. Details of the preparation and characterization are published elsewhere.[17,24] The experiments were carried out at the undulator beamline ID16 at the European Radiation Synchrotron Facility (ESRF), Grenoble. The incident energy was selected by a Si(111) two-crystal monochromator and the beam focused onto the sample position within a $100\times200\ \mu m^2$ spot using a toroidal mirror located downstream. Single crystals of $La_{0.82}Sr_{0.18}CoO_3$ samples were loaded in a Cu-Be diamond anvil cell (DAC) with ruby chips for pressure calibration. The sample was placed in a $Ta_{90}W_{10}$ gasket (gasket hole of 0.25 mm) filled with liquid N_2 as pressure-transmitting medium. Diamonds with thickness of 2 mm and culets of 0.6 mm were used.

The Co $K\beta$ emission line was measured at the beamline Raman spectrometer. The spectrometer was in the Rowland circle geometry with a 1 m diameter. We used a spherically bent Si(620) crystal analyzer operated at the nominal Bragg angle of 70.6° at the Co $K\beta$ emission line energy, and an avalanche photodiode as a detector. All the x-ray emission spectra under pressure were measured at an incident energy of 13 keV, which offers the best compromise between sample scattering length and transmission through the entrance diamond. The scattered beam was detected in transmission geometry at an angle of 12° in the forward direction. In this geometry, the sample in the gasket is homogeneous with respect to density and pressure gradient. The downside, however, is the strong absorption of the scattered intensity by the exit diamond. A typical count rate in the pressure cell at the maximum of the $K\beta$ line was ~500 counts/s, to be compared to 10^5 counts/s in the free-standing samples. For temperature-dependent measurements, the cell was mounted on a ^{4}He closed cycle refrigerator. Temperature was measured directly on the DAC by a thermocouple. The lowest temperature reached with this setup was 34 K. All XES spectra were normalized to the beam monitor and to the spectral area and aligned to have the main lines at the same energy.

Figures 1 and 2 show the evolution of the Co $K\beta$ $(3p\rightarrow1s)$ emission spectra in $La_{0.82}Sr_{0.18}CoO_3$ at 34 and 300 K, respectively, for different pressures up to 14.4 GPa. As evident from the insets of the figures, the intensity of the satellite structure on the low-energy side is suppressed with increasing pressure. The effect is more pronounced in the series measured at low temperature. It is well established that the variation of the spectral line shape with pressure is a direct consequence of the sensitivity of XES to the local spin state on the metal site.[21,25] In the presence of a $\underline{3p}$ core hole, the $K\beta$ final state manifold splits into two main components: an intense line and a broad satellite structure on the low-energy side which corresponds to an opposite alignment of the $\underline{3p}$ spin with respect to the $3d$ spin polarization.[26] As a rule of thumb, the more intense the satellite, the higher the spin state. As a reference for a LS state we show in Fig. 1 the XES of $LaCoO_3$ at 17 K.[27] In $La_{0.82}Sr_{0.18}CoO_3$ the decrease of the satellite component with increasing pressure mainly reflects a decrease of the local Co spin state. A more realistic description should take into account multiplet interactions and charge transfer effects, which complicate the simplistic atomic picture.[28]

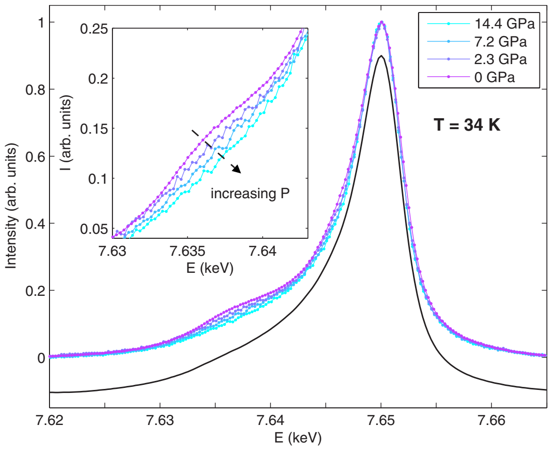

FIG. 1. (Color online) Co $K\beta$ emission spectra at 34 K and different pressures up to 14.4 GPa. The XES spectrum of $LaCoO_3$ at 17 K (black solid line) is shown as a reference for the LS ($S=0$) state. Inset shows a blowup of the satellite region. The intensity of the satellite structure is suppressed at 14.4 GPa.

To quantify the changes observed by XES in the sample with pressure, the spectra were analyzed by means of the integrated absolute difference (IAD) method. This method has proven to yield information about the spin state in transition metals.[27,29,30] The IAD is calculated from the integrated area of difference spectra between the XES emission lines at a given pressure and temperature and a reference spectrum, which in our case is the XES spectrum at $T=34$ K and the highest pressure of 14.4 GPa. In fact, any of the XES spectra can serve to calculate the IAD values. We have checked the consistency of our IAD values by using successively each of the spectra as reference. The identification of the IAD value at high pressure with $S=0$ comes from

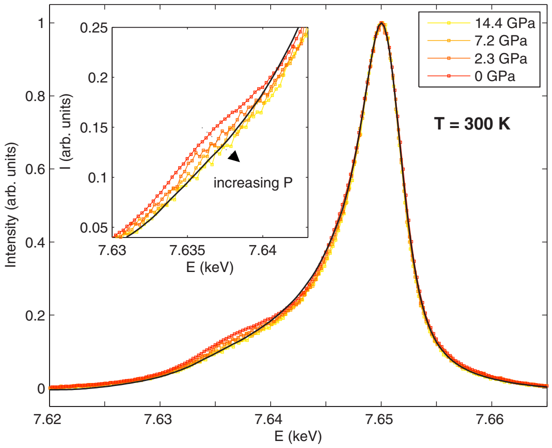

FIG. 2. (Color online) Co $K\beta$ emission spectra at 300 K and different pressures up to 14.4 GPa. Inset shows a blowup of the satellite region.

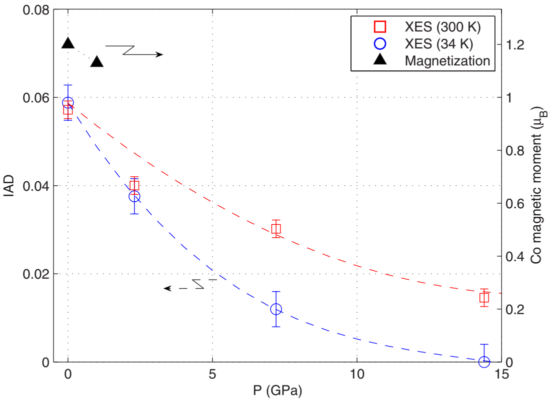

FIG. 3. (Color online) Left scale: pressure dependence of the integrated absolute difference (IAD) in $La_{0.82}Sr_{0.18}CoO_3$ up to 14.4 GPa at 300 and 34 K as deduced from the analysis of the Co $K\beta$ emission spectra (see text). Dotted lines through the data points are guides to the eyes. Right scale: pressure dependence of the Co magnetic moment (μ_{Co}) as obtained from magnetization measurements on $La_{0.82}Sr_{0.18}CoO_3$ under pressure up to 1 GPa. (Ref. [19])

the comparison with the model low-spin compound. In principle, reference spectra of known spin states could be further used to convert the IAD values to corresponding spin values. We obtain at ambient pressure nearly similar IAD values of 0.058(4) and 0.056(2) for the XES spectra at 34 and 300 K, respectively. As a reference, we note that $LaCoO_3$ at 800 K has an IAD value of 0.06, which corresponds to a spin value of $S=1$.[27] This value is compatible with a situation in which 50% of Co^{3+} is in the HS state and the other 50% in the LS state;[11] or alternatively with a situation in which all Co^{3+} ions are in the IS state. In both situations, we consider only the Co^{3+} spin state which is associated with the major amount of the Co ions (82%) in our sample, and neglect that of Co^{4+} ions (18%). The Co^{4+} spin state is assumed to be LS ($S=1/2$) and thus is expected to remain LS at high pressure. Because there is such a small fraction of LS Co^{4+} in the sample, we find within the experimental accuracy no indication of a distinctive XES signal from LS Co^{4+}.[31] Thus, the observed variation of the spin state with pressure is due to Co^{3+}. In any case, since the IAD analysis provides only relative values of the spin state, we restrict our discussion to the pressure-induced change of the spin state, regardless of its nature(e.g., IS, HS, or HS-LS). The change of the IAD values with increasing pressure for two different temperatures is displayed in Fig. 3. Upon increasing pressure, these values progressively decrease to achieve zero around 14.4 GPa at 34 K. This clearly indicates a gradual pressure-induced spin-state transition of Co^{3+} ions toward a LS state.

Apparently, high pressure favors the population of the LS Co^{3+} at the expense of the depopulation of higher-spin states. This can be attributed to the fact that the ionic radius of the LS Co^{3+} (0.545 Å) is smaller than that of HS Co^{3+} (0.61 Å),[32] and pressure causes an increase of the crystal field splitting between the t_{2g} and e_g orbitals and thereby results in a depopulation of electrons from the e_g orbital to a t_{2g} orbital.[19,33] This leads to the formation of a stable LS Co^{3+} state in $La_{0.82}Sr_{0.18}CoO_3$ at sufficiently high pressures. As a matter of fact, such a pressure-induced spin-state transition is intimately connected with the metallic conductivity of the system: a gradual depopulation of e_g electrons results in a strong suppression of the hopping conductivity, leading to an insulating state at high pressure. Thus, our high-pressure XES results provide microscopic proof of a pressure-induced magnetic collapse and clearly show that the observed pressure-induced metal-insulator transition in $La_{0.82}Sr_{0.18}CoO_3$ is driven by a simultaneous spin-state transition.

Next, we discuss the observed weak temperature dependence of the Co spin state in $La_{0.82}Sr_{0.18}CoO_3$ between 34 and 300 K as a function of pressure. Figure 3 shows IAD values of 0.058(2) and 0.056(2) at 34 and 300 K at ambient pressure, respectively, which are equal within the experimental accuracy. Thus, the spin state of $La_{0.82}Sr_{0.18}CoO_3$ exhibits no temperature dependence, in sharp contrast with what has been found in undoped $LaCoO_3$.[11,27] In the latter case, one observes at ambient pressure a large change of about 30% of the Co^{3+} ions to the HS state with increasing temperature, which is due to the thermal excitation from the LS ground state to the HS state.[11] This difference is also reflected in the observed different thermal expansion of the pure and doped compounds.[8] The ground state of our doped ferromagnetic sample is essentially different from that of undoped $LaCoO_3$. The Co^{3+} spin state is magnetic (HS and IS) already at 34 K. In fact, the creation of magnetic polarons as a result of Sr^{2+} doping leads to an internal transformation of LS Co^{3+} to HS or HS-IS states.[17,34] In this context, we would like to refer to nuclear magnetic resonance studies on $La_{1-x}Sr_xCoO_3$ ($0.1 \leq x \leq 0.5$),[35,36] which show in the ferromagnetic state clear evidence for magnetic phase separation. We thus believe that the above-mentioned factors are responsible for the absence of a temperature-induced change of the Co^{3+} spin state in $La_{0.82}Sr_{0.18}CoO_3$ at ambient pressure. As the pressure increases, the fraction of HS or IS Co^{3+} gradually transforms to a LS state and an energy gap is opened between the LS and the higher-lying HS or IS state. This leads to the observation of a temperature-dependent spin state at higher pressures. However, the amount of thermal excitation in $La_{0.82}Sr_{0.18}CoO_3$ is more than a factor of 2 smaller than that of undoped $LaCoO_3$. Such a small thermal excitation between 34 and 300 K is expected, since the crystal field splitting becomes very large at 14.4 GPa, so that much higher temperatures are required to induce a LS to HS or IS transition. This explanation is strongly supported by the observation of a dramatic increase of the spin-state transition temperature in $La_{1-x}Eu_xCoO_3$ due to chemical pressure:[37] a partial substitution of La^{3+} by smaller Eu^{3+} ions results in an enhancement of the crystal field splitting from about 230 K ($LaCoO_3$) to more than 2000 K for $EuCoO_3$.

Finally, we compare the observed pressure-induced decrease of the Co^{3+} spin state by XES with the pressure dependence of the Co magnetic moment (μ_{Co}) in $La_{0.82}Sr_{0.18}CoO_3$.[19] In order to compare the pressure-induced change of the Co magnetic moment with that of the Co^{3+} spin state, we have plotted in Fig. 3 the experimental values of μ_{Co} of $1.21\mu_B$ and $1.14\mu_B$ at ambient pressure and 1 GPa, respectively. Since these values are far from the saturation values of μ_{Co}, the magnetization data show only that the initial decrease of the Co magnetic moment with pressure follows in trend that of the Co spin state. In fact, even if one were to obtain the saturation values of μ_{Co}, magnetization measurements do not allow a direct determination of the spin state. In contrast, the XES technique provides a direct measure of the spin state independent of whether the system is magnetically ordered or not. This comparison clearly demonstrates the strength of the XES technique as a microscopic tool for the investigation of the Co spin state and its pressure dependence in an extended pressure range. Our XES data clearly prove a pressure-induced spin-state transition to a LS state. This spin-state transition is the driving mechanism of the pressure-induced metal-insulator transition in $La_{0.82}Sr_{0.18}CoO_3$.

In summary, we have investigated the effect of pressure on the Co spin state of conducting ferromagnetic single crystals of $La_{0.82}Sr_{0.18}CoO_3$ up to 14.4 GPa at 300 and 34 K using $K\beta$ x-ray emission spectroscopy. The analysis of the experimental results clearly reveals a gradual pressure-induced spin-state transition from the high or intermediate-spin to a low-spin state and thus provide microscopic evidence that the pressure-induced metal-insulator transition in this system is driven by a simultaneous spin-state transition. In contrast to $LaCoO_3$ we find that the pressure-induced LS Co^{3+} state is relatively stable against temperature. This is attributed to an enhancement of the crystal field splitting at high pressures.

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