

## A complete high-to-low spin state transition of trivalent cobalt ion in octahedral symmetry in $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$

The largest spin state variability of  $\text{Co}^{3+}$  is reported mainly for metal oxide compound, often within crystal structures where cobalt is coordinated by four to six oxygen ions. Low-spin (LS)  $\text{Co}^{3+}$  is found in  $\text{LiCoO}_2$ ,  $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ , and in  $\text{LaCoO}_3$  at low temperature.  $\text{LaCoO}_3$  is intensively studied and its controversial spin state cross-over upon heating is still debated [1,2]. High-spin (HS)  $\text{Co}^{3+}$  in a tetrahedral local symmetry was found in a mixed valent cobalt oxide  $\text{YBaCo}_4\text{O}_7$ . The pure HS  $\text{Co}^{3+}$  in a square pyramidal  $\text{CoO}_5$  coordination occurs in  $\text{Sr}_2\text{CoO}_3\text{Cl}$  and  $\text{BiCoO}_3$ . However, the pure HS  $\text{Co}^{3+}$  oxide in octahedral local symmetry is rarely documented. Also, there is a steady debate on the issue whether the octahedrally coordinated  $\text{Co}^{3+}$  has a mixed HS-LS state or an intermediate spin (IS) state in the new classes of cobaltates  $\text{RBaCo}_2\text{O}_{5.5}$  ( $\text{R}$  = rare-earth metal),  $\text{Sr}_{1-x}\text{Y}_x\text{CoO}_{3-\delta}$ ,  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$ , as well as in  $\text{LaCoO}_3$  at high temperature. All the extraordinary material properties of the cobaltates, including superconductivity, giant magnetoresistance, strong thermopower, metal-insulator transitions, as well as spin-blockade behavior are related to the spin state degree of freedom of the cobalt ion. Hence, if the debate around the IS state is settled the interpretations of the material properties of cobalt based metal oxides are simplified remarkably.

The complex metal oxide  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$  possesses a slightly distorted perovskite crystal structure. Figure 1 displays the unit cell of the body centered monoclinic crystal structure as well as the local oxygen coordination of the transition metal site. From the crystal structure refinement, the Co-O distances are unusually large, ranging from 1.96 to 2.00 Å. The Co-K EXAFS data reveal an average Co-O distance of  $1.98 \pm 0.02$  Å [3]. This distance is even larger than that in  $\text{LaCoO}_3$  at 1000 K. At 650 K the average distance in  $\text{LaCoO}_3$  was found to be 1.949 Å, a state which was proposed to have half of the cobalt ions in a HS state, whereas Co-O distance for IS  $\text{Co}^{4+}$  ion in  $\text{SrCoO}_3$  is 1.918 Å.

Based on soft-X-ray absorption spectroscopy in combination with multiplet calculations, we have demonstrated that the  $\text{Co}^{3+}$  ion in  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$  is high-spin, which is unique for  $\text{Co}^{3+}$  in octahedral oxygen coordination [3]. To investigate whether the HS state in  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$  can be converted to an IS or LS state on applying pressure, a  $\text{K}\beta$  emission experiment was carried out. The high pressure Co  $\text{K}\beta$  X-ray emission spectra were obtained at the Taiwan inelastic X-ray scattering beamline

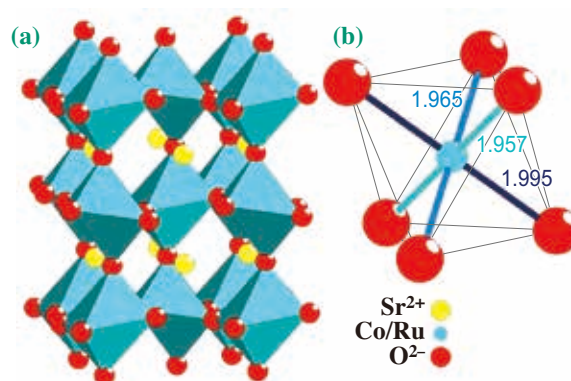


Fig. 1. Part of the  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$  crystal structure (left) and the local transition metal surrounding with bond lengths in Å to the neighboring oxygen ions (right).

**BL12XU.** Figure 2(a) shows the evolution of the Co  $\text{K}\beta$  X-ray emission line of  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$  as a function of pressure from ambient up to 39.6 GPa at room temperature. At ambient pressure, the Co  $\text{K}\beta$  emission spectrum reveals a main peak located at  $\sim 7650$  eV referred to as the  $\text{K}\beta_{1,3}$  line and a pronounced satellite peak located at  $\sim 7637$  eV corresponding to the  $\text{K}\beta'$  line. At high pressures, e.g., 39.6 GPa, the satellite peak nearly disappears and the main line gets narrower. This is similar to what happens for the  $\text{K}\beta$  emission spectrum of  $\text{LaCoO}_3$  at low temperatures, indicating that the LS state has been reached for  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$ . In fact, the spectral changes are alike those found for the complete spin state transition in FeS from 0 to 11.5 GPa and for  $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$  from 20 to 120 GPa, where  $\text{Fe}^{2+}$  also has the  $3d^6$  electronic configuration. This infers that the applied pressure induces a complete HS to LS transition in  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$ . The inset of Fig. 2(a) contains a plot of the so-called integrated absolute difference (IAD) as a function of pressure and the total IAD changes by about 0.15 in going from ambient pressure to 39.6 GPa. This 0.15 value is consistent with what is expected for a complete HS to LS transition.

Important is that the spectral changes with pressure are continuous without any signs for new features that otherwise could indicate the presence of spin states other than the HS and LS. This is apparent in Fig. 2(b), displaying a comparison between the difference spectrum of  $\text{K}\beta$  emissions taken at ambient pressure (AP) and at 39.6 GPa (black line) with the difference

spectrum of emissions taken at 15.8 GPa and at 39.6 GPa (green line). The black curve represents the spectral changes associated with a change in the average spin expectation value  $S$  from 2 to 0, and the green curve for a change of  $S$  from  $\approx 1$  to 0. Note that the difference spectra are identical apart from the expected scaling factor of two. This infers that the system at 15.8 GPa is in a  $\sim 1:1$  mixed HS:LS state, and not in an IS state, as otherwise the difference spectrum would show new features [4].

To understand the above experimental observations, the total energy level diagram of the cobalt ions as a function of Co-O distance was calculated (Fig. 3). Clearly, the ground state of  $\text{Co}^{3+}$  ions is either HS or LS (not IS) with a crossover at Co-O distance about 1.93 Å, where the HS and LS states are strongly mixed. Thus, Fig. 3 describes the evolution of the spin state during the compression induced by high pressure for  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$  and reversely, during the expansion upon increasing the temperature for  $\text{LaCoO}_3$ . Note that the IS states are remarkably unfavorable in energy in comparison to the HS and LS states.

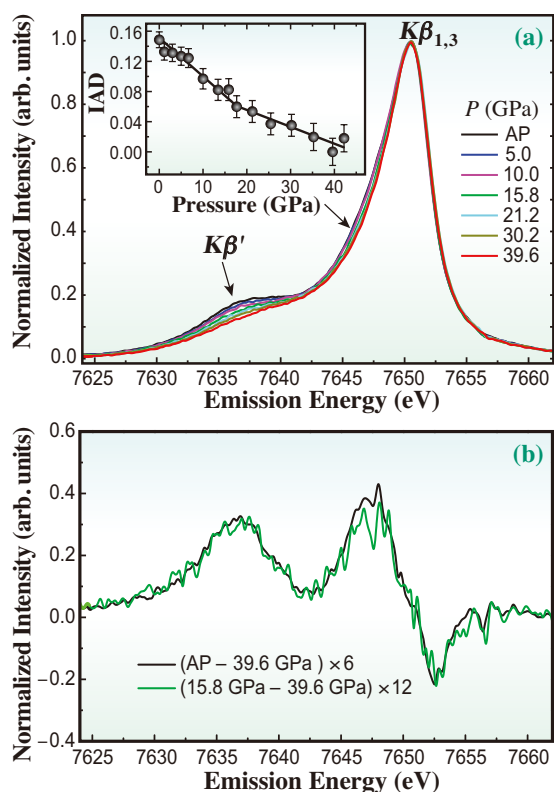


Fig. 2. (a) Evolution of the Co  $K\beta$  X-ray emission spectra of  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$  under pressure up to 39.6 GPa at room-temperature. The inset shows IAD values of Co  $K\beta$  emission spectra as a function of applied pressure with respect to 39.6 GPa. (b) Difference spectrum of the Co  $K\beta$  emissions taken at ambient pressure (AP) and 39.6 GPa (full black line) and taken at 15.8 GPa and 39.6 GPa (green dashed line).

In fact, the lowest of the IS states is already  $\sim 0.4$  eV ( $\sim 4000$  K) higher than the degenerated LS and HS at the Co-O distance 1.932 Å. These results allow us to draw an energy diagram depicting relative stabilities of the high, intermediate, and low spin states as functions of the metal-oxygen bond length for a  $\text{Co}^{3+}$  ion in an octahedral coordination.

A gradual high-to-low spin state transition in  $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{2.96}$  is completed by applying high hydrostatic pressure of up to  $\sim 40$  GPa. Across this spin state transition, the Co  $K\beta$  emission spectra can be fully explained by a weighted sum of the high-spin and low-spin spectra. We have not found any signs of the much debated intermediate spin state at any stage during the pressure induced spin state transition in this material.

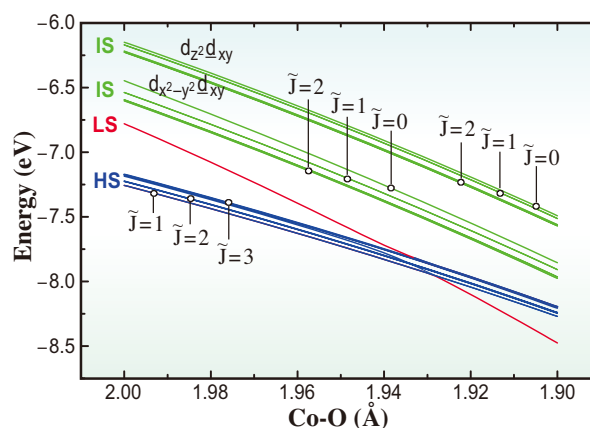


Fig. 3. Energy level diagram of a  $\text{CoO}_6$  cluster as a function of the Co-O distance.

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