The Spin State Transition in $LaCoO_3$; Revising A Revision

Using 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 lineshapes we find that $LaCoO_3$ at finite temperatures is an inhomogeneous mixed-spin-state system.

$LaCoO_3$ shows a gradual non-magnetic to magnetic transition with temperature, which has been interpreted originally four decades ago as a gradual population of high spin (HS, $t_{2g}^4e_g^2$, S=2) excited states starting from a low spin (LS, t_{2g}^6, S=0) ground state. This interpretation was changed after theoretical work of Korotin *et al.* in 1996, 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, $t_{2g}^5e_g^1$, S=1) type. Since then many more studies have been carried out on $LaCoO_3$ with the majority of them claiming to have proven the presence of this IS mechanism. In fact, this LDA+U work is so influential that it forms the basis of most explanations for the fascinating properties of the recently synthesized layered cobaltate materials, which show giant magneto resistance as well as metal-insulator and ferro-ferri-antiferro-magnetic transitions with various forms of charge, orbital and spin ordering. Here we revealed by using the Co-$L_{2,3}$ XAS spectrum 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.

Fig. 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 [3], but it is in fact essentially different in details. First of all, our set 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. The extended temperature range and especially the purity of the probed samples provide the required sensitivity for the spin-state related spectral changes.

Beamline

11A Dragon

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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 $2p^53d^{n+1}$ final states can be reached and with what intensity, starting from a particular $2p^63d^n$ initial state (n=6 for Co^{3+}). This makes the technique extremely sensitive to the symmetry of the initial state, e.g. the spin state of the Co^{3+}. 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. The CoO_6 cluster is taken to have the octahedral symmetry and the parameters are the same as the ones which succesfully reproduce the spectrum of LS $EuCoO_3$ [4]. 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 cross-over at about 10Dq=0.58 eV. 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. 3a. The corresponding effective activation energy is plotted in Fig 3b. 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 [5]. Here we would like to point out that these numbers are of the order k_{BT} and reflect total energy differences which include lattice relaxations as sketched in the inset of Fig. 3b. 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_{BT}. 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. 3a as derived from the XAS data. The results are plotted in Fig. 3c (red 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

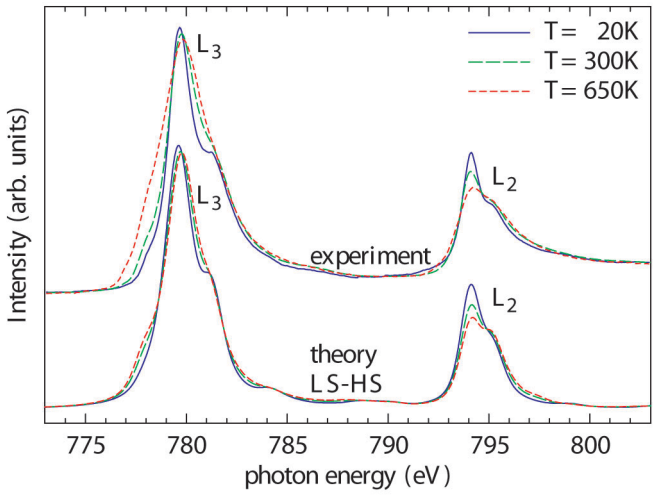

Fig. 1: Experimental and theoretical Co-$L_{2,3}$ XAS spectra of $LaCoO_3$ as a function of temperature.

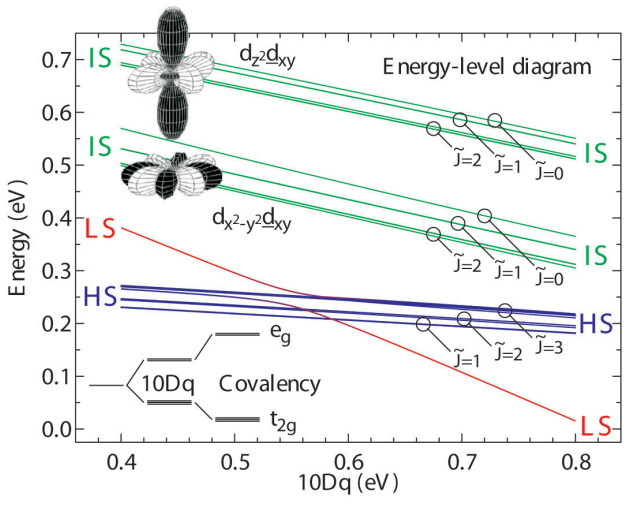

Fig. 2: Energy level diagram of a CoO_6 cluster as a function of the ionic part of the crystal field splitting 10Dq.

dependence is 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 to peak at 110 K. 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.

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 what the IS actually is. The IS state has one hole in the t_{2g} shell and one electron in the e_g shell. Due to the strong orbital dependent Coulomb interactions, the strong-Jahn-Teller states of the type $d_{z2}\underline{d}_{xy}$ and their x,y,z-cyclic permutations have much higher energies than the weak-Jahn-Teller $d_{x2-y2}\underline{d}_{xy}$ plus cyclic permutations. Here the underline denotes a hole. These weak-Jahn-Teller states indeed form the basis for the orbital ordering scheme as proposed for the IS scenario by Korotin. However, these real-space states do not carry a large orbital momentum, and are therefore not compatible with the values of $L_z/S_z = 0.5$ observed in the MCD measurements. Likewise, the strong Jahn-Teller-like local distortions in the IS state proposed by Maris *et al*. 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 110K. 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. A consistent picture has now been achieved which also explains available magnetic susceptibility, ESR and INS data.

We acknowledge the NSRRC staff for providing us with an extremely stable beam.

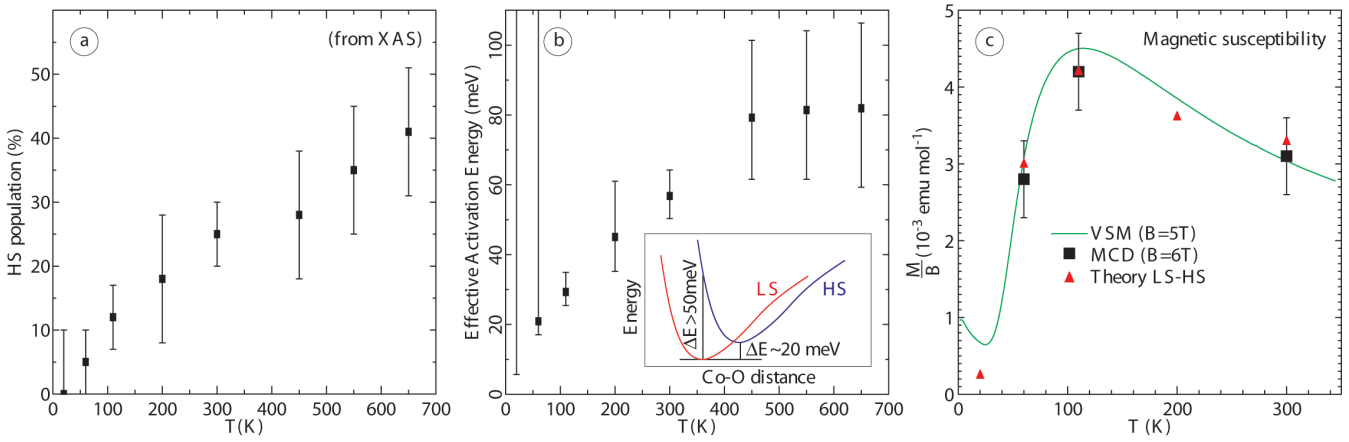

Fig. 3: (a) The percentage of the HS population as obtained from the XAS data. (b) Corresponding effective activation energy between the LS and the lowest HS state. The inset sketches the role of lattice relaxations. (c) Magnetic susceptibility measured by VSM (solid line), calculated from the cluster (red triangles) using the HS population of Fig. 3a.

Experimental Station

XAS chamber of the Universität zu Köln, Germany

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