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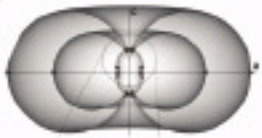
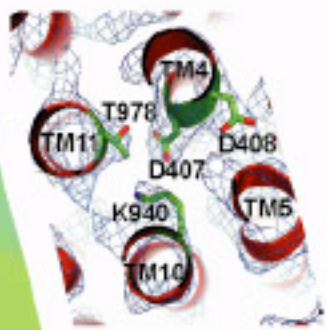
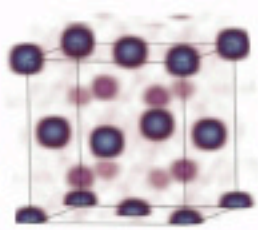
European Synchrotron Radiation Facility

Highlights

2006







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SCIENTIFIC HIGHLIGHTS

X-ray Absorption and Magnetic Scattering

Introduction

The Highlights in our selection this year are extremely diverse in their subject matter. This demonstrates the great versatility of the techniques used and the scientific interest in many fields of research. There are materials problems (ferroelectrics [Laulhé *et al.* p80] and negative thermal expansion [Sanson *et al.* p82]), catalysis [Newton *et al.* p78], geology [Muñoz *et al*. p79], studies at interfaces [Luches *et al.* p86], impurity problems [Sarigiannidou *et al.* p87] and dynamical studies [Goulon *et al.* p90], to name a few.

As in the past few years there are also many X-ray absorption studies which combine techniques, whether it be with diffraction (X-ray or neutron) or other spectroscopic methods. These combinations allow unique information to be obtained that would otherwise not be possible; see for example the catalysis study combining *in situ* time-resolved infrared and X-ray absorption spectroscopy [Newton *et al.* p78].

Studies with an emphasis on basic research also have a prominent place. For example, Kondo phenomena [Venturini *et al.* p94], spin states [Haverkort *et al.* p88], dynamics [Goulon *et al.* p90] and multipolar ordering [Mazzoli *et al.* p91 and McEwen *et al.* p92]. This is extremely important, showing the health of the entire scientific field where both basic and applied problems can be addressed and where the limits are only the imagination of the scientists.

Clearly, there are many other examples of outstanding research which could not be included for space reasons. There are contributions to our understanding of the physics of magnetism at interfaces (ferromagnetic/antiferromagnetic [1] and ferromagnetic/superconducting [2]), magnetic impurities [3] and magnetism in nanoparticles [4]. Important work on metal-insulator transitions [5] and undercooling phenomena in nanoparticles [6] has also been carried out. In addition, synchronised time-resolved UV-Vis/XAS studies of catalysts [7] has added to the suite of *in situ* studies in chemistry. Nevertheless, these studies only represent a small part of the important research work being under taken in this general research area. This large body of work gives us confidence in the scientific future for the research fields addressed by X-ray absorption and magnetic scattering.

With the strong growth of synchrotron research in Europe and around the World there will be many possibilities for making important gains in our scientific understanding and consequently, it is important to look beyond what we have today and will have tomorrow and look towards the scientific challenges of the future. This will give us the “Highlights” of the coming decades.

N. Brookes

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[3] K. W. Edmonds *et al., Phys. Rev. Lett.* **96**, 117207 (2006).
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[5] T. C. Koethe *et al., Phys. Rev. Lett.* **97**, 116402 (2006).
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K edge (identical to the Ga K-edge XLD of GaN single crystal), but its amplitude is 1.8 times smaller. This is precisely what one would observe for the Mn atoms in substitution with Ga atoms, whereas for other possible Mn sites occupation, *e.g.* N-substituted or interstitial sites, the spectral shape and amplitude of XLD signal should be drastically different [1]. Within the detection limit of the method, the presence of any secondary phases or metallic clusters have not been revealed. The XANES spectrum at the Mn K edge in contrast with XLD spectra are quite different from those at the Ga *K* edge. Two additional peaks at the low-energy side of the absorption edge are observed. These two peaks originate from both quadrupolar ($1s \rightarrow 3d$) and dipolar ($1s \rightarrow 4p$) transitions reflecting hybridisation of the Mn impurity 4*p* band with the 3*d* band located in the GaN gap. The presence of these two peaks in the XANES spectra indicates that the valence state of Mn is mainly 3+ (d^4) rather than 2+ (d^5), where only one peak is usually observed. To elucidate the microscopic origin of the magnetic behaviour of (Ga,Mn)N, we have performed XMCD measurements at the Mn *K* edge (**Figure 112**). A very intense XMCD signal (1.6% with respect to the edge jump) is observed mainly at the first peak of the XANES spectrum. Given the fact that only the orbital magnetisation of the absorbing atom gives rise to the K-edge XMCD signal, our result provides another strong argument in favour of the Mn^{3+} valence state in wurtzite (Ga,Mn)N. Indeed, in the case of Mn^{2+} where the 3*d* and 4*p* orbital moments are vanishingly small, the XMCD signal is at least one order of magnitude smaller. Moreover, the negative sign of the XMCD signal suggests that the Mn orbital magnetic moment is antiparallel to the applied field and, therefore, to the sample magnetisation. The inset of **Figure 112** shows the magnetisation curve recorded by monitoring the Mn *K*-edge XMCD signal as a function of applied field at 7 K. This magnetisation curve is a typical signature of a ferromagnetic system in the vicinity of a transition temperature. In conclusion, thanks to the element specificity of XLD and XMCD, we have demonstrated that wurtzite (Ga,Mn)N with 6.3% Mn is a intrinsic ferromagnetic DMS with a rather low Curie temperature of only 8K.

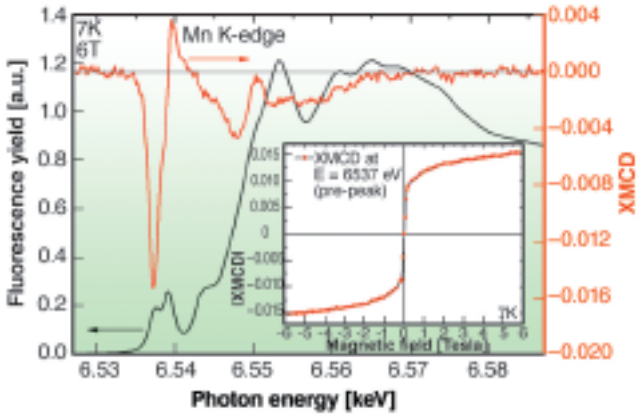

Fig. 112: Isotropic XANES spectrum (black line, left scale) and corresponding XMCD signal (red line, right scale) recorded at the Mn *K* edge measured under 6 Tesla in-plane field and at 7 K for a (Ga, Mn)N film with 6.3% Mn. Inset: magnetisation curve measured at 7 K by monitoring the amplitude of the Mn *K*-edge XMCD signal.

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[1] F. Wilhelm, E. Sarigiannidou, E. Monroy, A. Rogalev, N. Jaouen, H. Mariette and J. Goulon, *AIP Conference Proceedings* 879, 1675 (2007).

Principal Publication and Authors

E. Sarigiannidou (a,d), F. Wilhelm (b), E. Monroy (a), R.M. Galera (c), E. Bellet-Amalric (a), A. Rogalev (b), J. Goulon (b), J. Cibert (c), and H. Mariette (a), *Phys. Rev. B* **74**, 041306(R) (2006).
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Spin state transition in $LaCoO_3$ studied using soft X-ray absorption spectroscopy and magnetic circular dichroism

$LaCoO_3$ shows a gradual non-magnetic to magnetic transition with temperature, the nature of which has been highly debated over the last few decades. Starting from a low-spin (LS, $t_{2g}^6e_g^0$, S=0) ground state for the Co^{3+} ion at low temperatures, either a high-spin (HS, $t_{2g}^4e_g^2$, S=2) or an intermediate-spin (IS, $t_{2g}^5e_g^1$, S=1) first excited state becomes populated at elevated temperatures. In the recent past, local density approximation + Hubbard U (LDA+U) band structure calculations predict the IS state to be lower in energy than the HS [1]. Nowadays, this forms the basis of most explanations for the fascinating properties of the recently synthesised layered cobaltate materials, which show giant magnetoresistance and metal-insulator/magnetic transitions with various forms of charge, orbital, and spin ordering. In this work carried out at the ID08 beamline, we examined the validity of this prediction and have arrived at an unexpected conclusion.

We used soft X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (MCD) at the Co $L_{2,3}$ edge. **Figure 113** shows the XAS and MCD spectra taken at 60, 110 and 300 K, *i.e.* in the paramagnetic phase, using a 6 Tesla magnet. The MCD signal is only in the order of 1%,

but can nevertheless be measured very reliably due to the good signal to noise ratio, stability of the beam, and the accurate photon energy referencing. In the figure, the experimental MCD curves are compared to theoretical spectra calculated for a CoO_6 cluster. We are able to obtain good agreement for an inhomogeneously mixed LS-HS scenario (see **Figure 113**), but not for a mixed LS-IS.

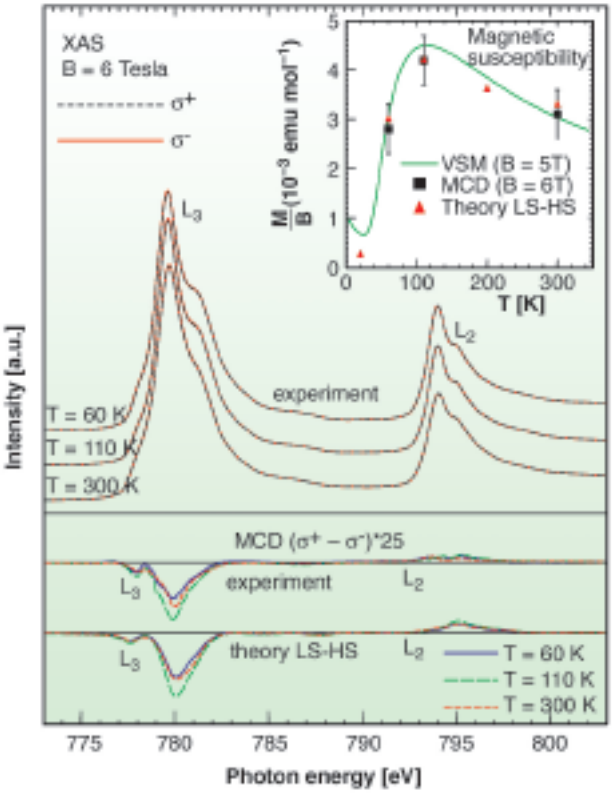

Fig. 113: Top: experimental Co-$L_{2,3}$ XAS spectra taken from $LaCoO_3$ at 60, 110, and 300 K using circularly polarised X-rays with the photon spin aligned parallel (σ^+) and antiparallel (σ^-) to the 6 Tesla magnetic field. Middle: experimental MCD spectra. Bottom: theoretical MCD spectra calculated in the LS-HS scenario. Inset: Magnetic susceptibility measured by VSM (solid line), calculated from the cluster (triangles) using the HS population obtained from the XAS spectra and extracted from MCD data (squares).

To check our data, we use the MCD sum-rules to extract the values for the orbital (L_z) and spin ($2S_z$) contributions to the induced moments. These results normalised to the magnetic field are plotted in the inset of **Figure 113**. They are in close agreement with the magnetic susceptibility as measured using a vibrating sample magnetometer (VSM).

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 ~1/2. This means first of all that the spin-orbit coupling must be considered in evaluating the energy level diagram, as is done in **Figure 114**. Second, and crucial for the spin-state issue, this large L_z/S_z ratio allows us to directly verify the LS-HS scenario and falsify the LS-IS. One should realise that a

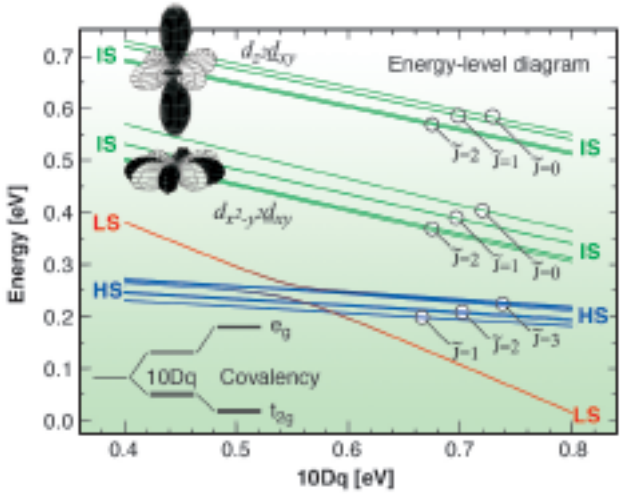

Fig. 114: Energy level diagram of a CoO_6 cluster as a function of the ionic part of the crystal field splitting $10Dq$.

t_{2g} electron has a pseudo orbital momentum of 1, which couples with the spin. For the HS state we find a lowest state that is a triplet, with $L_z = 0.6$, $S_z = 1.3$ and a g-factor of 3.2, in good agreement also with ESR experiments. For the IS state, the hole in the t_{2g} shell couples with the electron in the e_g shell due to the strong orbital dependent Coulomb interactions leading to a $d_{x^2-y^2}d_{xy}$ state plus their x, y, z-cyclic permutations (see **Figure 114**). The e_g electron in turn, couples to the lattice and this leads, according to LDA+U [1], to the formation of an orbital ordered state. This 'real-space' state, however, does not carry a large orbital momentum and is therefore not compatible with the values observed in our MCD measurements.

To summarise, we find 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 at elevated temperatures an inhomogeneous mixed-spin state system is formed. The large orbital momentum revealed by the MCD measurements invalidates existing LS-IS scenarios. Consequently, the spin-state issue for the new class of the layered cobaltates needs to be reinvestigated.

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