

Experiment Report Form

	Experiment title: $\text{Ca}_3\text{Co}_2\text{O}_6$	Experiment number: HE-1644
Beamlne: ID08	Date of experiment: from: 01-08-2004 to: 04-08-2004	Date of report: 18-02-2005
Shifts: 9	Local contact(s): Nick Brookes, Júlio Criginski Cezar	<i>Received at ESRF:</i>
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The peculiar magnetic and structural properties of $\text{Ca}_3\text{Co}_2\text{O}_6$ have attracted great interest in recent years [1-7]. The rhombohedral structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ consists of $[\text{Co}_2\text{O}_6]_\infty$ chains running along the *c*-axis. The intrachain and interchain couplings are ferromagnetic ($T_{c1} = 24$ K) and antiferromagnetic ($T_{c2} = 12$ K), respectively. In each chain, one $\text{Co}(1)\text{O}_6$ octahedron alternates with one $\text{Co}(2)\text{O}_6$ trigonal prism along the *c*-axis. The magnetism of $\text{Ca}_3\text{Co}_2\text{O}_6$ has been described as a planar Ising triangular lattice because of the observation of a magnetic field induced transition from a ferri- to a ferromagnetic state. The spin and valence state of Co ions on both the octahedra and trigonal prisms are still unclear as discrepancy persists among low-temperature neutron-diffraction [2], high-field magnetization [3-6] and magnetic susceptibility measurements [2,4]. Two scenarios have been proposed by Aasland *et al.* for the spin and valence state of the Co ions: (i) $\text{Co}(1)^{3+}$ low spin (LS) with $\mu=0\mu_B$ and $\text{Co}(2)^{3+}$ high spin (HS) with $\mu=4\mu_B$, (ii) $\text{Co}(1)^{4+}$ LS with $\mu=1\mu_B$ and $\text{Co}(2)^{2+}$ HS with $\mu=3\mu_B$ [2]. Vidya *et al.* have proposed a third scenario: (iii) $\text{Co}(1)^{4+}$ and $\text{Co}(1)^{2+}$ LS with an average $\mu=1\mu_B$, and $\text{Co}(2)^{3+}$ HS with $\mu=4\mu_B$ [8].

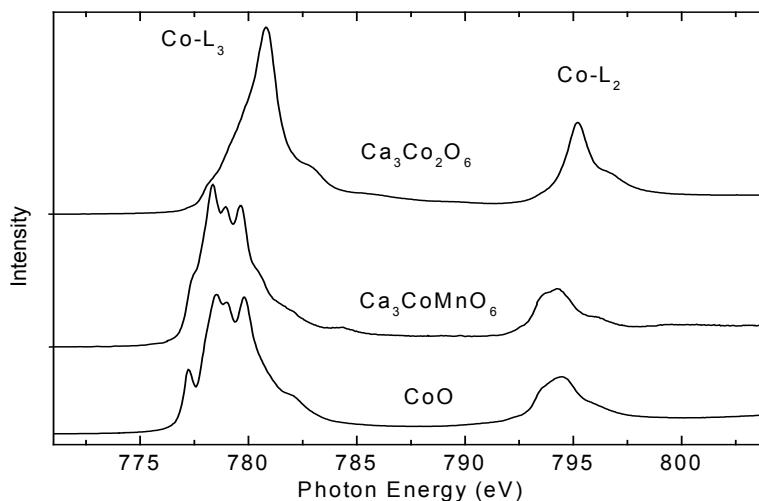


Fig. 1. The Co-L_{2,3} XAS (isotropic) of $\text{Ca}_3\text{Co}_2\text{O}_6$, $\text{Ca}_3\text{CoMnO}_6$ and CoO .

In an earlier work, we have carried out at the NSRRC-Taiwan a comparative study of the Co-L_{2,3} XAS spectra of Ca₃Co₂O₆, Ca₃CoMnO₆ and CoO. Ca₃CoMnO₆ is a useful material for comparison because a neutron diffraction study indicated that the Co ions here occupy only the trigonal prism site [9]. As shown in Fig.1. the Co spectrum of Ca₃Co₂O₆ is quite different from that of Ca₃CoMnO₆ and CoO, while the latter two have quite similar spectral structures. First of all, we can conclude that the Co ion in Ca₃CoMnO₆ is in a divalent state, which is further confirmed by the observation that the Mn ion is in a tetravalent state (not shown here). Secondly, we can conclude that there is no Co²⁺ ion in Ca₃Co₂O₆, be it in the octahedral or trigonal sites. We thus can reasonably exclude scenarios (ii) and (iii), and continue to work with the hypothesis that all Co ions are in the trivalent state.

During the 01-08-2004 to 04-08-2004 period, we have carried out x-ray magnetic circular dichroism (XMCD) measurements at the Co-L_{2,3} edges on single crystals of Ca₃Co₂O₆ at the ID8 beamline at the ESRF. The c axis is oriented along the magnetic field and the incident photon beam.

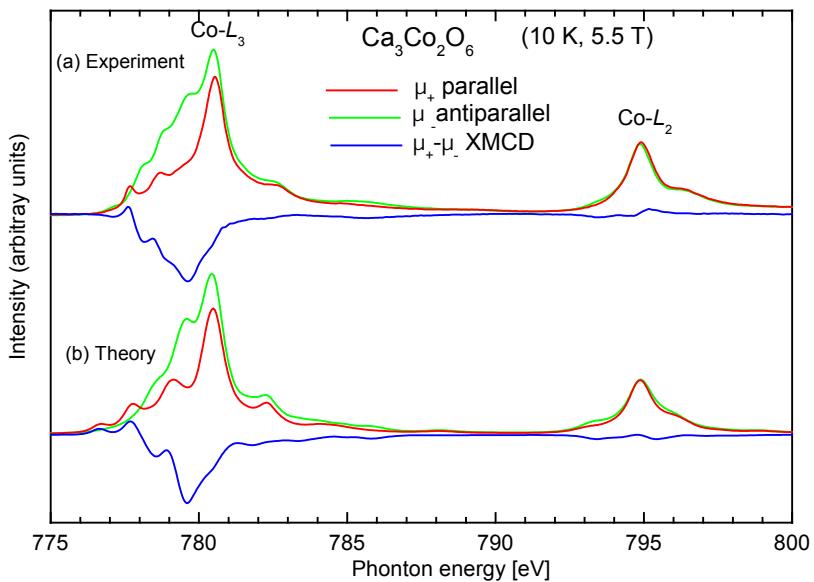


Fig. 2. The Co-L_{2,3} XAS and XMCD spectra of Ca₃Co₂O₆: (a) Experimental data taken at 10 K and 5.5 T. (b) Theoretical cluster calculations with Co(1) in the LS and Co(2) in the HS trivalent state.

Fig. 2 shows the Co-L_{2,3} XAS spectra for parallel (red line, μ_+) and antiparallel (green line, μ_-) alignment of the magnetization and photon spin, together with the difference spectrum (XMCD spectrum). The dichroic effect defined as $(\mu_+ - \mu_-)/(\mu_+ + \mu_-)$ is very large, up to 37%. The spectra are taken with the sample at 10 K under 5.5 T magnetic field, ensuring that the sample is fully magnetized according to magnetization measurements [5]. The main XMCD structures (blue line, $\mu_+ - \mu_-$) are positioned at a significantly lower energy as compared to the main peak of the individual XAS spectra. This suggests that the XAS spectra are composed of two different Co spectra, with only one of the two showing the XMCD effect. In other words, the data suggest that one of the two Co sites is in the non-magnetic LS state and that the other Co site is the HS state.

It is important to realize that the spin state of a Co³⁺ ion is very sensitive to the balance of the relative strengths of the crystal field and the Hund exchange. A famous example for this is LaCoO₃ [10]: at low temperatures (5K) LaCoO₃ is non-magnetic with a Co-O bond length of 1.9254 Å, and at high temperatures (650K) it is paramagnetic with a bond length of 1.9487 Å [11]. In Ca₃Co₂O₆, the trivalent Co(1) ion in the octahedral environment has the very short Co-O average bond length of 1.916 Å, and it is natural to expect that this ion is subjected to a large crystal field with the consequence that it probably will be in the LS state. In contrast, the trivalent Co(2) ion in the trigonal prism environment has the very large Co-O bond length of 2.062 Å, which is much larger than that of LaCoO₃ above 650 K, so that it is likely that this ion will be in the HS state.

To confirm our assignment for the Co(1) being in the trivalent-LS state and the Co(2) in the trivalent-HS, we have carried out CoO_6 cluster calculations which take into account the full atomic multiplet theory, local crystal field effects, and hybridization of the Co with the O ligands. Part of the one-electron parameters has been deduced from band structure calculations [12]. The results are shown in Fig.2. An excellent agreement between simulation and experiment can be observed. We indeed find that the Co(1) is in the LS state and does not contribute to the XMCD signal, and that the Co(2) is in the HS state and produces the entire XMCD.

An important result that can be directly obtained from the XMCD signal concerns the magnitude of the orbital moment of the Co ions. Using the sum rule developed by Thole et al. [13], we find that the Co(2) HS ion carries an orbital momentum of $1.2 \mu_B$. This value is exceptionally large, i.e. larger than the $1 \mu_B$ value that one usually encounters for 3d ions with an open t_{2g} shell in a cubic-like local environment. Such a large orbital moment can be associated with the rather unusual local environment of the Co(2): the quantum numbers t_{2g} and e_g are no longer useful in a trigonal prism surrounding, instead one is much better off using the magnetic angular momentum quantum numbers $m_l = -2, -1, 0, 1, 2$. The crystal fields in this surrounding lead to a large splitting between the $m_l = -1, 1$ orbitals on one hand, and the $m_l = -2, 0, 2$ on the other hand, with the latter set of orbitals lying lower in energy. For a HS d^6 configuration, this means in a simplified one-electron picture, that all the spin up $m_l = -2, -1, 0, 1, 2$ orbitals are occupied and that one of the spin down $m_l = -2, 0, 2$ orbitals is occupied (or a linear combination of them). Which of these three orbitals or which linear combination is indeed occupied depends on the relative strength of the spin-orbit interaction, the sign of the small crystal field splitting between the $m_l = -2, 2$ and $m_l = 0$ orbital, and the band formation involving these orbitals. In principle an orbital moment as large as $2 \mu_B$ is possible. Our cluster calculations, which reproduce the experimental spectra extremely well, yield a spin moment of $3.7 \mu_B$ and an orbital moment of $1.2 \mu_B$ for the Co(2) HS ion. The calculated total moment of $4.9 \mu_B$ is in excellent agreement with the magnetization measurements [4], and reproduces the orbital moment value as experimentally derived using the sum-rule. An article reporting these ESRF-based experimental data together with the successful theoretical analysis is in preparation and will be submitted soon for publication.

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