


**Experiment title:**

XMCD study of the behavior of Co orbital magnetic moment along crystal axes of the  $\text{LaCoO}_3$  single crystal in the range of two ferromagnetic phase transitions

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HE-2858

**Beamline:**

ID12

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**Local contact(s): Dr. Alevtina SMEKHOVA**

*Received at ESRF:*

**Dr. Serguei MOLODTSOV - Institut fuer Festkoerperphysik, Technische Universitaet Dresden, D-01062 Dresden, Germany**

**Dr. Vadim SIKOLENKO\* - Laboratory for Neutron Scattering PSI & ETHZ CH-5232, Switzerland**

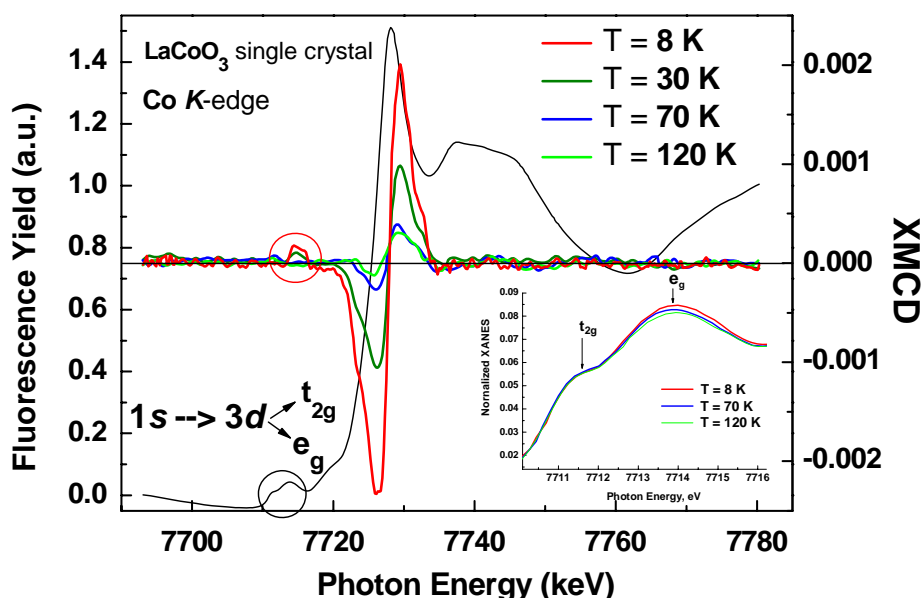
**Mr. Vadim EFIMOV\* - Joint Institute for Nuclear Research, Dubna, Moscow region, Russia**

The peculiar properties of  $\text{LaCoO}_3$  have been intensively studied since 1950's and a lot of controversial explanations of the results of magnetic susceptibility measurements appeared. In the ground state the  $\text{Co}^{3+}$  ions are found to be in the low-spin electronic configuration ( $\text{LS}; t_{2g}^6 e_g^0, S = 0$ ). With temperature increase the spin state of cobalt ions changes gradually in the range of  $T \sim 20$ -100 K followed by a transition into a metallic state at  $T \sim 500$ -600 K. The original interpretation of the low-temperature transition was done in terms of thermally-induced population of the low-lying high-spin state ( $\text{HS}; t_{2g}^4 e_g^2, S = 2$ ). Later, especially after LDA+U band structure calculations [1], another interpretation was put forward: the first transition near  $T \sim 100$  K could be due to a thermal activation of an intermediate-spin state ( $\text{IS}; t_{2g}^5 e_g^1, S = 1$ ) of  $\text{Co}^{3+}$  ions. This interpretation was supported by a number of experimental evidences.

Very recently a soft X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) at the Co  $L_{2,3}$  edge only at the 60 K, 110 K and 300 K as well as theoretical calculations for a  $\text{CoO}_6$  clusters have shown that the spin-state transition in  $\text{LaCoO}_3$  can be well described by a LS ground state and a triply degenerate HS excited state [2]. The large orbital momentum  $L_z/S_z \sim 0.5$  revealed by the XMCD measurements invalidates existing LS-IS scenarios [1].

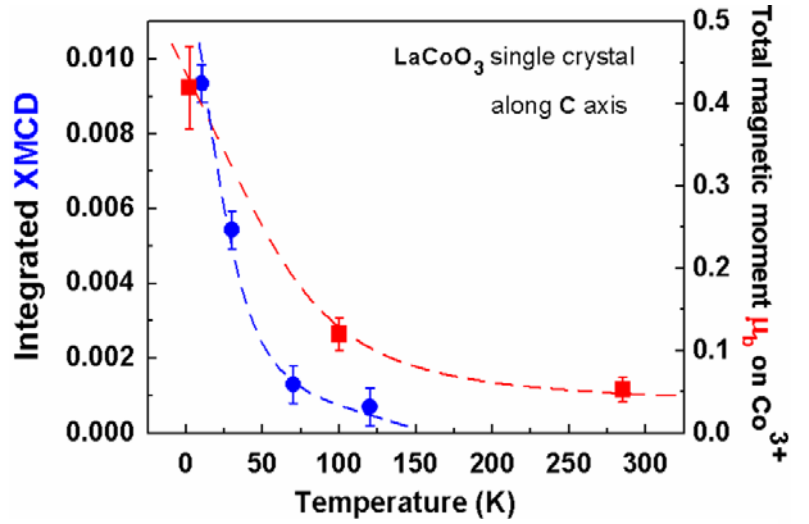
*The goal of the present work is XMCD study of the  $\text{LaCoO}_3$  single crystal at the Co K-edge in order to obtain accurately the magnitude of Co orbital magnetic moment and then to clarify nature of the spin-state transitions.*

**Figure 1** shows the temperature dependence of the normalized XANES and XMCD spectra for  $\text{LaCoO}_3$  single crystal at Co K-edge recorded in total fluorescence yield with electric field vector of X-ray perpendicular to the  $c$ -axis. A quite clear dichroic signal of the order of 0.03 % at  $T = 8$  K with respect to the edge jump is visible at preedge feature of Co. We found that the integrated XMCD signal, which is directly proportional to the orbital magnetic moment, is rapidly reduced to zero with increase of temperature up to 120 K (see **Fig. 1 and 2**). A preliminary calculation (not shown) by non-muffin-tin finite difference method FDMNES for XANES/XMCD simulations [3] for rhombohedral coordination of  $\text{Co}^{3+}$  (space group R-3c and structural

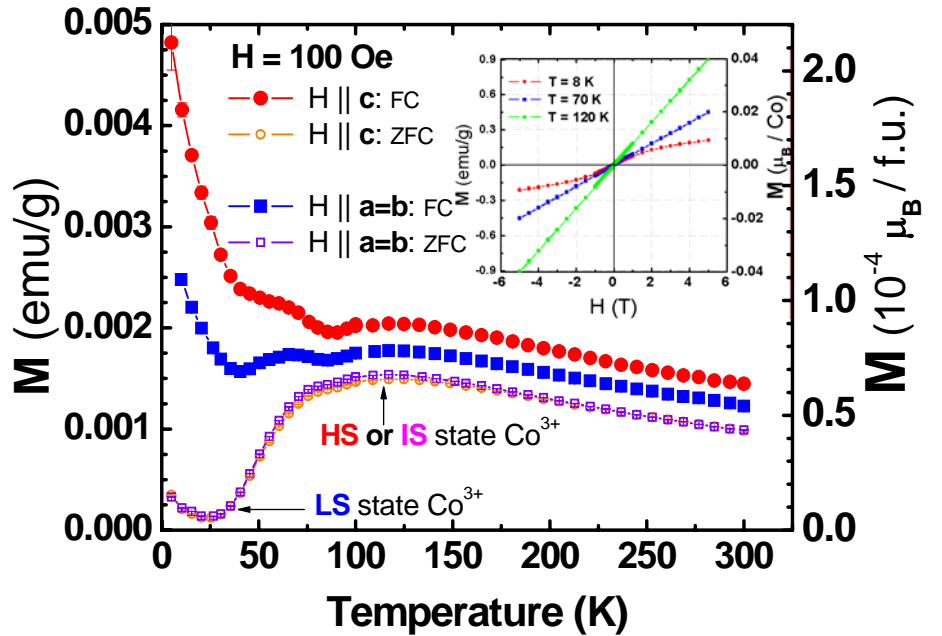


**Fig. 1:** Normalized XANES and XMCD spectra for  $\text{LaCoO}_3$  at the Co K-edge under applied magnetic field of 6 T which is parallel to  $c$ -axis. Inset shows the pre-edge region.

parameters:  $a = 5.4259 \text{ \AA}$ ,  $b = 12.991 \text{ \AA}$ ) with cluster radius  $8.0 \text{ \AA}$  and a core hole lifetime about  $1.3 \text{ eV}$  has shown that orbital moment at  $8 \text{ K}$  is equal to about  $0.09 \pm 0.03 \mu_B$ . It should be noted that our result (see **Fig. 2**) is consistent good with the temperature dependence behavior of total magnetic moment of  $\text{Co}^{3+}$  obtained by polarized neutron diffraction (see **Fig. 2**) [4] as well as with our SQUID-magnetization behavior curve (i.e. difference between of the field-cooled (FC) and zero field-cooled (ZFC) magnitude) (see **Fig. 3**) on the same  $\text{LaCoO}_3$  single-crystal along the  $c$ -axis. Moreover, the  $M(H)$  curves (see inset in **Fig. 3**) measured by SQUID indicate pure paramagnetic behavior. The discrepancy in the behavior of two curves on **Fig. 2** is most probably associated with absence of the *spin* moment contribution of cobalt and oxygen in total local magnetic moment. On the base above-considered result we can conclude that the XMCD data at the Co  $L_{2,3}$ -edges do not correlate well with our XMCD at the Co  $K$ -edge, SQUID-magnetization data and a polarized neutron diffraction study especially in helium temperature range. Such disagreement it could be attributed to a significant influence of crystal surface [5] and especially of  $\text{Co}^{2+}$  ions. It is very interesting to note that in the most recent XMCD data at the Co  $L_{2,3}$ -edges by T. Burnus *et. al.* [6] revealed that  $\text{Co}^{2+}$  ions in  $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  have a large orbital moment  $L_z/S_z \sim 0.47$  which is similar to one observed in  $\text{LaCoO}_3$  single crystal [2]. Thus, the question about the spin state of the Co ions in  $\text{LaCoO}_3$  is still open and is strongly related to the local chemical bonding.



**Fig. 2:** Temperature dependence of the integrated XMCD signals for  $\text{LaCoO}_3$  at the Co  $K$ -edge and the total magnetic moment of  $\text{Co}^{3+}$  obtained from by polarized neutron diffraction [4] under applied magnetic field of  $6 \text{ T}$ .



**Fig. 3:** FC and ZFC temperature dependence of the SQUID magnetization (left axis)/the calculated magnetic moment (right axis) for  $\text{LaCoO}_3$ . The inset shows the temperature dependence of  $M(H)$ -curves.

## References

- [1] M.A. Korotin, S.Yu. Ezhov, I.V. Solovyev, V.I. Anisimov, D.I. Khomskii and G.A. Sawatzky, *Phys. Rev. B* **54**, 5309 (1996).
- [2] M.W. Haverkort, Z. Hu, J. C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, N. B. Brookes, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, *Phys. Rev. Lett.* **97**, 176405 (2006).
- [3] Y. Joly, *Phys. Rev. B* **63**, 125120 (2001).
- [4] V.P. Plakhty, P.J. Brown, B. Grenier, S. V. Shiryayev, S. N. Barilo, S. V. Gavrilov, and E. Ressouche, *J. Phys.: Condens. Matter* **18**, 3517 (2006).
- [5] J.-Q. Yan, J.-S. Zhou and J.B. Goodenough, *Phys. Rev. B* **70**, 014402 (2004).
- [6] T. Burnus, M. W. Haverkort, Z. Hu, H. H. Hsieh, V. L. J. Joly, P. A. Joy, Hua Wu, A. Tanaka, H.-J. Lin,<sup>5</sup> C. T. Chen, and L. H. Tjeng, *Phys. Rev. B* **77**, 125124 (2008).