ESRF	**Experiment title:** X-ray natural circular dichroism in Langasite crystals	**Experiment number**: HE-3903
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Report

Scientific Background

The $La_3Ga_5SiO_{14}$ (LGS) is the prototype of the crystals family, which is widely studied for the striking piezoelectric and non-linear optical properties of its members, related to the non-centrosymmetric nature of its structure type [1,2]. The langasite structure belongs to the trigonal non- centrosymmetric P321 space group. The general formula is $A_3BC_3D_2O_{14}$, thus containing four different cationic sites. The decahedral A site and the octahedral B site form a layer at z=0, while the two tetrahedral sites C and D are located on the plane z=1/2. Half of D position is occupied by Ga atoms, another half is occupied by Si. Due to its atomic arrangement, this structure type is able to accommodate a large number of different cations with various sizes and valences, leading to a wide variety of isostructural compounds. Whenever one of the cations are substituted by ñmagnetic ionsò, these crystals provide interesting examples of coexisting magnetic order and optical or electrical properties and even may possess striking magnetic chirality [3]. XNCD is the most appropriate technique to study the hybridization of electronic states of opposite parity, which are responsible for the optical activity and to give a useful insight into electronic structure of the whole family of langasite compounds.

Experimental details

XNCD spectra in $La_3Ga_5SiO_{14}$ were measured at the Ga K-edge and at the $L_{2,3}$ edges of La. We have used the first harmonic of an APPLE-II helical undulator spectrum for the measurements at La L-edges and the second harmonic for the experiments at the Ga K-edge. The circular polarization rate for these photon energies was in excess of 90 %. X-ray absorption spectra were recorded at room temperature using total X-ray fluorescence yield detection mode. The XNCD spectra were obtained as the direct difference of two x-ray absorption spectra recorded with right- and left circularly polarized X-rays. The XNCD spectra have been recorded for two experimental configurations: a) X-ray wave vector of incident radiation is parallel to the crystal c axis and b) the wave vector is perpendicular to the c-axis.

Results

The space group of langasite allows the existence of the XNCD due to a pseudodeviator part of susceptibility tensor arising from electric dipole - electric quadrupole (E1.E2) interference term [4,5]. Surprisingly, the XNCD signal at the K-edge of Ga (due to *p-d* hybridization) was found to be 5 times more

intense than at the L-edges of La (due to *d-f* or *d-p* hybridization). At all edges, the XNCD signals were found to be twice bigger for experiments with the wave vector along the c axis and to have the opposite sign for measurements for the wave vector perpendicular to the c axis as expected from the angular dependence of XNCD for uniaxial crystal ~ $(3\cos^2\theta - 1)$. The experimental XNCD spectra measured at the Ga K-edge and at the La L_3 edges are shown on figures 1 and 2. On the contrary to XMCD spectra, the XNCD spectrum at the L_2 edge of La has exactly the same intensity and spectral shape as the L_3 one.

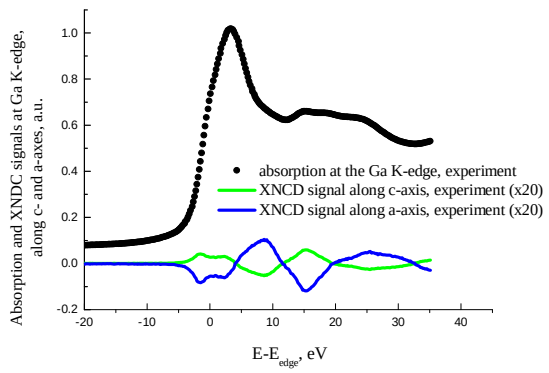

Fig. 1. The measured XANES spectra together with the XNCD signal along and perpendicular to the c-axis (multiplied by 20) near Ga K-edge.

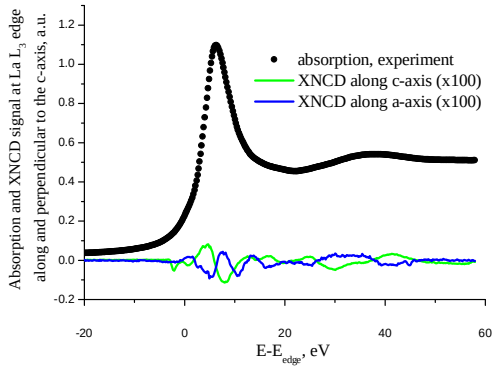

Fig. 2. The measured XANES spectra together with the XNCD signal along and perpendicular to the c-axis (multiplied by 100) near La L_3 edge.

In langasite crystal there are three different crystallographic Ga sites, so the XNCD signal is the sum of the contributions corresponding to each non-equivalent position. To disentangle these contributions we have performed ab-initio calculations of XNCD spectra using FDMNES code [6]. Firstly we have obtained a rather good general agreement between the theory and the experiment as illustrated on fig.3. We can see from the fig. 3 that the largest contribution to the XNCD gives the Ga(3) position, while the contribution due to the Ga(2) position is the smallest. On the other hand we do not observe the same agreement for the case of the La L-edges (see, fig.4). A plausible explanation could be the extended nature of both empty 6p and 4f orbitals of La ion.

Clearly more sophisticated calculations are needed and they are in progress.

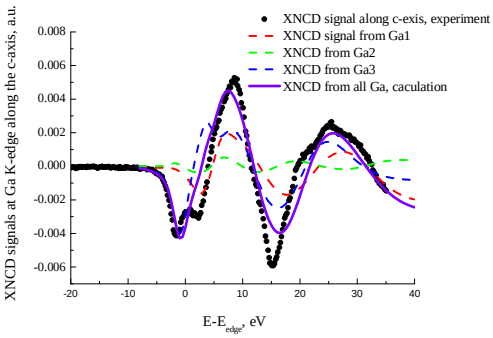

Fig. 3. The calculated XNCD corresponding to three different crystallographic positions 1(a) (Ga1), 2(d) (Ga2) and 3(f) (Ga3) and their sum in comparison with experimental result.

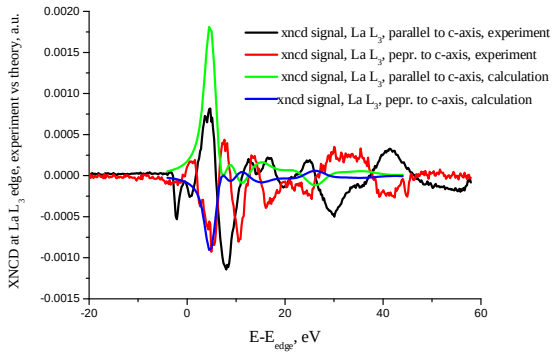

Fig. 4. The measured and the calculated XNCD signals along and perpendicular to the third rank axis near the La L_3 edge.

References

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Report Summary

XNCD signals in $La_3Ga_5SiO_{14}$ (LGS) were measured at the Ga K-edge and at the $L_{2,3}$ edges of La both along and perpendicular to the c axis. The calculations made using the multiple scattering method have shown the satisfactory agreement with experimental results and have allowed to separate the XNCD signal provided at the Ga K-edge by Ga atoms in three different crystallographical positions.