ESRF	**Experiment title:** X-ray natural dichroism of paramagnetic ions in corundum	**Experiment number:** HE 630
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Shifts: 15	**Local contact(s):** Andrei Rogalev	*Received at ESRF:*

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Report:

X-ray absorption measurements We are interested in the determination of the structural and electronic properties of rubies (α-Al_2O_3:Cr^{3+}) and sapphires (α-Al_2O_3:Fe-Ti). The introduction of paramagnetic impurities (Fe, Ti, Cr) in Al_2O_3 leads to angular and radial relaxation. These experiments have been made to measure these relaxations. In order to see the distorsions around the impurity ions (M) in Al_2O_3, it is necessary to measure XAS signals on single crystals for two independent orientations of the linear X-ray polarisation. Tanks to the analysis of both the isotropic and the dichroic signals, the two nearest M-O and M-Al distances can be reached [3]. The recording of the isotropic and dichroic EXAFS and XANES spectra at the Cr, Fe, Ti K-edge was planned for the 15 shifts. In fact, we have measured these spectra only at the Cr and Fe K-edge for several samples: three synthesized Al_2O_3:Cr^{3+} samples ($[Cr^{3+}]$ = 60, 800 and 10000 wt ppm) and two Al_2O_3:(Fe,Ti) samples (one synthesized crystal containing 1500 wt ppm of Fe and one natural crystal containing 1000 wt ppm of Fe). The spectra are presented in Fig.1 and Fig.2. These samples are cut so that the optical axis lies in the surface. We use a very efficient rotation technique proposed by J. Goulon [1] in order to obtain the isotropic and dichroic signals, and to get rid of diffraction peaks that have a devastating effect on the whole absorption spectrum (see Fig.3), we use a very efficient technique called the rotation technique and proposed by J. Goulon [1]. The photon flux is linearly polarized with $\vec{\epsilon}$ orthogonal to the normal of the sample surface. The crystals were placed on a rotating holder that allows the samples to be turned around the X-ray beam direction, perpendicular to the face of the sample. The optical axis of the samples stays perpendicular to the X-ray beam direction when the samples are turned.

For each energy $\hbar\omega$ of incident photon, the fluorescence intensity is measured by 8 detectors for rotation of the sample holder from 0 to 2π radians by step of $\frac{2\pi}{400}$. This process is carried out for 700 energy points, up to 1000 eV beyond the threshold. The recording of one EXAFS spectra requires about 10 hours. We did not have enough time to record the Ti K-edge.

EXAFS analysis The isotropic and the XNLD spectra have to be extracted from this amount of data. A filtering algorithm developped by Ch. Brouder [2] is used to obtain simultaneously both the isotropic signal μ_{iso} and the dichroic signal μ_{dichro}. The Cr K-edge EXAFS and XANES spectra of the three rubies are essentially identical except for signal to noise ratio. A standard procedure is used to analyse the isotropic part of the absorption spectra. A special procedure explained in [3] is used to analyse the dichroic signal. Final results are shown in Tab.1. This work is part of the PhD thesis by Amonmat Kiratisin and the paper collecting these results is under redaction.

	Al_2O_3	Al_2O_3:Cr^{3+}	Al_2O_3:Cr^{3+}	Cr_2O_3	Al_2O_3:Fe^{3+}	Al_2O_3:Fe^{3+}	Fe_2O_3
	[4]	isotropic data	dichroic data	[4]	isotropic data	dichroic data	[4]
M-O_1	1.86	1.93	1.92	1.97	1.92	1.90	1.94
M-O_2	1.97	2.01	2.01	2.02	2.10	2.05	2.11
M-M (f)	2.65	2.65	2.65	2.65	2.75	2.70	2.90
M-M (e)	2.79	2.79	2.85	2.89	2.88	3.04	2.97

Tab.1: Distances M-O and M-Al (Å) from the analysis of the isotropic and dichroic signal (M=Cr,Fe).

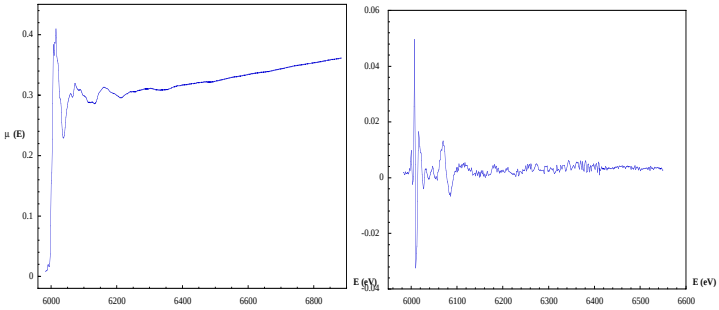

Fig.1: Isotropic (left) and dichroic (right) X-ray absorption spectra (K-edge) for Cr in ruby (1 %Cr).

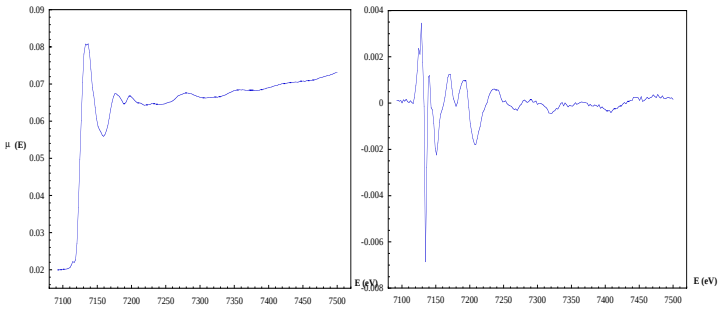

Fig.2: Isotropic (left) and dichroic (right) X-ray absorption spectra (K-edge) for Fe in synthesized sapphire

References

[1] J. Goulon et al. *J. Synchrotron Rad.* 7:182, 2000
[2] Ch. Brouder et al. *ICDIM, Johannesbourg*, 2000
[3] paper under redaction
[4] W. B. Pearson *Structure Reports* 24:507, 1960

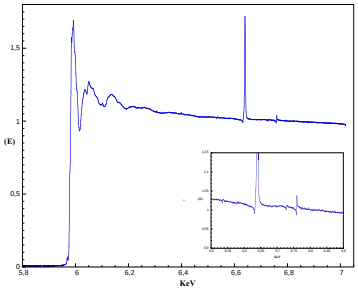

Fig.3: Cr K-edge XAS spectrum in ruby