

Report on the exp. MA145: Chemical environment and oxidation state of Co ions in CoAl_2O_4 films

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I. EXPERIMENTAL

The samples, few μm thick films of CoAl_2O_4 grown on a glass substrate, are labelled according to the preparation conditions and to the color obtain after each step of the process: for example, the sample 500G-800air5hB is grown at 500 °C, then annealed for 5 hours in air at 800 °C; it is green after growth and blue upon air annealing. The EXAFS experiment was performed at the Italian beamline GILDA of the European Synchrotron Radiation Facility (Grenoble-France) at the Co K-edge. The monochromator was equipped with a couple of 311 Si crystals and the harmonic rejection was achieved by two Pd-coated mirrors, working at an incidence angle of 3 mrad. The x-ray absorption spectra from the samples were measured in fluorescence mode with a photodiode. The x-ray absorption spectra from a series of standard compounds (namely, metallic Co, powders of CoO , CoAl_2O_4 , Co_3O_4 , $\text{Co(III) acetylacetonate}$ (Coacac_3)) were also measured in transmission mode. All of the samples were cooled at 77 K to limit thermal vibration. The analysis of the EXAFS spectra was performed by the FEFF8-FEFFTIT 2.98 package [1, 2]; the value of the S_0^2 parameter in the standard EXAFS formula [3] was determined by the analysis of the metallic Co. The Co-O backscattering phase and amplitude were calculated from a CoO cluster, providing to extend the calculation for different interatomic distances of the Co-O couple, down to 1.90 Å. The EXAFS signal from the first coordination shell of atoms around Co was selected by a Fourier filter, then fitted by a multiparameter single scattering fit into the R space; the fitting procedure in k-space led to the same results.

II. RESULTS

The EXAFS spectra are shown in Figure 1: it is evident from the Figure that the EXAFS spectrum of the sample 500G-800air5hB (i.e. the sample processed at the highest temperature) is very similar to the spectrum of CoAl_2O_4 , while the EXAFS signal from all the other samples is less structured. The corresponding Fourier transform moduli are reported in Figure 2(a): for all the spectra the peak present at $R \simeq 1.5$ Å is due to a Co-O correlation (or Co-N, the EXAFS spectroscopy being not able to distinguish between the two) and the corresponding first shell fit is also reported in the Figure. In Fig. 2(b) the first shell Fourier filtered spectrum and the cor-

responding first shell fit in k-space are shown for one of the deposited samples (sample 400B-500air1hG): as for all the other spectra, a good fit quality is obtained with a single Co-O coordination distance. The results of the EXAFS analysis for the first shell of atoms around Co are reported in Table I. The following points focus the main results:

- For the films, the Co-O distance varies in the range 1.96-2.02 Å (typical range for Co oxides, see the Table I), and depends on the preparation conditions, in particular on the annealing atmosphere (see samples 450B-599N₂1hB and 400B-500air1hG).
- The sample 500G-800air5hB has the same average Co site as the CoAl_2O_4 one. (N, R, σ^2 are the same).
- The EXAFS spectra of the samples 600G and 400B-500air1hG (the two green samples) are similar one to each other and different from all the others (see Fig. 1); correspondingly, the Fourier transform moduli exhibit similar features in the region up to $R = 6$ Å (see Fig. 2(a)). Presence of Co_3O_4 to be investigated.
- $N > 4$ for the samples 400B-500air1hG, 600G (the only green samples) and for the compound Coacac_3 (where Co is expected to have an octahedral coordination). For the two films, part of Co atoms are likely in octahedral sites. In the hypothesis that the measured site is the average of octahedral and tetrahedral sites, the fraction of Co atoms in octahedral sites is 5-25% for 400B-500air1hG and 20-50% for 600G.
- $N \lesssim 4$ for the sample heated in nitrogen atmosphere (450B-500N₂1hB), suggesting that a minor part of Co ions coordinate less than 4 O atoms: this could be related to the lack of O atoms in the annealing atmospheres.
- For the films, the Debye-Waller factor is lower for the samples annealed at higher temperatures.
- The samples 450B-500N₂B and 400B do not show any structures beyond the first shell (see Figure 2(a)), suggesting the absence of a medium range order.

TABLE I: Results of the EXAFS analysis for the films and for the standard compounds. N is the coordination number, R the interatomic distance and σ^2 is the Debye-Waller factor; the parameters without error bars were fix during fitting. Some pertinent crystallographic values are reported in parenthesis for comparison.

sample name	N_O	Co-O R_{Co-O} (\AA)	σ^2 ($\times 10^{-4} \text{\AA}^2$)
400B	4.1 ± 0.2	2.02 ± 0.01	74 ± 5
400B-500air1hG	4.3 ± 0.2	1.96 ± 0.01	60 ± 6
450B-500N ₂ 1hB	3.6 ± 0.3	2.01 ± 0.01	59 ± 10
500G-800air5hB	4.1 ± 0.3	1.96 ± 0.01	31 ± 5
600G	4.7 ± 0.3	1.99 ± 0.01	71 ± 7
CoO	6.2 ± 0.5	2.135 ± 0.01	66 ± 14
	(6)	(2.1259)	-
Co ₃ O ₄	(3;2)	(1.9164;1.9291)	-
CoAl ₂ O ₄	4.2 ± 0.3	1.96 ± 0.01	36 ± 6
Co(acac) ₃	5.6 ± 0.4	1.89 ± 0.01	19 ± 5
	(2;4)	(1.88;1.89)	-

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- [1] A. Ankudinov, B. Ravel, J. J. Rehr, and M. Newville, FEFFIT manual within the FEFF project, University of Washington, Seattle, USA (1992-1999).
- [2] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, Phys. Rev. B **56**, 7565 (1990).
- [3] J. J. Rehr and R. C. Albers, Rev. Mod. Phys. **72**, 621 (2000).

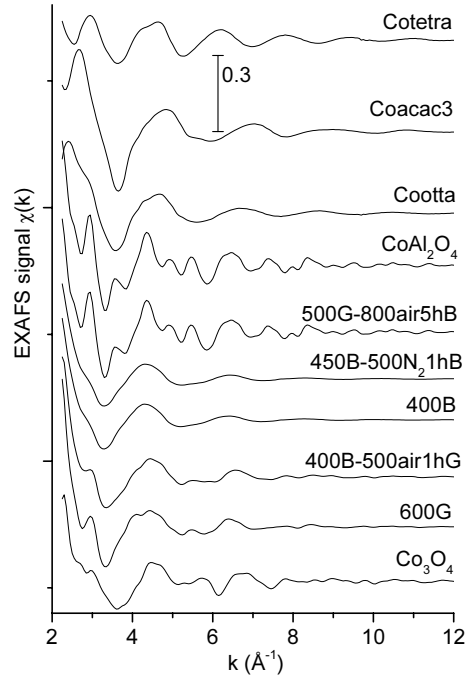


FIG. 1: Co K-edge EXAFS spectra of the investigated samples.

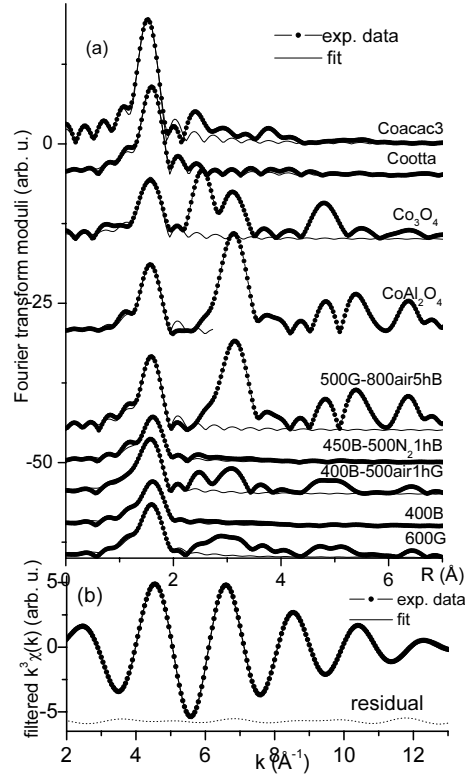


FIG. 2: (a) k^3 -weighted FT moduli and corresponding best fit curves of the Co-O coordination of the EXAFS spectra (transformed in the range 3-12 \AA^{-1}) recorded for the samples (the interatomic distance is not corrected for the backscattering phase shift); (b) Fourier-filtered EXAFS spectrum of the sample 500G-800air5hB in the range of fitting (markers): the corresponding fit (solid line) is superimposed on the data; the residual is also reported.