

**15.2-01** STRUCTURAL STUDIES OF COPPER<sup>II</sup> OXALATE COMPLEXES BY EXAFS SPECTROSCOPY. A. Michalowicz and R. Fourme, Laboratoire de Physicochimie Structurale, Université Paris-Val de Marne, 94010 Créteil and LURE (CNRS-Université Paris-Sud), B209C Campus d'Orsay, France.

In order to interpret magnetic properties of copper oxalate  $\text{CuC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$  ( $x < 1/2$ ) a compound for which single crystals are not available, the structure and packing were investigated by EXAFS spectroscopy. The transmission EXAFS spectra of copper oxalate at 300 and 15°K were recorded at LURE-DCI, using synchrotron radiation. Spectra of model complexes with known structures  $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  were also obtained. From the data analysis, three shells of light atoms were identified around each copper ion: 4 oxygen atoms ( $\text{Cu-O} = 1.98 \text{ \AA}$ ), 4 carbon atoms ( $\text{Cu-C} = 2.65 \text{ \AA}$ ) and 4 oxygen atoms ( $\text{Cu-O} = 3.9 \text{ \AA}$ ). Cu-Cu contributions include, 4 copper ions with  $\text{Cu-Cu} = 4.10 \text{ \AA}$  and  $\sim 8$  copper ions with  $\text{Cu-Cu}$  in the 5-5.5  $\text{ \AA}$  range. These results are consistent with the planar ribbon structure ... $\text{Cu-C}_2\text{O}_4\text{-Cu-C}_2\text{O}_4$ ... and the packing of non-parallel ribbons which was derived by Schmittler (Monatsber. Dtsch. Akad. Wiss. Berlin (1968), 10, 581) from powder X-ray diffraction patterns. They rule out two other models which were recently proposed (K.T. Mc Gregor and Z.G. Zoos, Inorg. Chem. (1976), 5, 100, A. Gleizes, F. Maury and J. Galy, Inorg. Chem., (1980) 19, 2074).

Finally, the EXAFS study of a new complex  $\text{CuC}_2\text{O}_4\text{Br}_2$  (synthesized by J.J. Girerd, Laboratoire de Spectrochimie des Eléments de Transition, Campus d'Orsay) will be reported and structural models compatible with the data will be discussed.

**15.2-02** EXAFS STUDIES OF THE STRUCTURE OF SOME AMORPHOUS COMPOUNDS. By P. Lagarde, LURE, Bat 209c, UPS, 91405 Orsay, France.

We have determined by EXAFS, jointly with W-ray scattering in some cases, the local structure of some amorphous materials:

I - Metallic alloys. The structure of  $\text{Cu}_x\text{Ti}_{1-x}$  with  $x = 0.66, 0.50, 0.33$  has been measured:  $\text{Cu-Cu} = 2.52$ ,  $\text{Cu-Ti} = 2.74$ ,  $\text{Ti-Ti} = 3.1 \text{ \AA}$ . The change of  $x$  does not affect the environment of the Cu atoms and no effect of an annealing up to 600 K can be detected. In Cu-Zr and Cu-Ti we did not find any dependence on the preparation mode (sputtering or quenching from the melt).

On Cu-Y and Ni-Y systems, EXAFS results show the evidence of two different distances of each pair of atoms: for instance, each Cu atom is surrounded in average by 2 Cu at 2.48, 4 Cu at 2.63, 4 Y at 2.85 and 2 Y at 3.15  $\text{ \AA}$ . Similar results are found for the Y atom and for Ni-Y.

II - Metal-metalloid compounds. Co-P and Ni-P metallic glasses (80% metal) have been studied also on both edges, especially on the soft X-ray range on P (2143 eV). Crystalline  $\text{Co}_2\text{P}$  and  $\text{Ni}_3\text{P}$  have been used as reference materials. The results are analyzed comparatively to the radial distribution functions obtained by X-ray scattering (Sadoc *et al.*, J. Non-Cryst. Sol. (1973), 12, 1).

The EXAFS results on these metallic alloys also compare favourably with small-angle scattering experiments (Flank *et al.*, J. Phys. C8 (1980), 41, 123).

**15.2-03** X-RAY ABSORPTION SPECTROSCOPIC STUDY OF  $\alpha$ - $\text{TiCl}_3$  AND  $\text{TiCl}_2$ . G. Vlaic, J.C.J. Bart, W. Cavigiolo, G. Navarra, Istituto G. Donegani, Novara (Italy) and S. Mobilio, Laboratori Nazionali di Frascati, INFN, Gruppo PULS, Frascati (Italy).

In order to characterize various titanium-chloride based polymerization catalysts we have studied  $\alpha$ - $\text{TiCl}_3$  and  $\text{TiCl}_2$  by means of EXAFS. The K threshold of Ti was measured at room temperature in a range of 1300 eV at 1 eV intervals using the X-ray beam of the Synchrotron Radiation Facility at the Frascati National Laboratories. Data analysis involved subtraction of the background using a fourth order polynomial expression of  $1/E$ . The smooth, isolated-atom like absorption was accounted for by Fourier filtering techniques. The Fourier transform was computed with a Gaussian window function and was backtransformed in the ranges of 1.52-2.36  $\text{ \AA}$  and 1.70-2.30  $\text{ \AA}$  for  $\text{TiCl}_2$  and  $\alpha$ - $\text{TiCl}_3$ , respectively. Iterative curve-fitting analysis with the theoretical phase and coordination numbers leads to Ti-Cl distances of 2.46(1)  $\text{ \AA}$  for  $\alpha$ - $\text{TiCl}_3$  (in agreement with the crystallographic value of 2.46  $\text{ \AA}$ ) and 2.42(1)  $\text{ \AA}$  for  $\text{TiCl}_2$ . The results are confirmed by Rabe's procedure (Phys. Rev. B17(1978) 1481) for the independency of  $R(\text{Ti-Cl})$  on the wave-vector  $k$ . The discrepancy with the available structural (powder) data for  $\text{TiCl}_2$  (Ti-Cl, 2.50  $\text{ \AA}$ ) calls for a redetermination of the latter crystal structure.

**15.4-01** AVERAGE SITE-OCCUPATION PARAMETERS IN 3-d TRANSITION METAL PHASES DETERMINED FROM CONVENTIONAL X-RAY AND SYNCHROTRON-RADIATION DIFFRACTION DATA. By H. L. Yakel, Metals & Ceramics Div., Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

The quantity and precision of conventional x-ray and synchrotron-radiation (SR) single-crystal Bragg diffraction data required to reliably estimate average site-occupation parameters in three phases, viz.,  $\text{CoFe}_2\text{O}_4$ ,  $\sigma(51.8\text{Fe}, 48.2\text{Cr})$ , and  $(\text{Fe}_7\text{Cr}_{16})\text{C}_6$ , are compared.

Results of the spinel experiment have been reported by the author (J. Phys. Chem. Solids (1980), 41, 1097). They show that, with differences ( $\Delta f$ ) of 3-5% in atomic scattering factors for iron and cobalt, a limited (819 observations of 36 independent reflection intensities), fairly precise ( $\sigma(I)/I \sim 4\%$ ) conventional Cu K $\alpha$  data set could not be used to fix the single site-occupation parameter for the structure with accuracy or precision. With 290 comparably precise SR diffraction data measured at energies just below the Fe and Co K absorption edges ( $\Delta f$ 's of 15-25%), this parameter was fixed to  $\pm 1\%$  at a value in agreement with results of neutron diffraction and Mössbauer spectroscopy experiments.

Over 8500 conventional Mo K $\alpha$  diffraction data representing about 1700 independent reflections were collected from a crystal of the Fe-Cr sigma phase (equilibrated for 1500 h at 740°C). Precisions of measurement varied from <1% for the relatively few intense diffraction maxima to  $\sim 5$ -10% for the more numerous weak reflections. Least-squares refinements in S.G.  $P4_2/mnm$  included occupation parameters for 4 of the 5 atom sites in the unit cell. Their final values and standard errors are listed below. About 300 SR diffracted intensity measurements from the same crystal were recorded at energies just below the Cr and Fe K edges ( $\Delta f$ 's of  $\sim 18$ -26% compared to 8% for Mo K $\alpha$ ). Values of site-occupation parameters derived from the SR data (see below) show greater precis-