

15.2-01 STRUCTURAL STUDIES OF COPPER^{II} 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 ~ 8 copper ions with Cu-Cu in the 5-5.5 \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 \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 Co_2P and Ni_3P 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 δ - TiCl_3 AND 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 δ - TiCl_3 and 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 \AA and 1.70-2.30 \AA for TiCl_2 and δ - TiCl_3 , respectively. Iterative curve-fitting analysis with the theoretical phase and coordination numbers leads to Ti-Cl distances of 2.46(1) \AA for δ - TiCl_3 (in agreement with the crystallographic value of 2.46 \AA) and 2.42(1) \AA for 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 TiCl_2 (Ti-Cl, 2.50 \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., CoFe_2O_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 (Δf) 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 α 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 (Δf '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 α 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 ~ 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 (Δf 's of ~ 18 -26% compared to 8% for Mo K α). Values of site-occupation parameters derived from the SR data (see below) show greater precis-

ion than, but do not differ significantly from, the conventional data results. All parameters are consistent with expectations based on neutron powder diffraction results (Kasper & Waterstrat, Acta Cryst. (1956), 9, 289; Algie & Hall, Acta Cryst. (1966), 20, 142).

Site	$\sigma(51.8\text{Fe}, 48.2\text{Cr})$			Coord.
	No. Fe Random	No. Fe Mo K α	No. Fe SR	
A(2a)	1.04	1.8(1)	1.80(3)	12
B(4f)	2.07	1.3(1)	1.09(3)	15
C(8i)	4.14	3.0(2)	3.05(7)*	14
D(8i)	4.14	7.0(2)	7.14(5)	12
E(8j)	4.14	2.5(2)	2.46(5)	14

Conventional Mo K α data comprising over 1200 observations of about 500 independent diffraction maxima were collected from a crystal of the τ carbide ($\text{Fe}_7\text{Cr}_{16}$)C $_6$ ($a_0=1.0595(1)\text{nm}$). Precisions of measurement averaged $\sim 3\%$ or better. Least-squares refinements of these data in S.G.Fm3m included occupation parameters for 3 of the 4 metal atom sites in the unit cell. Final values and their associated errors are listed below. SR diffraction data from this crystal have not yet been collected; based on the results of the σ -phase experiment, improved precisions but few significant differences would be anticipated in the occupation parameters derived from them.

Site	$(\text{Fe}_7\text{Cr}_{16})\text{C}_6$		
	No. Fe Random	No. Fe Mo K α	Coord.
4a	1.22	4.0(2)	12 (Cubo-octahedron)
8c	2.43	2.9(3)	16 (Friauf Polyhedron)
48h	14.61	15.8(7)*	12 + 2C
32f	9.74	5.2(4)	10 + 3C

* Fixed by composition and other occupation parameters.

15.4-02 X-RAY INTERFEROMETRY AT THE DARESBURY SYNCHROTRON RADIATION SOURCE. By M. Hart and D.P. Siddons, Wheatstone Laboratory, King's College, Strand, London WC2R 2LS, UK.

A new X-ray interferometric spectrometer has been constructed to exploit the properties of the radiation from the newly-commissioned SRS. The instrument is capable of high resolution in both energy and phase. It is built around a versatile diffractometer having three precision rotation axes. They are arranged as two identical high-resolution axes, with the third axis coincident with one of the other two. This third axis has lower resolution than the other two, but a wider range of rotational adjustment. This arrangement is suitable for a very wide range of X-ray optical experiments, and provides ample scope for adjusting the parameters of the optical system to suit the particular problem.

Provision is made for placing a solid-state detector in the final diffracted beam. In all the optical systems under consideration, this beam is in the same orientation as the primary beam, and so the SSD need only be translated. In the event of it proving desirable to detect off-axis X-ray beams, provision has been made for a second low-resolution axis to be placed coincident with the second fine axis so that a scintillation counter or other small detector may be rotated about this second axis.

The instrument is arranged primarily for diffraction in the vertical plane, but operation in the horizontal plane is possible, as are combinations of the two.

Initial operational experience with the diffractometer will be presented, including assessment of the relative merits of the various possible optical systems and some preliminary dispersion data.

15.4-03 THE CONFIGURATION OF THE FOUR IRON ATOMS IN DISSOLVED HUMAN HEMOGLOBIN AS STUDIED BY ANOMALOUS DISPERSION. By H.B. Stuhmann and H. Notbohm, European Molecular Biology Laboratory, EMBL-Outstation Hamburg, c/o DESY, Notkestrasse 85, 2000 Hamburg 52, West-Germany; Medizinische Hochschule Lübeck, Inst.f. Medizinische Molekularbiologie, Ratzeburger Allee 160, 2400 Lübeck 1, West-Germany.

The anomalous dispersion of iron at its K-absorption edge in small angle scattering of an aqueous solution of hemoglobin has been used to establish the geometrical arrangement of the four iron atoms in this protein. Though the anomalous contributions are about 0.001 to 0.01 of the total scattering, experiments with synchrotron radiation from the storage ring DORIS have shown that these effects can be measured with an average precision of about 10% at each of the 50 points of the scattering curve.

The anomalous scattering represents the convolution of the whole structure with the configuration of the four iron atoms of hemoglobin. The analysis in terms of multipoles suggests that tetrahedral symmetry of both the subunit arrangement and the iron structure is a dominant feature. The mean distance between the iron atoms of 26 Å as derived from this experiment compares well with those of crystallographic data.

15.4-04 PARTIAL OR COMPLETE CIRCUMVENTION OF THE PHASE PROBLEM IN CRYSTAL STRUCTURE DETERMINATION USING SYNCHROTRON RADIATION. By Karl F. Fischer, Institute of Crystallography, Universitaet des Saarlandes, D 6600 Saarbruecken, Germany (BRD).

Intensity differences taken at two or three wavelengths in the neighbourhood of an atomic absorption edge are used for determination of the sign or phase of single reflections (e.g. "Anomalous Scattering", edited by Ramaseshan and Abrahams, Copenhagen, 1975). F^2 -differences taken at two appropriately selected wavelengths around the absorption edge of one kind of atoms ("edge atoms") permit computation of a difference Patterson function $L(u)$. Its real part $L_c(u)$ contains main peaks corresponding to vectors between these edge atoms (e.g. Sakamaki, Hosoya, Fukamachi, Acta Cryst. (1980) A 36, 183). For an acentric crystal (space group P1) with k edge atoms and n "normal atoms" per unit cell, the imaginary part $L_s(u)$ of $L(u)$ yields k images of the normal atoms exhibiting the correct enantiomer and/or polarity of the structure. Measurements with a third wavelength eliminate problems caused by the anti-centrosymmetry of $L_s(u)$ and permit application to centrosymmetric crystal structures.

Detailed formalism, a computer program for this technique ("Lambda Method") and examples of applications are presented.