

13.X-1 STRUCTURES OF THE VARIOUS PHASES OF THE 100K SUPERCONDUCTOR  $Ba_2YCu_3O_7$ .

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'Oxygen deficient perovskite' oxides of the system (La,Sr,Cu), the crystal chemistry of which was extensively studied from 1984 by Raveau et al. in France, were shown in 1986 to be high temperature superconductors by Bednorz and Muller in Zurich. In 1987 Wu et al. in the U.S. showed that a similar (Y,Ba,Cu) material had an even higher superconducting transition temperature. This latter material seems to be the most suitable for detailed study, since its conductivity appears to be due to a single phase  $Ba_2YCu_3O_{7-\delta}$ , whose structure is now well established.

Conflicting X-ray diffraction results, due to microscopic twinning of the crystals, and the fact that the oxygen structure contributes only 5% to the total scattering, have been resolved by a number of neutron diffraction studies. (Capponi et al. at ILL Grenoble; Hinks et al. at Argonne; Beech et al. at NBS Washington, David et al. at RAL Oxford). The ideal  $Ba_2YCu_3O_7$  superconducting phase accommodates both  $Cu^{2+}$  and  $Cu^{3+}$  in characteristic oxygen environments in a novel 'oxygen deficient perovskite' structure, with (x,y)-planes of  $CuO_4$  squares sandwiching  $CuO_4$  chains along y. The oxygen environment clearly determines the copper valence state, which is essential to an understanding of the superconducting mechanism.

In Grenoble, using high resolution neutron powder diffraction, we have studied the oxygen content and structure as a function of temperature, between 5K and 1000K, in both oxidising and reducing atmospheres. We will report on the structures of the different phases, and the consequences for the superconducting mechanism.

## 13.X-2 SINGLE CRYSTAL PULSED NEUTRON DIFFRACTION

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Diffraction data from single crystals is obtained using the white-beam, stationary crystal, Laue technique. Separation of orders of the same reflection, which therefore fall on the same spot on the detector, is by their different times of arrival. The lecture will discuss the geometry of diffraction, the resolution of time-of-flight (TOF) diffractometers and their design. The integrated intensity of reflection is compared to that for the classical, monochromatic beam, moving crystal diffractometer and the overall speed of data collection is deduced. The success of the TOF technique is largely dependent on the provision of a suitable area, position-sensitive detector (PSD): its qualities are specified and a practical detector is described. Consideration is given to the suite of programs required to determine the crystal orientation matrix and to reduce the data to observed structure factors and, finally, some recent experimental results are cited.

## 13.X-3 NEW I.L.L. NEUTRON SINGLE-CRYSTAL DIFFRACTOMETERS : DESIGN AND RESULTS. By S.A. Mason, Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France.

A brief summary will be presented of new features of I.L.L. neutron single-crystal diffractometers, excluding instruments devoted mainly to powders, magnetic diffraction or small-angle scattering. The instruments concerned are D9 on the Hot Source, D19, D15 and D10 using thermal neutrons, and D16 and DB21 on Cold Source guide tubes.

Because neutron diffractometers are usually modular in conception (incident beam, sample environment, detection) most of the above instruments have been able to evolve to satisfy the changing needs of the scientists using them. However the availability of high-resolution position-sensitive detectors (P.S.D.'s), whether small for careful measurement of single or split reflections as for D9 or D15 ; or larger for the study of simultaneous reflections from macromolecules or more complicated patterns from partly-crystalline fibres, liquid crystals, etc. as for D16, D19 and DB21, has been a major impetus to re-thinking instrument design and data measurement algorithms.

The example of D19 will be considered in detail and some problems discussed. This instrument allows a wide choice of wavelength, resolution and sample environment. Coupled with the use of a  $4^\circ \times 64^\circ$  curved P.S.D. and of increasingly powerful computers and data analysis programs, these have led to successful experiments on single crystals of He, on crystalline DNA fibres, on very small mineral crystals (less than  $0.01 \text{ mm}^3$ ), and on several proteins.

## 13.X-4 POLARISED NEUTRON SCATTERING BY DYNAMIC POLARISED TARGETS.

By W. Knop, M. Krumpolz, K.H. Nierhaus, T.O. Niinikoski, V. Novotny, M. Rieubland, A. Rijllart, O. Schärpf, H.-J. Schink, H.E. Stührmann, R. Wagner, GKSS-WS D-2054 Geesthacht in collaboration with CERN Geneva, ILL Grenoble, MPI Berlin, Univ. Chicago, Univ. Mainz F.R. Germany

Polarised targets as used in high energy physics experiments may be of considerable interest in biological structure research using polarised neutrons. We report on various polarised targets which have been prepared from proteins (lysozyme, myoglobin, bovine serum albumin, ferritin, urease), transfer-ribonucleic acid and the large subunit of E.coli ribosomes (deuterated and native) dissolved in mixtures of heavy water with deuterated glycerol, ethylene glycol or 1,2-propandiol doped with a paramagnetic radical, sodium bis[2 deuterioxy-2-methylpropanoate(2-)] oxochromate- $d_{12}$ . Clusters of 700 to 6000 protons defined by the structures of the dissolved particles embedded in a fully deuterated matrix were polarised up to 75% within an hour by 4 mm microwave irradiation in a magnetic field of 2.5 tesla at a temperature of 0.3 K (DNP). The polarisation rate depends on the concentration of Cr(V), pH of the solvent, and molecular weight of the solute. Polarised neutron scattering from these targets changed by factors up to four when the polarisation direction of the neutron beam was inverted. The results agree with the predicted values. Spin contrast variation is very sensitive to inhomogeneities of the hydrogen distribution reflecting details of the internal macromolecular structures as could be shown in the case of the large ribosomal subunit. DNP fails with ferritin due to the magnetic mineral  $Fe_3O_4$  core of this cage protein. A single iron atom of the heme in myoglobin does not significantly affect DNP. Spin contrast variation is going to be used for *in situ* structure determinations (e.g. of one or two selected ribosomal proteins).