13. NEUTRON DIFFRACTION


Small-angle neutron scattering (SANS) experiments were performed on poly(ethylene terephthalate) (PET) with the Oak Ridge National Laboratory 30-m SANS instrument. An improved sample preparation technique which produces void-free films was developed. Single chain dimensions in amorphous undrawn films were measured for different label (deuterated chain) concentrations. The SANS radius of gyration was compared to the 1.544(1)Å for PET and the molecular weight was compared to the GPC molecular weight. The extent of the intermolecular reaction, both in the solid and the melt (temperatures from 200 to 300°C), was measured by following changes in the scattering curves over a period of time. Preliminary experiments on 100 K and 123 K and assistance received during my stay.

*Research sponsored by U.S. Army Research Office Grant No. DAAG-29-81-C-0187, and the National Science Foundation Grant No. DMR-77224459 through Interagency Agreement No. 40-636-77 with the U.S. Department of Energy under contract DE-AC05-84-OR21400 with Martin Marietta Energy Systems, Inc.

13.5-2 WATER MOLECULES IN NATURAL ZEOLITES STUDIED BY NEUTRON DIFFRACTION*. By A. Kyv, Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973 and G. Artioli, J. J. Pluth and J. V. Smith, The Department of Geophysical Sciences, The University of Chicago, IL 60637.

A series of neutron diffraction experiments using natural zeolites have been performed at the Brookhaven National Laboratory High Flux Beam Reactor in order to study the bonding of the water molecules and the cations in the zeolitic cavities. The ultimate aim of the studies is to develop models that will be useful for the understanding of reversible dehydration and ion-exchange properties of zeolite molecular sieves.

Precise structural data for natrolite, edingtonite, thomsonite and brewsterite collected in the temperature range 20K to 623K have yielded important information on the water molecules and their interaction with the cations and the framework oxygens. The hydrogen bonding is usually weak and the molecules adapt well to the local charge distribution in the framework. The c...0 distances vary in the ordered zeolites between 2.68 Å to 3.02 Å with 0<0<0 angles between 140 to 178°. The stronger bonds are accepted by oxygen atoms bonded to both Si and Al. In brewsterite there is Si/Al and cation disorder a complex hydrogen bond scheme is observed. The water oxygen atoms have fixed positions whereas the hydrogen atoms assume alternative positions to adjust to the varying local charge distribution caused by the disorder.

* Research carried out under contract with the U.S. Department of Energy and supported in part by its Office of Basic Energy Sciences.


ReO3 is a bright red metal which exhibits conductivity within a factor of six of copper at room temperature. Intense interest has developed in ReO3 due to a novel second-order phase transition in the metallic perovskite structured compound. A most unusual property of this transition is that the high pressure phase has a much larger (by a factor of seven) compressibility than the normal volume phase; this transition has been referred to as the "compressibility collapse".


This massive amount of information leads indirectly to the conclusion that the ReO3 structure undergoes a tetragonal distortion of the lattice involving...
displacement of the oxygen atoms from the linear O-Re-O chains of cubic ReO$_3$ to a "hinged" arrangement at the oxygens. This necessitates a doubling of the lattice and a change from simple cubic to a body centered geometry.

Until now, due to a large X-ray form factor mismatch, design limitations in X-ray single crystal pressure cells and a limited range in accessible pressure for the neutron powder measurement, no direct evidence of the high pressure ReO$_3$ structure has been obtained. For the first time, we have been able to obtain direct structural information at 15 kbar using the newly designed single crystal neutron diffractometer at WNR. This was accomplished by developing a novel geometry for the high pressure experiment which maximizes the available information using time-of-flight techniques and does not require the sample to be remounted in order to solve the structure (good for high symmetry systems > orthorhombic, with possible extensions to lower symmetry groups). This method consists of a cylindrical high pressure cell mounted along the beam axis (i.e. mounted on the incident beam collimator) so that the incident beam enters through the bottom of the cell. The sample is isolated inside a hydrostatic fluid chamber and the diffracted beam is scattered at 90° to the incoming beam.

As predicted, ReO$_3$ does undergo a lattice doubling with a hinging of the oxygen atoms. At ~15 kbar, the Re-O-Re angle is 165.4° (Re-Re-O 7.3°) with almost no change in the Re-O distance from the zero pressure structure. The "compressibility collapse", therefore, results from a rotation of Re-O octahedra.

13.5-4 ANTIFERROMAGNETIC STRUCTURE OF LaFeO$_3$. FROM HIGH RESOLUTION NEUTRON DIFFRACTION. BY T. Peterlin-Neu­haieler and E. Steichele, Technischen Universitét München, E 21, D-80046 Garching, BRR.

The rare earth orthoferrites belong to the orthohombi­cally distorted perovskite structures (space group D$_{16}$ - Pmnm) and show an antiferromagnetic ordering of the iron ions at room temperature. The determination of the Fe moment direction from the intensities of magnetic Bragg peaks may become difficult from powder measurements when some of the relevant reflections overlap. This problem is most serious with the light rare earth perovskites, as here the difference of the cell edges a and b is very small. For LaFeO$_3$, the a/b ratio is only 1.002, compared to 1.0175 for PrFeO$_3$. With a high resolution time-of­flight neutron diffractometer (E. Steichele and P. Arnold, Phys. Letters (1973) 44A, 165) and a carefully prepared sample the orthorhombic splitting could be re­solved.

The sample was prepared from a 1:1 molar mixture of La$_2$O$_3$ and Fe$_2$O$_3$, pressed to pellets with force of 15 tons, sub­sequently heated twice to 1420° C with grinding of the pellets in between. The diffractometer resolution could be improved to $\Delta d/d = 4 \times 10^{-4}$ for the (101) and (011) reflexions, which are purely magnetic peaks. Diffraction measurements were performed in the fixed backscattering geometry between $d = 2\theta = 9.2$ Å and $d = 3\theta = 3.4$ Å, where the experimental resolution was $1 \times 10^{-4}$. For higher order reflexions no magnetic contributions could be observed due to the reduced magnetic form factor of the iron ion. Individual peaks were fitted with a combined Gauss-Lorentz function (Gaussian in the tails), which approximated well the expected triangular resolution function. The result of such a least squares fit for the (101) and (011) reflexions is shown in the figure below. The experimental linewidth is about twice the instrumental resolution and the correlation splitting of the clearly separated peaks is $1.2 \times 10^{-4}$.

For a pure G - type configuration mostly found in rare earth perovskites one would expect an intensity ratio $R = (101) : (011) = 3 : 1$, whereas our experimental result is $R_{exp} = 2.32 \pm 0.12$. This implies that the spin must be canted with respect to the x-axis. From the experimental result two extreme orientations can be derived: With the moment in the z-plane the deviation from the x-axis would be $\pm 4^\circ$ and with the moment in the y-plane the deviation from the x-axis would be $\pm 19^\circ \pm 4^\circ$. In order to design the spin a unique orientation in space the intensities of other magnetic peaks are being evaluated. We also find that the magnetic peaks are by about 20% wider than the purely nuclear peaks probably due to finite magnetic domain sizes.

This work was supported by funds of the Bundesministerium für Forschung und Technologie.