

**13.4-01** HIGH RESOLUTION POWDER DIFFRACTION AT THE ZING-P' AND IPNS-I PULSED NEUTRON SOURCES. By J. D. Jorgensen and F. J. Rotella, Solid State Science Division, Argonne National Laboratory, Argonne, IL 60439.

A high resolution time-of-flight powder diffractometer has been operated at Argonne's ZING-P' pulsed neutron source for over 2 1/2 years. The diffractometer achieves  $\Delta d/d = 0.003$  (FWHM) for  $0.5\text{\AA} < d < 2.5\text{\AA}$  using time-focussed detectors in back-scattering ( $2\theta = 160^\circ$ ). The unusually large detector area (0.08 steradians) results in competitive count rates even though the time-averaged flux on the sample is relatively low. Using a Rietveld code modified for pulsed source time-of-flight data a number of relatively complex structures with up to 50 parameters have been successfully refined. In many cases, the precision of atomic positions is comparable to single crystal results. Refinements for standard samples (e.g.,  $\text{Al}_2\text{O}_3$ ) give results as good as or better than the best two-axis diffractometers. Instrumental background is unusually low. Fourier maps constructed from the powder data after initial refinement of known atom positions have been used to locate atoms not included in the starting model. At IPNS-I the next generation of powder diffractometers will allow computer processing of signals from individual detectors in order to achieve time-focussing at smaller scattering angles where mechanical time-focussing is not practical. This will allow large detector areas at scattering angles optimized for samples in special environments.

**13.5-01** THE NEUTRON DIFFRACTION STUDY OF  $\text{N}_2\text{O}_4$  AT 20, 60 AND 100K; AN EXAMPLE OF CONTROLLED SINGLE CRYSTAL GROWTH BY USE OF A CRYOSTAT.\* By A. Kvikic and R. K. McMullan, Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973

A procedure has been developed for neutron diffraction studies of single crystals grown from the gas phase by controlled cooling in a cryostat (DISPLEX model CS 202). The construction of the sample bulb provided a temperature gradient at a small tungsten metal surface for nucleation at the center of the diffractometer. The bulb was made of glass and had a volume from which crystals of suitable size were produced over a range of pressures. The appearance of Bragg reflections was observed as a means of monitoring crystal development and crystal quality. One dominant crystal could usually be formed by repeated heating/cooling with accurate temperature control ( $\pm 0.1^\circ\text{C}$ ) in a high vapor pressure range.

The method has been applied to a neutron diffraction study of the cubic phase of  $\text{N}_2\text{O}_4$  at 20, 60 and 100K. The unit cell dimension a changed from 7.7546(6) Å at 100K to 7.6937(6) Å at 20K. The molecule is planar with an observed N-N distance of 1.756(1) Å independent of temperature in the 20-100K region. The reduction of low-frequency rigid-body motion with temperature, however, increases the observed N-O distance slightly from 1.186(1) Å at 100K to 1.1893(5) Å at 20K. The molecular dimensions in the solid state agree with those found in the gas-phase (McClellan, Gundersen, Hedberg, J. Chem. Phys. (1972), 56, 4541). The planarity of the molecule despite the long N-N bond has been attributed (Redmond and Wayland, J. Phys. Chem. (1968), 72, 3038) to a weak long range  $\sigma$  bond interaction between the cis oxygen atoms. This O...O distance is 2.678(1) Å at 20K.

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**13.5-02** NEUTRON DIFFRACTION INVESTIGATION OF THE STRUCTURE OF  $\text{LiMoO}_2$ . By D. E. Cox, Physics Department, Brookhaven National Laboratory, Upton, NY 11973, U. S. A.; D. W. Murphy, D. B. McWhan, and R. J. Cava, Bell Laboratories, Murray Hill, NJ 07974, U. S. A.

A neutron diffraction study has been made on the rutile-related compound  $\text{LiMoO}_2$  formed by intercalation of  $\text{MoO}_2$  with Li. Rietveld refinement of powder data collected at 4.4K with 2.46Å neutrons reveal that the Li atoms form an ordered array in the distorted rutile-type lattice of  $\text{MoO}_2$  with approximately octahedral coordination. The unit cell is monoclinic, with  $a = 5.56\text{\AA}$ ,  $b = 5.21\text{\AA}$ ,  $c = 5.86\text{\AA}$  and  $\beta = 118.8^\circ$ , which corresponds to a roughly 5% expansion perpendicular to and a 1% contraction parallel to the pseudo-tetragonal rutile c axis in the original  $\text{MoO}_2$  cell. The paired Mo atoms in  $\text{LiMoO}_2$  are 2.46Å apart, compared to 2.51Å in  $\text{MoO}_2$  [B. G. Brandt and A. L. Skapski, Acta Chem. Scand. 21, 661 (1967)].

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**13.5-03** ON THE AMBIGUITY OF CATION DISTRIBUTION IN SPINEL FERRITES MEASURED BY NEUTRON DIFFRACTION AND MOSSBAUER EFFECT METHODS. By S. Ligenza\* and L. Chełmicki\*\*, Joint Institute of Nuclear Research, Laboratory of Neutron Physics, Dubna, USSR

The cation distribution measurements in polycrystalline Mn-Zn ferrites were carried out at 4.2K by two methods: neutron diffraction /ND/ and high-field Mössbauer effect /ME/. It has been found that the concentration of iron ions at tetrahedral sites as determined from ME experiments, is about 0.08 higher than that obtained from ND measurements. We presumed that this additional iron ions are situated randomly at 16c tetrahedral sites in spinel lattice. In our analysis of neutron diffraction patterns for ideal spinel structure the 16c sites are not taken into account. To test our supposition the calculation of neutron intensity peaks for iron ions at 16d and 8a sites only. It appears that for additional 0.08 iron content at 16c sites the reliability factor R does not change much, from that obtained for iron ions situated at 16d and 8a sites.

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