

21-Crystallography at Non-Ambient Temperatures and/or Pressures; Phase Transitions

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21.02 – Low Temperature Crystallography

MS-21.02.01 LOW TEMPERATURE MOLECULAR CRYSTAL STRUCTURE BY HIGH RESOLUTION NEUTRON POWDER DIFFRACTION. By R. M. Ibberson, ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, UK.

Low temperatures and high resolution neutron powder diffraction are a powerful combination that enable the precise and accurate determination of moderately complex molecular crystal structures to be performed.

The inherently high resolution of powder diffractometers operating at pulsed neutron sources, such as HRPD at ISIS, permits the routine collection of high quality powder data that contain several hundred resolved reflections. High resolution powder diffraction data, particularly if recorded at low temperatures, contain a wealth of information from Bragg reflections collected for d -spacings much shorter than 1\AA . The technique provides a rapid alternative to single-crystal neutron diffraction for unit cell volumes up to 1500\AA^3 and can be the only appropriate method for (i) crystals that undergo reconstructive first-order phase transitions and (ii) low melting point materials for which growing single crystals has practical difficulties.

This paper discusses recent high resolution neutron powder diffraction research at ISIS and assesses the future potential of its application. Examples discussed will include:

- ab-initio* structure determination
- precise bond length, bond angle and a.d.p. analysis
- phase transition studies.

MS-21.02.02 SINGLE CRYSTAL X-RAY DIFFRACTION EXPERIMENTS AROUND 20 K. By P. Luger*, Institute for Crystallography, Freie Universität Berlin, Germany.

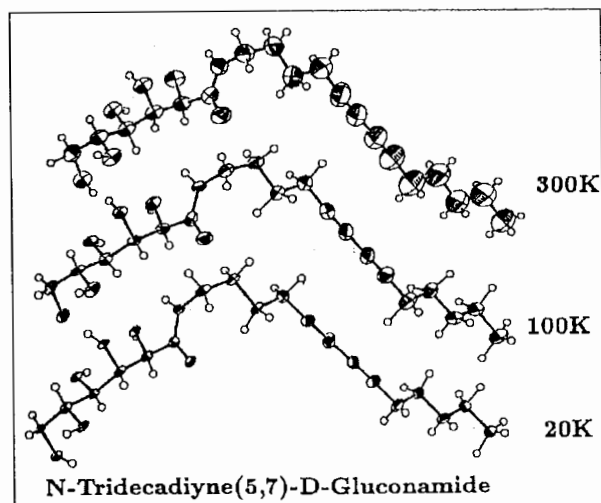
Performing single crystal X-ray diffraction experiments at temperatures much below 100 K involves considerable technical effort. We have installed low temperature equipments on single crystal X-ray diffractometers to cover a temperature range down to 50 K or even 20 K with single and double stage closed-cycle refrigerators. A rather small and inexpensive 50 K cryostat (Displex CS 1003) was mounted on a conventional Siemens-AED with quarter-circle χ -movement. A large Huber full-circle Eulerian cradle (400 mm diameter) with offset χ -circle was equipped with a double stage He refrigerator (Displex DE 202, Air Products). In both cases a Be vacuum chamber was fixed around the cold head. Two types of temperature dependent structural problems were investigated with these devices:

- For a number of flexible organic molecules, data sets were collected at various temperatures down to 20 K to allow a study of positional and thermal parameters versus temperature. An analysis of the individual atomic vibrational parameters as a function of the distance from the molecular centre of mass showed almost site-independent values at 20 K. Compounds considered in this study were crown ethers, amphiphilic molecules (Fig. 1) and a lysergic acid derivative.
- High resolution X-ray data sets ($\sin \theta / \lambda \geq 1.0 \text{\AA}^{-1}$) were collected for a number of small organic molecules at temperatures down to 20 K to obtain charge-density distributions. It was shown a dramatic intensity increase occurs for high order reflections when the temperature is lowered from 100 K to 20 K. Generally the 20 K data sets lead to a significant signal-to-background

improvement with increasing scattering angle so that high-order refinement provides very accurate atomic parameters. Inclusion of high-order reflections in Fourier maps enhanced the bond and lone-pair maxima in the dynamic deformation density maps without increasing the noise level.

It can be concluded that the low temperature setup at 20 K delivers high-quality data suitable for accurate structure and charge-density determination, which seems to justify the considerable technical effort.

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MS-21.02.03 STRUCTURE AND MAGNETIC PROPERTIES FROM NEUTRON DATA BELOW 10K. By B.N. Figgis* and P.A. Reynolds, Chemistry Dept., University of Western Australia, Nedlands, Western Australia 6009, Australia.

The results of a series of accurate neutron structure determinations on classical transition metal complexes, performed at the ILL over the last 10 years at temperatures of 4.2K or below, will be summarized. The results on the ammonium M(II) Tutton salts, $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, often deuterated, with M from V to Cu, provide a unique body of information on O-H-O and O-H-N hydrogen-bonding interactions. Comparison with 85K and 300K X-ray structures for some metals gives information about the nature of the thermal motion present, including anharmonicity and, possibly, TDS.

Polarized neutron diffraction on the same complexes, performed also at the ILL, gives magnetic structure factors which reflect the magnetization density in the crystal. Earlier work was restricted to complexes with orbitally non-degenerate ground terms, where the magnetization density can be identified, within a scale factor, with the spin density. Examples of covalence obvious from spin transfer to the ligand group, and of spin polarization, which destroys any simple relationship between the covalent transfer of charge and spin in chemical bonding, will be presented. A conceptually simple picture we call "differential covalence", based upon UHF theory, allows rationalization of covalence and spin polarization effects.

More recently, experiments which involve complexes with orbitally degenerate ground terms have been performed. Some of the complexities that this brings will be outlined, and it will be shown that in some cases, at any rate, covalence and spin polarization effects can still be identified.