

05.1-26 MOLECULAR DISORDER IN ICE Ih NEAR THE MELTING POINT BY SINGLE CRYSTAL NEUTRON DIFFRACTION. By W.F. Kuhs, Institut Laue-Langevin, Grenoble, France.

The structure of ice Ih has very often been related to the structure of water and studies of ice are considered as preparatory work for a better understanding of the structure of the liquid, still very much disputed. The different phases of the water substance may be viewed as a basically tetrahedral network of hydrogen bonded water molecules, which are increasingly randomized when going from the crystalline state towards the vapour phase. Obviously the closest resemblance of the liquid and the crystalline state occurs very close to the melting point. We report on a single crystal neutron diffraction study on heavy ice at 223K and 1 degree below the melting point. High resolution data ( $\sin\theta_{\max}/\lambda = 0.96 \text{ \AA}^{-1}$ ) of excellent quality were obtained from the considerably improved four-circle diffractometer D9 at the Institut Laue-Langevin. The temperature stability of a new, 2-stage Displex cryo-refrigerator was excellent with  $\text{rmsd}$  of  $0.02^\circ$  over a period of several days. Special precautions were taken to avoid vapour transport of the sample within the cryostat. Structure refinements including higher order parameters to describe the molecular disorder converged at a R-factor of 2%. Spatial information on the molecular disorder is obtained, the magnitude of which is in quantitative agreement with spectroscopic estimates (obtained from the FWHM of the uncoupled stretch vibration band). However, the extent of the molecular disorder clearly is less than predicted by molecular dynamics simulations.

05.1-27 STRUCTURAL BEHAVIOUR OF  $\text{NiS}_2$  UP TO 5.4 GPa. By T.Fujii, F.Marumo and K.Tanaka, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Midori, Yokohama 227, Japan.

Pyrite-type crystals of  $\text{NiS}_2$  show a phase transition at about 4.6 GPa under room temperature from a low-pressure, semi-conductor phase to a high-pressure, metallic phase. Changes of the cell-dimension and atomic positions were examined by the single-crystal X-ray diffraction method with the aid of a diamond-anvil cell up to 5.4 GPa. A crystal of  $\text{NiS}_2$  with dimensions  $0.10 \times 0.10 \times 0.04$  mm was set into the diamond-anvil cell together with a piece of ruby crystal for pressure calibration. Measurements of the cell-dimension and diffraction intensities were carried out at pressures of 3.2, 4.9 and 5.4 GPa with Ag K $\alpha$  radiation on a four-circle diffractometer.

The cell-dimension linearly decreases within experimental errors from  $5.6845(4) \text{ \AA}$  at the ambient pressure to  $5.5745(4) \text{ \AA}$  at 5.4 GPa without showing an appreciable discontinuity at the transition pressure, though the transition is supposed to be of the first order. The pressure dependence of the individual bond lengths were examined. The Ni-S length decreases with increasing pressure, whereas the S-S length is practically constant up to the transition pressure and decreases rapidly above it within the experimental pressure range. Decrement of the Ni-S length is smaller above the transition pressure than below it. These facts suggest that the S-S bond is softened and the Ni-S bond hardened on the phase transition from the semi-conductor to the metallic phase. The expected discontinuity in the bond lengths at the transition point are not so large as can be recognized with the accuracy of this experiment.

05.1-28 EFFECTS OF ELECTRIC FIELD ON INCOMMENSURATE-COMMENSURATE PHASE TRANSITIONS OF  $(\text{NH}_4)_2\text{SO}_4$ -GROUP CRYSTALS. By M.Ozeki, T.Kimura, Y.Tsutsumi, Department of Applied Physics, Waseda University, Japan.

Effects of electric field on the incommensurate-commensurate phase transitions of  $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$  (abbreviated as TMA-Zn), TMA-Co, TMA-Fe,  $[\text{N}(\text{CH}_3)_4]_2\text{BeF}_4$  (AFB),  $(\text{NH}_4)_2\text{SO}_4$  (AS)-group crystals, were studied by using X-rays. The diffraction spectra were acquired by the two dimensional reciprocal method (J.Kobayashi, et al, Phys.Rev.Letters,1963,11, 410-414). When electric field was not applied, any diffraction spectra were not observed issued from the nearly commensurate domains. With the application of electric field, those spectra appeared and coexisted with the incommensurate ones in some crystals, and did not in others. Thus the crystal of AS-group could be classified into the two types, according to whether such coexistence of the two kinds of spectra takes place or not. TMA-Zn, Co, and Fe belong to the former type, TMA-Cu and AFB to the latter. As an example of the former type, Fig.1 shows schematically the scattering intensity of  $(40-2/5-\delta)$  of TMA-Zn as functions of temperature and wave vector. Temperature dependences of the deviation parameters  $\delta$  differ between the two types. In the substances that show the coexistence,  $\delta$  decrease steeply with decreasing temperatures, while this feature is diminished in the others as shown in Fig.2. On approaching the incommensurate-commensurate transition temperatures, the widths of the incommensurate spectra invariably diverge.

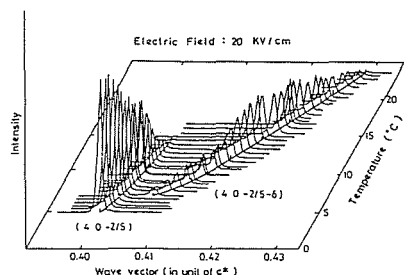


Fig.1

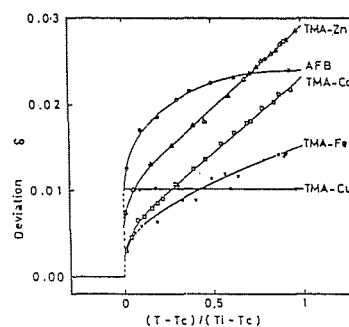


Fig.2