12-Amorphous, Imperfectly Ordered and Quasi-periodic Materials

PS–12.02.10 MOLECULAR ORIENTATION IN PLASTIC CRYSTAL OF 1-BROMOADAMANTANE. By H.Takakura*, M.Shiono and N.Achiwa, Department of Physics, Kyushu University, Higashi-ku, Fukuoka, Japan.

Some of adamantane 1-monosubstituted derivatives have plastic phase just below melting point. 1-bromoadamantane ($C_{10}H_{15}Br$, Br-ADM) is one of the suitable compounds for studying molecular orientation and phase transition property because bromine atom has relatively large X-ray scattering amplitude. Br-ADM has semi-ordered and ordered phases below plastic phase (Clark,T., et al , J.Chem.Soc.Faraday Trans. ,1977,**73**, 1224-1231.). X-ray single crystal Bragg data in three phases were measured at 244K,298K and 340K. Temperature dependence of lattice parameters were also determined from 244K to 340K. The plastic phase crystallizes in the cubic space group ($Fm3m$, $a = 10.079(1)$Å). The Crystal structure was analyzed by using rigid-model and then we proceeded to maximum entropy (ME) analysis. The most plausible ME-map is shown in Fig.1. It can be deduced that the molecule oritents its molecular principal Br-C axis along six equivalent $< 100 >$ directions rotating around the molecular principal Br-C axis. Moreover,it seems that the center of mass of each split molecule slightly deviates along the four-fold axis. The semi-ordered phase crystallizes in the orthorhombic space group ($Pmcn$, $a = 10.120(2)$Å, $b = 6.902(1)$Å, $c = 13.626(2)$Å) where tumbling motion of molecules around the Br-C axis occurs. The ordered phase crystallizes in the monoclinic space group ($P2_1/c$, $a = 10.134(1)$Å, $b = 6.868(1)$Å, $c = 13.315(2)$Å, $\beta = 90.05(1)°$) and the Br-C axis orients alternatively in (011) and ($0\bar{1}1$) directions propagating along the c-axis. This structure is quite similar to that of Cl-ADM (Foulon,M. et al, Acta Cryst. ,1989,B45,404-411.) which shows only ordered phase below plastic phase.
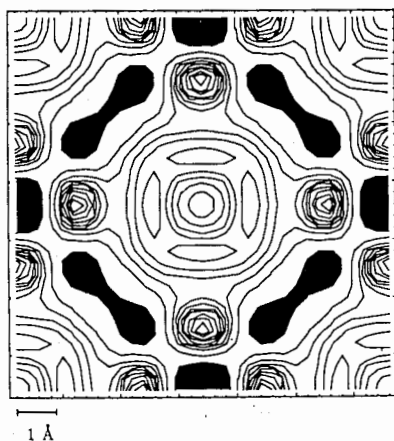

1 Å

Fig.1 The most plausible ME-map in (001) plane.

PS–12.02.11 INVESTIGATION OF THE REAL STRUCTURE OF NON-STOICHIOMETRIC SPINELS WITH DIFFERENT COMPOSITIONS. By S. V. Tsybulya, L. P. Solovyeva and G. N. Kryukova, Institute of Catalysis of the Russia Academy of Sciences, Novosibirsk, Russia

The structure of several nanometer-sized non-stoichiometric spinels has been investigated by X-ray powder profile analysis (Rietveld and Warren-Averbach methods) and HREM. The Mg-Al-spinel was derived from the aluminium hydroxide which has been modified by magnesium (9.4%MgO-90.6% Al_2O_3) at 1273 K. Vacancies in the 8a tetrahedral and 16d octahedral positions and atoms in the 8b (tetrahedron A*) and 16c (octahedron B*) positions have been found. The structure formula is $(Mg_{0.36}, Al_{0.6}) A^*_{0.05} [Al_{1.72}] [B^*_{0.05}] O_4$. It was found that the cations occupy A* and B* positions due to the formation of stacking faults. The model of stacking faults has been proposed. The Zn-Al spinel was derived at 1023 K from α-Al (OH)$_3$ and ξ-Zn (OH)$_{\hat{z}}$. The particles of this spinel consist of incoherent microblocks with sizes of 50 Å. The structure formula has been determined as $(Zn_{0.3}, Al_{0.7}) [Al_{1.7}] O_4$ where the vacancies are at the octahedral sites. Few anions (ca. from 0. 2 up to 4) seem to be OH^--groups. The Co_3O_4 spinel was prepared from cobalt nitrate. The structure formula of this sample is $Co_{0.94} [Co_2] [Co_{0.06}]^* O_4$ where * is assigned to the 16c octahedral position. Due to the presence of cations at the 16c position there are clusters or stacking faults with the structure of CoO in this sample.

PS–12.02.12 CONNECTION BETWEEN THE AVERAGE HEXAGONALITY AND ANOMALOUS PHOTORESPONSE OF FAULTED ZnS POLYTYPES.
M. Farkas-Jahnke and M. Somogyi, Research Institute for Technical Physics, HAS, H-1325 Budapest P.O.Box 76, Hungary

According to recent investigations (M.Farkas-Jahnke, S. Mardix 1993, to be published) the lattice parameters of ZnS polytype crystals can be related to the hexagonality of their stackings. As the hexagonality means the proportions of the hexagonal stackings to the whole number of stackings, this concept can be used also for polytypes with stacking faults, and the average value of lattice parameter parallel to the hexagonal c-axis of the crystal can be correlated to the average hexagonality of a randomly faulted lattice region. The average hexagonality of the investigated region, and also the relative rate of occurrences of four and five layer structure elements can be obtained by using a direct method based on the diffracted intensity distribution measured along row lines with Miller indices /h-k/≠3n on oscillational X-ray patterns of the crystals. In such faulted regions of the lattice, where a random distribution of hexagonal and cubic stackings are present, the lattice will have an average hexagonality, and correspondingly a common average lattice parameter value. This corresponds to an energy gap between the hexagonal and the cubic energy gap value.
Photoresponse measurements were taken from crystal parts connecting pure 2H, 4H, 3C or other periodic polytype regions to such randomly faulted regions. Appearence of photoactivity could be correlated to these adjoining pure and faulted regions and also to the presence of asymmetrical structure elements /hcc or hhc stackings/ among the five layer stucture elements of the faulted lattice.