12-Amorphous, Imperfectly Ordered and Quasi-periodic Materials

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 aluminum hydroxide which has been modified by magnesium (9.45% MgO-90.6% Al₂O₃) at 1273 K. Vacancies in the 8a tetrahedral and 16d octahedral positions and atoms in the 8b (tetrahedral A') and 16c (octahedral B') positions have been found. The structure formula is 

\[ \text{Mg}_{1.9} \text{Al}_{0.1} \text{A}^{3+}_{0.2} \text{Al}^{3+}_{1.8} \text{(OH)}_4 \]  

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 a-Al(OH)₃ and Zn(OH)₂. The particles of this spinel consist of incoherent microblocks with sizes of 50 Å. The structure formula has been determined as (Zn₆₋₃, Al₃₋₂) (Al₃₋₃)O₄, where the vacancies are at the octahedral sites. Few anions (ca. from 0.2 up to 4) seem to be OH−-groups. The Co₃O₄ spinel was prepared from cobalt nitrate. The structure formula of this sample is Co₆₋₃ (Co₅₋₂) (Co₃₋₁)O₄, 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 Co²⁺ in this sample.

PS-12.02.10 MOLECULAR ORIENTATION IN PLASTIC CRYSTAL OF 1-BROMOADAMANTE. 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 (C₉H₈Br, 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. The crystal structure was analyzed by using rigid-model and then we proceeded to maximum entropy (ME) analysis. The best plausible ME-map is shown in Fig. 1. It can be deduced that the molecule orients 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 (Pmna, a = 10.120(2) Å, b = 6.902(1) Å, c = 13.624(2) Å) where tumbling motion of molecules around the Br-C axis occurs. The ordered phase crystallizes in the monoclinic space group (P2₁/c, a = 10.134(1) Å, b = 6.865(1) Å, c = 12.315(2) Å, β = 90.05(1°) and the Br-C axis orientates alternatively in (011) and (c01) directions parallel to the c-axis. The structure is quite similar to that of Cl-ADM.

![Fig. 1 The most plausible ME-map in (001) plane.](image)

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Investigation of the Real Structure of Non-Stoichiometric Spinels with Different Compositions. By V. Tsybul'skii, L. P. Solov'eva and G. N. Kryukova, Institute of Catalysis, Siberian Scientific Center, Novosibirsk, Russia