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PS-12.02.13 DISORDER IN THE PLASTIC PHASE OF HEXACHLOROORTHOTANNE. By A. Oriarte and A. Muñoz, Departamento de Física de la Materia Condensada, Instituto de Ciencia de Materiales, Universidad de Sevilla, Spain.

Hexachloroorthotanne is a molecular crystal which shows an orientationally disordered cubic phase between 344 K and the melting point at 458 K. Neutron diffraction experiments (Gerlach, Hohlfeld, Prandl & Schulz, 1981, Acta Cryst. A37, 904–908) showed that the orientational probability is maximum along the (100) and [111] direction for the chlorine and carbon atoms, respectively. X-ray diffuse scattering (Gerlach & Prandl, 1988, Acta Cryst. A44, 128–131) and quasielastic neutron scattering (Gerlach, Dorner, Prandl & Lefebvre, 1988, Acta Cryst. A44, 251–257) work has also been carried out.

In this work we present a molecular dynamics simulation of the plastic phase using intermolecular potentials in order to explain the nature of the disorder. The calculated atomic probability distributions are in good agreement with the experiment. The molecular probability distribution, not accessible by diffraction methods, is also obtained. The origin of the disorder is studied from the correlations of the molecules with their surrounding neighbours, which reflect in the diffuse scattering patterns.


Diffraction pattern from iron amorphised by boron is recorded using X-ray diffractometry. The Interference component was separated after different corrections dependent on radiation and substance properties and normalisation of this pattern has to be performed. Fourier transform of this component gave the atomic radial distribution function based on which the short-range order model was obtained, namely, icosahedron with the nearest interatomic distance between Fe atoms equal to 2.52 Å. Interference components of amorphous Fe were noticeably different before and after annealing suggesting the displacement of the upper part of icosahedron relative to the lower one. Icosahedral short-range order was confirmed by calculation of the theoretical interference component, such a displacement giving markedly different results. In connection, the fit of the icosahedral model to amorphous Fe was considered in the energetic context. Configurational (potential) energy of cluster - icosahedron calculation was calculated on the basis of coordinates with Lennard-Jones type atomic interaction (the interaction type was chosen the structure of the short-range order to be due to interaction energy (potential pit) at the nearest interatomic distances). The energy of the system was calculated in approximation of atomic pair additivity to 1-J potential (φ-12):

\[ \phi(r) = \varepsilon \left( \frac{r_i}{r} \right)^{12} - 2 \left( \frac{r_i}{r} \right)^6 \]

where \( \varepsilon \) is the deep of potential pit, \( r_i \) the atomic diameter taken as a length unit. Icosahedron centered at the origin was arranged so that two opposite tops were located at vertical axis and the plane from which polar angle \( \theta \) was measured has gone through one of the equatorial atoms in the upper half of icosahedron. The six upper atoms were displaced by \( d \) relative to the lower ones. Energy values of icosahedra deformed were calculated as functions of values of displacement \( d \) and an angle \( \theta \) of turn relative to an axis. The potential energy surface represented the picture of equal value energy lines (isolines).

On this surface there was a stable local minimum at \( E = -5.52 \) eV/atom except global minimum at \( E = -2.79 \) eV/atom and the shortest distance between them has gone through the saddle point \( E = -2.39 \) eV/atom. Consequently, in the case of Fe the potential barrier value is equal to 0. 13eV=340 K at \( \varepsilon = 2000 \) K. Notice that points \( E = E_1 \) at the energy surface correspond to the shortrange orders in icosahedron and icosahedron with displacement.

PS-12.02.15 TOPOLOGICAL EQUIVALENCE CLASSES OF A TWO DIMENSIONAL RANDOM NETWORK WITH COORDINATION NUMBER 3 ON THE BASE OF FIBRE BUNDLES. By V. V. Manzhale*, Department of Inorganic Chemistry, L'viv State University, Ukraine.

The translational invariance principle is known to be not adequate for the description of disordered solid's structure. Therefore we propose a new approach based on the local invariance principle which has an empirical ground - the existence of short range order (SRO). So the local approach is available not only for the description of amorphous solids but crystalline [1] and quasicrystalline [2] ones too. It turns out that the local approach can be formulated in natural way within a mathematical tool of a fibre bundle theory. As an example we consider a simple case, namely the model of a two dimensional random network with coordination number three. To construct the corresponding fibre bundle we introduce the notion of the short range order configuration (SROC), which differs from that of the SRO essentially. The set of all the SROC's which can be realized in the structure forms the short range order configuration space (SROCS). We have shown that the principal bundle \( P \) and the associated one \( E \) have the form:

\[ \phi(S^2, S^2, (1,2) \times S^2, (1,2) \times S^2) \]

respectively. The basis \( S^2 \) (two dimensional sphere) arises from boundary conditions which must be imposed on an atomic system. In this respect we used the isotropy property of most glasses. The fibre (the SROCS) \( D^2 \times S^2 \) is a direct product of the...
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closed disk D² and the circle S¹. The structure group SO(1,2) x SO(2) is a direct product of pseudoorthogonal group SO(1,2) and orthogonal one SO(2)=S¹. The topological classes of random configurations result from the classification of the bundle P. And we have shown that they are in one to one correspondence with two integer numbers (m₁, m₂). Hence there are an infinite number of topologically stable equivalence classes of random configurations in this case. This is an exact result.

References

12.03 - Glasses and Polymers

DS-2.03.01 X-RAY DIFFRACTION OF POLYMERS-RECENT RESULTS ON POLYSACCHARIDES

By P. Zugenmaier Institute for Physical Chemistry, TU Clausthal, D-392 Clausthal-Zellerfeld, Germany.

Polymer fibers exhibit poor X-ray patterns which are not suitable for a full structural evaluation as for example the data obtained from a single crystal analysis.

A method will be described which allows with the use of potential energy calculations, additional data of various sources and X-ray intensities from X-ray fiber pattern, a structure determination with regard to conformation and packing of polymers. Results on polysaccharide structures as derivatives of amylose and cellulose and solvent inclusion complexes will be discussed.

DS-12.03.02 STRUCTURAL DISORDER OF POLY(VINYLDENE FLUORIDE), By Yasuhiro Takahashi, Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

Poly(vinylidene fluoride) (PVDF) possesses several polymorphs. In the present paper, the crystal structures and structural disorders of PVDF are described.

Form I: The molecule assumes the slightly deflected planar zigzag conformation. Two chains are contained in the unit cell with parameters, a = 8.58 Å, b = 4.91 Å, c = 4.58 Å and the space group C2/c. The crystal structure assumes the statistical structure in which two chains related by the mirror symmetry occupy a crystal site with equal probability. A diffuse streak scattering is observed on the line binding 110 and 001 reflections. This streak is interpreted by the kink band of GT₆ conformation parallel to the (110) plane in the crystallite of the planar zigzag molecule (Γ₉-trans, C₈-gauche, C₈ minus gauche). The rather regular arrangement of GT₆ in P₇ conformation is found in the incommensurate form which is observed as extra spots on the fiber diagram of polar II. On the equator and the first layer line, the diffuse streak scatter.