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

Hexachloroethane is a molecular crystal which shows an orientationally disordered cubic phase between 344K and the melting point at 458K. Neutron diffraction experiments (Gerlach, Hohlwein, Prandl & Schulz, 1981, Acta Cryst. A37, 904-908) show 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, 128-135) 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.

PS-12.02.14 MODEL OF THE SHORT-RANGE ORDER OF AMORPHOUS IRON AND ITS ENERGETIC STABILITY.

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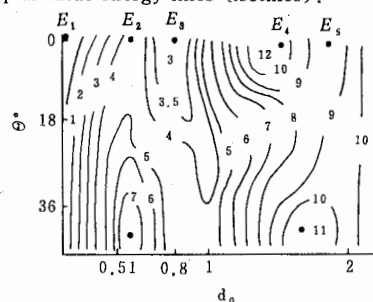
Diffraction pattern from iron amorphized by boron is recorded using X-ray diffractometry. The interference component was separated after different corrections dependent on radiation and substance properties, and normalization of this pattern has to be performed. Fourier transform of this component gave 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 this connection, fit of the icosahedron model to amorphous Fe was considered in the energetic context.

Configuration (potential) energy of cluster - icosahedron 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 L-J potential (6-12):

$$E_N = \sum_{i \neq j} \varphi(r_{ij}), \quad \varphi(r) = \epsilon \left[\left(\frac{r_1}{r} \right)^{12} - 2 \left(\frac{r_1}{r} \right)^6 \right],$$

where ϵ - the deep of potential pit, r_1 - 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 θ 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 θ 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 $E_0 = -2.52$ /atom except global minimum at $E_0 = -2.79$ /atom and the shortest distance between them has gone through the saddle point $E_1 = -2.39$ /atom. Consequently, in the case of Fe the potential barrier value is equal to $0.13\epsilon \approx 340$ K at $\epsilon = 2600$ K. Notice that points E_0 and E_1 at the energy surface correspond to the short-range 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.

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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 simplest 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 of 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:

$$P(S^2, SO_0(1,2) \times SO(2)),$$

$$E(S^2, D^2 \times S^1, SO_0(1,2) \times SO(2))$$

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) $D^2 \times S^1$ is a direct product of the

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opened disk D^2 and the circle S^1 . The structure group $SO_0(1,2)_x$ $SO(2)$ is a direct product of pseudoorthogonal group $SO_0(1,2)$ and orthogonal one $SO(2) \approx S^1$. 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 $\{m_1, m_2\}$. Hence there are an infinite number of topologically stable equivalence classes of random configurations in this case. This is an exact result.

References

1. Manzhar V. V., *Krystallographiya*. 1990, 35, p. 1367.
2. Manzhar V. V., *Krystallographiya*. 1990, 35, p. 807.

12.03 - Glasses and Polymers

DS-12.03.01

FIBER DIFFRACTION OF POLYMERS-RECENT RESULTS ON POLYSACCHARIDES.

By P. Zugenmaier Institute for Physical Chemistry, TU Clausthal, D-3392 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(VINYLDIENE 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, $a = 8.58 \text{ \AA}$, $b = 4.91 \text{ \AA}$, $c = 2.56 \text{ \AA}$ and the space group $Cm2m$. 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 $GT\bar{G}$ conformation parallel to the (111) plane in the crystallite of the planar zigzag molecule (T: trans, G: gauche, \bar{G} : minus gauche). The rather regular arrangement of $GT\bar{G}$ in TT 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-

ings are observed on the lines binding 110 and 110, 020 and 220, 110 and 200, 111 and 201 reflections. These streaks are attributed to two kinds of glides (alip planes) parallel to the planes (100) and (110).

Form II Two chains with $TGT\bar{G}$ conformation are contained in the rectangular unit cell with parameters, $a = 4.96 \text{ \AA}$, $b = 9.64 \text{ \AA}$, $c = 4.62 \text{ \AA}$ and the space group, $P2_1/c$. In the crystal, four molecules with different orientations statistically occupy a crystal site with different probabilities. This statistical structure is caused by two kinds of anti-phase domain structures: one is the domain concerning the direction of the molecule on the c-projection and the other is the domain concerning the pointing direction, up and down of the molecule.

Streak II This is the intermediate form between forms II and III and transforms to form III by heat-treatment. In form III, the molecule assumes $T_3GT_3\bar{G}$ conformation. On the fiber diagram of streak II, diffuse streak scatterings are observed from the reflections of form II along ζ -direction. These are attributed to the kink bands of TT conformation parallel to the (001) in the crystallite of $TGT\bar{G}$ conformation. Streaks are going to the sharp spots of form III during heat-treatment. This shows that the molecular conformation gradually changes from form II of $TGT\bar{G}$ to form III of $T_3GT_3\bar{G}$ during the heat-treatment.

DS-12.03.03 TIME RESOLVED X-RAY DIFFRACTION OF ORGANIC POLYMERS AROUND THE GLASS TRANSITION. By A. Mahendrasingam, W. Fuller*, A. Turner, *D.J. Blundell, *D. MacKerron, **R.J. Oldman, Department of Physics, Keele University, England, *ICI plc, Wilton, England and **ICI plc, Runcorn, England.

A comparative study of structural transitions in the organic polymers poly(aryl-ether-ether-ketone) (PEEK) and polyethylene terephthalate (PET) in response to mechanical stress and temperature around the glass transition has been made using the UK SERC Daresbury Laboratory X-ray Synchrotron Radiation Source with a FAST TV detector. The studies of PEEK are of particular interest. Close to the glass transition ($\sim 152^\circ\text{C}$) annealing (without further drawing) of originally cold drawn specimens show a dramatic loss of orientation in the high angle fibre diffraction pattern which after ~ 10 seconds is regained and followed by crystallisation. Complementary time-resolved small angle x-ray fibre diffraction studies have allowed changes in the gross organisation of polymer chains to be correlated with the changes in polymer conformation and packing indicated by changes in the high angle diffraction.