

10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

K (Dyachenko, O.A., Gritsenko, V.V., Mkyan, Sh.G., Shilov, G.V., & Atovmyan, L.O. *Izv. AN SSSR. Ser. Khim.*, 1991, 2062-2070), $(\text{ET})_8[\text{Hg}_4\text{Cl}_{12}(\text{PhBr})_2]$ (6) which is metallic to 10 K, $(\text{ET})_8[\text{Hg}_4\text{Br}_{12}(\text{PhCl})_2]$ (7) with $T_{\text{MI}} = 90$ K, $(\text{ET})_8[\text{Hg}_4\text{Br}_{12}(\text{PhBr})_2]$ (8) with $T_{\text{MI}} = 125$ K (Gritsenko V.V., Dyachenko, O.A., Shilov, G.V., Lyubovskaya, R.N., Afanasyeva, T.V., Lyubovskii, R.B. & Makova, M.K. *Izv. AN. Ser. Khim.*, 1992, 894-902), $(\text{ET})_8[\text{Hg}_4\text{Br}_{12}(\text{MePhCl})_2]$ (9), $(\text{ET})_4[\text{Hg}_3\text{I}_8]$ (10) (Takhirov, T.G., Krasochka, O.N., Dyachenko, O.A., Atovmyan, L.O., Aldoshina, M.Z., Goldenberg, L.M., Lyubovskaya, R.N., Merzhanov, V.A. & Lyubovskii, R.B. *Mol. Cryst. Liq. Cryst.*, 1990, 185, 215-226), $(\text{ET})_4[\text{Hg}_2\text{I}_6]$ (11), $(\text{ET})_2[\text{Hg}(\text{SCN})_2\text{Cl}]$ (12) with $T_{\text{MI}} = 50$ K (Konvalikhin, S.V., Shilov, G.V., Dyachenko, O.A., Lyubovskaya, R.N., Aldoshina, M.Z. & Lyubovskii, R.B. *Izv. AN. Ser. Khim.*, 1992, 903-909), $(\text{ET})_2[\text{Hg}(\text{SCN})_2\text{Br}]$ (13) with $T_{\text{MI}} = 140$ K, $(\text{ET})_2[\text{Hg}(\text{SCN})\text{Cl}_2]$ (14) with $T_{\text{MI}} = 35$ K (Konvalikhin, S.V., Shilov, G.V., Dyachenko, O.A., Aldoshina, M.Z., Lyubovskaya, R.N. & Lyubovskii, R.B. *Izv. AN. Ser. Khim.*, 1992, 2323-2331), $(\text{ET})_2[\text{Hg}(\text{SCN})_2\text{Br}_{0.66}\text{Cl}_{0.33}]$ (15) with $T_{\text{MI}} = 70$ K and $(\text{d}_8\text{-ET})_4[\text{Hg}_2(\text{SCN})_4\text{Cl}_2]$ (16) with $T_{\text{MI}} = 86$ K. The named compounds are characterized by a variety of electroconducting properties including superconductors (1-4), metals (5-8, 12-16) and semiconductors (9-11). As a result of a comparative study of the crystal structures of the compounds (1-16) and organic conductors related to them, a variety of the types of ET packing in the conducting layers and the anion structures have been shown. The factors affecting the structural design and electroconducting properties of the organic conductors and superconductors are discussed.

10.02 - Fullerenes

MS-10.02.01 SYNCHROTRON X-RAY STUDY OF THE ORIENTATIONAL ORDERING IN SINGLE CRYSTAL C_{60} . By P. Wochner, P. C. Chow, G. Reiter, S. C. Moss, University of Houston, Houston, TX 77204-5506 USA; J. D. Axe, J. C. Hanson, R. K. McMullan, Brookhaven National Laboratory, Upton, NY 11973 USA; P. Zschack, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA; M. C. Nelson, University of Illinois, Urbana, IL 61801 USA.

The determination of both the single molecule and intermolecular interaction potentials provides a key to the understanding of the orientational ordering transition at 260K. These potentials can be extracted, respectively, from Bragg (P. C. Chow et al., *Phys. Rev. Lett.*, 1992, 69, 2943-2946) and diffuse X-ray scattering experiments which probe the orientational pair correlations between C_{60} molecules as a function of their separation (J. R. D. Copley and K. H. Michel (preprint)). We will show that even in the orientationally disordered state, with continuously re-orienting C_{60} molecules, a given molecule will show preferential orientation resulting in deviations from a spherical distribution. These deviations allow us to evaluate the probability of orientation

$P(\tilde{\omega})$ and the effective single molecule potential energy $V(\tilde{\omega})$, where $\tilde{\omega}$ is the set of Euler angles.

In a large single crystal, grown by J. Z. Liu and colleagues at UC Davis, we have observed anisotropic zone boundary diffuse scattering, extending well above the first-order transition temperature T_c , which is strongly dependent on the scattering wave vector, \tilde{Q} . This scattering is associated with the form factor variation for a single molecule in the crystal field, which is then modulated by the scattering from coherent orientational correlations. We will present current progress in our determination of the interaction potential.

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MS-10.02.02 CRYSTAL STRUCTURES OF C_{60} AND OF $(\text{HYDROQUINONE})_3\text{C}_{60}$. By H.-B. Bürgi and M. Foertsch, Laboratory of Crystallography, University of Bern, Switzerland; R. Restori and D. Schwarzenbach*, Institute of Crystallography, University of Lausanne, Switzerland; O. Ermer, Institute of Organic Chemistry, University of Köln, Germany.

Pure C_{60} undergoes a phase transition at 250K. The low-temperature structure (cubic $\text{Pa}\bar{3}$) shows a twofold orientational disorder; the corresponding populations are in thermal equilibrium (Bürgi, H.-B. et al., *Angew. Chem. Int. Ed.*, 1992, 31, 640-643). We now report the high-temperature structure (cubic $\text{Fm}\bar{3}\text{m}$) determined from published synchrotron X-ray data (Chow, P. C. et al., *Phys. Rev. Lett.* 1992, 69, 2943-2946). The room-temperature scattering density distribution has been parametrized in terms of a combination of oriented symmetry-related molecules, and of a freely spinning molecule. Corresponding populations are 61% and 39%. The oriented part of the model is obtained, in good approximation, by imposing symmetry $\text{m}\bar{3}\text{m}$ on the energetically more favourable major orientation in the low-temperature structure of C_{60} . The orientational probability density distribution has been calculated from the molecular libration tensors. It shows maxima for C_{60} orientations possessing $\bar{3}\text{m}$ crystallographic site symmetry. It is also relatively large for the C_{60} orientations with cubic site symmetry $\text{m}\bar{3}$. The smallest energy barrier for reorientation between different $\bar{3}\text{m}$ orientations *via* a $\text{m}\bar{3}$ orientation appears to be less than 2 kJ mol^{-1} . On average, 75% of the intermolecular contacts of the oriented molecules are longer than those observed in the low-temperature structure, the other

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25% are less favourable. The second orientation of C_{60} found in the low-temperature structure could not be identified at room temperature.

The orientational disorder of C_{60} in the structure of (hydroquinone) $_3C_{60}$ (trigonal, $R\bar{3}m$) has been investigated at four temperatures, 100K, 200K, 293K and 373K. C_{60} occupies clathrate-like cages with symmetry $\bar{3}m$ (Ermer, O., *Helv. Chim. Acta* 1991, 74, 1339-1351). At 100K, C_{60} shows a threefold orientational disorder, the crystallographic molecular symmetry being $2/m$. At higher temperatures, disorder increases: at 373K, it is represented by two sets of oriented symmetry-related molecules with site symmetry $\bar{1}$. One is near the orientation found at 100K, the other places a molecular threefold axis close to the crystallographic threefold axis. As for pure C_{60} , this parametrization permits to determine a probability density function of molecular reorientation.

MS-10.02.03 DEFECTS AND PHASE TRANSITIONS IN C_{70} and C_{60} .

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Two subjects will be addressed in some detail.

(i) Phase transitions in C_{70} [G. Van Tendeloo et al. *Europhys. Lett.* 21 (1993) 329]. Crystals grown from the vapour under reduced helium pressure exhibit two different morphologies: the majority is cubic, a few % only is hexagonal. Electron diffraction on fragments obtained by crushing under liquid nitrogen shows that at room temperature the crystal structures are respectively predominantly FCC and HCP with a c/a ratio close to ideal consistent with their morphology. In most cases the structure is faulted.

At liquid nitrogen temperature the HCP crystals exhibit an orientationally ordered phase with a superstructure which can be described as monoclinic with $a_m = a_H$, $c_m = 2a_H$, $b_m = c_H$ and β close to 120° . This low temperature phase can occur in six orientation variants with respect to the hexagonal room temperature phase. The layers of molecules are stacked according to the HCP mode ($c/a \cong 1.82$) with their long molecular axis parallel to b_m . Rows parallel to a_m consist of parallel molecules having the same azimuthal orientation, but in adjacent rows the molecules differ 180° in orientation. A second orientational stacking mode of the same type of layers leading to $b_m = 2c_H$ is occasionally found (orientational polytypism). With increasing temperature the different orientational degrees of freedom of the molecules are gradually excited. In a first transition (~ 276 K) the orientational order disappears as a consequence of the free rotation about the long molecular axis; hereby c/a remaining 1.82. At 337 K c/a decreases to 1.66; subsequently the ABAB stacking is irreversibly changed into a rhombohedral ABCABC stacking by a shear transformation; finally, at higher temperatures the structure becomes FCC.

(ii) The defect structure of C_{60} [S. Muto, G. Van Tendeloo, S. Amelinckx, *Phil.Mag* (1993) in the press].

The orientational disorder-order transition from face centered cubic into simple cubic causes fragmentation of single crystals into domains related by the 90° symmetry rotation, lost in the phase transition; also translation variants are produced. This domain structure has been studied by diffraction contrast electron microscopy. A further transition from this primitive cubic structure into one with doubled cell parameters, termed "2a₀" superstructure has been observed by electron diffraction.

All the defects which commonly occur in low stacking fault energy face centered cubic alloys are also found in C_{60} at room temperature. High resolution electron microscopy has allowed to image these defects on a molecular scale and we will discuss some of these defects in detail:

- (i) Twin interfaces and the lattice relaxation along them.
- (ii) Intrinsic and extrinsic stacking faults and their relation with partial dislocations.
- (iii) Lines of partial vacancies along the intersection lines of stacking faults.
- (iv) Interaction of stacking faults and twin boundaries.
- (v) Surface reconstruction of C_{60} , probably because of the presence of oxygen at the surface.

MS-10.02.04 PHASE TRANSFORMATIONS OF C_{60} UNDER NONHYDROSTATIC PRESSURE

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Fullerenes under pressure present several new phenomena depending on pressure and temperature conditions. Under hydrostatic compression, C_{60} molecules are stable up to 20GPa (Duclos *et al. Nature*, 1991, 351, 380). However, application of nonhydrostatic pressure above 15 GPa transforms fullerenes into polycrystalline diamond at room temperature, the color of the bulk sample being yellowish by transparency (Nùnez Regueiro *et al. Nature*, 1992, 355, 237). Furthermore, application of nonhydrostatic pressure at high temperature give rise to black non insulating samples. We report on the x ray synchrotron radiation and electron diffraction characterization of these transformations.

Electron diffraction patterns of samples transformed at room temperature present continuous rings corresponding to all f.c.c. diamond reflections or diffuse rings of an amorphous phase. The diffraction patterns evolve continuously from diamond rings to amorphous rings and the sample morphology, as observed by optical and electron microscopy, is not lamellar. From the dark-field images, we deduce that the size of the crystallites varies from 20 to 1000Å in the different chips. In all samples the amorphous phase exists, the largest proportion of well crystallized diamond material was found when the applied pressure was the least hydrostatic. We have analyzed the diffuse pattern of samples which seemed totally amorphous by using x ray synchrotron radiation at DCI (LURE). It corresponds to sp^3 -type carbon and is always mixed with a small amount of polycrystallized f.c.c. diamond. Several simulations and fits show that this sp^3 amorphous phase contains, together with staggered C-C bonds, some amount of eclipsed C-C bonds as found in Lonsdaleite. Simulation spectra of theoretical phases containing C_{20} or C_{24} polyhedra do not agree with our measurements and the number of eclipsed C-C bonds must be limited.

On the contrary, samples obtained in a belt press at moderate pressures and high temperatures are black non insulating and amorphous. Electron diffraction and x ray synchrotron radiation characterization of this phase show its sp^2 -character, affected by preferential orientation.