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## Short Communication

Structural phase transitions in single crystal C<sub>60</sub>

R. Moret<sup>(1)</sup>, P.A. Albouy<sup>(1)</sup>, V. Agafonov<sup>(2)</sup>, R. Ceolin<sup>(2)</sup>, D. André<sup>(3)</sup>, A. Dworkin<sup>(3)</sup>,  
H. Szwarc<sup>(3)</sup>, C. Fabre<sup>(4)</sup>, A. Rassat<sup>(4)</sup>, A. Zahab<sup>(5)</sup> and P. Bernier<sup>(5)</sup>

<sup>(1)</sup> Laboratoire de Physique des Solides(\*), Bât. 510, Université Paris-Sud, 91405 Orsay, France

<sup>(2)</sup> Laboratoire de Chimie Physique, Faculté de Pharmacie, 2bis boulevard Tonnellé, 37042 Tours, France

<sup>(3)</sup> Laboratoire de Chimie Physique des Matériaux Amorphes(\*\*), Bât. 490, Université Paris-Sud, 91405 Orsay, France

<sup>(4)</sup> Laboratoire d'Activation Moléculaire(\*\*\*) , Ecole Normale Supérieure; 24 rue Lhomond, 75231 Paris, France

<sup>(5)</sup> Groupe de Dynamique des Phases Condensées(\*\*\*\*), Université de Montpellier, 34060 Montpellier, France

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**Résumé .** — Des cristaux de C<sub>60</sub> ont été étudiés à basse température par diffraction des rayons X. Nous avons mesuré l'intensité (*I*) de réflexions caractéristiques de la transition cubique à faces centrées-cubique simple, jusqu'à 23 K. Cette transition de mise en ordre orientationnel intervient à  $T_0 = 259 \pm 1$  K avec une hystérésis d'environ 1 K, mais sans discontinuité de l'intensité à  $T_0$ . Des anomalies significatives de  $d(I)/d(T)$  sont observées vers 155 K et 85 K. Elles impliquent des modifications au niveau des réorientations des molécules de C<sub>60</sub> et leur origine est analysée.

**Abstract .** — X-ray diffraction has been employed to study the low temperature structural behavior of C<sub>60</sub> crystals. The intensity (*I*) of selected reflections which appear at the face-centered cubic-simple cubic transition was measured as a function of temperature down to 23 K. This orientational ordering transition is found at  $T_0 = 259 \pm 1$  K. It displays a hysteresis of about 1 K but no discontinuity of the intensity at  $T_0$ . Anomalies in  $d(I)/d(T)$  around 155 K and 85 K are clearly revealed. They are associated with changes in the C<sub>60</sub> molecular reorientations and their origin is discussed.

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The understanding of the orientational ordering mechanism of the  $C_{60}$  molecules at low temperature in pure fullerene  $C_{60}$  remains an important issue for this new class of molecular solids. Combining results from various types of measurements it appears that the details of the molecular reorientations and their associated dynamics are rich and still partly unravelled. At room temperature, X-ray diffraction studies established that crystalline  $C_{60}$  adopts a face-centered cubic (fcc) structure where the molecules are orientationally disordered [1, 2]. This results from rapid and continuous rotations of the  $C_{60}$  truncated icosahedra, as shown by  $^{13}C$  NMR [3, 4] and recent quasielastic neutron scattering measurements [5]. Differential scanning calorimetry [2, 6] and X-ray powder diffraction [2] revealed a first-order transition near 250 K associated with a symmetry change from fcc to simple cubic (sc) at 250-260 K.

The structure of the low temperature phase has been studied by both high resolution X-ray [2] and neutron [7, 8] powder diffraction methods. From these results the following picture for the orientational ordering of the  $C_{60}$  molecules has been proposed [7, 8]: below the first-order transition at  $T_0 \approx 260$  K the  $C_{60}$  molecules perform rapid rotational jumps about one or several  $\langle 111 \rangle$  directions (their frequency is 10-100 kHz at 160 K [3, 6, 9]). Two inequivalent orientations of the molecules, related by  $60^\circ$  rotations about  $\langle 111 \rangle$ , and corresponding to anticlockwise rotations  $\phi$  of  $38^\circ$  and  $98^\circ$  with respect to the ideal  $Fm\bar{3}m$  configuration, appear to be energetically preferred. A frequency dependent elastic anomaly in the sound velocity and attenuation at  $\approx 160$  K supports the existence of 2 such energy minima [9]. As the temperature is reduced the orientation that optimizes the electrostatic interactions ( $\phi = 98^\circ$ ) is favored at the expense of that ( $\phi = 38^\circ$ ) which minimizes the van der Waals contribution to the free energy. Furthermore, evidence for a possible anomaly in the cell parameter near 155 K has been reported. It was tentatively associated with a change from multi  $\langle 111 \rangle$  rotation axes ( $T > 155$  K) to a single rotation axis ( $T < 155$  K) for each molecule. Finally, at about 90 K, the cell parameter variation exhibits a cusp which was attributed to the freezing of the rotational degrees of freedom of the molecules.

In this paper we present the results of a X-ray single-crystal study of the orientational ordering transition. This first-order transition is found at  $T_0 = 259 \pm 1$  K and it exhibits a hysteresis of about 1 K. Of particular interest is the first report of anomalies in the slope of the superstructure reflection intensity  $I(T)$  near 155 K and 85 K.

The starting  $C_{60}$  material was extracted from arc-generated carbon soot with hexane-toluene mixtures and purified by column chromatography on neutral alumina. Characterization by chromatography, infrared and mass spectroscopy indicated no trace of impurity.

Single crystals, shaped as distorted octahedra, were grown by slow evaporation from toluene solutions of pure  $C_{60}$ . Typical dimensions were of the order of 100  $\mu m$ . Characterization by X-ray precession photography and 4-circle diffractometry confirmed the fcc cubic symmetry with  $a = 14.15$  Å. The precession photographs also reveal a pattern of diffuse lines running along  $\langle 111 \rangle$  directions and which can be attributed to close-packed stacking faults in the fcc lattice. Such faulting has been previously observed, in particular in  $C_{60}$  films [11].

X-ray intensity measurements were performed using a home-built three-axis diffractometer (lifting-detector geometry) consisting of a rotating anode generator ( $CuK\alpha$ , fine focus, 55 kV, 20 mA), a doubly-bent graphite (002) monochromator and a linear position sensitive detector (PSD). The sample was attached to the cold end of a modified Displex cryogenerator. Good thermal stability (0.01 K) was assured by a flow of helium gas and the temperatures were accurate to within 0.1 K.

In a preliminary stage, oscillation photographs were made between 295 K and 25 K in order to probe extended regions of the reciprocal lattice. The fcc-forbidden superstructure reflections clearly appear on photographs taken at 250 K and below. Apart from the intensity buildup of these reflections as  $T$  was lowered, no further modification (such as lattice distortion or new

satellite reflections) could be found. No attempt was made to follow the lattice parameter evolution.

Some reflections were selected for intensity measurements as a function of temperature. These were performed by scanning through the peak position while integrating the intensity with the PSD. Figure 1 shows the temperature dependence of the integrated intensity (above background) of the (623) reflection between 23 K and 260 K. The transition occurs at  $T_0 = 259 \pm 1$  K. Sweeping the temperature up and down across the transition (see the inset) reveals a hysteresis of about 1 K but no discontinuity of  $I(T)$ .

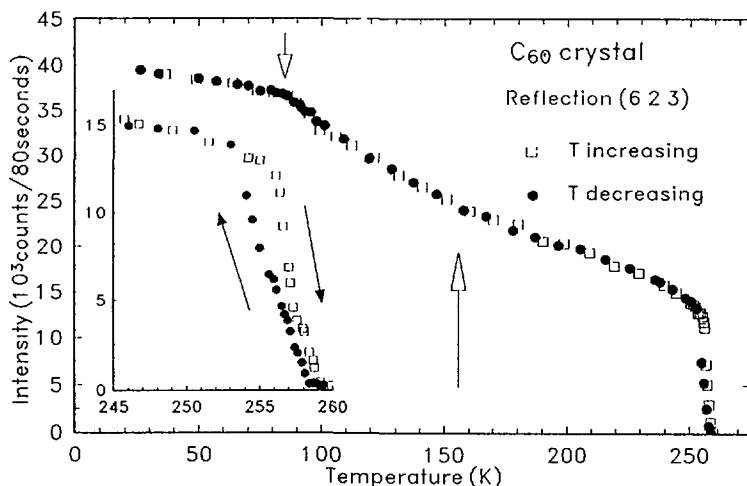


Fig. 1. — Temperature dependence of the integrated intensity of the (623) fcc forbidden reflection. Data were taken both on cooling and heating. Two anomalies are clearly visible near 155 K and 85 K. An expanded view of the hysteresis below 260 K is displayed in inset.

Below 250 K the intensity still increases appreciably ( $I(23 \text{ K})/I(250 \text{ K}) \approx 2.4$ ) in agreement with the results of Heiney *et al.* [2]. The temperature dependence of the intensity exhibits 2 anomalies at about 155 K and 85 K. The first one is found at  $T = 155 \pm 10$  K with an inflexion of  $I(T)$  (change of curvature,  $d^2I/dT^2$  becomes positive below 155 K) and a sudden increase of  $-dI/dT$ . A second anomaly in the intensity was observed at  $T = 85 \pm 5$  K, with a break in the rate of increase of the intensity ( $-dI/dT$  smaller below 85 K). The two anomalies are reproducible both on cooling and heating the sample (see Fig. 1) and a very similar behavior of  $I(T)$  was obtained for the (612) reflection.

These results shed light on some aspects of the orientational ordering in solid  $C_{60}$ , as discussed now. Beginning with the first-order transition at  $T_0$  it is worth noting that the value of  $T_0$  appears to depend on the particular sample. For instance the transition was found at  $254 \pm 1$  K for a second crystal from a different batch. Previous studies have shown that the characteristics of the transition depend on the crystallinity [4, 10] of the sample and also on its purity, as solvated crystals exhibit a lower transition temperature [9]. Another factor to consider is the existence of close-packed stacking faults in the fcc crystals. These defects are probably intrinsic to the growth mechanism of these van der Waals solids [11] and their concentration may vary, even for crystals taken from the same preparation. Their influence on the

molecular ordering remains to be quantitatively evaluated.

The first order nature of the transition is clearly demonstrated by the small hysteresis at  $T_0$ . Its magnitude ( $\delta T \approx 1$  K) compares well with that obtained by differential thermal analysis ( $\delta T \approx 1$  K) [12] but it is smaller than that reported from sound velocity measurements ( $\delta T \approx 2.5$  K) [9]. The same factors which were invoked for  $T_0$  (crystallinity, purity, stacking faults) can probably account for the variability of  $\delta T$  as well. The fact that we observe no discontinuity of  $I(T)$  can be understood if the two phases coexist in the crystal and this may again be influenced by the nature and concentration of defects.

It is very likely that the anomaly observed at  $T = 155$  K bears the same origin as the weak change of slope in the cell parameter previously detected by high resolution neutron measurements at the same temperature [8]. A quantitative change in the dynamics of the molecular reorientations cannot account for these effects. An interesting suggestion by David *et al.* [8] is that above 155 K each molecule rotates about different  $\langle 111 \rangle$  directions, while it rotates about a single  $\langle 111 \rangle$  axis below 155 K. In both temperature ranges long-range intermolecular correlations must preserve the cubic symmetry. However it is not clear to us at the moment that this would cause a larger rate of increase of  $I(T)$  below 155 K. On the other hand David *et al.* also find that the relative proportion of the  $\phi = 98^\circ$  configuration of the  $C_{60}$  molecule increases as the temperature decreases. Although this behavior was found to be initiated as high as 260 K, it would be tempting to associate 155 K with the temperature at which the stabilization of the  $\phi = 98^\circ$  configuration becomes sizeable. According to this model the progressive removal of the orientational disorder between the  $\phi = 38^\circ$  and  $\phi = 98^\circ$  configurations would be responsible for the faster increase of the intensity below 155 K.

The lower anomaly at  $85 \pm 5$  K leads to a reduced temperature dependence of the intensity at low temperature and it is probably related to the cusp in the lattice parameter reported by David *et al.* [8] at about 90 K. The authors suggested that this effect corresponds to the freezing of the molecular rotations, which hinders a complete stabilization of the  $\phi = 98^\circ$  configuration over the  $\phi = 38^\circ$  one, thus leading to some residual static disorder. The break in  $I(T)$  (Fig. 1) with a smaller ( $-dI/dT$ ) at low temperature may be attributed to the saturation of an order parameter below 85 K and thus appear to confirm this model. Actually, the behavior of  $I(T)$  is similar to that found in a number of materials such as the organic conductor  $(TMTSF)_2ClO_4$  (TMTSF is the molecule of tetramethyltetraselenafulvalene) where the orientational ordering of the  $ClO_4^-$  tetrahedra at 24 K can be quenched under moderately rapid cooling rates, leading to a saturation of the superstructure reflection intensity [13]. It would be interesting to investigate possible cooling rate effects in the present case and for instance it may be feasible to achieve a better orientational ordering of the  $C_{60}$  molecules under slower cooling rates.

The most significant result of our single crystal X-ray diffraction study is that two well defined anomalies in the temperature dependence of the intensity of fcc forbidden reflections were found at about 155 K and 85 K, below the first-order orientational ordering transition at 259 K. These results compare well with a recent neutron diffraction study by David *et al.* [8]. While the 85 K anomaly is likely to be due to the freezing of the molecular reorientations, the origin of the 155 K effect is still uncertain. Model calculations and fits to the  $I(T)$  curve should help to clarify this interesting issue.

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