Determination of molecular orientational angles in the low-temperature phase of C_{60}

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The low-temperature structure of C_{60} is simple cubic, however, orientational long-range order is far from being complete. According to current understanding C_{60} molecules can adopt two orientational states obtained by rotations about [1 1 1] axes through angles close to 98° and 38°. We present results of an elastic diffuse neutron-scattering investigation being clearly incompatible with these values and yielding rotational angles close to 102° and 42° instead. The significance of this finding is the following: While the previous angles can be interpreted as an attempt to reconcile icosahedral molecular symmetry with long-range cubic lattice symmetry the new angles can be understood as the result of an optimized arrangement of nearest-neighbor molecules. The molecular orientational states, therefore, are indicative of the dominant role of short-range interactions in this system. [S0163-1829(97)02430-2]

Solid C_{60} undergoes a phase transition from a face-centered cubic (space group $Fm\overline{3}m$) to a simple cubic structure (space group $Pa\overline{3}$) at $T_c \sim 260$ K.[1–4] In contrast to the orientationally largely disordered state above T_c the low-temperature structure exhibits orientational long-range order. This ordered phase is currently described by a two-state model where molecules are found in two energetically nearly degenerate orientations. These two states are presumably adopted at random, their fractions, however, depend on temperature. The two orientations are obtained from a given standard orientation by rotations about [1 1 1] axes through angles close to 98° and 38° (Refs. 5–7) (for a detailed review see Refs. 8 and 9). We have performed elastic diffuse neutron-scattering experiments whose results are clearly at variance with these values but show that the rotational angles are close to 102° and 42°. This may appear as a relatively small correction, however, is highly significant with regard to the physical meaning pertaining to these two different sets of orientations: The 98°/38° angles align molecular symmetry axes along crystallographic [1 1 0] directions as closely as possible thus underlining the presumed strong influence of long-range structural order. By way of contrast the 102°/42° angles arise from an attempt to optimize the mutual arrangements of neighboring molecules and thereby emphasize the importance of local molecular configurations for the structural state of C_{60}.

The random occupation of major ($\sim 98°$) and minor ($\sim 38°$) orientations presents a disturbance of the long-range order of the low-temperature phase and consequently gives rise to the appearance of diffuse scattering. The present investigation deals with the elastic part of this scattering which is due to static disorder while the inelastic part takes its origin in the dynamics of the system. A proper separation of these two contributions can only be achieved in neutron-scattering experiments since x rays do not permit us to sufficiently discriminate elastic from inelastic processes. The fractions of molecules adopting the two different orientations in the low-temperature phase of C_{60} vary with temperature[5,6] and thus, in general, will lead to a corresponding change both in the intensity of the elastic scattering and its distribution in reciprocal space.

Elastic diffuse scattering, which is characteristic of static disorder, was indeed observed in neutron investigations both in powders[10,11] and in single crystals.[12,13] Due to the averaging over reciprocal space the powder experiments did not provide enough detail to clarify the exact nature of the disorder. However, they established clearly that a narrow energy resolution is indispensable in order to be able to distinguish between static and dynamic effects. On the other hand, the early measurements on single crystals did provide specific information on the $(1\,\overline{1}\,0)$ scattering plane, however, they suffered from small samples and an inadequate energy resolution (about 2.1 meV).

This situation led us to reinvestigate the elastic diffuse scattering with improved energy resolution in a large C_{60} single crystal of about 100 mg. The experiment was performed on the triple-axis spectrometer VALSE located at a cold neutron guide position of the Laboratoire Léon Brillouin in Saclay, France. The measured energy resolution was 0.8 meV. Since the radial variation of the scattering in ques-
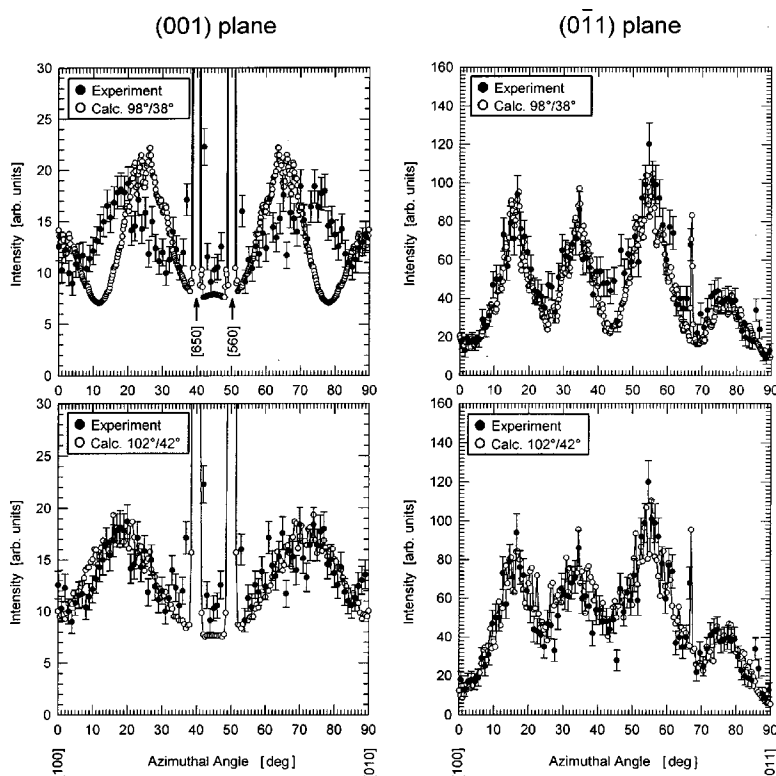
FIG. 1. Comparison of selected data on experimental and calculated elastic diffuse scattering. The left-hand side of the figure summarizes data for the scattering plane (0 0 1), the right-hand side for the scattering plane (0 $\bar{1}$ 1). Experimental points measured at 150 K (black dots with error bars) are compared with calculations (open symbols). In the upper half of the figure the calculations are based on orientational angles of 98° and 38° for the major and the minor orientation, respectively, in the bottom half the calculations were done with 102° and 42°. In the calculations an occupational fraction of 0.70 was chosen for the major orientation which is representative for published work on fractional occupations as a function of temperature (Refs. 5 and 6). The experimental data were obtained by performing circular scans in reciprocal space at constant momentum transfer close to $Q=3.5$ Å^{-1}. The scans cover an arc of 90° between two main directions of symmetry defining the respective scattering plane. The symmetry directions are indicated at the end points of the abscissa which gives the azimuthal angle over one quadrant. The two strong peaks in the (0 0 1) scattering plane (left-hand side of the figure) at about 40° and 50° are due to Bragg peaks closely approached by the scans and are identified by arrows. Their maxima (several orders of magnitude larger than the diffuse scattering and therefore not shown in the figure) are of comparable intensity as is expected for a merohedrally twinned crystal. Occasional ''spikes'' in the data of the (0 $\bar{1}$ 1) plane (right-hand side of the figure) likewise are due to Bragg peaks which, however, are lying farther off. Their tails usually are reproduced in the calculations by allowing for finite Q resolution.

tion is essentially determined by the molecular structure factor the major part of the required information has to be gained from the azimuthal dependence of the scattering intensity. Most of the measurements, therefore, were done on arcs of circles whose radii were chosen at values of transferred momentum Q near 3.5 Å^{-1} where the structure factor of the C$_{60}$ molecule exhibits its first maximum. Diffuse scattering in three scattering planes [(0 0 1), (0 $\bar{1}$ 1), and (1 1 1)] was examined at several temperatures between $T_c \sim 260$ and 10 K.

The experimental results were compared to model calculations of elastic diffuse scattering performed within the framework of the two-state orientational model. In the following we will not discuss results relating to the scattering intensity as a function of temperature[14] but rather concentrate on information which can be derived from characteristic patterns of elastic diffuse scattering and their temperature dependence.

Experimental results from two scattering planes obtained at 150 K are shown in Fig. 1 (upper half) together with calculated distributions of elastic diffuse scattering to be ex-

pected from the 98°/38° model. Significant discrepancies between the experimental data and the calculations are observed, especially in the (0 0 1) plane, where not even a rough agreement is found.

In order to obtain a better understanding of the deviations between experiment and simulation the parameters entering the calculations were systematically varied. Deviations from the published temperature dependence of the lattice parameter[5] and the bond lengths of the C$_{60}$ molecule[15] were considered within reasonable limits, yet as expected the resulting changes in the scattering patterns proved to be negligible. On the other hand, significant changes were obtained by varying the angles and the fractions of the two molecular orientations, however, in a qualitatively different way. While variations of the fractions of the two orientational variants over a wide range influence mainly the intensities of the calculated scattering patterns these patterns are also shifted and strongly distorted by changes of the orientational angles.

An important aspect of these calculations lies in the observation that changes in the arrangement of neighboring molecules are not reflected to the same extent in all scatter-

ing planes. In particular, it turned out that position and shape of the scattering pattern in the (0 0 1) plane are considerably more sensitive to changes of the orientational angles in comparison with the two other planes investigated. This sensitivity of position and shape represents a considerable advantage. The information which can be gained from intensity variations as a function of orientational angles is limited by uncertainties in quantities such as the Debye-Waller factor and the instrumental resolution which enter the calculations. On the other hand, the overall shape and, specifically, the positions of the maxima of the scattering patterns are practically not influenced by these factors and therefore can be considered highly reliable.

In the determination of the orientational angles various modifications of the standard 98°/38° model were examined. First, the angles were allowed to vary both independently and on the assumption that their difference equals a constant value. Then several types of continuous angular distributions about various pairs of angles were simulated, however, proved to be unsatisfactory. Finally, good agreement was achieved for a model where the 98°/38° orientations were replaced by pairs of discrete angles $98° \pm 4°$ and $38° \pm 4°$, respectively, and the sign of the orientational distortions was chosen at random.

Since this result was somewhat surprising we tried to analyze the local next-neighbor configurations corresponding to the $\pm 4°$ distortions. As originally pointed out by David[3] favorable orientations of neighboring molecules are characterized by electron-rich double bonds facing charge-depleted regions provided by adjacent hexagonal and pentagonal faces. Configurations of neighboring molecules for the angles $98° \pm 4°$ and $38° \pm 4°$ are shown in Fig. 2. It turns out that only the $+4°$ rotations improve the positions of double bonds relative to adjacent hexagonal and pentagonal faces while the $-4°$ rotations obviously lead to a loss of symmetry in the next-neighbor configurations.

This raised the question whether the experimentally obtained diffuse scattering pattern may be explained solely by the intuitively reasonable $+4°$ configuration but taking into account symmetry operations related to merohedral twinning. Twinning is known to be inherently present in C_{60} (Refs. 5 and 6) and Bragg peak intensities observed in this experiment are likewise compatible with the presence of two merohedral fractions amounting to about 50% each. We performed calculations based exclusively on the $+4°$ configuration but allowing for merohedral twinning as obtained by mirror reflection about a (1 1 0) plane of the simple cubic unit cell. The results shown in the bottom half of Fig. 1 are indeed found to be in good agreement with the experimental data as is the case also for the (1 1 1) plane not displayed in the figure.

Further calculations were performed using varying occupational fractions of the major orientation between 0.60 and 0.85 in order to describe all available experimental data measured in the temperature range between 250 and 10 K. (Complete data sets in all three scattering planes were measured at 250, 150, and 80 K. Additional, though less complete data sets were taken at 10, 50, 120, and 200 K.) Again, good agreement was obtained in all three scattering planes, however, the rotational angles yielding the best results in the calculations were found to increase slightly from 101.5°/
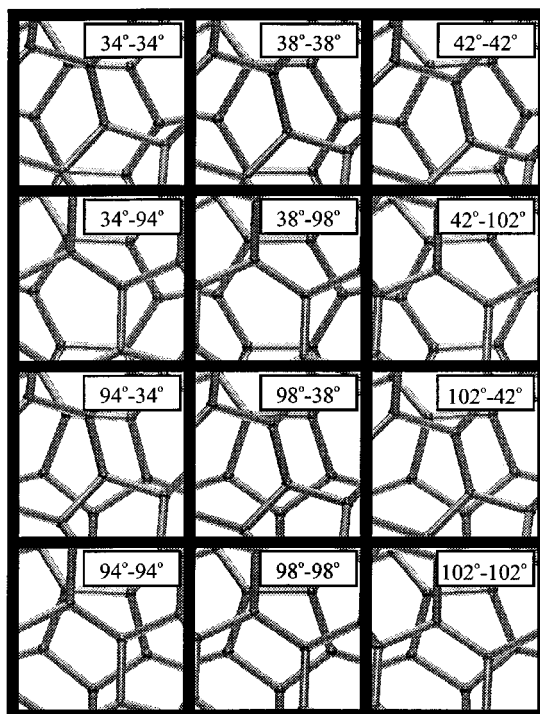

FIG. 2. Schematic representation of changing configurations of neighboring molecules viewed along [1 1 0] directions as a function of orientational angles. Each of the four rows corresponds to one of the four possible mutual arrangements occurring in the two-state model of the low-temperature phase of C_{60}. From top to bottom the contacts between background/foreground molecules arise from minor/minor, minor/major, major/minor and major/major orientations. In all pictures a ''short'' hexagon-hexagon double bond (displayed in the foreground) faces either a pentagon or a hexagon of the adjacent molecule (displayed in the background). The respective orientational angles are indicated in the legends. The first number refers to the background and the second number to the foreground molecule. On increasing the orientational angle, i.e., in turning from left to right in the figure, an advance of symmetry is observed and the configurations become progressively more advantageous with respect to the electronic charge distribution. Note that the ''gain'' is obviously largest for two molecules both adopting the minor (hexagon) orientation and smallest for two molecules both occupying the major (pentagon) orientation. A description of the elastic diffuse scattering based on the presently accepted angles $\sim 98°$ and $\sim 38°$ is clearly inconsistent with our experimental data. Interestingly, however, it is possible to reproduce the experimental results satisfactorily by properly mixing angle combinations of 102°/42° and 94°/34°. Nevertheless it is by far more convincing to do the calculations with a crystal made up of molecules exhibiting orientations of 102° and 42° together with its merohedral twin.

41.5° at 80 K to 102.5°/42.5° at 250 K. In all we estimate the uncertainty of the orientational angles to be no more than $\pm 1°$.

The variation with temperature has to be discussed in the following context: By inspecting Fig. 2 one can see that the necessary rotational shift towards a configuration of maximum local symmetry is largest for 38°/38° and smallest for 98°/98° contacts. On the other hand, the fraction of the major (98°) orientation is reported to increase from about 60% below T_c to about 80% around 100 K (Refs. 5 and 6) and though other published data on the temperature dependence

of the fractional occupations exhibit some scatter it is well established that the fractional occupation of the major orientation increases considerably at the expense of the minor orientation at low temperatures.

The above observations suggest that the orientational angles determined in our calculations and which are found to change with temperature are related to the respective fractions of the two orientations. The number of 42°/42° and 102°/42° contacts will decrease and the number of 102°/102° contacts correspondingly increase upon cooling. It may be that, as a consequence, the resulting orientational angles will take on slightly lower values at lower temperatures.

We briefly compare our results with the measurements of Chaplot et al.[12,13] which is the only neutron-scattering experiment reported so far investigating elastic diffuse scattering in the low-temperature phase of C_{60} single crystals. The angles obtained by Chaplot et al. at 10 K are 100° and 42° for the pentagon and the hexagon orientation, respectively, while we found 101.5° and 41.5°. The difference is not large though the 100°/42° combination is less satisfactory when applied to our data. At 250 K Chaplot et al. report agreement with their experimental data for 100° and 45°, however, prefer a description based on 100° and 42° together with random deviations $\Delta\varphi = 2°$ (rms) as being more convincing. It is indeed not easy to distinguish between these alternatives and the angles proposed in the present investigation by relying exclusively on data obtained in the $(0\bar{1}1)$ scattering plane as Chaplot et al. did in their experiment. However, the highly discriminating intensity pattern in the (0 0 1) plane shows clearly, that the 102°/42° combination (without any random deviations) is the only one leading to satisfactory agreement between the intensity distributions obtained from experiment and calculations.

In addition, we note that the triple peak structure of the data pertaining to the $(0\bar{1}1)$ plane shown in Fig. 1 for 150 K is completely conserved up to 250 K in our experiment. It presents a rather stable pattern which is also found in the calculations performed by Chaplot et al. in order to describe the situation at 250 K, however, is no more visible in their experimental data obtained at this temperature (see Fig. 4 in Ref. 13). This discrepancy has to be ascribed to insufficient discrimination of inelastic scattering in the experiment of Chaplot et al. due to a rather coarse energy resolution.

It is the principal outcome of this experiment that the low-temperature Pa$\bar{3}$ structure of C_{60} is characterized by two orientational states defined by the angles 102° and 42° at 150 K rather than by any other angle. This result is particularly convincing in view of the underlying physical meaning. Its significance is understood best by opposing the molecular arrangements leading to the 102°/42° and 98°/38° orientations, respectively. The 98° orientation can be seen as an attempt to accommodate the icosahedral symmetry of the molecule within the cubic symmetry of the lattice. It is unique in that a molecular symmetry axis approaches a crystallographic symmetry axis as closely as possible [strictly speaking the minimum value is attained at 97.621° (Ref. 7), where the angle between the fivefold axis of the C_{60} molecule and the crystallographic [1 1 0] direction is only 2.113°]. On the other hand, the 102°/42° orientations optimize the local configuration of a given molecule and its 12 nearest neighbors with respect to electrostatic interactions. The slight variations of the orientational angles with temperature are due to the respective changes of the pentagon and the hexagon fractions.

Apart from the 98°/38° orientations other pairs of angles have been proposed in investigations of solid C_{60} the majority of which, however, lie not too far from these values. Since these orientations can be regarded as mixtures of the ''long-range optimized'' 98°/38° and the ''short-range optimized'' 102°/42° angles but do not exhibit any peculiar distinguishing properties we do not discuss them in detail in the present context.

In summary, the new rotational angles determined in this experiment indicate the dominant influence of the local next-neighbor configuration on the structural state of C_{60} molecules at low temperatures.

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