Two-Stage Rotational Disordering of a Molecular Crystal Surface: C_{60}

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We propose a two-stage mechanism for the rotational surface disordering phase transition of a molecular crystal, as realized in C_{60} fullerite. Our study, based on Monte Carlo simulations, uncovers the existence of a new intermediate regime, between a low-temperature ordered (2×2) state, and a high-temperature (1×1) disordered phase. In the intermediate regime there is partial disorder, strongest for a subset of particularly frustrated surface molecules. These concepts and calculations provide a coherent understanding of experimental observations, with possible extension to other molecular crystal surfaces.

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Surface-specific thermal disordering phenomena, such as, for instance, surface melting [1], are of considerable interest. Conceptually, they demonstrate how a chunk of the metastable phase (e.g., the liquid phase within the solid domain of stability) can be imprisoned in full equilibrium by restricting it to an interface region of space. Practically, they provide at a temperature below the triple point a germ of the disordered phase that makes a major difference to all surface-related properties, as well as to the bulk transformation kinetics.

In molecular crystals, thermal surface disordering is richer than in atomic solids. Because of the presence of rotational degrees of freedom, the bulk develops rotational and positional melting transitions that are separate, and both of which might possess a surface counterpart. One is thus led to seek the existence of a well-defined surface rotational melting for a molecular crystal. However, until recently, very little phenomenology has been gathered addressing that issue.

The situation recently changed after the discovery of the C_{60} molecule [2] and its subsequent availability in macroscopic quantities [3] in its crystalline form, the fullerite. Here the near sphericity of the molecules favors rotational disordering at a relatively low temperature, when positional disorder and evaporation are still irrelevant owing to a sufficiently large cohesion [4]. On the theoretical side, the remarkable symmetry of the molecule leads to considerable simplifications with the help of symmetry adapted functions [5], such as those originally used for the CD_4 molecules [6].

Bulk measurements showed that C_{60} fullerite undergoes a first-order rotational melting transition at 260 K, characterized by fixed orientations of the molecules in the space group $Pa\bar{3}$ at low temperature transforming to a plastic phase with rotational isotropy, space group $Fm\bar{3}m$, at high temperature [7–9]. In the $Pa\bar{3}$ phase, the fullerite structure is composed of four sublattices. Neutron powder diffrac-

tion studies [10] of this phase have revealed the orientational configuration of the C_{60} molecules. The optimal orientation is such that, for all adjacent couples of C_{60}, an electron-rich double bond of one molecule faces an electron-poor pentagon of the other. In the $Fm\bar{3}m$ phase, the molecules are still not completely free to rotate since they are still correlated, and moreover they feel a crystal field of cubic symmetry [5,11]. However, in this phase, angular correlations are short ranged, and molecules are all equivalent, as opposed to the $Pa\bar{3}$ phase, with four inequivalent molecules and long-range angular correlations.

The structure of a free (111) surface of fullerite can differ from that of a bulk (111) plane due to the lowering of the number of neighbors. The first experiments showing a specific surface disordering were high-resolution reflection electron-energy-loss spectra (EELS) obtained by Goldoni *et al.* [12]. This technique is sensitive to the surface layer only because of the short escape depth of the scattered electrons. The authors reported an abrupt jump at about 230 K in the energy of the C_{60} triplet exciton. This discontinuity is an indication that the fullerite (111) surface undergoes the rotational disordering phase transition at a temperature some 30 K lower than the bulk. A similar transition temperature (230 ± 20 K) was observed in LEED studies of C_{60} films [13] but the incertitude in the temperature was too large to interpret it as a specific surface effect.

At first sight, such a lowered surface transition temperature is reminiscent of ordinary, positional surface melting of solids, where surface premelting precedes and initiates the bulk transition [1]. However, it soon appeared that in fullerite the surface disordering took place in the topmost layer only [12,14], in contrast with standard surface melting, where the liquid film grows progressively, invading the crystal. At the same time, a conceptual difference was also noted. Positional order in a crystal is forced exclusively by interparticle interaction; rotational ordering instead involves both intermolecular angular interactions and a cubic

crystal field that would be present and effective on each molecule even if all the surrounding molecules were perfect spheres. A surface molecule thus feels not only less rotational interactions but also a crystal field which may generally frustrate bulk order [15]. On the other hand, due to the weak short-range nature of intermolecular potentials, the molecules in the second layer, immediately below the surface, are already very close to a bulk situation. The system, between 230 and 260 K, can thus be regarded as an ordered solid with a disordered surface.

We now underline the fact that experimental data suggest in fact not one but *two* surface transitions, the second one taking place at even lower temperatures. There is a less marked discontinuity at about 160 K in the triplet exciton energy revealed by EELS [12]. It was explained as a consequence of the molecular rotation relaxation time which at this temperature becomes similar to the exciton lifetime. However, independent evidence for a transition or crossover at that lower temperature is the presence at about 160 K of a shoulder in the LEED intensity of the $Pa\bar{3}$ diffraction spots versus temperature, absent in the bulk x-ray intensity [16]. Helium atom scattering (HAS) diffraction studies of the (111) surface of fullerite by Glebov *et al.* [17] clearly showed a change from a (2×2) to a (1×1) structure taking place at 235 K. But, in addition, the behavior of the Debye-Waller factor (DWF) of the (0,0) Bragg spot between 140 and 235 K was completely unexpected. Instead of decreasing monotonically with increasing temperature, the DWF started increasing at about 140 K and reached a maximum at 235 K. This was explained as a consequence of preempted disordering of C_{60} molecules at low coordination defect sites. This behavior, found to be reversible, cannot be explained if the surface layer were totally ordered below 235 K.

In this Letter, we studied the surface orientational ordering of fullerite by classical Monte Carlo (MC) simulation. We considered a C_{60} molecule as a rigid body, and used the potential developed by Lamoen *et al.* [18] to model the intermolecular interactions. That model considers 210 interacting centers on each fullerene: 60 are localized on the carbon atoms, 60 are at the center of the single bonds, and 3 are distributed along each of the 30 double bonds to take their spatial extension into account. The repulsive part of the intermolecular potential is a sum of Born-Mayer terms between all the interacting centers (c), and the attractive part is made of R^{-6} van der Waals interactions between the atoms (a)

$$V = \sum_{a_1 a_2} \frac{A}{r_{a_1 a_2}^6} + \sum_{c_1 c_2} B_{c_1 c_2} \exp[-C_{c_1 c_2} r_{c_1 c_2}]. \quad (1)$$

Our MC simulations were based on a standard Metropolis, acceptance-rejection algorithm. The molecules were placed in a semi-infinite fcc lattice with a (111) surface. We considered twelve nonequivalent molecules, four in the first layer (the surface layer), four in the second layer, and four in the third layer. All other molecules in the system were assumed to be copies of this twelve-molecule basic cell, with periodic boundary conditions applied in two dimensions. In the direction of the bulk, the second layer was reproduced at the fourth layer, shifted horizontally in order to simulate the fcc stacking. The center of mass of the molecules was held fixed to lattice sites, while the temperature-dependent lattice parameter of the structure was set to the experimental value [19]. The twelve molecular orientations were allowed to change randomly. We performed a complete calculation of the energy at each MC step.

Earlier theoretical studies of the rotational bulk phase transition have shown the usefulness of a set of order parameters based on the cubic harmonics [5]. We used an efficient and original algorithm to generate these cubic harmonics. Starting from generating functions of the irreducible representations k (A_1, A_2, E, T_1, T_2) of the cubic group O_h, it is possible to expand them into a Taylor series and to extract from that expansion the number of irreducible representations for each manifold l of the intermolecular potential. Using the generators $\Gamma(k)$ of each irreducible representation, one can construct automatically the cubic harmonics [20]:

$$[\Gamma^{(k)}(g)]E^{(l,k)}(\vec{r}) = E^{(l,k)}[\Gamma^{(T_1)}(g)\vec{r}], \quad (2)$$

where g belong to O_h and $E^{(k,l)}$ is the integrity basis of order l for the irreducible representation k. Since the cubic harmonics must be homogeneous polynomials of the coordinates, this system can be solved easily, and one obtains analytical expressions for all the cubic harmonics, to be used with the atomic coordinates of the 60 atoms of the molecule. In particular, the following expression was calculated:

$$h_n^{(l,k)} = \sum_{a=1}^{60} E^{(l,k)}(\vec{r}_a^n), \quad (3)$$

where $\vec{r}_a^n$ is the position vector of atom a in the nth molecule in the unit cell. Using the C_{60} atomic coordinates automatically introduces the icosahedral symmetry of the molecules. Another advantage of this method is to naturally allow for a future inclusion of internal molecular vibrations, not treated at this stage. Because of the icosahedral symmetry, $h_n^{(l,k)}$ differ from zero for $l = 6, 10, 12, 16, 18 \cdots$. We used $l = 10$ throughout. For each molecule (index n), we calculated a scalar order parameter

$$\eta_n^{(l,k)} = |\langle h_n^{(l,k)} \rangle|^2, \quad (4)$$

where $\langle h_n^{(l,k)} \rangle$ is an average over the configurations generated by the MC algorithm. For all the irreducible representations of the O_h group, this parameter was traced as a function of the temperature to observe the phase transition as it has the largest amplitude in the ordered phase.

As mentioned in [21], T_{1g} and T_{2g} are the two primary order parameters. We adopted the irreducible representation T_{2g} as the best indicator of the rotational phase transition, as the corresponding order parameter vanishes in the disordered phase [5]. Figure 1 shows the temperature dependence of that order parameter for the twelve molecules
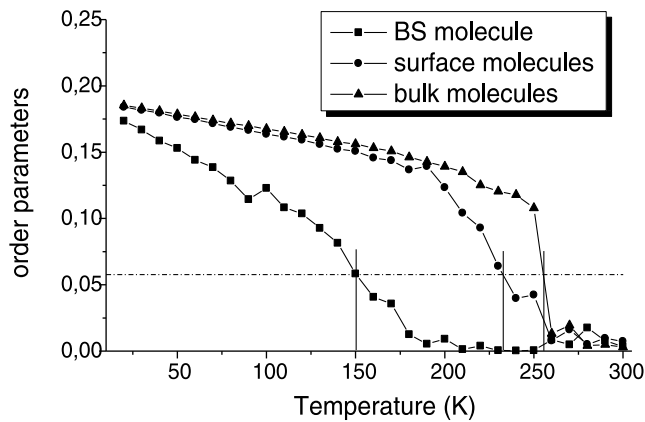
FIG. 1. Variation of the order parameter $\eta_n^{(l,k)}$ corresponding to $l = 10$ and $k = T_{2g}$ versus temperature. The curves correspond to the three behaviors observed in our Monte Carlo simulations. The triangles are the arithmetic means of the order parameters associated with the bulk molecules. The circles are the arithmetic means of all the surface molecules, except the molecule BS which has a behavior pointed out by the squares.

of our system. The eight bulklike molecules of layers 2 and 3 (represented by triangles), plus all their infinite copies, undergo a clear phase transition at 250 K. This value is affected by size, in particular by artificial correlations built in a small system such as the one we considered. By comparison, the mean-field theory transition temperature was even smaller, namely, 200 K [18]. However, only the dominant part of the multiple-order parameters was originally used in the mean-field molecular equations of Ref. [18]. An extension of the number of coupled-order parameters leads to an increase of the mean-field transition temperature [9,22].

At low temperature, the molecules in the (111) surface (represented by circles in Fig. 1) keep the same orientation as in the bulk, corresponding to the (2×2) superstructure observed in HAS diffraction. In this configuration, shown, for example, in Ref. [23], one can immediately distinguish two types of molecular orientations. Three molecules in the surface (2×2) unit cell have only a twofold axis normal to the surface and the $Pa\bar{3}$ threefold axis 30° off. The fourth molecule, which we denote as BS, has instead the threefold axis normal to the surface. Calculations performed by rotating one molecule while keeping a fixed orientation of all the other molecules show that the "crystal field" angle-dependent potential felt by the rotating molecule is different, and shallower for the BS molecule than

for the three other molecules. This suggests that the rotational thermal behavior of the BS molecule must differ from that of the other surface molecules [15].

In fact, with increasing temperature, the four surface molecules do behave differently. The BS practically becomes a quasifree rotator above about 150 K, whereas the other three molecules do so only above a much higher phase transition temperature, which is about 230 K. Notice that a partially ordered phase (with respect to molecular orientations) exists in solid CD_4 [6,24]

In the low-temperature phase, the surface symmetry is threefold due to the local threefold axis of the BS molecule. At 150 K, we observe a dramatic reduction of threefold order with strong rotational disordering of the BS molecule. Although strictly speaking the threefold order of that molecule cannot vanish, it does, however, become too small to assimilate it to a free rotator, in which case the surface symmetry would become sixfold because the BS molecular environment is characterized by a sixfold axis. Thus 150 K represents a crossover temperature, where there is no strict change of surface symmetry and probably no proper surface phase transition, but there is nonetheless a change from essential order to essential disorder for BS molecules only.

Hence our system exhibits altogether four phases or regimes (see Table I): (i) a fully ordered $Pa\bar{3}$ state (effective $p3$ surface symmetry) below 150 K, as it was recently confirmed by scanning tunneling microscopy (STM) measurements [23]; (ii) an intermediate regime between 150 and 230 K with one essentially disordered and three ordered surface molecules per unit cell ($p6$ effective symmetry of the surface layer) over a $Pa\bar{3}$ ordered bulk; (iii) a disordered surface layer on an ordered $Pa\bar{3}$ bulk between 230 and 250 K; (iv) a fully rotationally disordered $Fm\bar{3}m$ ($p6m$ symmetry of the surface layer) above 250 K.

In the simulations, full thermal disordering of the molecules takes place at the topmost layer only, in agreement with evidence from EELS [12]. In addition, the main surface transition temperature (230 K) agrees very well with the observations by LEED, EELS, and HAS. The intermediate BS-disordered regime between 150 and 230 K can explain the weaker experimental anomalies mentioned above, in particular the feature at 160 K in the triplet exciton energy, signaling in our interpretation an approximate change of surface symmetry from $p3$ to $p6$.

We note that in LEED and HAS diffractions, this change is not picked up since the unit cell remains (2×2) up to

TABLE I. Ordering phase transitions in C_{60} fullerite with a (111) surface.

Temperature	Bulk	Surface	surf. sym.
Below 150 K	Ordered	Ordered	$p3$
150–230 K	Ordered	1 of 4 mol. disordered / 3 of 4 mol. ordered	$p6$
230–250 K	Ordered	Disordered	$p6m$
Above 250 K	Disordered	Disordered	$p6m$

230 K. We suggest instead that STM experiments be carried out in the appropriate temperature interval to test in more detail our predicted two-stage surface disordering. Our model provides a plausible explanation for the behavior of the (0,0) Debye-Waller factor in HAS diffraction [17], its increase between 140 and 235 K due to the BS molecule rotating freely in that temperature interval. Because of the resulting partial disordering of the (2×2) surface cell, the intensity of some diffracted beams is reduced and transferred to the specular spot [25], which compensates the thermal attenuation of the elastic reflection [17]. Our proposed selective thermal disordering of BS molecules may also provide an explanation of the anomalous features observed near 160 K in x-ray powder diffraction intensities [26,27]. Such anomalies were also observed by David [28] in high-resolution neutron scattering. If these anomalies were not reported later on, it was probably due to the increasing quality (and then the grain size) of the C_{60} powder, decreasing the surface/bulk ratio.

In summary, the study of fullerite may prove of paradigmatic importance to a much broader class of molecular crystals. Our work indicates that rotational thermal surface melting of a molecular crystal differs from ordinary, positional surface melting, in one important aspect, with several consequences. The rotational ordering forces comprise both crystal fields and intermolecular interactions, while the former is missing in the positional case. At the surface, both interactions and crystal fields are different from the bulk. When, as in fullerite, the crystal field is quantitatively very important in the bulk, its heavy change at the surface may lead to an early thermal disordering taking place strictly in the first layer, since in all other layers the crystal field is bulklike. Moreover, crystal fields may differ so much between one surface molecule and the other, to cause surface thermal disordering to take place in separate stages, the weaker molecules disorder much earlier than the stronger molecules.

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