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Heterophase fluctuations near the 260-K transition and the absence of reflections with half-integer indices in a C_{60} single crystal

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A diffuse-neutron-scattering investigation of the 260-K order-disorder transition in a C_{60} single crystal reveals the presence of ordered clusters within a narrow temperature range above the transition temperature. This cluster state is metastable and gives evidence for heterophase fluctuations. In addition, during an excursion to lower temperatures we investigate regions near reciprocal-lattice points with half-integer indices where recently additional superlattice intensities were reported to have been observed by electron-microscopic methods. At three selected reciprocal-lattice points, i.e., (0.5,0.5,5.5), (2.5,2.5,0.5), and (3.5,3.5,5.5), no superlattice reflections can be found down to 10 K.

C_{60}, the newly discovered modification of carbon, shows an order-disorder phase transition near 260 K.[1,2] At low temperatures, the C_{60} molecules crystallize in a long-range-ordered configuration as borne out by the observation of sharp superlattice reflections below the transition temperature. Above 260 K, the orientation of the C_{60} molecules is dynamically disordered but the centers of the molecules form a fcc lattice.

This phase transition has been investigated by a series of methods, e.g., x-ray and neutron diffraction, NMR, specific heat, and ultrasound techniques.[1,3–7,11] It was found that the transition is a first-order transformation characterized by a small hysteresis of a few degrees. At the transition temperature, the lattice constant shows a discontinuous change, i.e., a small decrease of 0.4% upon ordering. Investigations of macroscopic quantities such as specific heat and ultrasound attenuation show a λ-shaped anomaly near the transition temperature.[6–11]

In the present paper we report on an elastic diffuse-neutron-scattering investigation of a C_{60} single crystal revealing the presence of ordered clusters within a narrow temperature range above the order-disorder transition temperature. These clusters may be ascribed to heterophase fluctuations.

A 4-mg C_{60} single crystal was synthesized using the sublimation technique.[12] The neutron measurements were done on the triple-axis spectrometer VALSE located on a cold neutron guide position of the Laboratoire Léon Brillouin in Saclay (France). The incident neutron energy was 14.7 meV and a pyrolytic graphite filter was put into the incident beam in order to eliminate higher-order contaminations. Pyrolytic graphite crystals were used as both monochromator and analyzer and the collimations were 30 min. The mosaic spread of the crystal was about 40 min. The sample temperature during the measurements was controlled by a closed-cycle cryostat.

The (4,4,5) reciprocal-lattice position corresponding to a superlattice reflection in the ordered phase was investigated by radial scans along the [1,1,1] direction as a function of temperature, especially near 260 K. At 255 K, a sharp (4,4,5) superlattice reflection was observed whose width was determined by the instrumental resolution. Increasing the temperature to 260 K and 262 K, respectively, did not induce any noticeable changes either in the intensity or in the width of the peak. During further heating to 262.5 K, the intensity of the superlattice reflection dropped to about 20% of its original value while its width was still limited by the instrumental resolution [Fig. (1a)].

Subsequently the temperature was increased in several steps comprising a few tenths of a degree at a time. After each temperature change the region near the (4,4,5) reciprocal-lattice point was investigated by a series of scans in order to study the reproducibility and the time behavior of the measured intensity distribution. It was observed that the superlattice reflection was broadened after each temperature step [Fig. (1b)]. At constant temperature, however, the measured intensity distribution did not show any further evolution, even after 20 h at the same temperature. AT 264 K, a flat background was observed.

The crystal was heated to 300 K and then the temperature was decreased again. Upon cooling through the transition region, a similar scanning procedure was applied after each temperature step. Again, near 263 K, a broad diffuse intensity distribution was observed at the (4,4,5) superlattice point. After further temperature steps, the distribution became narrower and its intensity increased (Fig. 2). At constant temperature, however, the diffuse scattering did not exhibit any variation with time. Finally, between 262 K and 260.7 K the intensity of the superlattice reflection increased abruptly to its original value. The intensity behavior during cooling and heating is shown in Fig. 3. The corresponding widths of the intensity distributions are displayed in Fig. 4.

The present series of measurements confirms the first-order nature of the phase transition since in both directions of the temperature variation a discontinuous change of the superlattice reflection intensity is observed. During this intensity jump, the measured width of the reflection remains within the limits of the experimental resolution.

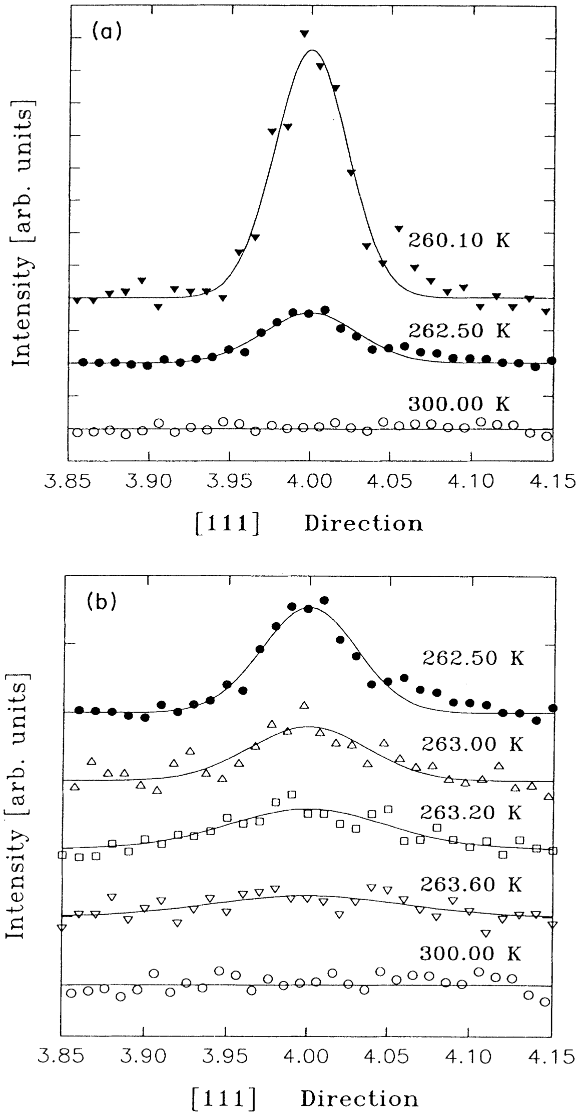

FIG. 1. The (4,4,5) superlattice reflection scanned along the [111] direction (in reciprocal lattice units) at different temperatures during heating. (a) An abrupt intensity change is seen between 260.1 and 262.5 K but the width of the peak remains within the experimental resolution. At higher Q values the intensity distributions exhibit a small shoulder which decreases in intensity like the main peak. This shoulder may be related to an intensity contribution from a stacking fault streak taking its origin at the (445) point and extendng along the [111] direction. (b) Peak broadening is observed at the indicated temperatures. The curves represent Gaussian fits to the data.

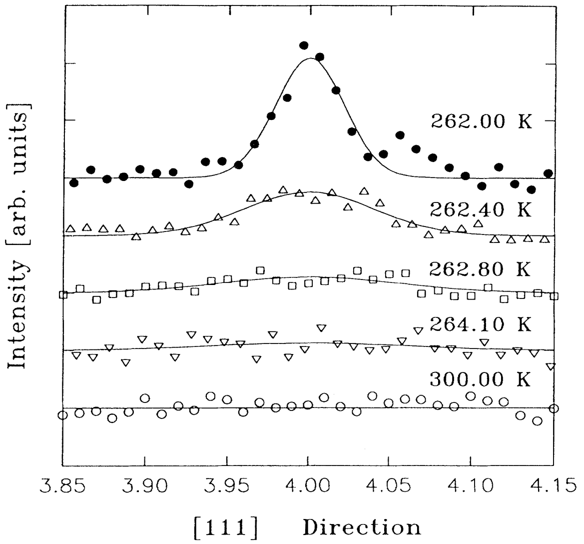

FIG. 2. The (4,4,5) superlattice reflection scanned along the [111] direction at different temperatures during cooling. A broad diffuse intensity distribution appears which becomes narrower upon cooling. The curves represent Gaussian fits to the data.

On the other hand, the experiment shows the presence of ordered clusters within a temperature range of a few degrees above the transition temperature. These ordered clusters are stable over the time scale of the experiment. From the observed broadening of the superlattice reflection a typical cluster size of about 70 Å can be deduced at temperatures of about one degree above the transition point. The cluster state occurs likewise on heating and on cooling but its formation shows a small

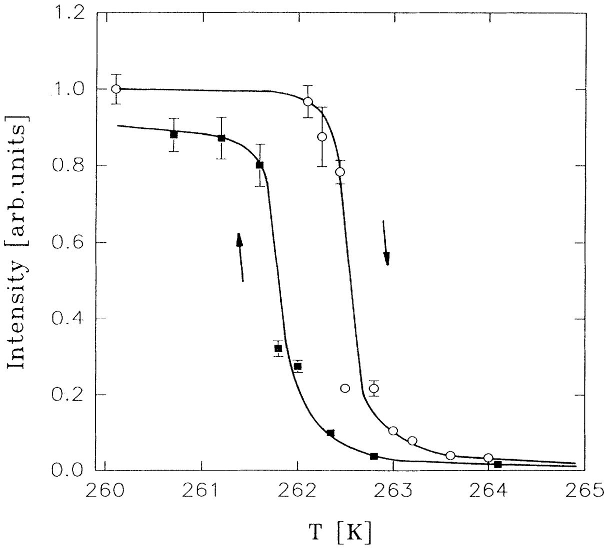

FIG. 3. The peak intensity of the (4,4,5) superlattice reflection vs temperature. (○) during heating, (■) during cooling.

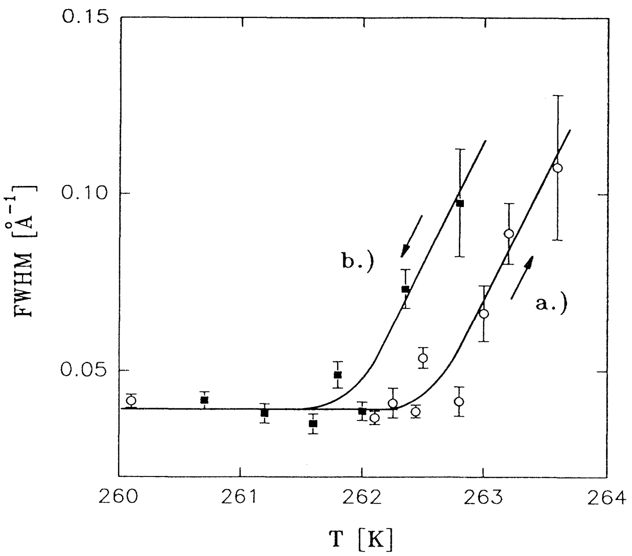

FIG. 4. The full width at half maximum (FWHM) of the intensity distribution as a function of temperature observed at the (4,4,5) superlattice point. (○) During heating, (■) during cooling.

hysteresis (Fig. 4) linked to the one observed for the transition temperature, in agreement with earlier results. Moreover, the ordered clusters have the same lattice parameter as the long-range-ordered phase since the broadened intensity distribution near the (4,4,5) point is always centered at the same position as the sharp (4,4,5) superlattice reflection.

The formation of clusters near first-order phase transitions has been treated in the past, especially in theoretical work.[8–10] Near first-order phase transitions thermal fluctuations induce long-lived metastable structural states which have been called heterophase fluctuations. These heterophase fluctuations increase in size when the transition temperature is approached. Generally, it is conjectured that they are responsible for the λ-shaped behavior of some macroscopic quantities near the transition point.[8]

Nevertheless, experiments giving direct evidence for heterophase fluctuations are rare. In some works it is conjectured that in many solid-state systems, heterophase fluctuations are suppressed by the strain energy related to volume and shape changes of crystals occuring at first-order phase transformations. In the present case of a C_{60} single crystal, the strain energy is low as borne out by the small hysteresis and C_{60}, therefore, is a candidate for the formation of heterophase fluctuations as shown in this experiment. We cannot definitively show that the heterophase fluctuations are intrinsic properties of the C_{60} material and consequently cannot rule out that the heterophase fluctuations nucleate or are stabilized near crystal-lattice defects. It should be noted, however, that typical values of the volume fraction ($\sim$ 10%) and the cluster size ($\sim$70 Å) of the heterophase fluctuations are large when compared to the density and size of crystal-lattice defects possibly interacting with them.

Furthermore, it should be noted that the present results on the intensity behavior near the (4,4,5) superlattice point are qualitatively in good agreement with measurements of ultrasonic attenuation in a C_{60} single crystal near 260 K reporting a λ-shaped behavior and, in particular, showing pronounced tails towards higher temperatures.[11] These tails in the ultrasonic attenuation may be attributed to the cluster formation observed in this experiment. Likewise, the ultrasonic results indicate a similar small hysteresis.

Finally, in addition to the reported measurements near 260 K, we also investigated some selected regions near fcc reciprocal-lattice points, i.e., (0.5,0.5,5.5), (2.5,2.5,0.5), and (3.5,3.5,5.5), where recently superlattice reflections with half-integer indices have been found by electron microscopic methods, especially at low temperatures.[13] These reflections were presented as evidence for the formation of a low-temperature superstructure in pure C_{60}. The structure of the phase was described to be fcc with a lattice parameter $2a$ where a is the lattice parameter of the dynamically disordered high-temperature fcc lattice.

We made reference scans at room temperature and at 150 K where only a flat background could be observed. After further cooling to 10 K, measurements with good counting statistics gave no evidence for the appearance of superlattice reflection intensities at the three selected Q positions. Again, at all three reciprocal-lattice points only a flat background could be observed. Further data evaluation showed that the reported additional superlattice reflections, if present, should be lower than 10^{-2} of the peak intensity of the (4,4,5) reflection.

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