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# First-order orientational-disordering transition on the (111) surface of $C_{60}$

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The temperature dependences of the triplet exciton, of the vibrational modes, and of the low-energy diffraction pattern of the (111) surface of well-ordered $C_{60}$ films indicate that this surface undergoes a first-order orientational order-disorder phase transition at 225±3 K, well below the temperature of the corresponding phase transition in the bulk of the same samples, which we find to be 260 K. The bulk phase transition is therefore initiated by the surface. To our knowledge, this is the first example of a surface orientational phase transition, a phenomenon that should occur on several other molecular crystal surfaces. [S0163-1829(96)07127-5]

Surface order-disorder phase transitions may initiate the corresponding first-order phase transitions in the solid. Surface melting has been observed to occur on surfaces of several solids[1] at temperatures substantially lower than the bulk melting point. This transition can be regarded as a complete or incomplete wetting of the ordered solid by a disordered layer.

In this paper we show that also orientational order-disorder transition in a molecular crystal may have a surface counterpart that occurs at lower temperature. This kind of surface phase transition is expected to occur on a large class of molecular crystals.

Solid $C_{60}$ undergoes an orientational order-disorder transition at $T_B = 260$ K and a glassy transition at about 90 K.[2–4] At temperatures above $T_B$ the quasispherical $C_{60}$ molecules rotate around their center.[5] The molecules are all equivalent and the lattice is fcc.[2] When the temperature is lowered below 260 K the rotation stops and a first-order phase transition occurs. The new lattice is simple cubic (sc) with a basis of four molecules that differ by their orientation.[3] Each molecule performs thermally activated jumps between two minima of the orientational potential. Below 90 K the jumping time becomes very long and the solid is left in an orientational glassy state.[2–4]

The $C_{60}(111)$ surface is known to have a $(2\times2)$ superstructure at $T < 230 \pm 20$ K,[2,6] which results from the low-temperature orientational ordering of the surface $C_{60}$ molecules, since the ideal (111) surface of the low-temperature sc crystal has a basis of four inequivalent $C_{60}$ molecules in a $(2\times2)$ lattice.[6] Here we show that the $C_{60}(111)$ surface undergoes a first-order transition at 225±3 K, 35 K below the temperature of the bulk transition, when the surface structure changes from $(2\times2)$ to $(1\times1)$. This transition has been first found by measuring the temperature dependence of the surface triplet exciton spectrum and then confirmed by a jump in the scattering cross section of some vibrational modes in high-resolution electron energy-loss spectroscopy (HREELS), and by low-energy electron diffraction (LEED). The high surface sensitivity of the electron scattering mechanism that excites the triplet exciton in $C_{60}$ is proved in the Appendix.

Ordered $C_{60}$ layers were grown on an Au(110) substrate by sublimation from a Ta crucible in UHV ($10^{-10}$ torr). The $C_{60}$ powder had a purity better than 99.5% and was degassed at 730 K in UHV for hours before growing the samples. An ordered close-packed monolayer (ML) was grown, keeping the sample at 700 K during deposition.[7] The other 1–30 layers were grown slowly on top of this layer, keeping the sample at 400 K. LEED data and scanning tunneling microscope (STM) studies[7] show that these layers are well ordered and flat. The corrugation induced by the substrate in the first layer vanishes from the third layer on.[7] The thickness of the film was determined by Auger spectroscopy at low coverages[8] (see the Appendix) and by the growth time at high coverages. The LEED pattern observed above ~240 K is that of a well-ordered (111) surface of an fcc crystal and surface primitive vectors of about 10 Å. A clear $(2\times2)$ superstructure was observed at lower temperatures. Auger spectroscopy did not show any surface contamination within the detection limit (1%).

The spectra were measured with a Leibold Heraeus ELS 22 spectrometer with a resolution of 20 meV for the electronic excitations and 5 meV for the vibrational excitations. The vibrational spectra were measured in specular geometry with an incidence angle of 70°, the spectra of the exciton were collected 15° out of the specular direction. The temperature was measured by a Chromel-Alumel thermocouple inserted in a small hole in the Au substrate with an accuracy of 2–3 K. The intensity of the LEED spots was measured using a photodiode.

Figure 1 shows the energy loss spectrum of the triplet exciton as a function of temperature $T$. This is the lowest-energy structure of the electron energy-loss (EEL) spectra and it is excited by exchange scattering.[8–10] Its energy is about 0.3 eV below the $T_{1g}$ singlet exciton[11] and is close to the measured energy of the triplet exciton in solution[12] (1.6 eV) and in solids (1.5 eV).[13] Our spectra are sensitive to the topmost $C_{60}$ layer because the sampling depth in the case of exchange scattering is half the escape depth of the scattered electrons. For low-energy electrons (2–100 eV) in $C_{60}$ the escape length is of the order of the molecular diameter[8,14] (see the Appendix). At the energy at which the spectra were

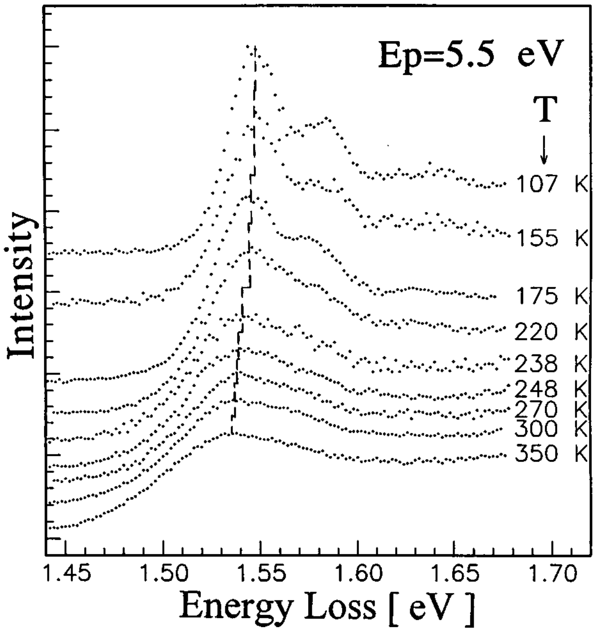

FIG. 1. EEL spectra of the triplet exciton of $C_{60}(111)$ as a function of temperature.

recorded (5.5 eV) the escape length (10 Å) is such that more than 75% of the triplet exciton signal comes from the first molecular layer. Therefore Fig. 1 shows the surface triplet exciton.[8] Samples of various thickness, from 5 to about 30 $C_{60}$ layers, show similar spectra. The peak at 1.549 eV at 100 K is attributed to the pure electronic transition and the peaks and shoulders at higher energies are associated to $h_g$ phonon assisted transitions.[8,15]

The structures in the surface triplet exciton spectrum broaden and shift as the temperature increases. The energy $E_1$ of the half height point in the low-energy side of the pure electronic transition is plotted as a function of $T$ in Fig. 2. $E_1$ remains constant up to 150 K, then decreases almost linearly. A jump of about 7 meV occurs at 224 K within 2 K. After this jump $E_1$ decreases almost linearly with a slope of 0.14 meV/K between 230 and 350 K, with a possible kink barely above the noise level at 260 K. In order to understand if the 224-K jump is due to the broadening of the excitonic structures or to their shift we have fitted the triplet exciton spectrum between 1.4 and 1.7 eV with nine Gaussian peaks, i.e., one peak for the pure electronic transition and eight peaks for the $h_g$ phonon replicas (six losses and two gain peaks). The energy differences between the pure electronic peak and the phonon replicas have been determined by fitting the 110-K spectrum (Fig. 2 top panel) and have been kept constant in the fits of the other spectra. The free parameters in the fits for $T > 110$ K were the intensities of the peaks, the width and energy of the pure electronic transition, the common width of the phonon assisted transitions, and the background. This term was simulated by a constant plus a Gaussian peak, which mimics the tail of the electronic transitions at energies higher than 1.8 eV.

Figure 2 shows the energy $E_0$ of the pure electronic transition as a function of $T$ as obtained from our fitting. The temperature dependence is similar to that of $E_1$, with a constant region up to 150 K followed by a decrease, a jump at 225 K ($T_S$), and a possible kink at about 260 K. The magnitude of the jump (6 meV within 2 K) is similar to that of $E_1$. The width of the pure electronic peak is constant (30 meV) up to 150 K, and increases, reaching 40 meV at 225 K and 50 meV at 350 K without jumps within the error (4 meV).

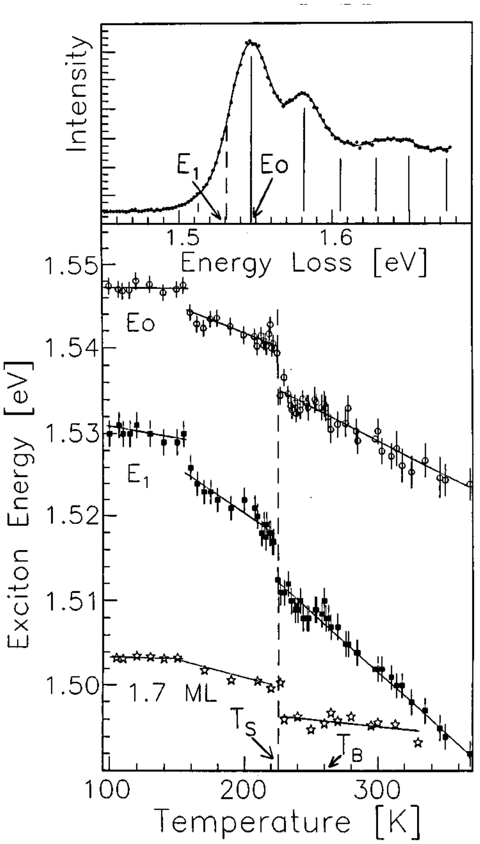

FIG. 2. Top: fit of the triplet exciton EEL spectrum at 110 K. The bars show the energies of the Gaussian peaks used in the fit. Bottom: Energy of the half height point in the low-energy side of the main excitonic peak $E_1$, of the pure electronic transition $E_0$ in thick films, and in a 1.7-ML film as a function of $T$. The data for the 1.7-ML film have been shifted downwards by 40 meV. The jump at $T_S = 225$ K indicates the surface phase transition. The solid lines are guides to the eye.

The surface origin of the observed temperature dependence has been checked by monitoring the triplet exciton of a 1.7-ML film. The spectrum of the first $C_{60}$ layer in contact with the substrate does not show any triplet exciton, being metallic.[16] Therefore the 1.55-eV peak in the 1.7-ML spectrum originates from the incomplete second $C_{60}$ layer only. The strong similarity between the temperature dependence of the energy of the triplet exciton in this sample and in the 30-ML sample indicates that the 225-K jump is a surface effect.

In order to relate the change in the electronic states at $T_S$ with the surface structure we have measured the temperature dependence of the LEED pattern of the $C_{60}(111)$ surface. The intensity of the half integer spots vanishes at about 235 K (Fig. 3). This is only an upper limit for $T_S$, because the jump of the intensities of the diffraction peaks is appreciably broadened by the surface defects in a surface phase transition. The presence of steps, vacancies, and domain

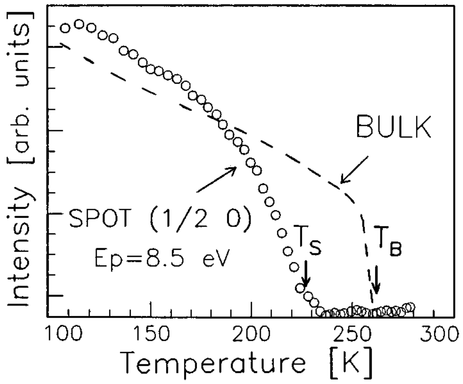

FIG. 3. Intensity $I$ of the $(\frac{1}{2}\ 0)$ LEED spot vs $T$. The data have been corrected for the Debye-Waller factor estimated from the integer order spots. The dashed line is the bulk x-ray (236) intensity from Ref. 3.

boundaries can locally change the transition temperature $T_c$. The intensity of the diffraction peaks of the low-temperature phase starts to decrease appreciably below $T_c$ because the disordered phase nucleates at steps and domain boundaries before $T_c$ is reached, and then gradually expands over the rest of the surface.[17] The diffraction peaks, which measure the long-range order of the surface, are much more sensitive to the effects of surface defects than the surface exciton, which is mainly localized on a single molecule[18] and feels the nearest-neighbor molecules only. Therefore the profiles of the diffraction intensities versus $T$ are less defined than that of the exciton energy versus $T$. Since the jump in the triplet exciton energy occurs at a temperature very close to that at which the $(\frac{1}{2}\ 0)$ spots vanish, we associate this jump to the $(2\times2)\rightarrow(1\times1)$ structural transition, i.e., to the orientation disordering of the surface $C_{60}$ molecules. The first-order character of the transition is pointed out by the discontinuity of $E_0$ and $E_1$.

We have checked the bulk transition temperature of our $C_{60}$ samples by measuring the HREELS cross section of a vibrational mode at 89 meV. This mode is dipole forbidden in the disordered phase, while it is dipole allowed in the sc phase.[19] Thus it can be excited by dipole scattering in the sc phase. The depth of the sampled layer in the case of dipole scattering is $\sim 1/q$, where $q$ is the component of the momentum transferred by the scattered electron parallel to the surface.[20] The sampling depth is larger than 100 Å in our experimental geometry for dipole scattering, i.e., a factor 10 larger than that of the impact scattering process and to detect the triplet exciton. Figure 4 shows the vibrational HREEL spectra of our samples at 300 and 115 K. The main differences are in the intensities of the peaks at 92 and 178 meV. In the high-temperature phase the 92-meV peak is mainly excited by impact scattering, but the symmetry lowering induced by the surface may cause some weak dipole activity of the vibrational modes that contribute to this structure. As expected, when the temperature is lowered this peak increases in intensity and shifts by about 1 meV to lower energy because of the additional dipole contribution from the 89-meV excitation of the bulk ordered phase. The intensity of the 89-meV bulk peak vs $T$ has been measured by fitting the HREEL spectra in the region between 50 and 110 meV with four Gaussian peaks, two for the dipole active $t_{1u}$ peaks at 66 and 72 meV,[16] one for the high-temperature 92-meV peak, and one for the 89-meV contribution. The energies of the first three peaks have been determined by fitting the 300-K spectrum and have been kept constant at the other temperatures. The intensity of the bulk 89-meV excitation is shown in the inset (a) of Fig. 4 as a function of $T$. It decreases continuously as $T$ is increased, as observed by bulk infrared spectroscopy,[19] and vanishes at 260±3 K. Therefore the molecules start to rotate at 260 K when they are a few layers below the surface. This indicates that the phase transition shown by the triplet exciton data and by the LEED data is a genuine surface effect, since it occurs at a temperature much lower than that at which the molecules in the bulk of the same samples lose their orientational order. The temperature at which the intensity of the 89-meV mode vanishes is the bulk transition temperature $T_B$ of well ordered and pure single crystals. This indicates that our samples have negligible crystal imperfections and $C_{70}$ impurities density, since these defects decrease $T_B$ by 10–20 K.[21] It also shows that the strain induced by the substrate in the molecular layer in contact with it is relaxed in the first few layers close to the substrate, as shown by the absence of corrugation in the STM images of films 3 or more layers thick,[7] and does not affect the bulk transition temperature.

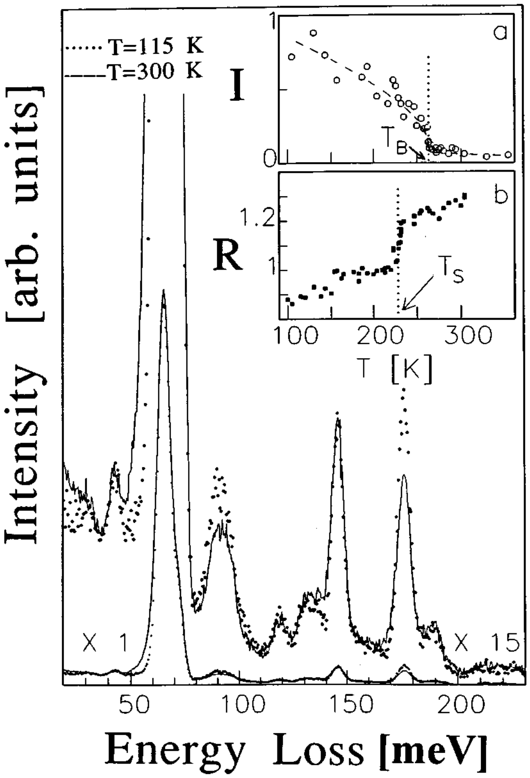

FIG. 4. HREEL spectra of $C_{60}(111)$ at 115 K (dots) and at 300 K (solid line) showing the dipole active vibrational excitations. The spectra have been normalized to the same elastic peak intensity. Inset (a): intensity $I$ of the dipole active 89-meV peak from the fitting the 50–110-meV region (see text), showing the bulk phase transition at $T_B$. Inset (b): ratio $R$ between the intensities of the 146-meV peak and of the 178-meV peak as a function of $T$.

The strong temperature dependence of the dipole active 178-meV $t_{1u}(4)$ peak is in striking contrast with that of the other peaks. The inset (b) of Fig. 4 shows the ratio of the intensities of the $t_{1u}(3)$ peak at 146 meV, which is almost independent on $T$, and of the $t_{1u}(4)$ peak. The ratio drops by 20% at $\sim$228 K in the range of 5 K. The same ratio measured by infrared spectroscopy in the bulk changes by less than 3% in the range 200–300 K.[22] The cross section of a bulk dipole excitation in HREELS is proportional to its optical absorption coefficient measured by infrared adsorption.[20] Therefore the 20% intensity jump of the 178-meV mode in HREELS at 228 K cannot be due to the bulk phase transition, which can only explain a jump of less than 3%. The 228-K jump is caused by an increased contribution of the surface layer related to the surface structural transition. This change could be caused by the decoupling the surface $t_{1u}(4)$ mode from the corresponding band of the bulk mode. The dispersion of this mode in the bulk is less than 0.3 meV.[23] If the surface phase transition shifts the vibrational energy of the surface molecule by 0.3 meV or more a well localized surface mode forms decoupled from the bulk. Its localization at the surface could increase its cross section in a HREELS experiment. Alternatively the phase transition could cause the switching on of the dipole cross section of a mode with different symmetry at nearly the same energy. The jump of the intensity of the 178-meV phonon in a temperature range of the order of our experimental accuracy points again to a first-order phase transition.

The decrease of the triplet exciton energy $E_0$ with temperature and the jump at $T_S$ cannot be explained in terms of energy gap dependence on the expansion of the lattice parameter $a$. The lattice expands as the temperature is increased[4] and, according to high-pressure studies,[24] the gap increases for increasing $a$. A possible explanation for the general decrease of $E_0$ and of the band-to-band transitions at about 2 eV (Ref. 8) is the phonon contribution to the particle self-energy.[25] Another contribution to this shift comes from orientational effects. According to calculations,[26] the band structure of $C_{60}$ is sensitive to the orientation of the molecule, with a band-gap difference up to 0.2 eV between different orientations. Below the order-disorder transition the population of the two configurations corresponding to the two minima in the orientation potential varies from 85% and 15% below 85 K to 60% and 40% close to 260 K.[27] The minority orientation brings nearest-neighbor molecules into closer contact along [110] than the ground-state majority orientation.[2] This effect should increase the bandwidth, decrease the energy gap, and contribute to the observed shift. The band-gap sensitivity to the orientation can also explain the energy jump at $\sim$225 K, when the molecules assume random orientations. In a large class of these orientations the minimum distance $r$ between carbon atoms in adjacent molecules is shorter than that in the low-temperature majority orientation by more than 0.3%. The $C_{60}$-$C_{60}$ distance $d$ in the surface plane could not increase at the transition, if the deeper layers lock the positions of the surface molecules. The observation of a simple $(1\times1)$ LEED pattern above 225 K favors this hypothesis. If the first layer expands, it should become incommensurate with the substrate, giving rise to a superstructure and a periodic corrugation of the first layer. This corrugation is not visible in the LEED pattern. It is likely that the distance between the first and second layers increases at the transition, since the lattice parameter expands by 0.3% in the bulk at $T_B$.[2] The decrease of the average value of $r$ could be enough to compensate for the increase of the spacing between the first and second layers. Moreover this expansion decreases the contribution to the screening of the electron-electron and electron-hole interaction, which arises from the polarization of the neighboring molecules. Assuming a vertical expansion of the first layer by about 0.3% induced by the surface phase transition, the polarization energy[10,28] decreases by about 0.5% (3 meV) and the exciton binding energy increases by about 6 meV. This value is comparable to the energy jump observed at $T_S$. The shift at higher temperatures can only be explained by electron phonon interaction.[25,29] The total energy shift of the triplet exciton between 100 and 300 K is comparable to that of the bulk singlet excitons at 1.8–2.0 eV measured by optical absorption and second-harmonic generation.[18,29] The exciton shift above $T_S$ in the 1.7-ML film is appreciably smaller. It is likely that the bonding with the substrate strongly reduces the amplitude of the vibrations and librations of the chemisorbed first layer, decreasing the effect of the electron-phonon renormalization of the gap of the second layer.

The exciton energy of the multilayer shows a weak kink at about 260 K, the amplitude of which is, however, very close to the noise level. This structure could be a sign of the disordering of the second and deeper layers, which occurs close to 260 K, and affects the binding energy of the surface exciton by allowing the system to expand horizontally.

The energy and linewidth of the exciton and the intensity of the 178-meV phonon are constant within the noise up to about 155 K. From this temperature on they start to depend on $T$. At this temperature the rotational relaxation time is about $10^{-5}$ s,[2] i.e., of the order of the exciton lifetime. Therefore the exciton feels the effects of the molecular rotational jumps between the favored and the unfavored orientations during its lifetime only above 155 K. Below this temperature the exciton is not sensitive to the molecular dynamics. The shift of the exciton energy above 155 K and the jump at 225 K can be attributed to similar mechanisms. Between 155 and 225 K the exciton shifts because during an increasing fraction of its lifetime the molecules assume the unfavored orientation. At 225 K it shifts because the molecules can rotate freely and many more orientations are sampled during its lifetime.

Theoretical calculations on the effect of a surface on the orientational order-disorder transitions in a van der Waals solid has been recently performed with either a four-state Pott model and a continuum orientational potential with four minima, both on a semi-infinite Lennard-Jones fcc lattice.[30] At the present stage these calculations do not show surface phase transition at least for reasonable coupling parameters. It is therefore likely that fine details of the $C_{60}$-$C_{60}$ potential are important for a proper description of the surface dynamics in solid $C_{60}$.

In conclusion we have measured the temperature of the orientational order-disorder transition both on the surface and in the bulk of well-ordered $C_{60}$ films, finding that they differ by 35±4 K. This is an example of a surface orientational phase transition, a phenomenon that should occur also on several other molecular crystal surfaces, if the molecular units have high symmetry, and that can provide valuable information on the details of the intermolecular potential.

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## APPENDIX

The escape depth *l* of electrons in $C_{60}$ has been measured as a function of their kinetic energy utilizing Auger, photoemission, and EELS spectra. The escape depth of electrons at 69 eV has been determined by measuring the intensity of the Au *NOO* Auger signal of the clean Au surface and of that covered by 1 ML $C_{60}$. This coverage has been obtained by dosing $C_{60}$ with the Au sample kept between 500 and 750 K. At this temperature only the first $C_{60}$ layer adsorbs, forming a close-packed quasihexagonal layer (the $6\times5$) structure.[7] The first $C_{60}$ layer attenuates the 69-eV Auger signal by a factor $7.3\pm0.7$. This value corresponds to an escape depth of $4.1\pm0.2$ Å. Similar values have been obtained using the Auger signal of Pt (43 and 64 eV), Ni (61 eV), and Si (92 eV) substrates. These signals are attenuated by a factor between 6.5 and 10 by a $C_{60}$ monolayer. The escape depth at 15 eV has been measured using the photoemission spectra of the clean Au substrate and same surface covered by 1 and 2.2 $C_{60}$ ML. The coverages have been estimated by the attenuation of the Au Auger signal, since it is known that $C_{60}$ grows layer by layer if the substrate temperature is above 350 K.[31] The $C_{60}$ layer gives a small contribution to the total photoemission spectrum in the region from the Fermi energy $E_F$ to a binding energy of 1.7 eV.[32] Therefore most of the signal comes from the Au *s*-*p* band in this energy region. The intensity of the spectrum between $E_F$ and 1.7 eV decreases by a factor 2.9 when a first $C_{60}$ layer is added, and by a factor 9 when an additional 1.2 ML is added. These values correspond to an escape depth of 7.5 Å. This is only an upper limit for *l*, since there is a small contribution to the photoemission intensity near the Fermi level that comes from the extra electron transferred from the substrate to the lowest unoccupied molecular orbital (LUMO) derived states of $C_{60}$.[16] Our estimates of *l* agree very well with the data reported in the literature.[14]

In order to estimate the escape depth at lower kinetic energies we have measured the EELS spectrum of 1 ML and of $2.0\pm0.1$ ML of $C_{60}$ on Au(110) in the off specular geometry. In this geometry impact scattering dominates the spectrum. The spectrum of 1 ML $C_{60}$ (Fig. 5) shows strong phonon peaks below 0.5 eV, a broad shoulder at 0.8 eV, and another maximum at about 2 eV. The 0.8-eV structure is due to electronic excitations within the partially filled LUMO derived states, while the 2-eV peak is due to highest occupied molecular orbital (HOMO-)–LUMO transitions.[16] The spectrum of the 2-ML film is the superposition of that of the second layer and that of the first layer, attenuated by the anelastic scattering processes suffered by the incoming and outcoming electrons when they pass through the surface $C_{60}$ layer. The spectrum of the second layer is almost identical to that of bulk semiconducting $C_{60}$,[16] since the second layer is weakly affected by the substrate (the triplet exciton is now visible). It has vanishing intensity after the phonon region at energies higher than 0.7 eV, shows the triplet exciton at 1.55 eV, and a strong peak at 2.2 eV (HOMO-LUMO transitions). Therefore the signal below 1.5 eV in the 2-ML spectrum originates from the layer in contact with the substrate. The escape depth has been evaluated measuring the attenuation of the signal of the 2-ML spectrum in the region between 0.7 and 1.5 eV with respect to that of the 1-ML spectrum. For instance, for a primary electron energy of 2.3 eV, the spectrum is attenuated by about a factor 3.5. Since the electrons in EELS have to cross the second $C_{60}$ layer twice, this attenuation corresponds to an escape depth of about 13 Å. The measured escape depth is about $19\pm5$ Å at 1.4 eV and $9\pm3$ Å at 7 eV. Therefore the interpolated value of 1 is about 10 Å at the primary electron energies used to study the triplet exciton spectrum. The escape depth we have measured at low kinetic energies is appreciably shorter than that observed in many other solids. This low value is very likely related to the anomalously high cross section for electron capture of the $C_{60}$ molecule.[33] This high cross section is present also in the solid state, as shown by the very strong resonances of the high-energy phonon modes of $C_{60}$ in the HREELS spectra at low primary electron energies.[34]

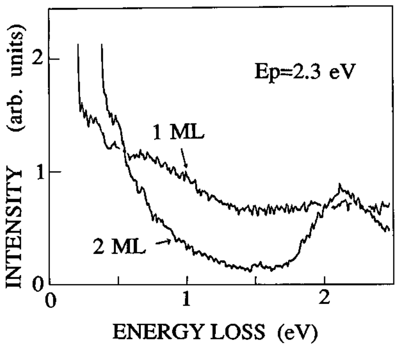

FIG. 5. Electron energy-loss spectrum of 1 ML and of 2 ML ordered $C_{60}$ films on Au(110) at a primary electron energy of 2.3 eV. The different intensity between 0.7 and 1.5 eV is caused by the attenuation of the signal of the first layer by the second layer (see text).

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