

Auger spectroscopy of a fullerite film on an iridium surface

E. V. Rut'kov, A. Ya. Tontegode, and Yu. S. Grushko*

*A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences,
194021 St. Petersburg, Russia*

**Institute of Nuclear Physics, Russian Academy of Sciences, 188350 Leningrad Oblast',
Gatchina, Russia*

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A technique has been developed for producing a flux of C_{60} molecules in ultrahigh vacuum and has been used to grow fullerite films on iridium. The Auger spectrum of carbon from the fullerite has been obtained at high resolution ($\Delta E/E \lesssim 0.1\%$). This spectrum has a characteristic shape which is different from the spectra of diamond, graphite single crystals, polycrystalline graphite, metal carbides, and SiC. The C_{60} molecules begin to desorb from the fullerite at ≥ 600 K, and from the iridium at ≥ 900 K; the flux depends weakly on T . At ≥ 1200 K the C_{60} molecules effectively decay in the adsorbed film on the Ir, forming graphite.

The C_{60} fullerene molecules which were recently observed,¹ with the unusual shape of a hollow sphere made up of 20 hexagons and 12 pentagons, having an outside diameter $\sim 7 \text{ \AA}$ and an inside diameter $\sim 4.5 \text{ \AA}$, have attracted an immense amount of interest, both scientific and practical. This interest intensified even further after Krätschmer *et al.*² developed a technique for producing macroscopic amounts of this substance. A high- T_c superconductivity at 30 K has been observed for the fullerite crystal Rb_3C_{60} , made up of C_{60} molecules and a rubidium dopant. Learning about the properties of C_{60} molecules and of fullerite films grown from them on metal surfaces is thus a matter of current interest; this was the goal of the present study. This study was also stimulated by the authors' many years of experience in research on the interaction of carbon with metal surfaces, which is summarized in Tontegode's monograph *Carbon on the Surfaces of Transition Metals*.³

The present experiments were carried out in two pieces of high-vacuum apparatus: a high-resolution Auger-electron spectrometer ($\Delta E/E \lesssim 0.1\%$) and a magnetic mass spectrometer (with a sensitivity $\sim 10^{-16}$ Torr), both described in Ref. 4. A thin iridium tape (20 μm thick) was annealed in vacuum at 2200 K for use in producing a source of a flux of C_{60} molecules. A droplet of a benzene solution of C_{60} was then placed on the tape, and the benzene was evaporated. This procedure was repeated many times. As a result, a fullerite film $\sim 1000 \text{ \AA}$ thick was produced on the iridium. The mass spectrometry showed that a flux of C_{60} molecules desorbs from the film in the temperature range $600 < T < 1100$ K (C_{60}^+ and C_{60}^{++} ions were observed in the mass spectrometer). The density of this flux is surprisingly insensitive to the tape temperature.

The same C_{60} source was produced in the Auger spectrometer to study the

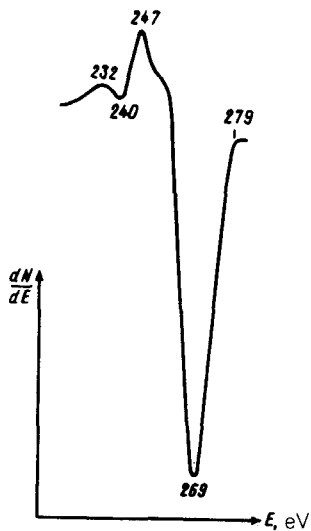


FIG. 1. Auger spectrum of carbon from a fullerite film on an iridium surface.

adsorption and desorption on the surface of an iridium tape and also to study the formation of a fullerite film on it. The thickness of the deposited fullerite film was inferred from the shrinkage of the Auger peak of iridium. To record Auger spectra of the carbon we used a deposited film ~ 8 – 10 monomolecular layers thick; this film completely screened the metal. Figure 1 shows, in differential form, the C_{kvv} Auger spectra of this fullerite film; Fig. 2 shows C_{kvv} Auger spectra of a graphite single crystal, polycrystalline graphite, diamond, metal carbides, and silicon carbide, recorded on the same apparatus. The shape of the C_{kvv} Auger spectrum of the fullerite is seen to be quite different from that of other states of carbon. The carbon Auger peak from polycrystalline graphite is the closest in shape to the fullerite Auger peak. However, there is a substantial difference in energy, 3.0 eV (272 eV for polycrystalline graphite versus 269 for the fullerite), of the negative swings of the Auger peaks. High-resolution Auger spectroscopy thus makes it a simple matter to distinguish a fullerite film from other states of carbon; this capability is important for the diagnostics of surface carbon. Auger and electron spectroscopy had been used previously⁵ to obtain C_{kvv} Auger spectra of a nanofilament carbon material (tubular solid-state C_{60+18n}); these spectra differed from the Auger spectra of a graphite crystal.

We were interested in the initial stages of the adsorption of C_{60} on iridium. To study them we deposited the fullerene on an Ir tape at 300 K to a submonolayer coverage, 1×10^{14} moles C_{60} per 1 cm². We then heated the tape in steps and monitored the surface carbon by Auger spectroscopy.

The C_{60} molecules begin to desorb from the metal at temperatures ($T \gtrsim 900$ K) considerably higher than the corresponding temperature for desorption from a fullerite film ($T = 600$ K), because of the higher binding energy. The lifetime of the C_{60} molecules depends weakly on the substrate temperature, apparently reflecting the particular features of the thermal desorption of this polyatomic entity. At $T \geq 1200$ K, the C_{60} molecules effectively decay in the adsorbed layer on the Ir, forming graphite.

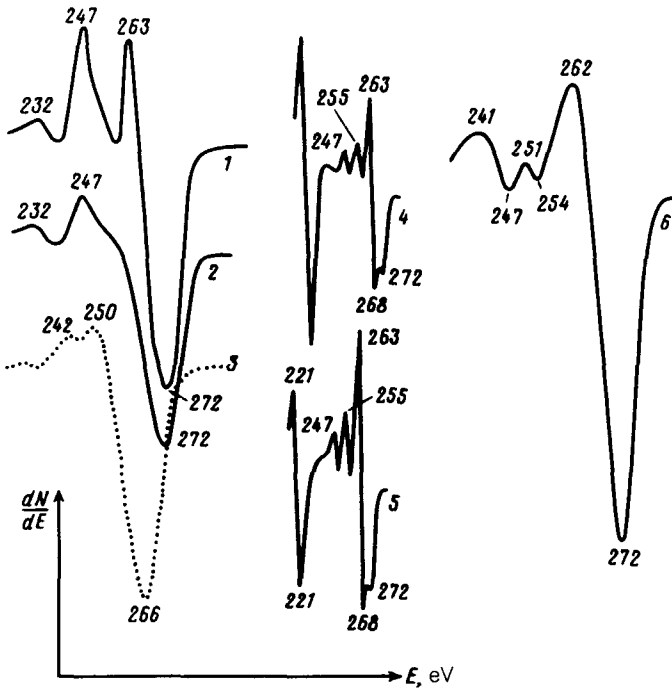


FIG. 2. Auger spectra of carbon. 1—From a graphite single crystal; 2—from polycrystalline graphite; 3—from diamond; 4—from surface molybdenum carbide, MoC; 5—from bulk molybdenum carbide, Mo₂C with the surface carbide, MoC; 6—silicon carbide, SiC.

Only in the form of C₆₀ molecules can surface carbon be removed from the iridium at such low temperatures, $T \sim 900$ K; chemisorbed C atoms, in contrast, can be removed from iridium only at $T > 200$ K.⁶

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Monte Carlo study of expanded matter at low temperatures

S. M. Stishov and A. V. Smirnov*

Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Russia

**Information and Computation Center, Kurchatov Institute Russian Science Center, 123182 Moscow, Russia*

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A system of Lennard–Jones particles at a low density and a low temperature has been studied by the Monte Carlo method in an NVT ensemble.

Under certain conditions, a spatially disordered state of the matter may have a potential energy lower than that of a crystalline state.

The expanded state of matter, corresponding to negative pressures, occurs only rarely naturally, but it does occur. States with negative pressure which are reached by slowly cooling a superheated liquid are well-known examples.¹ Of greater interest from the physics standpoint, however, is the case in which the system or subsystem is extended by internal factors, such as the electron–gas pressure in a metal and the pressure associated with a zero energy in a quantum crystal or liquid. In such cases the total pressure of the system need not necessarily be negative.

Our interest in expanded matter, i.e., in matter at a negative pressure, stems from the problem of the relative stability of the crystalline and noncrystalline (spatially disordered) states. To clarify the formulation of the problem we consider a classical system of particles interacting with a binary Lennard–Jones (6–12) potential. We imagine that we have been able to stretch out our system in such a way that the smallest distance between particles satisfies $r_1 > 1.244\sigma$, where σ and 1.244σ correspond to the vanishing of the potential $\Phi(r)$ and its second derivative $d^2\Phi/dr^2$ (Fig. 1).¹ We recall that the potential energy of the system can be written in this case as

$$E = \left\langle \frac{1}{2} \sum_{ij} \phi(r_i - r_j) \right\rangle = (N\rho/2) \int \phi(r)g(r)d^3r, \quad (1)$$

where $\phi(r)$ is the interaction potential, $g(r)$ is the radial profile of the particles, and ρ is the density.

For a crystal at $T=0$, in which case the radial profile $g(r)$ is a sum of δ -functions, and in the approximation of nearest-neighbor interactions (Fig. 1), we have $E = (N/2)\phi(r_1)Z$, where Z is the coordination number. We now spread out the δ -function and describe the distribution of nearest neighbors by a Gaussian function (Fig. 1). As the width of the Gaussian increases, the energy of the system calculated from expression (1) decreases until the tail of the Gaussian overlaps significantly with the region of strong repulsion. The physical nature of this effect is quite clear. The reason is that the derivative $d\Phi/dr$ falls off rapidly with increasing r at $r > 1.244\sigma$ (1.244σ is the inflection point). If we go through a similar procedure for the point r_2 in the region of strong repulsion, the energy of the system will obviously increase with increasing width of the distribution.

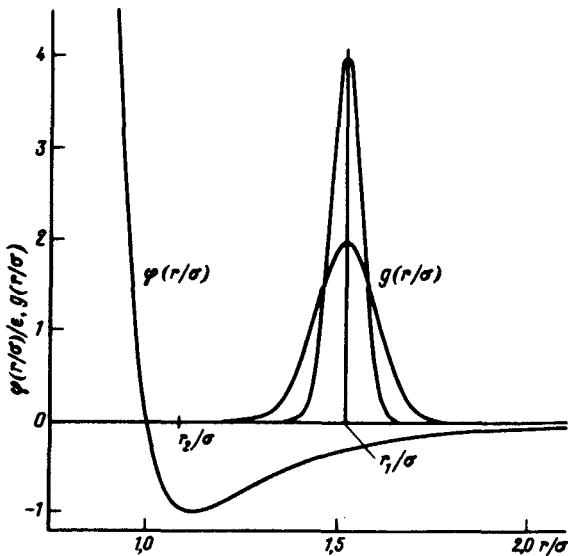


FIG. 1. Diagram used in calculating the potential energy of the Lennard-Jones system at a low density (see the text proper).

It thus seems extremely likely that the lowest-energy state in the approximation of a nearest-neighbor interaction, at a low density, will correspond to either an extremely specific crystal with static displacements of the particles from the lattice sites or a spatially disordered amorphous body. This conclusion can of course serve as only a starting point for a more accurate study of the question.

Unfortunately, the situation shown schematically in Fig. 1 is difficult to study in its pure form, without incorporating an additional interaction which stabilizes the system. Essentially any system of particles with a realistic interaction becomes unstable² at low densities, and this tendency causes difficulties in efforts to evaluate the energy of spatially disordered phases. Nevertheless, as we will see below, numerical calculations by the Monte Carlo method form a basis for drawing completely definite conclusions.

The thermodynamic properties of a system with an interaction

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad r \leq r_c,$$

$$\phi(r) = 0, \quad r > r_c,$$

were studied by the classical Monte Carlo method in an isochoric ensemble of N particles in a cube of volume V with periodic boundary conditions. A specific realization of this simulation method is described in Ref. 3. The cutoff radius r_c is taken to be 2.5σ . Analysis shows that increasing this radius to 4.2σ does not alter the conclusions of this study.

As we have already mentioned, one of the goals of this study was to learn about the disordered state of a system of Lennard-Jones particles at temperatures close to absolute zero. Here is an outline of the calculations: A system consisting of $N=432$ particles at the sites of a crystal lattice, at a density $N/V = 0.4\sigma^{-3}$, is heated to the

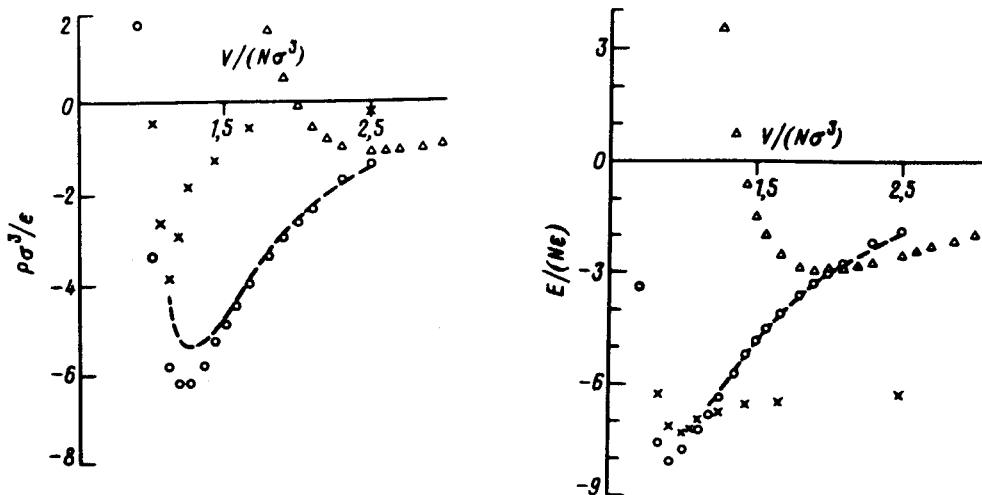


FIG. 2. The energy per particle, E/N , and the pressure P of a system of Lennard-Jones particles (the cutoff radius for the potential is $r_c = 2.5\sigma$) versus the volume V/N at $T=0$. \circ —Face-centered-cubic lattice; Δ —diamond lattice; \times —amorphous state; dashed curve—amorphous state obtained by extrapolating from the stability region (see the text proper).

point that the crystal fractures. It is then put in a state of a given density at $T = 1.0\epsilon$. It is then cooled in steps of $\Delta T = 0.1\epsilon$ to $T = 0.1\epsilon$ at a fixed density. After each cooling step, $10^3 N$ configurations are generated by the Monte Carlo method, and the next cooling step is carried out. A prolonged relaxation at $T = 0.003\epsilon$ is carried out to determine the energy and pressure of the disordered system at $T=0$: $2.5 \times 10^4 N$ configurations are generated by the Monte Carlo method. Further simulation leads to essentially no change in the average energy of the system for the densities and temperatures considered.

We believe that this procedure makes it possible to reach a disordered state with the energy closest to the lowest attainable: At normal density, the energy of the resulting amorphous state is essentially independent of how this state was prepared.³ In the case at hand, however, the energy of the amorphous phase which arises from the fracture of the fcc lattice, at $T = 0.003\epsilon$ in the region in which this phase is unstable ($N/V < 0.826\sigma^{-3}$), is about 0.3ϵ higher than the energy of the amorphous phase produced from the supercooled liquid even after a prolonged relaxation ($4 \times 10^4 N$ configuration) (a possible reason for this difference is discussed below). The radial profiles $g(r)$ for these two amorphous structures are essentially identical.

Figure 2 shows the energy as a function of the volume for an fcc lattice and a disordered (amorphous) structure. The energies of the fcc lattice were calculated analytically for $\rho = N/V < 0.826\sigma^{-3}$. The volume dependence of the energy of the amorphous phase was found through Monte Carlo calculations. It can be seen from Fig. 2 that the energy of the amorphous system changes only very slightly as the density is reduced by a factor of more than 2. This result looks questionable. The

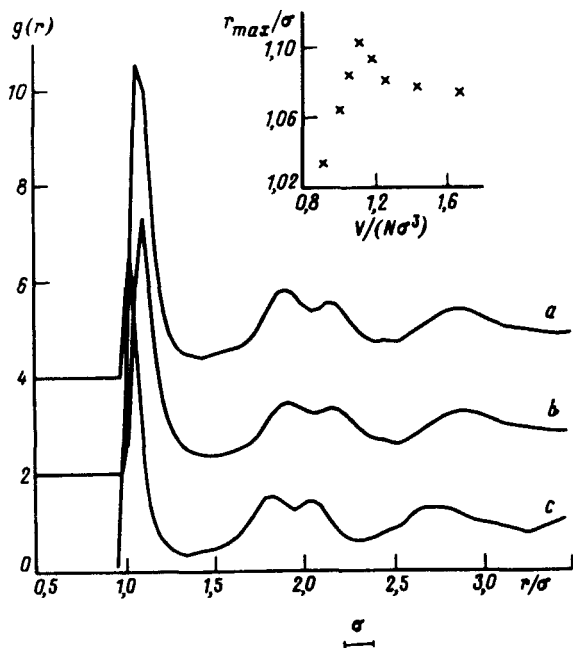


FIG. 3. Radial profiles $g(r)$ for various volumes V/N in a supercooled Lennard-Jones system at $T = 0.1\epsilon$. a — $V/N = 0.91\sigma^3$; b — $1.11\sigma^3$; c — $1.43\sigma^3$. Curves a and b have been shifted for clarity. The inset shows the position of the first peak in the radial profile, r_{\max} , versus the volume.

situation can be clarified by analyzing Figs. 3 and 4. The radial profiles $g(r)$ for the three densities considered in Fig. 3 look quite ordinary. However, the coordinate of the first maximum, r_{\max} , on the $g(r)$ curve undergoes an irregular shift as a function of the density. As the volume is increased, the distance between nearest neighbors increases, as we would naturally expect. When the values $\rho \approx 0.9$ and $\partial P/\partial V \approx 0$ are reached (Fig. 2), however, the derivative $\partial r_{\max}/\partial V$ reaches zero and then changes sign. The results are summarized by Fig. 4, which shows projections of the centers of gravity of

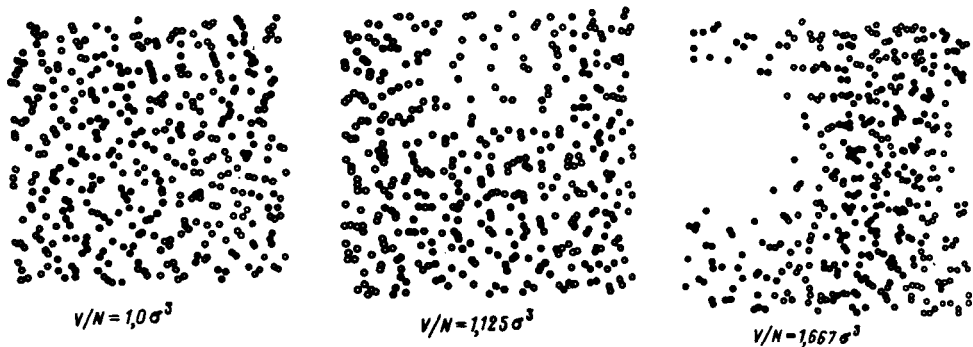


FIG. 4. Projections of the center-of-mass of particles in a Lennard-Jones amorphous system for different values of the volume ($T=0.003\epsilon$).

the particles onto the plane for various densities. We see from Figs. 2 and 4 that discontinuities form at a low density in the amorphous phase, and a "Swiss-cheese" structure arises. The interatomic distances and the pressure relax to lower values, and the effective density of the material actually increases. Similar discontinuities are observed in the amorphous phase which arises upon destruction of the fcc phase at low temperatures. The reasons for the small variation in the energy of the amorphous system with increasing volume thus become apparent. The appearance of these voids seems to explain the small difference in the energies of the amorphous phases prepared in different ways, as was pointed out earlier. The size and shape of the voids must be a factor here.

The porous low-temperature structure of the amorphous phase is essentially an analog of a high-temperature two-phase state of a substance corresponding to the coexistence of a liquid and a gas.

These results do not conflict with physical intuition. An omnidirectional expansion of a body at a low temperature results in rupture of the body when the instability condition $\partial P/\partial V > 0$ becomes satisfied at some critical density. Curiously, the rupture of an amorphous body occurs at a density higher than in the case of a crystal. The rupture evidently occurs at "weak spots."

However, as we have already mentioned, the situation of greatest interest is that in which the system is extended by internal factors. Let us imagine a case in which the energy of the binary interaction is only a fraction of the overall interaction in a system, and there exists a purely bulk contribution to the total energy of the system, E' , of the form $f(N/V)$. If the form of the function $f(N/V)$ is such that the contributions to the pressure and the bulk modulus are positive, then the state of the system may stabilize at a density $\rho < 0.9$. In this case conditions would not favor the formation of the Swiss-cheese structure, and the spatial distribution of the particles would be substantially more nearly uniform.

To determine the behavior of the binary-interaction energy as a function of the volume for this case, we extrapolated the energy of the amorphous phase out of the stability region to low densities by scaling the interparticle distances and then calculating the energy. Curiously, the results of this extrapolation are essentially independent of the initial density. The curve found in this manner seems to set an upper bound on the energy of the *relaxed* amorphous state at large volumes, while a lower bound is set by the curve characterizing the porous structure. We note that the extrapolation curve in Fig. 2 is close to the energy of the fcc phase; at large volumes it runs a bit below the latter. We thus reach the completely plausible conclusion that under certain conditions the amorphous state may serve as the ground state.²⁾

To complete this discussion of the results, we note that a "porous" diamond becomes more favorable than a close-packed or amorphous phase from the energy standpoint at low densities (Fig. 2). Since the stabilizing energy E' does not alter the relative positions of the energy levels, we easily conclude that there is the possibility in principle that the following sequence of phase transitions occurs as the density of the substance changes: "porous" crystalline phase \leftrightarrow amorphous medium \leftrightarrow dense crystalline phase. A sequence of this sort has been observed experimentally,⁵ but of course

we cannot assert that the amorphous medium observed experimentally is a stable, rather than metastable, phase.

¹⁾At $r_1 > 1.244\sigma$ the potential becomes complex.

²⁾To those who may perceive a violation of the Nernst theorem in this assertion, we would point out that the spatial disorder and the entropy are not related in a single-valued way.⁴

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