

## Low temperature microhardness of Xe-intercalated fullerite C<sub>60</sub>

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The Vickers microhardness of Xe-intercalated polycrystalline fullerite C<sub>60</sub> (Xe<sub>x</sub>C<sub>60</sub>,  $x \simeq 0.35$ ) is measured in a moderately low temperature range of 77 to 300 K. A high increase in the microhardness of the material (by a factor of 2 to 3) as compared to that of pure C<sub>60</sub> single crystals is observed. It is shown that the step-like anomaly in the temperature dependences of the microhardness of pure C<sub>60</sub> single crystals recorded under the orientational fcc-sc phase transition ( $T_c \simeq 260$  K) is also qualitatively retained for Xe<sub>x</sub>C<sub>60</sub>, but its onset is shifted by 40 K towards lower temperatures and the step becomes less distinct and more smeared. This behavior of  $\bar{H}_V(T)$  correlates with x-ray diffraction data, the analysis of which revealed a considerable influence of xenon interstitial atoms on the peculiar features of fullerite thermal expansion due to orientational phase transitions (see the paper by A.I. Prokhvatilov et al. in this issue).

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### Introduction

The physical and mechanical properties of crystalline C<sub>60</sub> are considerably affected by intercalation of the crystal by different impurities, where the environment itself may be considered as an impurity source [1]. This is related to the weak van der Waals interaction between the C<sub>60</sub> molecules as well as the presence of comparatively large interstitial sites in the fullerite lattice. As a result, the crystal easily absorbs impurities and is easily amenable to intercalation. The most dramatic effect due to intercalation is the superconductivity that occurs with alkali metals [2].

Of possible intercalants, gases occupy a highly important place for C<sub>60</sub>. The high interest in this type of impurity is dictated by several facts [1]. Gases are commonly used to transmit pressure to solid C<sub>60</sub>. In this case gas atoms and molecules can diffuse into the cavities of the fullerite lattice and form interstitial solutions. Considering the arrangement of the centers of gravity of its molecules, fullerite C<sub>60</sub> forms a face-cen-

tered cubic (fcc) lattice through the whole range of existence of its solid phase. For each C<sub>60</sub> molecule in the lattice there are two tetrahedral sites as well as one octahedral site, which may be occupied by impurity atoms or molecules. Besides their occupation, chemical interaction between impurities and the C<sub>60</sub> molecules (including polymer bond formation) is possible.

This paper is concerned with the influence of interstitial gaseous impurities on the mechanical properties of solid C<sub>60</sub>. In particular, xenon was selected because being a rare gas eliminates the intercalant-matrix chemical interaction. The atomic diameter of Xe (3.92 Å) is almost two times larger than the effective diameter of a tetrahedral site (2.2 Å) and close to that of an octahedral one (4.1 Å), so that one might expect xenon to only occupy the octahedral sites of the C<sub>60</sub> lattice. The large diameter of the Xe atom makes its entry into the lattice difficult and possible only at elevated pressure and temperature [3]. The effect of xe-

non on the mechanical properties of fullerite  $C_{60}$  has not previously been studied. In fact the only related study so far, has been in [4], that has shown the remarkable result of almost a hundredfold increase in the microhardness of a  $C_{60}$  single crystal grown in vacuum, and kept in an argon atmosphere.

The mechanical properties of  $Xe_xC_{60}$  were studied by using the microindentation technique. As shown in the previous papers [5–8], the temperature dependence of microhardness of pure  $C_{60}$  single crystals displays a step-like anomaly, the position of which is correlated with the temperature  $T_c \simeq 260$  K of the fcc–sc phase transition. It is known [9,10] that intercalation of an impurity into the  $C_{60}$  lattice results, as a rule, in a decrease of  $T_c$  and a broadening of the phase transition temperature range. The research reported in this paper concerns the influence of xenon saturation of the  $C_{60}$  lattice on both the microhardness value and the anomaly of its temperature dependence in the vicinity of the phase transition point.

### Experimental procedure

$C_{60}$  powder was saturated with xenon at a Xe pressure  $p \simeq 200$  MPa and a temperature  $T \simeq 575$  °C, for 36 hr [3]. To prepare the specimens for micro-indentation studies, the saturated powder of  $Xe_xC_{60}$  was pressed into tablet-shaped samples  $\sim 10$  mm in dia and  $\sim 5$  mm in height, using hydrostatic pressure ( $p \simeq 0.5$ – $1.0$  GPa) [11,12]. From the x-ray structural data [13], the degree of filling of the octahedral sites with xenon amounted to  $(35 \pm 5)$  % ( $x \simeq 0.35$ ). Prior to measuring, the tablet surface was polished on a benzol-moistened chamois leather.

The Vickers microhardness at room temperature was measured with a standard unit PMT-3 and in the temperature range of 77–300 K with a freely suspended indenter system [14]. The time of load endurance was 10 s. To reveal the relation between microhardness and indentation load, the load,  $P$ , was varied between 0.005 and 0.2 N, at room temperature. The temperature dependence  $H_V(T)$  was measured at  $P \simeq 0.05$  N as it was found that there was no influence of indentation load on microhardness in the vicinity of this load. The measurement was made in the course of cooling. The microhardness was calculated by the expression  $H_V = 1.854P/(2a)^2$ , where  $2a$  is the impression diagonal. For each temperature or load 10 indents were applied to the surface, and then the values of microhardness were averaged over those indentations. The averaged value,  $\bar{H}_V(T)$ , was considered statistically to be a representative mechanical property of the material studied.

### Experimental results

A typical impression on the polished surface of a  $Xe_xC_{60}$  polycrystal is shown in Fig. 1. The impression exhibited good faceting, indicating a high microplasticity of the material in question. The impressions remained sharp with decreasing temperature down to 77 K. At the same time cracks were commonly formed round the observed impressions, even at low load. These are mainly lateral (secondary) cracks, dipping at a low angle to the sample surface (clearly seen in Fig. 1). One may speculate that the cracks propagate along the grain boundaries which are the weakest sites of the pressed material due to a high density of defects, particularly pores, in them.

The average values of microhardness,  $\bar{H}_V(T = 300$  K), of  $Xe_xC_{60}$  polycrystal for different loads are shown in Fig. 2. As is evident,  $\bar{H}_V(T = 300$  K) is almost independent of indentation load, and only at a high value of  $P \geq 0.15$  N can one observe reduced microhardness, supposedly due to active crack propagation. To avoid the influence of crack formation and consider  $\bar{H}_V(T)$  as a characteristic of plasticity, measurements of the temperature dependence of microhardness were made at a low load of  $P \simeq 0.05$  N.

The temperature dependences of microhardness for the  $Xe_xC_{60}$  polycrystal and for the pure  $C_{60}$  single crystal studied in [6] (indentation plane (001)) are illustrated in Fig. 3. A comparison of these curves allows us to recognize the principal differences in the micromechanical behavior between the two materials. These differences are:

1. At room temperature the microhardness of the  $Xe_xC_{60}$  polycrystal is approximately three times higher than that of the pure  $C_{60}$  single crystal; and as the temperature is decreased down to 77 K, this discrepancy reduces to two times.

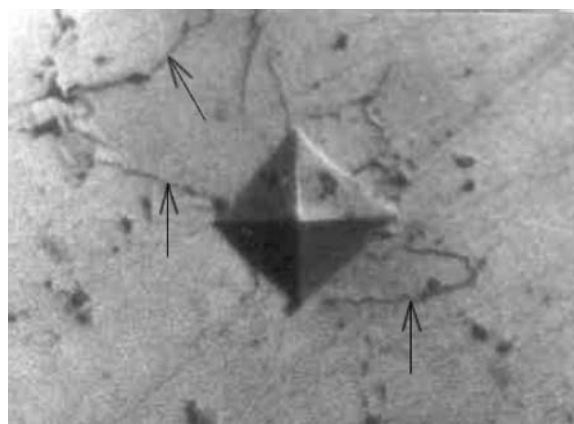


Fig. 1. The impression on the  $Xe_xC_{60}$  polycrystal surface for indenter load  $P \simeq 0.2$  N and room temperature. The area of brittle fracture in the form of lateral (secondary) cracks is marked by arrows. The impression diagonal is about 30  $\mu$ m.

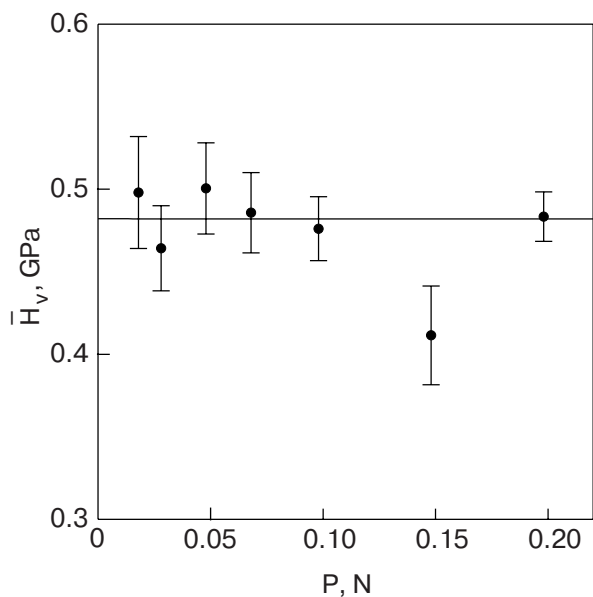


Fig. 2. The dependence of average microhardness  $\bar{H}_V$  of  $\text{Xe}_x\text{C}_{60}$  on indenter load  $P$  at room temperature. The standard deviations for  $\bar{H}_V$  are indicated as bars.

2. As temperature is decreased from 300 to 225 K, the microhardness of  $\text{Xe}_x\text{C}_{60}$  polycrystal increases linearly by  $\sim 20\%$ , while for the fcc single crystal of pure  $\text{C}_{60}$  it remains almost unchanged (down to 260 K).

3. The step-like anomaly in the dependence  $\bar{H}_V(T)$  for pure  $\text{C}_{60}$ , clearly seen under the transition from fcc

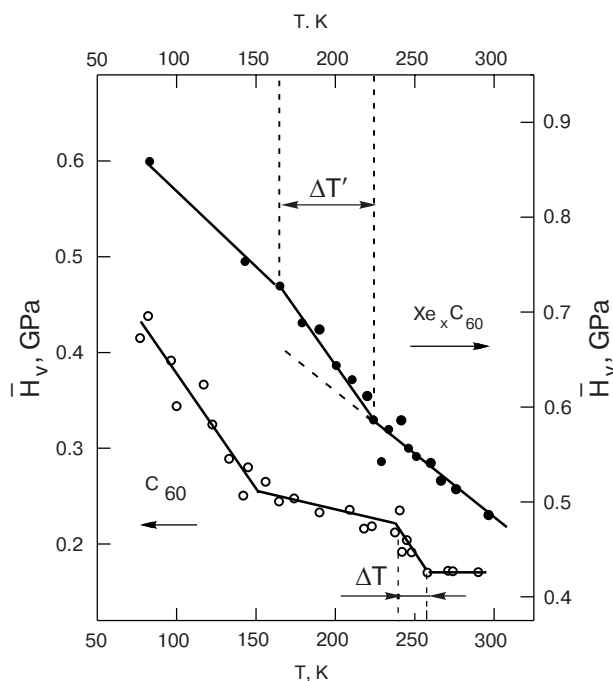


Fig. 3. The temperature dependence of  $\bar{H}_V$  for the  $\text{Xe}_x\text{C}_{60}$  polycrystal (upper curve) and pure  $\text{C}_{60}$  single crystal (lower curve) [6]. The standard deviations for  $\bar{H}_V$  are about 3%.

to the sc phase below 260 K, changes significantly. Such an anomaly is observed for  $\text{Xe}_x\text{C}_{60}$  too, but the step edge is shifted towards lower temperatures (down to 220 K) and the step itself becomes less steep and highly smeared ( $\Delta T' \approx 60$  K for the intercalated fullerite as compared to  $\Delta T \approx 20$  K for pure  $\text{C}_{60}$ ).

4. In the case of pure crystalline  $\text{C}_{60}$ , the low temperature edge of the step in the  $\bar{H}_V(T)$  curve is adjacent to an area of rather slight variations in microhardness. Below 150 K this area turns into a region of drastic growth in  $\bar{H}_V(T)$ . As for the  $\text{Xe}_x\text{C}_{60}$  polycrystal, an analog of the first area can also be observed below 160 K, but we could not detect the second range because of lack of microhardness measuring technique for temperatures below 77 K.

### Discussion

Before proceeding to a discussion of the anomalies observed in the microhardness of  $\text{C}_{60}$  on its saturation with xenon, some important results obtained in comparative x-ray diffraction studies of pure  $\text{C}_{60}$  and  $\text{Xe}_x\text{C}_{60}$  polycrystals should be mentioned [13]. Introduction of Xe conserves the fcc structure of the greater part of the material (90%), but in  $\text{Xe}_x\text{C}_{60}$  there also exists  $\sim 10\%$  of another phase (more probably, polymerized  $\text{C}_{60}$  molecules). Besides, considerable distortions of the fcc lattice by the Xe atoms cause the fcc-sc transition temperature,  $T_c$ , and the glass transition point,  $T_g$ , to decrease. This correlates with the anomalies in the temperature dependence of microhardness: The saturation with xenon results in a substantial hardening and an embrittlement of the fullerite and similarly, in a shift of the anomalies in the  $\bar{H}_V(T)$  curve.

Investigations performed by several teams of researchers (see [8] and the references *ibid.*) have revealed that macro- and microplastic deformation of fullerite  $\text{C}_{60}$  at room and at moderately low temperatures is determined by the glide of dislocations in the  $\{111\}\langle 110 \rangle$  slip system; the system is kept efficient even after the fcc-sc transition. As the saturation of fullerite with xenon produces no change in its lattice structure, the scientific treatment of the observed difference in microhardness between the pure  $\text{C}_{60}$  single crystals and  $\text{Xe}_x\text{C}_{60}$  polycrystals should be limited to a discussion of some possible differences in those structural factors and mechanisms which dictate the dislocation mobility in these materials.

On the qualitative level, one should distinguish two effects caused by the influence of intercalation. These are (1) a rather substantial increase in the absolute values (background) of microhardness  $\bar{H}_V$  and (2) a certain transformation of subtle peculiarities in

the temperature dependence  $\overline{H}_V(T)$  under the fcc-sc transition. The origin of these effects may generally be accounted for by different physical and structural factors. The first effect may be caused by the different morphology of the Xe-intercalated sample and by the influence of Xe atoms on the elastic properties and the mobility of the dislocations. The other one is probably connected with the influence of the Xe impurity on the dynamics of the orientational degrees of freedom of the C<sub>60</sub> molecules, and therefore, on the dislocation-orientational interaction. Below is discussed the influence of these factors in detail.

First of all, we shall consider a possible influence of the morphologies of the materials compared. One of these is a reasonably perfect single crystal, while the other is a polycrystal with inclusions of another phase. The difference in morphology between the two materials is due to the specific features of the intercalation technology [3,12]; unfortunately, at present there is no other way of preparing macroscopically homogeneous single crystals adequately saturated with xenon. The very high microhardness of the Xe<sub>x</sub>C<sub>60</sub> polycrystal as compared to that of the C<sub>60</sub> single crystal may be caused by two factors: (i) the hardening effects of both the intergrain boundaries and secondly (ii) the minor second phase particles within the crystalline grains. By the Hall-Petch relation [15], the yield stress and microhardness of a polycrystal are higher than those of a single crystal by an amount inversely proportional to the square root of polycrystal grain size. The second-phase fine particles form local barriers which impede dislocation slip, reducing appreciably the plastic compliance and increasing the microhardness of the material (that mechanism of hardening is well known in the physics of ageing alloy plasticity [16]). It should also be noted that any porosity induced from pressing the specimens should have an opposite effect, deteriorating the mechanical properties [17,18]. The softening due to this factor appears to be slight.

We now turn to the effect of gaseous impurities on dislocation mobility in the bulk of a separate crystalline grain. A high Xe concentration in the lattice, as well as its almost identical size with that of the octahedral site which it occupies, suggest that as a first approximation by concentration, the intercalation does not disturb the macrostructural homogeneity of the material inside the grains. Because of this, separate impurity atoms produce no effective local barriers to dislocation slip in the sense of the term «local barrier» used in the physics of plasticity of weakly and moderately concentrated solid solutions [16]. At the same time, in a highly concentrated solid solution second order-in-concentration effects, and in particular, the

presence of microclusters with a short-range order of impurities, are supposed to be of a certain importance. For example, in some unit cells of the lattice the impurity atoms occupy all octahedral sites while other unit cells remain unoccupied. Such microclusters may be effective centers of dislocation drag, thus enhancing the material's microhardness.

One more thing should be mentioned: for fullerite C<sub>60</sub> and many atomic cubic crystals, a significant influence on the plastic compliance may be exerted by dislocation drag by the Peierls relief which becomes essential for a low density of local barriers with low height [19]. It may therefore appear that the effect of gaseous impurities on the microhardness of fullerite is partially due to the change of the Peierls relief caused by the influence of a great number of interstitial atoms on the lattice parameter and intermolecular interaction. Unfortunately, even the sign of that influence cannot be predicted without detailed microscopic calculations.

Finally, one more important factor should be pointed out, namely, a considerable enhancement in the elastic moduli at the transition from pure crystals to highly concentrated solid solutions. According to a well known law in materials science [20], the basic value of the microhardness of a material as a local characteristic of plasticity is proportional to the Young modulus. Independent measurements of the elastic moduli of intercalated fullerenes (for example, by acoustic techniques or by Brillouin-light-scattering measurements) would enable one to determine the individual contributions to enhancement of their hardness but at present such data is not available.

Above we have discussed the principal factors that dictate the order of magnitude of the yield stress and microhardness and the general background of their temperature dependences in a wide range of moderately low temperatures for both pure and atomic impurity-intercalated fullerite C<sub>60</sub>. From the general conclusions of the theory of thermally activated dislocation motion [21,22], the background should be rather smooth and involve no distinct features like kinks which are seen in the dependences  $\overline{H}_V(T)$  for pure and intercalated fullerenes C<sub>60</sub>. It would therefore appear reasonable that these observed anomalies are caused by the effect of the orientational degrees of freedom of the C<sub>60</sub> molecule on the dislocation mobility [6,23]. A direct support for this suggestion may be the correlations between the anomalies in the  $\overline{H}_V(T)$  dependences and the anomalies of thermal and acoustic properties which may be considered as an indicator of the orientational phase transitions in fullerite C<sub>60</sub>: the fcc-sc phase transition and the orientational glass transition. The absolute contribution of disloca-



tion-orientation interaction to dislocation drag forces is not high but it has peculiarities as mentioned above and therefore can be qualitatively identified in the background of contributions from other factors. In conclusion, the effect of interaction on subtle anomalies like kinks in the temperature dependences of the lattice parameter,  $a(T)$ , and the microhardness,  $H_V(T)$ , is considered to be caused by the influence of gaseous impurities on the libration and rotation dynamics of  $C_{60}$  molecules.

It is evident that intercalation of the fullerite lattice by a great number of interstitial atomic impurities has an appreciable effect on the dynamics of the orientational degrees of freedom of the  $C_{60}$  molecules, producing a shift along the temperature scale and a smearing of the orientational fcc-sc and orientational glass transitions. This is supported by the x-ray diffraction data for  $Xe_xC_{60}$  [13] testifying that the values of temperature  $T_c$  and the glass transition point  $T_g$  decrease by 30–40 K. The comparison between the dependences  $\bar{H}_V(T)$  for pure and Xe-saturated fullerites shown in Fig. 3 and their correlation with the x-ray diffraction data for the temperature dependences of the lattice parameter,  $a(T)$  [13], indicate that the dislocation-orientational interaction determines the characteristic anomalies in the temperature dependence of the microhardness even in the presence of gaseous impurities. The influence of gaseous impurities on the orientation dynamics of the  $C_{60}$  molecules and the parameters of the lattice-orientation interaction can be estimated quantitatively by analyzing simultaneously x-ray diffraction, thermal, mechanical and acoustic data [24]. Although such data is available for pure  $C_{60}$  fullerite [6,25], no such data is available for  $Xe_xC_{60}$ , making these estimations difficult at present.

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