

## Pressure-induced orientational ordering in $C_{60}$ single crystals studied by Raman spectroscopy

K.P. Meletov\* and D. Christofilos

*Physics Division, School of Technology, Aristotle University of Thessaloniki, Thessaloniki GR-54006, Greece*

S. Ves

*Solid State Physics Section, Department of Physics, Aristotle University of Thessaloniki, Thessaloniki GR-54006, Greece*

G. A. Kourouklis

*Physics Division, School of Technology, Aristotle University of Thessaloniki, Thessaloniki GR-54006, Greece*

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Raman spectra of  $C_{60}$  single crystals have been measured as a function of hydrostatic pressure up to 15 GPa at room temperature. Several modes exhibit a reversible softening with pressure in the range 0–0.4 GPa. This behavior is associated with the orientational ordering phase transition from the fcc to the partially ordered sc phase. New Raman lines appear above 0.4 GPa, some of them exhibit a softening up to 2.5 GPa. Abrupt changes in the slope of a number of phonons are observed around 2.5 GPa. Also a redistribution of intensity among  $A_g(2)$  and  $H_g(7)$  modes, typical of mode interaction, takes place at pressures exceeding 2.5 GPa. These effects are connected to the phase transition from the partially ordered sc phase to the rotation free orientationally ordered sc phase of  $C_{60}$  occurring at 2.5 GPa at room temperature.

### INTRODUCTION

The interest in molecular dynamics and phonon spectra of fullerenes is connected both with their unique molecular structure and the versatility of their phonon spectra, as well as with the potential of Raman scattering to investigate possible phase transitions and material transformations.<sup>1–5</sup> In particular, Raman scattering has been used to study the new phases in alkali metal intercalated  $C_{60}$  compounds<sup>6,7</sup> and the pressure-induced phase transitions in  $C_{60}$  and  $C_{70}$ .<sup>8,9</sup> Raman scattering has also been used for the study of the stability of the  $C_{60}$  molecule at very high pressures.<sup>4,10,11</sup> The interest in this problem is connected with the extremely high hardness of the  $C_{60}$  molecule, which has been predicted theoretically as being higher than that of diamond.<sup>12</sup>

Recently, Raman scattering has been used to investigate the photodimerization of  $C_{60}$  under UV illumination.<sup>13</sup> The reaction mechanism and the photodimerization kinetics were studied using the irreversible softening of the pentagon pinch mode (PP-mode) as the probe of the photodimerization reaction.<sup>14,15</sup> At the same time van Loosdrecht *et al.*<sup>5</sup> have reported that the softening of PP-mode is reversible when the laser power density varies in a region below some threshold, above which it becomes irreversible. The softening of the PP-mode under high pressure up to about 0.6 GPa has been reported by Chandrabhas *et al.*<sup>8</sup> and it was explained as the Raman indication of the pressure-induced orientational ordering phase transition.<sup>16</sup> In an x-ray powder-diffraction study of  $C_{60}$  (Ref. 17) as a function of pressure it was found that the rotation free orientationally ordered sc phase appears at pressures higher than 2.5 GPa.

In this investigation we report the results of a high-pressure Raman study of  $C_{60}$  single crystals at room temperature and pressures up to 15 GPa. We have determined the pressure dependence of the intramolecular phonon modes and have shown that the two phase transitions at 0.4 and 2.5 GPa induced by pressure are manifested by the changes observed in the Raman spectra. All changes observed are reversible in the pressure region under investigation. According to our results the majority of the phonon modes exhibit a softening with pressure up to 0.4 GPa. At higher pressures new lines appear. The majority of the modes exhibit positive pressure shifts. The reversibility of the pressure dependence of the phonon modes in this pressure region indicates that the observed softening is due to the phase transition, namely to the pressure-induced orientational ordering phase transition,<sup>16</sup> which occurs at room temperature and at 0.45 GPa according to differential thermal analysis measurements.<sup>18</sup> The slopes of the pressure dependence of some intramolecular modes is changed at 2.5 GPa and a redistribution of intensity among  $A_g(2)$  and  $H_g(7)$  modes is observed. These observations are connected to the phase transition to the rotation free orientationally ordered sc phase of  $C_{60}$  occurring at 2.5 GPa at room temperature.<sup>19,20</sup>

### EXPERIMENTS

Single crystals of  $C_{60}$ , used in the present study, were grown from starting material obtained by the Krätschmer method.<sup>21</sup> The purity of the material, determined by mass spectrometry, was found to be better than 99%. Crystals having well-faceted mirrorlike surfaces and typical dimensions of about  $100 \times 50 \times 20 \mu\text{m}$  have been

selected and used for the present measurements. High pressure was generated using the gasketed diamond-anvil cell of the Mao and Bell type.<sup>22</sup> The 4:1 methanol-ethanol mixture was used as pressure transmitting medium and the well-known ruby fluorescence technique<sup>23</sup> was used for pressure calibration. The pressure was measured with accuracy of  $\sim 0.1$  GPa.

The Raman spectra were recorded on a triple monochromator (DILOR-XY 500) equipped with LN<sub>2</sub> cooled CCD detector system and/or on a SPEX Ramalog 5 spectrometer. The spectral width of the system was approximately  $4\text{ cm}^{-1}$ . The  $514.5\text{ nm}$  line of an Ar<sup>+</sup> laser was used for excitation, and the beam was focused to a spot of approximately  $50\text{ }\mu\text{m}$  in diameter. The power, measured directly before the cell, was kept always below  $10\text{ mW}$ . The spectra were recorded in the backscattering geometry using a  $\lambda/4$  plate for the depolarization of the laser beam; no attempt for polarization measurements was made. The experimental results were obtained for a number of different samples and data were recorded for both increasing and decreasing pressure cycles.

## RESULTS

The Raman spectra of C<sub>60</sub> crystals were measured in two frequency regions from  $200$  to  $800\text{ cm}^{-1}$  and from  $1350$  to  $1700\text{ cm}^{-1}$ . In the intermediate region appears the Raman mode of diamond at  $1333.4\text{ cm}^{-1}$  which is many orders of magnitude stronger than the Raman modes of C<sub>60</sub>. The high-frequency region of the spectrum at various pressures and room temperature is shown in Fig. 1. In this region appears the most intense  $A_g(2)$  double-bond stretching pentagon pinch mode, due to the out-of-phase dilatory vibration of the pentagonal and hexagonal rings of the molecule. At ambient pressure the spectrum contains three intramolecular modes  $H_g(7) = 1422\text{ cm}^{-1}$ ,  $A_g(2) = 1467\text{ cm}^{-1}$ , and  $H_g(8) = 1570\text{ cm}^{-1}$ . In Fig. 2 the Raman spectra of C<sub>60</sub>, in the low-frequency region, are shown at various pressures and room temperature. The initial spectrum at ambient pressure contains five intramolecular modes:  $H_g(1) = 272\text{ cm}^{-1}$ ,  $H_g(2) = 435\text{ cm}^{-1}$ ,  $A_g(1) = 496\text{ cm}^{-1}$ ,  $H_g(3) = 710\text{ cm}^{-1}$ , and  $H_g(4) = 772\text{ cm}^{-1}$ . The most intense  $A_g(1)$  mode corresponds to the in-phase dilatory breathing vibrations of the pentagonal and hexagonal rings. The frequencies of the observed phonon modes at ambient pressure are close (within  $2\text{ cm}^{-1}$ ) to the previously reported ones.<sup>1,5</sup> It is important to note that the Raman measurements were performed with special care in setting the laser power at such a level in order to get the maximum value ( $1467\text{ cm}^{-1}$ ) for the frequency of the  $A_g(2)$  PP-mode. For higher laser power, a decrease in the frequency of the  $A_g(2)$  mode, up to  $4\text{ cm}^{-1}$ , was found. When the laser power density was higher than some critical value this decrease of the  $A_g(2)$  mode frequency became irreversible and was accompanied by visual observation of damage on the crystal surface. The critical value of laser power density varies from sample to sample and for the most resistant ones, was approximately  $200\text{ W/cm}^2$ . The laser power density was kept approximately three times

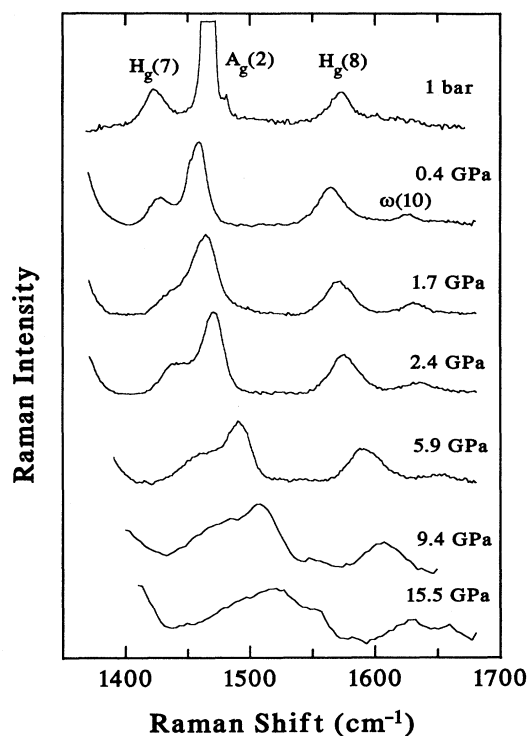


FIG. 1. Raman spectra of C<sub>60</sub> single crystal in the high-frequency region at room temperature and for various pressures.

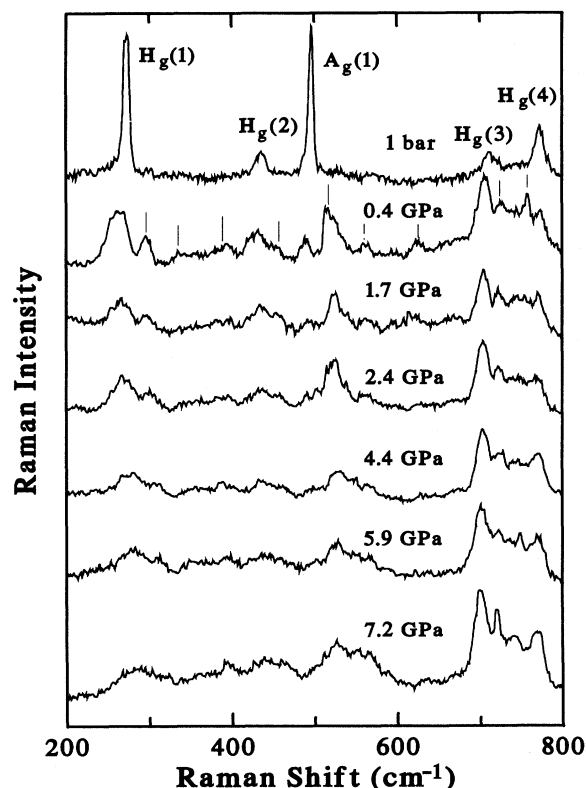


FIG. 2. Raman spectra of C<sub>60</sub> single crystal in the low-frequency region at room temperature and for various pressures.

smaller than this value for all measurements including those performed at high pressure.

In Fig. 3 the pressure dependence of  $H_g(7)$ ,  $A_g(2)$ ,  $H_g(8)$ , and a mode marked  $\omega(10)$  is shown for a number of increasing pressure runs. The solid symbols denote data taken for decreasing pressure in all runs. The peak positions were determined by fitting Lorentzian line shapes to the experimental data. The experimental data for  $A_g(2)$  and  $H_g(8)$  modes were fitted to a linear model by a least-squares method, in the pressure region above 0.4 GPa, giving slopes  $5.5 \text{ cm}^{-1}/\text{GPa}$  and  $4.8 \text{ cm}^{-1}/\text{GPa}$ , respectively. The solid lines in Fig. 3 correspond to this fit. The  $H_g(7)$  mode shows also a linear pressure dependence, but its slope changes drastically at a pressure of 2.5 GPa. Below this pressure, the slope is  $9.3 \text{ cm}^{-1}/\text{GPa}$ , while above the slope decreases by more than a factor 2 to become  $4.1 \text{ cm}^{-1}/\text{GPa}$ .

Figures 4 and 5 display the pressure dependence of the low-frequency intramolecular phonon modes. In addition to the  $H_g(1)$ ,  $H_g(2)$ ,  $A_g(1)$ ,  $H_g(3)$ , and  $H_g(4)$  modes, several new modes appear in the partially ordered sc phase, marked as  $\omega(1)$ – $\omega(9)$ . Solid symbols again represent data taken for decreasing pressure. The solid lines are linear least-squares fittings. The vertical lines in Figs. 3–5 show the pressures 0.4 and 2.5 GPa in

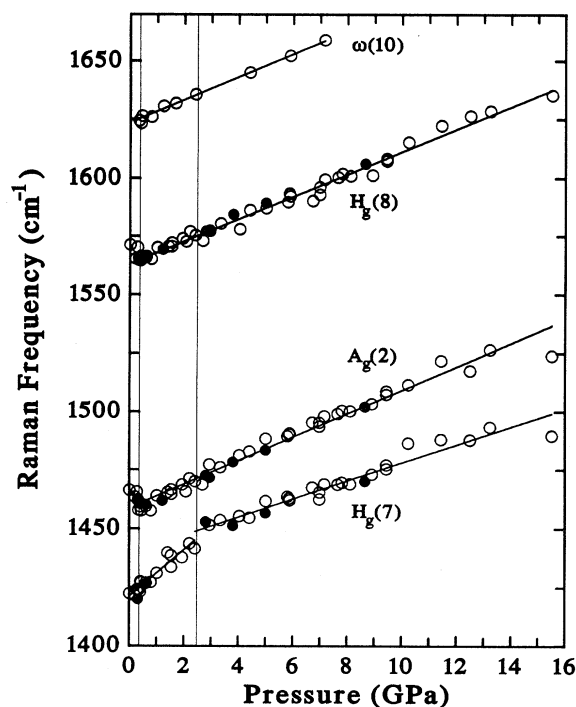


FIG. 3. Pressure dependence of the intramolecular mode frequency of  $H_g(7)$ ,  $A_g(2)$ ,  $H_g(8)$ , and  $\omega(10)$ . The mode  $\omega(10)$  appears in the sc phase above 0.4 GPa. Data are taken in different experimental runs for increasing pressure (open symbols) and decreasing pressure (solid symbols) cycles. Vertical error is approximately indicated by the size of the symbols. The lines are linear least-squares fits to the experimental data. Vertical lines indicate the transition pressures 0.4 and 2.5 GPa.

which changes in the pressure dependence of phonon frequencies are observed. When the pressure increases up to 0.4 GPa several of the observed phonon modes shift to lower frequencies. The total frequency shifts in this pressure region vary from  $10 \text{ cm}^{-1}$  for  $H_g(1)$  and  $A_g(2)$  down to  $5 \text{ cm}^{-1}$  for  $H_g(2)$ ,  $A_g(1)$ , and  $H_g(3)$  modes. For some of them this is shown in Fig. 6, in which it is clearly shown that the same pressure-induced softening behavior of the  $A_g(2)$  is also exhibited by several other modes whose frequencies span the spectral region under investigation. Above 0.4 GPa the pressure-induced shift of the phonon modes is positive except for the  $H_g(3)$ ,  $H_g(4)$ ,  $\omega(8)$ , and  $\omega(9)$ , which are clustered in the  $700$ – $800 \text{ cm}^{-1}$  region and exhibit a softening up to the highest pressure reached in our experiments. This pressure effect is accompanied by a line broadening of all Raman lines and the appearance of one new mode at high frequencies (Fig. 3) and nine at lower frequencies. At the same time the intensities of the low-frequency peaks change: the most intense  $A_g(1)$  mode becomes weaker and the  $H_g(3)$  mode becomes stronger than  $H_g(4)$ . When the pressure exceeds 2.5 GPa a gradual redistribution of intensity among  $A_g(2)$  and  $H_g(7)$  modes takes place. It

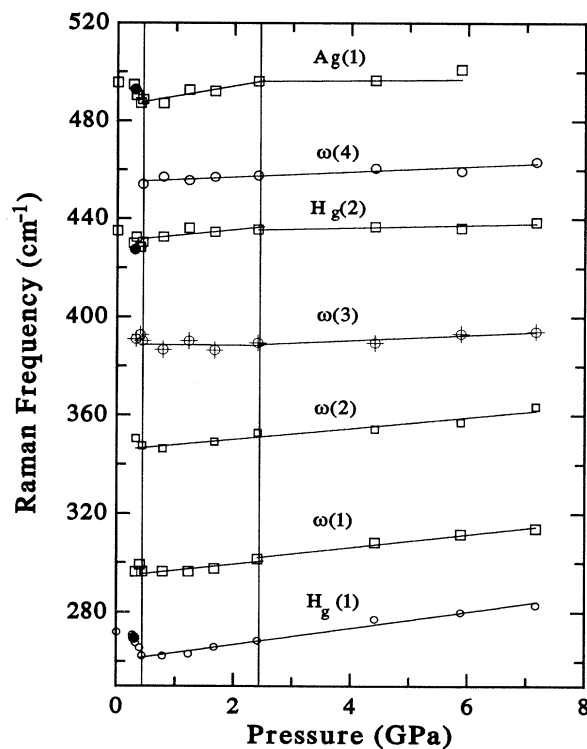


FIG. 4. Pressure dependence of the low-energy intramolecular mode frequency of  $H_g(1)$ ,  $H_g(2)$ , and  $A_g(1)$  phonon modes and  $\omega(1)$ ,  $\omega(2)$ ,  $\omega(3)$ , and  $\omega(4)$  modes which appear in the sc phase. Data are taken in different experimental runs for increasing pressure (open symbols) and decreasing pressure (solid symbols) cycles. Vertical error is approximately indicated by the size of the symbols. The lines are linear least-squares fits to the experimental data. Vertical lines indicate the transition pressures 0.4 and 2.5 GPa.

is remarkable to note that all pressure-induced changes, namely, the softening of modes, the broadening of Raman lines, the appearance of new phonon lines, and the changes in the peak intensities are reversible with pressure. The slopes of a number of low-frequency modes change, the most drastic changes are observed in the slopes of  $A_g(1)$ ,  $H_g(4)$ ,  $\omega(8)$ , and  $\omega(9)$  modes. The absolute values of the slopes are smaller than those of the high-frequency modes and vary from  $-3.9 \text{ cm}^{-1}/\text{GPa}$  up to  $+3.6 \text{ cm}^{-1}/\text{GPa}$ .

In Fig. 7 are shown the relative integrated intensities  $I_{A_g}/(I_{A_g}+I_{H_g})$  of the  $A_g(2)$  phonon mode (upper symbols) and  $I_{H_g}/(I_{A_g}+I_{H_g})$  of the  $H_g(7)$  mode (lower symbols) as a function of pressure. The solid lines are linear least-squares fittings to the experimental data. The relative integrated intensities were determined from the fitted Lorentzian line shapes. The vertical lines in Fig. 7 correspond to 0.4 and 2.5 GPa. In the pressure range 0.4–2.5 GPa the relative integrated intensities of  $A_g(2)$  and  $H_g(7)$  lines are almost constant. Above 2.5 GPa a gradual transfer of intensity from the stronger  $A_g(2)$  mode to the weaker  $H_g(7)$  mode takes place. At a pressure of  $\sim 7.2$  GPa, the relative intensities of these modes become almost equal. The data, on releasing pressure,

show that this transfer of intensity is also a reversible effect with pressure (the solid symbols in Fig. 7 represent data taken upon releasing pressure).

## DISCUSSION

The vibrational spectrum of a free  $C_{60}$  molecule contains 46 modes, with symmetries:

$$\Gamma = 2A_g + 3F_{1g} + 4F_{2g} + 6G_g + 8H_g + A_u + 4F_{1u} + 5F_{2u} + 6G_u + 7H_u, \quad (1)$$

and with allowance for the high symmetry ( $I_h$ ) and degeneracy the total number of modes becomes 174,<sup>5,24</sup> from these, two  $A_g$  and eight  $H_g$  are Raman-active modes.<sup>1</sup> A detailed discussion of the group-theoretical aspects of the vibrational properties in the solid phase of  $C_{60}$  is given by Dresselhaus *et al.*<sup>24</sup> In the crystal, the degeneracy is lifted from the crystal field and additional modes may appear in the Raman spectrum from the splitting of the degenerated modes.<sup>5,24</sup> In fact, the intramolecular modes  $H_g(7)$  and  $A_g(2)$  in a free molecule should change their symmetry in the face-centered-cubic (fcc) ( $T_h^3$ ) crystal structure to give rise to modes with

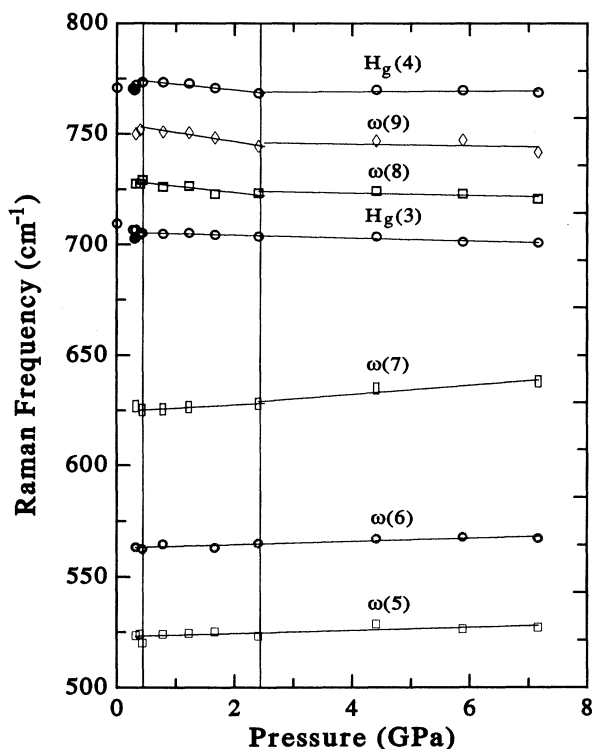


FIG. 5. Pressure dependence of the low-energy intramolecular mode frequency of  $H_g(3)$  and  $H_g(4)$  modes and of  $\omega(5)$ ,  $\omega(6)$ ,  $\omega(7)$ ,  $\omega(8)$ , and  $\omega(9)$  modes which appear in the sc phase. Data are taken in different experimental runs for increasing pressure (open symbols) and decreasing pressure (solid symbols) cycles. Vertical error is approximately indicated by the size of the symbols. The lines are linear least-squares fits to the experimental data. Vertical lines indicate the transition pressures 0.4 and 2.5 GPa.

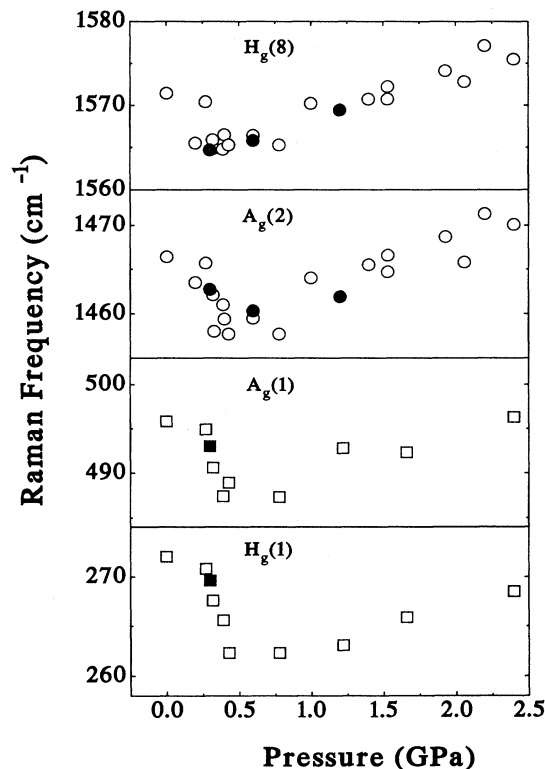


FIG. 6. Pressure dependence of the mode frequency of  $H_g(8)$ ,  $A_g(2)$ ,  $A_g(1)$ , and  $H_g(1)$  modes showing in more detail the pressure-induced softening in the 0–0.4 GPa pressure region. Data are taken in different experimental runs for increasing pressure (open symbols) and decreasing pressure (solid symbols) cycles. Vertical error is approximately indicated by the size of the symbols.

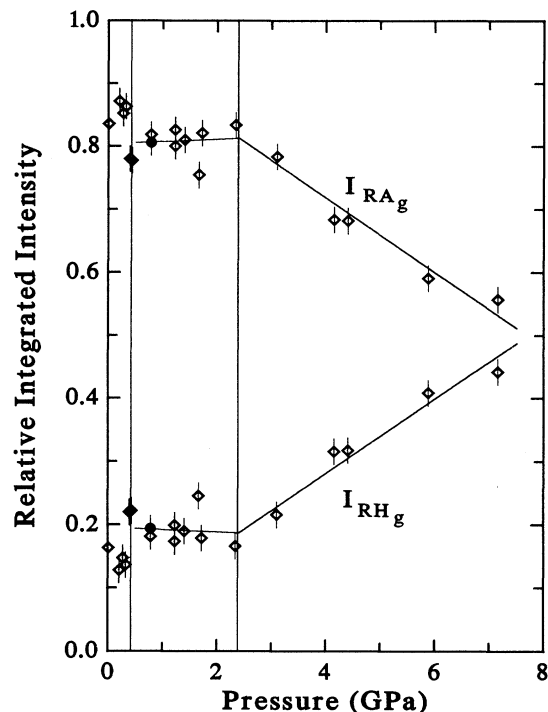


FIG. 7. The pressure dependence of the relative integrated intensities of  $A_g(2)$  and  $H_g(7)$  modes. Solid symbols correspond to data obtained upon releasing pressure. The lines are linear least-squares fits to the experimental data. Vertical lines indicate the transition pressures 0.4 and 2.5 GPa.

symmetry characters:  $A_g \rightarrow A_g$  and  $H_g \rightarrow E_g + F_g$ .<sup>24</sup> The orientational ordering phase transition to the simple cubic (sc) ( $T_h^6$ ) crystal structure, is accompanied by further removal of degeneracy and the resulting modes have symmetry characters:  $A_g \rightarrow A_g + F_g$  and  $H_g \rightarrow A_g + 2E_g + 5F_g$ .<sup>24</sup> Similar symmetry changes occur in the alkali-metal intercalated  $C_{60}$  compounds. Instead of the ten Raman-active  $A_g$  and  $H_g$  molecular modes, all gerade modes are expected to be active in the solid  $C_{60}$ . Raman and IR measurements on  $C_{60}$  thin films and single crystals<sup>25,26</sup> have shown the existence of a great number of additional weak bands in the spectra. These lines were assigned to silent and higher-order modes. The activation of these additional modes has been attributed to mode combination or symmetry breaking, caused by isotope and crystal-field effects.<sup>27</sup> In a recent paper<sup>28</sup> it has been shown that in  $C_{60}$ , the crystal-field effects play a dominant role in the activation of the silent modes. The Raman spectra of  $C_{60}$  in the low-temperature orientationally ordered sc phase, as well as the Raman spectra of intercalated compounds of  $C_{60}$ , show the appearance of new lines.<sup>3,5,7,29</sup> It should be noted that the Raman spectra of  $C_{60}$  in the orientationally disordered fcc phase, contain mostly the strong basic lines, attributed to the modes of the free molecule with  $A_g$  and  $H_g$  symmetry characters.<sup>1,3,5</sup> The absence of additional modes in this phase is connected, in our opinion, with the fact that this phase may be considered as a structure with fcc translational symmetry, only in the approximation of spheri-

cal distribution of charges in the  $C_{60}$  molecule. In fact the real distribution of charges is nonuniform due to the different charge densities for double and single carbon-carbon bonds.

The changes in the pressure dependence of the basic Raman modes of  $C_{60}$  at 0.4 GPa and the appearance of new modes above this pressure is connected with the orientational ordering phase transition from the fcc to the sc crystal structure. The first Raman indication of this transition was observed by Chandrabhas *et al.*<sup>8</sup> as a softening of  $A_g(2)$  PP-mode at pressures up to 0.6 GPa. At normal pressure this transition takes place at 249 K (Ref. 16) and the transition temperature increases with pressure at a rate of 10.4 K/kbar.<sup>18</sup> The appearance of the additional Raman modes in the low-temperature sc phase of  $C_{60}$  was reported by van Loosdrecht *et al.*<sup>3</sup> These authors reported also on the characteristic changes in the intensities of intramolecular modes of  $C_{60}$  in going to the new phase. The intensity of  $A_g(1)$  mode decreases while the intensities of  $H_g(4)$  and  $H_g(3)$  increase with the later becoming the most intense mode in the low-frequency region. We have observed all these typical features of the low-temperature sc phase in the pressure-induced orientationally ordered sc phase at room temperature. It is known that the photodimerization of  $C_{60}$  under intense UV illumination, results in similar changes to the Raman spectra, namely, the softening of  $A_g(2)$  PP-mode and the appearance of modes in the spectrum.<sup>13</sup> The fundamental difference between the pressure-induced and photodimerization effects, is the reversibility of all pressure-induced effects. Therefore the observed pressure behavior of the Raman spectra near 0.4 GPa is due to the orientational ordering phase transition.

An interesting result, in our opinion, is the softening of almost all intramolecular modes of  $C_{60}$  in the pressure region below the orientational ordering phase transition. This result correlates with the unusual temperature dependence of intramolecular modes of  $C_{60}$ , reported by van Loosdrecht *et al.*<sup>3</sup> They have found that the phonon frequencies decrease when temperature decreases to the transition temperature and noted that this result was not completely understood. The softening of the intramolecular modes of  $C_{60}$  has also been observed in the intercalated  $C_{60}$  compounds  $A_6C_{60}$ ,  $A = K, Rb, Cs$ .<sup>29</sup> In this case the Raman-active modes are insensitive to the  $A$  atom, and therefore to the lattice expansion caused by doping with alkali-metal atoms with larger ionic radius. This softening has been attributed<sup>29</sup> to the elongation of the intramolecular bond lengths induced by charge transfer and the resulting softening of the force constants.

The pressure-induced softening of intramolecular modes in pristine  $C_{60}$  may also be caused by charge transfer. The orientational ordering phase transition leads to the freezing of random rotations of the  $C_{60}$  molecules. In the sc phase the molecules are oriented in one of the two equivalent standard orientations, in which the twofold molecular axes are aligned along the crystallographic axes. The simple cubic structure requires that each of the four molecules in the unit cell rotates about a different [111] direction preserving the threefold axes along the [111] direction required by the cubic symmetry.<sup>30</sup>

The neutron powder-diffraction patterns showed that the principal rotation angle was about 98°. <sup>31</sup> This angle is such that the six electron-poor centers of the pentagonal faces of a given molecule face the short electron-rich bonds of the neighboring molecules. This, precisely, may lead to the elongation of intramolecular bond lengths and the resulting softening of the force constants.

The pressure dependence of the observed phonon modes exhibit drastic changes in the slopes of the pressure-induced shifts in a number of modes at 2.5 GPa. The most impressive change in the slope of the  $H_g(7)$  mode is accompanied with the redistribution of intensity among the  $H_g(7)$  and  $A_g(2)$  modes above 2.5 GPa. The dependence in the pressure range 0.4–2.5 GPa implies that the crossing of these two modes would have happened at around 9 GPa. Above 2.5 GPa the crossing behavior is changed to an anticrossing one with the repulsion of the phonon modes and the redistribution of their intensity. The change in the crossing behavior of the  $A_g(2)$  and  $H_g(7)$  modes to the anticrossing one is connected to the symmetry changes occurring in going from the fcc to the sc structure of C<sub>60</sub>. These modes have different symmetries in the molecule and in the solid phase, which excludes the interaction of these modes in the fcc structure. In the rotation free sc phase both  $H_g(7)$  and  $A_g(2)$  modes contain  $A_g$  and  $F_g$  symmetry components and the interaction between them becomes possible. This leads to the repulsion of these modes and the redistribution of intensity from the stronger mode to the weaker one. This behavior cannot be attributed, in our opinion, to the change of resonance conditions due to the pressure-induced shifts of the electronic transitions. It is known that the pressure-induced shift of the absorption spectrum can change the resonance conditions of Raman scattering resulting in changes of the intensities of the Raman modes. <sup>9</sup> According to Matus *et al.* <sup>2</sup> the maximum of the Raman cross section in C<sub>60</sub> is located at the excitation energy of 2.7 eV. Taking into account the negative sign of the pressure-induced shift of the absorption spectra of C<sub>60</sub> <sup>32,33</sup> the intensity of the  $A_g(2)$  PP-mode should increase with pressure. The observed behavior of the Raman intensities is just opposite and therefore can-

not be associated with the pressure-induced change of the resonance conditions in the Raman scattering.

In a recent x-ray powder-diffraction study <sup>17</sup> of C<sub>60</sub> under pressure it was found, that, at room temperature, the rotation free orientationally ordered sc phase occurs at pressures higher than 2.5 GPa. The x-ray results obtained for 0.55 and 1.3 GPa indicate the presence of a reduced degree of orientational order reflecting the rotation of molecules along [111] directions. At ambient pressure this transition occurs near 85 K. <sup>20,34,35</sup> The change in the slopes of the pressure dependence of a number of modes and the pressure-induced intensity redistribution among  $A_g(2)$  and  $H_g(7)$  Raman modes near 2.5 GPa are the manifestation of this phase transition. It is interesting to note that the slope of the pressure dependence of the transition temperature, estimated from our data, is approximately equal to 8.6 K/kbar. This value is close to the value 10.4 K/kbar, reported earlier for the first order orientational melting phase transition. <sup>18</sup>

In conclusion, the pressure dependence of the intramolecular phonon modes of C<sub>60</sub> indicates singularities at 0.4 and 2.5 GPa, associated with the orientational melting and the rotation free orientational ordering phase transitions, respectively. The pressure-induced softening of the majority of molecular modes of C<sub>60</sub> in the pressure range below 0.4 GPa is connected with the charge transfer taking place during the orientational ordering phase transition. The phase transition to the rotation free orientationally ordered phase, accompanied by symmetry changes, causes the interaction between  $A_g(2)$  and  $H_g(7)$  modes.

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\* Permanent address: Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow district, 142432, Russia.

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