Energy spectrum and phase transitions in C_{70} fullerite crystals at high pressure

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Measurements have been made of the Raman, optical absorption, and luminescence spectra of single crystals and pellets of the fullerite C_{70} at $T=300$ K and at pressures up to 12 GPa. The baric shift $d\omega/dP$ and the Grüneisen parameters of the Raman-active intramolecular phonon modes have been determined. It has been established that the $d\omega/dP$ value for certain phonon modes abruptly changes at pressures of $P_1 \approx 2$ GPa and $P_2 \approx 5.5$ GPa, as do the half-widths of the Raman lines. These features in the Raman spectrum are associated with phase transitions at high pressure. The baric shifts of the absorption and luminescence edges of C_{70} crystals have been determined and are -0.12 eV/GPa and -0.11 eV/GPa, respectively, for absorption and luminescence. The baric shift of the absorption edge decreases significantly with increasing pressure and is -0.03 eV/GPa at 10 GPa. These data have been used to determine the deformation potential of the fullerite C_{70}, which is about 2.1 ± 0.1 eV. © *1997 American Institute of Physics.* [S1063-7761(97)01601-6]

1. INTRODUCTION

The discovery of the family of multiatomic carbon molecules known as the fullerites has resulted in intensive study of the physical properties both of the molecules and crystals themselves and of various compounds based on them.[1,2] The fact that most of the attention in this case has been devoted to the fullerite C_{60} is mainly associated with the discovery of superconductivity at relatively high temperatures in compounds of C_{60} with the alkali metals.[3,4] A definite role in this is played by the circumstance that the method developed for synthesizing the fullerenes preferentially yields C_{60} and that it is more available than the other representatives of the family, in particular C_{70}.[5]

Nevertheless, a fairly great amount of attention has been paid to the study of the properties of the fullerene C_{70}. This is associated both with the high intensity of the studies of many-atom carbon clusters as a whole and with the successes in obtaining fairly pure starting material and single-crystal samples of C_{70}. Unlike C_{60}, the C_{70} molecule has the shape of a rugby ball and consists of twelve pentagons and twenty-five hexagons.[6] The molecule belongs to the D_{5h} point group, and the C_{70} crystal has hcp structure with parameters $a_0=1.01$ nm and $c_0=1.68$ nm and belongs to the space group P_{6_3}/mmc.[7] Annealing crystals with the hexagonal structure in high vacuum causes it to be altered, and it becomes predominantly cubic, with a small concentration of the hexagonal phase.[8] It should be pointed out that most C_{70} single crystals grown from the vapor phase have a cubic structure, although about 10% of the crystals are obtained with a hexagonal structure.[9]

Much interest and attention have been devoted to the molecular dynamics and the phonon spectrum of C_{70} crystals, which have been studied in a number of theoretical and experimental papers.[10–14] According to theoretical calculations of the molecular dynamics, the C_{70} spectrum contains fifty-three Raman-active vibrations, classified in the D_{5h}

point group as $12A_1' + 22E_2' + 19E_1'$. In a C_{70} crystal, which contains four molecules per unit cell, the number of active modes increases significantly because of lowering of the symmetry and Davydov splitting. The first detailed measurements of the Raman and IR absorption spectra in C_{70} films made it possible to determine the frequencies of the intramolecular vibrations active in Raman scattering and IR absorption and to compare them with the results of numerical calculations.[14] Measurements of the temperature dependence of the Raman spectra of C_{70} single crystals made it possible to determine the frequencies of the intermolecular phonon modes and the critical variations of the Raman spectra associated with the orientational-ordering phase transition at $T=276$ K.[10,15] The structural aspects of the orientational-ordering phase transitions were studied by x-ray and electron diffraction.[9] Detailed studies of the thermodynamics of these transitions were carried out by differential thermal analysis.[16]

In our opinion, there is special interest in studying the energy spectrum and the phase transitions in C_{70} crystals at high pressure. They are a source of additional information on the intermolecular interaction and are needed for qualitative numerical calculations of the band structure and the energy spectrum of C_{70}. The first measurements of the Raman spectrum at high pressure were made on a powdered mixture of C_{60}/C_{70} fullerenes.[17] Measurements of the Raman spectra of C_{70} single crystals at high pressure made it possible to establish the features in the baric dependence of the phonon frequencies associated with phase transitions of the orientational ordering of the molecules in the crystal.[18] Measurements of the IR absorption spectra of C_{70} at high pressure made it possible to determine the baric shift coefficients and the Grüneisen parameters of the IR active modes.[19] The baric shift of the fundamental absorption edge was studied in Ref. 20.

This paper presents the results of detailed measurements of the Raman spectra and the optical absorption and luminescence spectra of single crystals of the fullerite C_{70} at high

TABLE I.

ω_i, cm^{-1}	$d\omega_i/dP$, cm^{-1}/GPa $P<2.0$	$d\omega_i/dP$, cm^{-1}/GPa $2.0<P<5.5$	$d\omega_i/dP$, cm^{-1}/GPa $P>5.5$	γ_i	ω_i, cm^{-1} (Ref. 14)	ω_i, cm^{-1} (Ref. 15)	$d\omega_i/dP$, cm^{-1}/GPa (Ref. 17)
256	3.2	3.2	3.2	0.226	261	257	1.65
412	0.1	0.1	0.1	0.004	411	410	-
509	-	1.0	1.0	0.036	501	506	0.38
570	−0.3	−0.3	−0.3	−0.01	573	570	−0.06
708	−0.3	−0.3	−0.3	−0.008	704	710	-
737	0.9	0.9	0.9	0.022	739	738	0.12
776	0.8	0.8	0.8	0.019	770	768	-
1061	3.7	5.4	1.5	0.063	1062	1062	1.1
1181	7.1	9.4	3.5	0.109	1186	1184	4
1228	5.3	6.3	3.1	0.078	1231	1229	3.2
1254	7.8	7.5	0.9	0.113	1260	1258	-
1367	6.3	8.2	5.3	0.083	1370	1369	1.1
1432	5.2	4.5	3.0	0.066	-	1438	-
1445	6.0	7.6	3.6	0.075	1448	1448	-
1468	6.0	6.3	5.0	0.074	1471	1469	-
1511	3.8	7.8	2.2	0.046	1517	1517	4.5
1565	4.2	5.9	3.3	0.049	1569	1566	2.73

pressure. The baric shifts and the Grüneisen parameters are determined for a large number of intramolecular phonon modes. The baric shift of the fundamental absorption and luminescence edge is determined, as well as the deformation potential of crystalline C_{70}. Characteristic singularities caused by phase transitions are revealed in the baric dependence of the phonon frequencies at pressures of about 2 GPa and about 5.5 GPa.

2. EXPERIMENT

Single crystals of the fullerene C_{70} were grown from solution in toluene. The starting C_{70} material was obtained by the method described in Ref. 5, and, according to the data of a mass-spectrometric analysis, its purity was at least 98.5%. The Raman and luminescence spectra were measured on single-crystal samples of C_{70} with a size of $100\times80\times20$ μm^3. The optical absorption spectra were measured on thin polycrystalline pellets of C_{70}, fabricated from separate crystallites of the starting material. The pellets were fabricated in a high-pressure chamber with diamond anvils whose working areas are parallel to within arc minutes. To do this, a crystallite placed between the parallel working areas was squeezed with no gasket in a sequential loading cycle until its coloration in the unloaded state became clear red. Measurements show that pellets with a uniform thickness from 1 to 5 μm are obtained in this case.

The optical measurements at high pressure were made by means of a high-pressure chamber with diamond anvils of Merill–Basset type.[21] The working area of the anvils was 600 μm across, the diameter of the working opening of the stainless steel gasket was 250 μm, and the thickness of the gasket after preliminary compression was 80 μm. A 4:1 methanol–ethanol mixture was used as a medium to transmit the pressure. The pressure in the working volume of the chamber was determined with an accuracy of 0.05 GPa from the shift of the R_1 luminescence line of ruby microcrystals.[22]

The Raman and luminescence spectra were measured by means of a Dilor-XY triple spectrometer with an optical multichannel recording system. An argon laser ($\lambda=488$ nm) and a He–Ne laser ($\lambda=632.8$ nm) were used as radiation sources. The radiation power directly in front of the high-pressure chamber was $\lesssim0.5$ mW, and the excitation spot diameter, allowing for defocusing by the diamond anvils, equalled about 10 μm. The absorption spectra were measured on an MDR-23 monochromator by the technique described in Ref. 20.

3. RESULTS AND DISCUSSION

In the Raman spectra of C_{70} single crystals at normal pressure and room temperature, seventeen vibrational modes were observed, whose frequencies ω_i are given in the first column of Table I. These frequencies are essentially identical with the data of Refs. 14 and 15 for C_{70} films, shown in the right-hand part of the table. They are also very close to the phonon frequencies in the Raman spectra of C_{70} crystals of hexagonal modification, measured at $T=23$ K and normal pressure.[10] Some of the frequency difference of the separate modes is possibly associated with the presence of stresses in the C_{70} films and with heating of the crystals by the argon laser radiation at $\lambda=488$ nm, in the strong-absorption region of the C_{70}. The presence of stresses in the C_{70} films increases the phonon frequencies somewhat, whereas heating the crystals has the opposite effect. It should be pointed out that a reversible decrease of the phonon frequencies in the Raman spectra of fullerite as the laser radiation power increases was observed earlier in C_{60} crystals.[23] It was associated with the formation of a large number of excited triplet states; however, in our opinion, it is not impossible that it can be associated with significant local heating of the crystal. We observed a similar effect in C_{70} crystals. To explain it, it is necessary to specially investigate the value of the local heating in the laser excitation spot and its effect on the Ra-
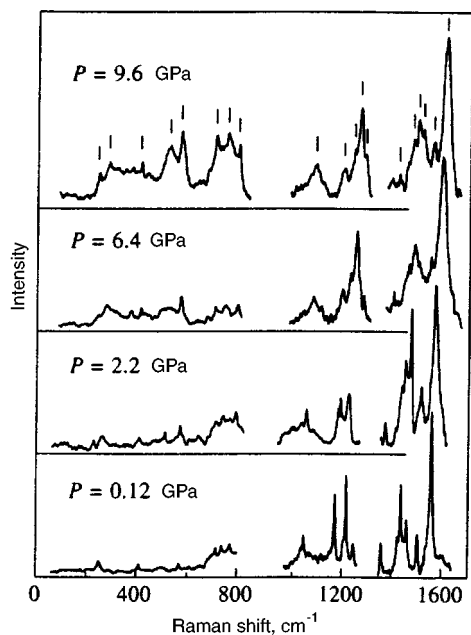
FIG. 1. Raman spectra of C_{70} single crystals at various pressures, $T = 300$ K.

FIG. 2. Baric dependence of frequencies of the phonon modes of C_{70} single crystals in the interval 1350–1650 cm^{-1}.

man spectra. In this paper, we strove to set the laser power at the minimum possible level in order to reduce the effect of laser heating.

All the observed Raman modes relate to intramolecular modes; the intermolecular, rotational, and vibrational modes are located in the 10–60-cm^{-1} frequency interval[10] and were not considered in this work. Figure 1 shows segments of the Raman spectra of C_{70} crystals in the 200–800-cm^{-1} and 1000–1650-cm^{-1} frequency regions at several pressures. No spectra were recorded in the 800–1000-cm^{-1} region, since there are no Raman-active phonon modes of C_{70} in this region. The region close to $\omega \approx 1332$ cm^{-1} has also been eliminated from the Raman spectrum, since a very strong diamond vibration is located in this region, and the contribution to the Raman spectrum from the diamond anvils is dominant. The experiments were done at room temperature, but, as indicated above, some local heating of the crystal in the laser-excitation spot is not excluded. The phonon modes of C_{70} observed in experiment at all pressures are noted on the upper spectrum of Fig. 1 by dashes. The frequencies of the overwhelming majority of the phonons increase with increasing pressure. The two phonon modes at 570 and 708 cm^{-1} are exceptions, since their frequencies decrease with increasing pressure. A relative redistribution of the intensity of the phonon modes with increasing pressure is also observed in the Raman spectra and is associated with a change in the resonance conditions of the excitation because of a significant baric shift of the optical absorption spectrum.[20] Most importantly, a significant strengthening of the low-frequency part of the Raman spectrum should be noted. A similar effect was also observed in the Raman spectra of C_{60} crystals. Changing the excitation wavelength from $\lambda = 488$ nm to $\lambda = 632.8$ nm in these spectra at $P \gtrsim 3.4$ GPa partially cancels the negative baric shift of the absorption spectrum and at first causes a partial reconstruction of the
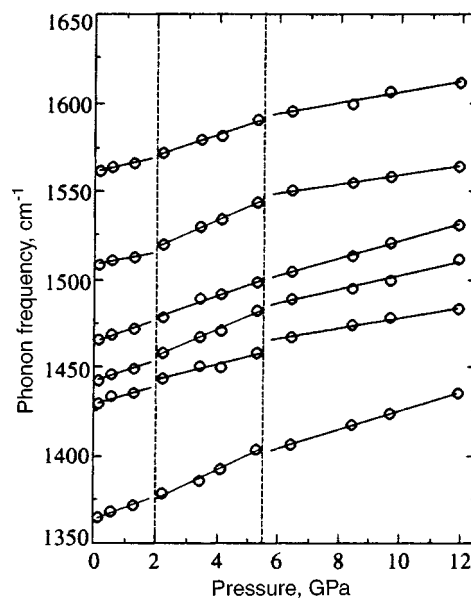
initial intensity distribution. However, increasing the pressure further again changes the resonance conditions of the excitation and alters the intensity of the lines in the Raman spectrum.

The baric dependence of the phonon frequencies is shown in Figs. 2–4, corresponding to three different energy intervals. The vertical dashed lines in these figures indicate the pressures of 2.0 and 5.5 GPa, at which the slope of the baric dependence of virtually all the phonon modes abruptly changes. When $P \approx 2.0$ GPa, new phonon modes also appear in the spectrum and are indicated in Figs. 3 and 4 by black dots. The solid straight lines are linear approximations of the experimental baric dependences of the phonon frequencies,
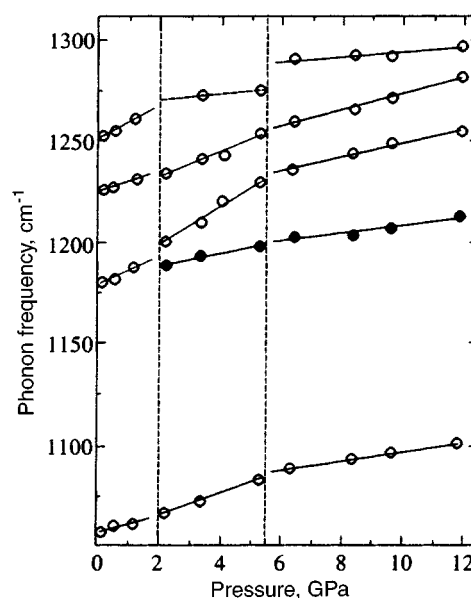

FIG. 3. Baric dependence of frequencies of the phonon modes of C_{70} single crystals in the interval 1050–1300 cm^{-1}.
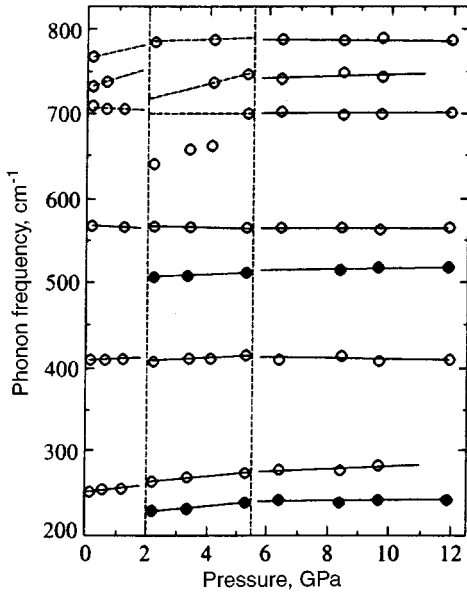
FIG. 4. Baric dependence of frequencies of the phonon modes of C_{70} single crystals in the interval 200–800 cm^{-1}.

drawn independently in three pressure ranges: $P < 2.0$ GPa, $2.0 < P < 5.5$ GPa, and $P > 5.5$ GPa. For some phonon modes, these lines are shown by a dashed line, which reflects inadequate statistics of the experimental data.

Figure 5 shows the pressure dependence of the width of the most intense line, for the 1565-cm^{-1} phonon. It clearly shows the abrupt increases in the line width at the boundaries of the three pressure regions, whereas the dependence is described by a virtually identical linear function in the intermediate regions. These data are unambiguous evidence that there are two phase transitions in the C_{70} crystal in the $P_1 = 2.0 \pm 0.2$ GPa and $P_2 = 5.5 \pm 0.5$ GPa regions. It should be pointed out that the measurements at high pressure were made in two loading cycles with direct application of pressure. In the first loading cycle, measurements were made for pressures of 0.55 and 4.1 GPa (the black dots in Fig. 5); then the pressure was dropped to zero and a second loading cycle
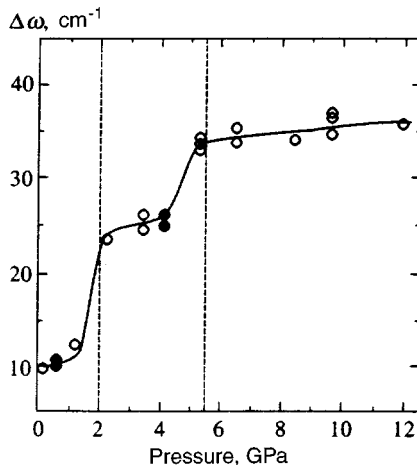

FIG. 5. Raman line width for the phonon with frequency 1565 cm^{-1} vs. pressure.

was carried out on the same sample. The closeness of the data obtained for the position and half-width of the line in the two loading cycles indicates that the phase transition in the $P = 2.0 \pm 0.2$ GPa region, at least, is reversible with respect to pressure.

The Raman data from the C_{70} crystals at high pressure do not make it possible to unambiguously determine the nature of the observed phase transitions. As is well known, orientational-ordering phase transitions that occur in two stages take place in C_{70} crystals, as in C_{60} crystals. In a C_{60} crystal at normal pressure, the first stage of the orientational-ordering phase transition occurs at $T \approx 260$ K and corresponds to freezing out of the random rotations of the molecule.[24] After this, the molecules occupy two energetically equivalent orientational positions, between which they can jump. These jumps completely freeze out at $T \approx 85$ K, which corresponds to the second stage of the orientational-ordering phase transition.[25] The orientational phase transitions at high pressure and $T = 300$ K also occur in two stages, at $P_1 \approx 0.4$ GPa and $P_2 \approx 2.4$ GPa, with the baric shift coefficient of the phase-transition temperature being equal to about 100 K/GPa for both stages.[26–30] According to x-ray and electron diffraction data, the orientational ordering in C_{70} crystals at normal pressure also occurs in two stages, which presumably correspond to freezing out of the rotations of the molecule along the short and long axes at $T_1 \approx 335$ K and $T_2 \approx 276$ K, respectively.[9]

It is tempting to associate the phase transitions that we observed at high pressure with orientational ordering of the molecules. However, to do this, it must be assumed that the laser radiation heats the crystal to a fairly high temperature, the value of which we estimated earlier as about 100 K.[18] In this case, an estimate of the baric shift coefficient of the phase-transition temperature gives a value significantly lower than in the C_{60} crystal. The observed data do not rule out the possibility that both phase transitions that we observed at high pressure are associated with orientational ordering, but additional studies, using other methods, are needed to reliably explain their nature.

The baric shift coefficients $d\omega_i/dP$ of the phonon modes are given in Table I for three pressure intervals. Their values varied between -0.3 and 9.4 cm^{-1}/GPa for various modes and pressure intervals. The Grüneisen parameters γ_i of the intramolecular phonon modes are determined from these data:

$$\gamma_i = -\frac{\partial \omega_i / \omega_i}{\partial V / V} = \frac{B_0}{\omega_i^0}\frac{\partial \omega_i}{\partial P}. \tag{1}$$

It was assumed in this case that the equation of state of crystalline C_{70} is described by a Murnaghan-type dependence:

$$P = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \tag{2}$$

(where V_0/V is the relative variation of the volume of the crystal) with a bulk modulus of $B_0 = 18.1 \pm 1.8$ GPa and that $B_0' = dB_0/dP = 5.7 \pm 0.6$ is the same as in the case of crys-
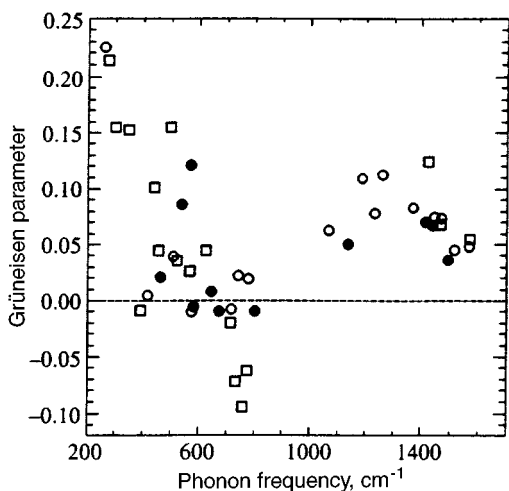
FIG. 6. Grüneisen parameters γ_i of various intramolecular phonon modes of the fullerites C_{60} and C_{70}.

FIG. 7. Initial sections of the luminescence spectra of a C_{70} crystal at various pressures, GPa: *a*) 0, *b*) 0.44, *c*) 0.82, *d*) 1.6. The inset shows the baric dependence of the position of the luminescence edge.

talline C_{60}.[31] The values of the Grüneisen parameters for the intramolecular phonon modes of C_{70}, determined for the initial pressure region, are given in Table I.

Figure 6 shows the dependence of the Grüneisen parameters of fullerite crystals on the frequency of the intramolecular phonon modes. The open dots show the data of this paper, the black dots show the data from IR absorption in C_{70} films,[19] and the squares show the data from Raman scattering in C_{60} crystals.[32] As can be seen from the figure, a distinct correlation is observed between the results of the work using Raman scattering and the IR absorption in C_{70} crystals. This dependence, on which three characteristic regions can be distinguished, also agrees well with the data from Raman scattering in C_{60} crystals. The vibrations are stiffest in the initial region of phonon frequencies, from 200 to 350 cm^{-1}, and correspond to the maximum values of the Grüneisen parameters. Several vibrations in which the Grüneisen parameters are close to zero occur in the frequency region close to 400 cm^{-1}. Next, another group of vibrations, in which the Grüneisen parameters again assume rather large values, occurs in the 450–600-cm^{-1} region. A large group of the highest-frequency vibrations, in the region from 1100 to 1600 cm^{-1}, has approximately the same parameters. Finally, a group of vibrations with negative Grüneisen parameters occurs in the frequency region from 700 to 800 cm^{-1}, whose values for C_{60} are higher in absolute value than the corresponding values for C_{70}.

Negative values of the Grüneisen parameters for crystal phonon modes are evidence of structural instability of the crystal and closeness of the phase transition. In the case of intramolecular modes, they can be evidence of changes of the conformation and instability of the molecule. Negative Grüneisen parameters in the C_{60} molecule characterize the $H_g(3)$ and $H_g(4)$ modes, which correspond to flattening of the molecules (the squashing mode).[12] From this viewpoint, it is not especially surprising that the absolute value of the negative values of the Grüneisen parameters is significantly greater in C_{60} crystals than in C_{70}. This is possibly associated with the initially higher symmetry of the C_{60} molecule
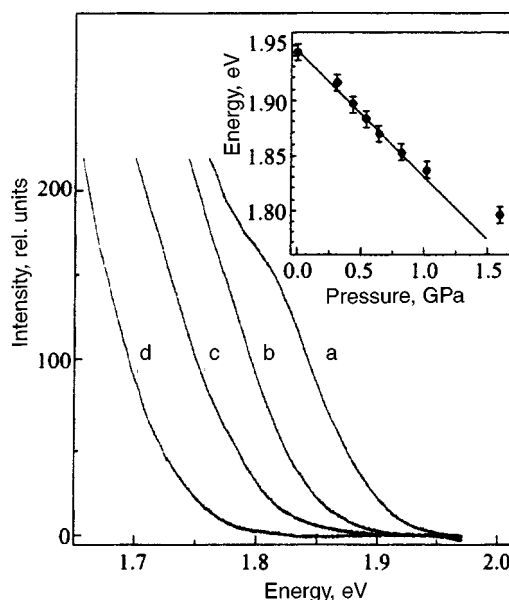
and the stronger influence of weak variations of the conformation of the molecule on the spectrum of intramolecular vibrations.

Figure 7 shows the initial sections of the luminescence spectra of C_{70} crystals at $T = 300$ K and various pressures. Curve a corresponds to normal pressure, and curves b, c, and d correspond to pressures 0.44, 0.82, and 1.6 GPa, respectively. The luminescence spectrum is very extensive, and its low-frequency edge lies beyond the limits of spectral sensitivity of the optical multichannel analyzer. C_{60} crystals are likewise characterized by photoluminescence spectra that extend to 1 eV in the low-frequency region. The spectra were measured at constant laser-excitation power density and were corrected for the spectral sensitivity of the recording apparatus. Thus, the intensity distribution in the luminescence spectra reflects the true picture, and its scale is identical for all pressures. This makes it possible to determine the position of the edge of the spectrum accurately at any pressure.

The luminescence spectrum shifts toward the red as pressure increases, while its shape changes little. However, we are mainly interested in the baric shift of the luminescence edge. It was determined as follows: the initial section of the spectrum was approximated by a parabola, and the part adjacent to it in the higher-energy region was approximated by a straight line parallel to the x axis. The intersection of these two curves was taken as the point from which the luminescence edge was measured for each pressure. The spectral edge is at about 1.94 eV at normal pressure, and it shifts toward lower energies as pressure increases. The baric shift of the luminescence spectrum is thus negative, which is characteristic of molecular crystals, whose molecules in the electron ground state possess a center of inversion and zero dipole moment. The baric dependence of the position of the luminescence edge, determined by the method indicated above, is shown in the inset to Fig. 7. The straight line in the
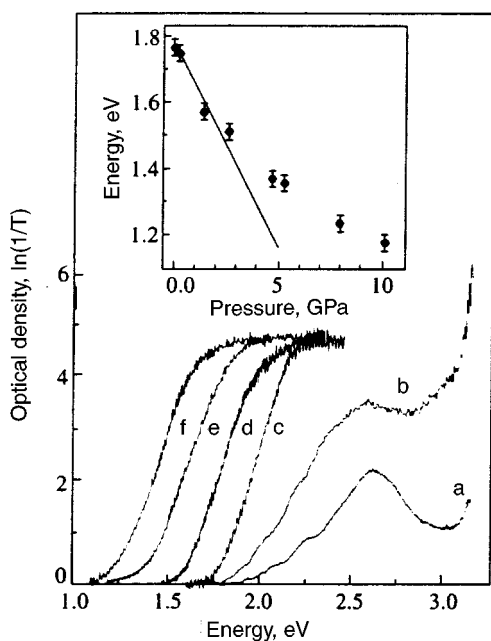
FIG. 8. Absorption spectra of the fullerite C_{70} at various pressures. Curve a shows the absorption of a solution of C_{70} in toluene; curve b shows the absorption of a thin pellet of C_{70} at normal pressure. Curves c, d, e, and f show the absorption of a thin pellet of C_{70} at pressures of 0.2, 1.4, 4.7, and 8.0 GPa, respectively. The inset shows the baric dependence of the position of the absorption edge.

minescence spectrum, shifts toward lower energies as pressure increases. The baric dependence of the position of the absorption edge is shown in the inset of Fig. 8, where the straight line is the tangent to this dependence at the beginning region of pressures, and its slope defines the baric slope of the spectrum. This value equals about -0.12 eV/GPa and agrees fairly well with the baric shift of the luminescence spectrum. The baric shift of the absorption spectrum strongly decreases with increasing pressure and is about -0.03 eV/GPa at $P=10$ GPa. The same behavior is characteristic of C_{60} crystals, as it is for molecular crystals as a whole.[33]

As is well known, molecular crystals of the fullerites C_{60} and C_{70} are semiconductors with a rather large band gap. Its value can be determined by the position of the optical absorption edge and by the beginning of the luminescence spectrum of the crystal. Our data on the baric shift of the absorption edge and the beginning of the luminescence spectrum essentially determine the pressure dependence of the band gap of the C_{70} crystal. They make it possible to determine the deformation potential of the fullerite C_{70}:

$$\mathscr{D} = \frac{\partial E_g}{\partial \ln(V_0/V)} = -B_0 \frac{dE_g}{dP}. \qquad (3)$$

Its value, determined from Eq. (3) with parameters $B_0 = 18.1 \pm 1.8$ GPa and $dE_g/dP = -0.115 \pm 0.005$ eV/GPa, is $\mathscr{D} = 2.1 \pm 0.1$ eV.

This value of the deformation potential is somewhat less than the value $\mathscr{D} \approx 1.3$ eV determined in Ref. 32 for C_{60}. Unlike C_{60}, for which there are theoretical band structure calculations at normal and high pressures, and the deformation potential has been determined both numerically and experimentally, there are no such data for the C_{70} crystal. For this reason, it is not currently possible to compare experimental results for the baric dependence of the electron and phonon spectrum of the C_{70} crystal with the results of other papers. Nevertheless, we assume that our results can be useful for further development of theoretical and experimental studies of the energy spectrum of C_{70}.

inset is the tangent to the initial region of this dependence, and its slope defines the baric shift of the spectrum, whose value is about -0.11 eV/GPa.

Figure 8 shows absorption spectra of the fullerite C_{70} at $T = 300$ K and various pressures. Curve a corresponds to the absorption of a solution of C_{70} in toluene and is given for comparison with the absorption spectrum of a thin pellet of C_{70} (curve b), obtained by the method explained above (in the section on experimental technique). As can be seen from the figure, these two spectra have identical structure, which reflects the rather low level of mechanical stresses in the pellet that unavoidably arise in the process of fabricating it. Curves c, d, e, and f correspond to the absorption of a thinner pellet at pressures of 0.2, 1.4, 4.4, and 8.0 GPa, respectively. The position of the absorption edge, determined by the same method as for the luminescence spectrum, is about 1.8 eV for normal pressure. This value is about 1.84 eV, however, for the solution of C_{70} in toluene, and the difference of ~ 0.04 eV between them determines the so-called crystal shift of the electron terms in molecular crystals.[20] The difference between the position of the absorption edge and the beginning of the luminescence spectrum, corresponding to 0.14 eV, can be a consequence of the chosen method of determining the spectral edge. It is also not impossible that it has a well-defined physical meaning. We cannot assert that the chosen procedure of determining the position of the spectral edge is sufficiently accurate when the spectra have no clearcut edge structure. All the same, there is no doubt that it can be used to accurately determine the baric shift of the spectrum, which is our main goal.

The absorption spectrum of crystalline C_{70}, like the lu-

[1] E. Rohlfing, D. M. Cox, and A. J. Kaldor, J. Chem. Phys. **81**, 3322 (1984).

[2] H. W. Kroto, J. R. Heath, S. C. O'Brien et al., Nature **318**, 162 (1985).

[3] K. Holczer, O. Klein, Sh.-M. Huang et al., Science **252**, 1154 (1991).

[4] P. W. Stephens, L. Mihaly, P. L. Lee et al., Nature **351**, 632 (1991).

[5] W. Kratschmer, K. Fostiropulos, and D. Huffman, Chem. Phys. Lett. **170**, 167 (1990).

[6] J. R. Heath, S. C. O'Brien, Q. Zhang et al., J. Opt. Soc. Am. **107**, 7779 (1985).

[7] V. P. Dravid, S. Liu, and N. M. Kappes, Chem. Phys. Lett. **185**, 75 (1991).

[8] J. E. Fischer, P. A. Heiney, A. R. McGhie et al., Science **252**, 1288 (1991).

[9] M. A. Verheijen, H. Meekes, G. Meijer *et al.*, Chem. Phys. **166**, 287 (1992).

[10] P. H. M. van Loosdrecht, M. A. Verheijen, H. Meekes *et al.*, Phys. Rev. B **47**, 7610 (1993).

[11] R. E. Stanton and M. D. Newton, J. Phys. Chem. **92**, 2141 (1988).

[12] D. E. Weeks and W. G. Harter, J. Chem. Phys. **90**, 4744 (1989).

[13] Z. Slanina, J. M. Rudzinski, M. Togasi *et al.*, J. Mol. Struct. **202**, 169 (1989).

[14] D. S. Bethune, G. Meijer, W. C. Tang *et al.*, Chem. Phys. Lett. **179**, 181 (1991).

[15] N. Chandrabhas, K. Jayaram, D. V. S. Muthy *et al.*, Phys. Rev. B **47**, 10 963 (1993).

[16] E. Grivei, B. Nysten, M. Gassart *et al.*, Phys. Rev. B **47**, 1705 (1993).

[17] D. W. Snoke, Y. S. Raptis, and K. Syassen, Phys. Rev. B **45**, 14 419 (1992).

[18] A. A. Maksimov, K. P. Meletov, Yu. A. Osipyan *et al.*, JETP Lett. **57**, 816 (1993).

[19] H. Yamawaki, M. Yoshida, Y. Kakudate *et al.*, J. Phys. Chem. **97**, 11 161 (1993).

[20] K. P. Meletov, V. K. Dolganov, and Yu. A. Ossipyan, Solid State Commun. **87**, 639 (1993).

[21] A. Jayaraman, Rev. Sci. Instrum. **57**, 1013 (1986).

[22] D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **44**, 1 (1973).

[23] P. H. M. van Loosdrecht, P. J. M. van Bentum, M. A. Verheijen *et al.*, Chem. Phys. Lett. **198**, 587 (1992).

[24] P. A. Heiney, J. E. Fischer, A. R. McGhie *et al.*, Phys. Rev. Lett. **66**, 2911 (1991).

[25] W. I. F. David, R. M. Iberson, T. J. S. Dennis *et al.*, Europhys. Lett. **18**, 219 (1992).

[26] G. A. Samara, J. E. Schirber, B. Morosin *et al.*, Phys. Rev. Lett. **67**, 3136 (1991).

[27] N. Chandrabhas, M. N. Shashikala, D. V. S. Muthy *et al.*, Chem. Phys. Lett. **197**, 319 (1992).

[28] K. Meletov, D. Christofilos, G. Kourouklis, and S. Ves, Phys. Lett. **236**, 265 (1995).

[29] K. Meletov, D. Christofilos, S. Ves, and G. Kourouklis, Phys. Rev. B **52**, 10 090 (1995).

[30] A. P. Jephcoat, J. A. Hriljac, L. W. Finger *et al.*, Europhys. Lett. **25**, 429 (1994).

[31] S. J. Duclos, K. Brister, R. G. Haddon *et al.*, Nature **351**, 380 (1991).

[32] K. P. Meletov, G. Kourouklis, D. Christofilos, and S. Ves, Zh. Éksp. Teor. Fiz. **108**, 1456 (1995) [JETP **81**, 798 (1995)].

[33] K. P. Meletov, V. K. Dolganov, O. V. Zharikov *et al.*, J. Phys. (Paris) **2**, 2097 (1992).

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