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Bulk modulus of C_{60} studied by single-crystal neutron diffraction

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The compressibility of solid C_{60} has been investigated by single-crystal neutron diffraction at pressures up to 5 kbar and temperatures between 70 and 300 K. Ar and He were used as pressure-transmitting mediums at temperatures above and below 200 K, respectively. In this way, a large temperature region could be explored while avoiding intercalation of gaseous species. At room temperature, a very sharp fcc-to-sc transition was observed proving fully hydrostatic loading conditions. Measurements slightly above the glass transition showed that the reduction of the bulk modulus due to the pressure-induced reorientation of the C_{60} molecules (as monitored by the diffraction intensity) may be as large as 30%. Measurements below the glass transition showed that the bulk modulus of the pentagon phase is about 10% larger than that of the hexagon phase. [S0163-1829(99)01415-0]

I. INTRODUCTION

The compressibility of C_{60} has already been investigated by numerous groups,[1–10] either at room temperature,[1–3,5,8–10] at low temperatures[4] or at both.[6,7] Widely different values have been reported for the bulk modulus at room temperature and the volume decrease at elevated pressures. The reasons for these discrepancies are not fully clear. Presumably, they are due to inhomogeneous and/or nonhydrostatic loading of the samples in some of the experiments. We therefore thought it worthwhile to investigate the compressibility of C_{60} using a technique leading to purely hydrostatic pressure conditions, i.e., single-crystal neutron diffraction with a gas as the pressure-transmitting medium. The drawback of this technique is its limitation to rather moderate pressures, i.e., 5 kbar at the moment. Further, special care has to be taken in order to avoid gas intercalation, which is known to alter the compressibility of C_{60}.[9] On the other hand, single-crystal neutron diffraction allows one to measure the relative volume with high precision in a wide temperature range and at many intermediate pressures between zero and $p_{\max}$. In this way, we were not only able to settle the question of the room temperature and the low-temperature compressibility, but also to quantify the contribution of the pressure-induced molecular reorientations to the bulk modulus. Furthermore, molecular reorientations could be monitored by using the diffraction intensities. This allowed us to determine the energy difference between the pentagon and the hexagon orientation as a function of pressure and hexagon orientation, on which basis a variety of experimental data can be understood in a consistent way. The paper is organized as follows: Sec. II describes the experimental technique. The experimental results and the analysis of the data are presented in Sec. III. In Sec. IV, we compare our results with those published in the literature, and Sec. V is devoted to the conclusions.

II. EXPERIMENT

The sample was a large single crystal (~100 mg) grown from the vapor phase.[11] It was inserted to an aluminium gas pressure cell in a standard ''orange'' cryostat. The maximum operating pressure of this cell was 500 MPa (5.0 kbar). Hydrostatic pressure is achieved by means of a gas intensifier system. Since it is known that He and also Ne enters into the C_{60} lattice under pressure entailing significant changes of the compressibility,[9] Ar was used as a pressure transmitting medium for measurements at $T=260$ K and 299 K. However, Ar would have been inappropriate for measurements at low temperatures because of its high melting point, and therefore measurements at $T=150$ K and below were performed using He as the pressure-transmitting medium. Fortunately, we learned from dilatometric measurements of Grube[12] that uptake of He by the C_{60} crystal can be avoided (at least on the time scale of the measurements) if the sample is cooled below 200 K before it is pressurized. The drawback of the procedure of first cooling the sample and then pressurizing it, is a reduction of the plasticity of the seal, which makes it difficult to reach the maximum operating pressure of the cell. We were able to reach 500 MPa at $T=200$ K and could then cool the sample to any temperature below 200 K. Attempts to load the sample at $T=70$ K led only to pressures of ~200 MPa.

The neutron measurements were carried out on the IN3 spectrometer located at a thermal neutron guide of the high-flux reactor of the Institut Laue-Langevin, Grenoble. The spectrometer was operated in the diffractometer mode using Cu111 and pyrolithic graphite as monochromator and analyzer, respectively. The wavelength chosen was $\lambda=2.33$ Å. The lattice constants were determined from longitudinal scans through the (10,2,2)-Bragg peak, whereby the sample orientation was checked after each change of the pressure or

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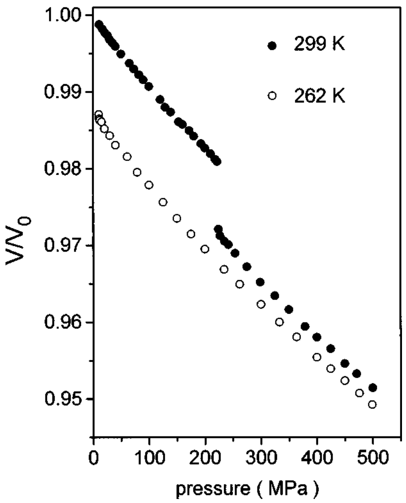

FIG. 1. Relative volume V/V_0 (normalized to the zero pressure volume at $T=299$ K) versus pressure for $T=299$ K and 262 K, respectively. We note that cooling the sample to 261 K induced the phase transition at $p=10$ MPa.

temperature. The precision of the d values after averaging over three individual measurements is typically $\Delta d/d=3\times10^{-5}$.

III. RESULTS AND ANALYSIS

The relative volume V/V_0 vs pressure measured at $T=262$ K and 299 K with Ar as pressure transmitting medium is plotted in Fig. 1. At $T=299$ K, the pressure-induced fcc-sc phase transition was observed at $p=224$ MPa, in excellent agreement with the data of Samara *et al.*[13] and Grube[12] for nonintercalating pressure-transmitting media. We note that the transition was confined to a very narrow pressure region (<4 MPa), indicating purely hydrostatic loading conditions. Nevertheless, we found clear evidence for a two-phase behavior in this pressure range (see Fig. 2). The ratio of the two phases depended not only on the pressure and the temperature, but also on the rate of pressure or temperature change. After entering the two-phase region from above or below by a sudden change in pressure at constant temperature, the newly appearing phase gained gradually in weight with a time constant of the order of hours. Similarly, when entering the two-phase region by a change in temperature at constant pressure, we were not able to adjust the ratio of the two phases at will, even when the temperature was changed only at a rate of the order of 100 mK/h: the phase transition, once started, continued to proceed after stabilizing the temperature. A similar rate dependency has been observed in measurements of the specific heat capacity near the order-disorder transition by Pitsi, Caerels, and Thoen[14] and was interpreted as evidence for a very long internal relaxation time of the order of 10 h.

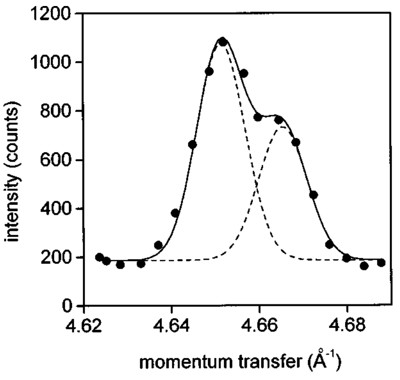

FIG. 2. Longitudinal scan through the (10,2,2)-Bragg peak at $T=299$ K and $p=224$ MPa. The position of the peaks at 4.651 Å and 4.665 Å^{-1} correspond to the lattice constant of the fcc and the sc phase, respectively.

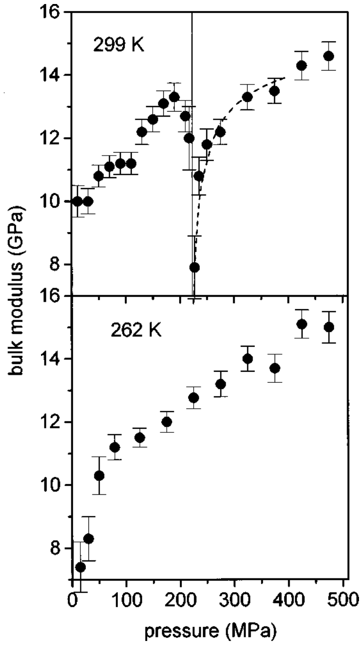

FIG. 3. Bulk modulus, calculated by numerical differentiation of the data shown in Fig. 1. The vertical line in the upper graph denotes the phase transition pressure. The phase transition pressure at $T=262$ K (lower graph) is close to zero. The dashed line depicts the pressure dependence of the bulk modulus calculated from Landau theory by Fradkin (Ref. 15), downshifted in pressure by 110 MPa and upshifted in bulk modulus by 2 GPa.

The bulk modulus obtained by numerical differentiation of the data plotted in Fig. 1 is shown in Fig. 3. Except in a narrow region around the critical pressure, the bulk modulus softens only moderately on approaching the phase transition from above or below. For pressures above the transition, the data are well described by calculations based on Landau theory reported by Fradkin.[15]

It is well known that in the low-temperature phase the C_{60} molecules are locked into distinct orientations about 60° apart, in which hexagonal or pentagonal faces of one molecule face double bonds of adjacent molecules.[16] The fraction of molecules being in the pentagon orientation increases with decreasing temperature at zero pressure,[16] but decreases with increasing pressure,[4] because it occupies a larger volume. Below a certain temperature, called the glass temperature T_g, the kinetics of reorientational motions becomes so slow that the fraction of molecules being in one or the other orientation remains practically constant during the time of the experiment. For experiments on a time scale of hours, T_g is about 85 K at zero pressure[16] and increases to ~120 K at $p=500$ MPa.[12,17,18] It follows from these facts that the pentagon-to-hexagon orientation ratio in the glass phase will

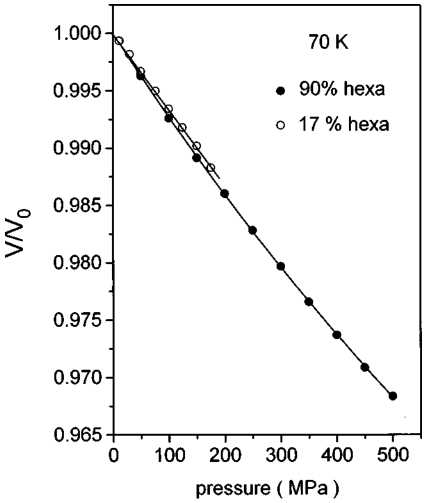

FIG. 4. Relative volume V/V_0 as a function of pressure after cooling to $T=70\,\mathrm{K}$ at 500 MPa (full circles) or at 10 MPa (open circles), i.e., for phases with ~90% or 17% hexagon occupancy, respectively. The lines denote a fit with Murnaghan's equation.

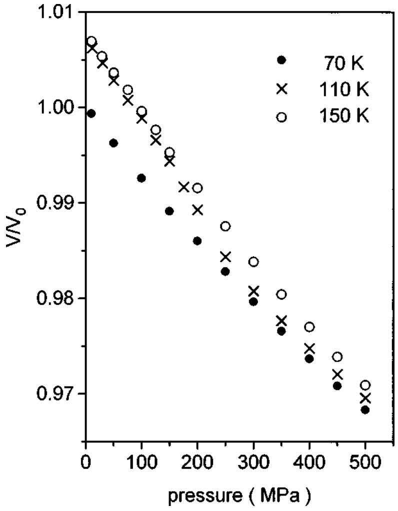

FIG. 5. Relative volume V/V_0 versus pressure at three different temperatures normalized to the zero pressure volume at $T=70\,\mathrm{K}$. In all three runs, the sample was cooled under a pressure of 500 MPa, after which the pressure was stepwise released.

depend on the pressure at which the sample is cooled below T_g.

We have performed measurements at $T=70\,\mathrm{K}$ after cooling the sample at $p=10\,\mathrm{MPa}$ and at 500 MPa, leading to a hexagon occupation of about 17% and 90%, respectively. The precision with which the occupation values can be given will be discussed later. The relative volume vs pressure observed at $T=70\,\mathrm{K}$ is plotted in Fig. 4. The data for the pentagon phase cover only the pressure range 10–180 MPa because of technical problems mentioned in Sec. II. The data for the hexagon phase can be very well described by Murnaghan's equation[19] $B=B_0+B_1\cdot p$ with $B_0=13.2\,\mathrm{GPa}$ and $B_1=10$. Interestingly, B_0 is ~10% higher for the ''pentagon'' phase (B_1 cannot be evaluated with any precision due to the insufficient pressure range). Since in both phases investigated the fraction of molecules taking on the minority orientation was non-negligible, a nearly 15% difference in B_0 has to be expected between a pure hexagon and a pure pentagon phase.

Releasing the pressures at temperatures of 110 or 150 K, respectively, leads to a markedly larger volume change than pressure release at 70 K (Fig. 5). The rather sudden onset of this effect observed at $T=110\,\mathrm{K}$ below 250 MPa is clear evidence that it is related to the onset of reorientational motions. This idea is strongly supported by a concomitant change of the (10,2,2)-Bragg peak intensity (Fig. 6). We note that, by chance, the intensity of the (10,2,2)-Bragg peak changes nearly linearly with the hexagon occupation, and hence the intensity change can be taken as a direct measure of the hexagon occupancy. A glass-transition pressure of ~220 MPa at $T=110\,\mathrm{K}$ appears somewhat too low when compared to the results of Sundquist *et al.*,[17,18] but it fits very well to the results of Grube[12] obtained by high-resolution dilatometry.

At $T=150\,\mathrm{K}$, the changes with pressure are more gradual, but again, the extra volume and the extra intensity behave in a very similar manner (Fig. 6, open symbols), corroborating the idea of a close relation of these two quantities. For a more quantitative understanding of this phenomenon, we have tried to model it starting from the following assumptions:

(i) The volume changes linearly with hexagon occupation n_h

$$V=V_p-\Delta V_{p-h}\cdot n_h, \tag{1}$$

where V_p is the volume of a pure pentagon phase and ΔV_{p-h} the volume difference between a pure pentagon and a pure hexagon phase.

(ii) The hexagon occupation n_h is related to the energy difference ΔG between the hexagon and the pentagon orientation by a Boltzmann equation

$$[n_h/(1-n_h)]=\exp(-\Delta G/kT), \tag{2}$$

whereby ΔG depends in the following form on n_h and pressure p

$$\Delta G=\Delta G_p\cdot(n-n_h)+\Delta G_h\cdot n_h-p\cdot\Delta V. \tag{3}$$

Here, ΔG_p and ΔG_h denote the energy needed to switch a single molecule in a pure pentagon or hexagon phase, respectively. They need not be the same, and the data of

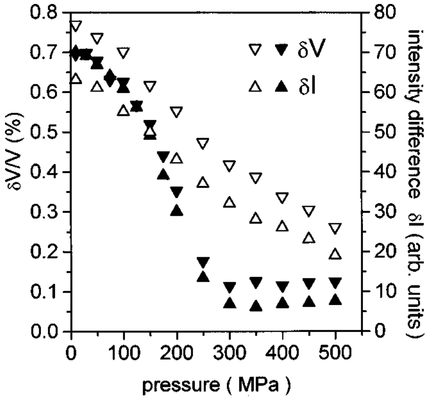

FIG. 6. Left-hand scale: difference in relative volume between 70 and 110 K (full down triangles) or 150 K (open down triangles) on decreasing the pressure after cooling the sample under a pressure of 500 MPa. Right-hand scale: difference in intensity of the (10,2,2)-Bragg peak between 70 and 110 K (full up triangles) or 150 K (open up triangles).

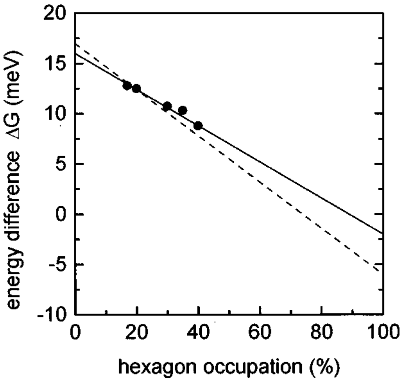

FIG. 7. Energy difference ΔG between the pentagon and the hexagon orientation versus hexagon occupation. The points denote values deduced from neutron diffraction data (Ref. 20). The full line depicts the dependency used in the model calculations of this work, whereas the dashed line was found to give the best description of specific heat data (Ref. 23).

David, Ibberson, and Matsuo[20] have indeed shown a significant dependence of ΔG on n_h (see Fig. 7). Similarly, it has been shown by Gugenberger *et al.*[21] that any attempt to describe the specific heat data of Matsuo *et al.*[22] around the glass transition with a constant ΔG leads to somewhat unsatisfactory results, whereas Herrmann[23] has shown that an ansatz like that of Eq. (3) is perfectly consistent with the data. In our calculations, we assumed a somewhat smaller difference between ΔG_p and ΔG_h than Herrmann[23] to achieve consistency with the results derived from diffraction data of David, Ibberson, and Matsuo[20] (Fig. 7). Still, our value of ΔG_h is slightly negative. At first glance, such an assumption may seem surprising, but it simply means that a pure hexagon phase is in a local minimum of the free energy. Such a behavior was predicted[24] by supercell calculations based on an empirical potential (i.e., the split-bond charge model of Ref. 25), and it is supported by observations of Andersson, Soldatov, and Sundqvist[18] that when a structure is frozen and then heated after changing the pressure at low T, relaxation will start at a higher temperature when the frozen-in structure was close to a pure hexagon phase than when it was close to a pure pentagon phase.

Since we found (Fig. 4) that the pentagon phase has a slightly higher bulk modulus than the hexagon phase, ΔV is assumed to be pressure dependent

$$\Delta V(p)=\Delta V_0+\int_0^p\left(\frac{dV_h}{dp}\bigg|_h-\frac{dV_p}{dp}\bigg|_p\right)dp. \tag{4}$$

From our data we obtain $\Delta V_0=(0.88\pm0.06)\%$, and the integral is evaluated with $B_0=13.16\,\mathrm{Pa}$ and $B_1=10$ or $B_0=14.7\,\mathrm{Gpa}$ and $B_1=9$ for a pure hexagon or a pure pentagon phase, respectively (although we cannot derive a precise value for B_1 of the pentagon phase, our data indicate that its value is lower than that for the hexagon phase, which means that the difference in bulk modulus decreases with increasing pressure).

(iii) The bulk modulus in the absence of molecular reorientation is assumed to be a linear function of n_h. In order to account for a certain softening of the lattice with increasing temperature, the coefficient B_0 for temperatures above 70 K is reduced according to

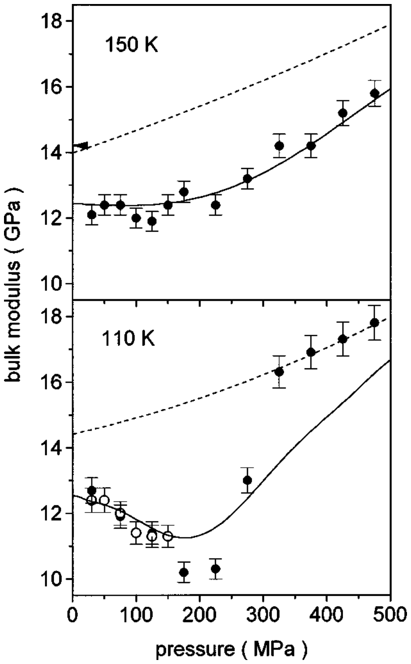

FIG. 8. Bulk modulus versus pressure evaluated from the data shown in Fig. 5. Open and full symbols refer to pressure increase from 10 MPa or pressure release from 500 MPa, respectively. Full and dashed lines are calculated from models including or excluding the contribution of the pressure-induced change of the hexagon occupation, respectively. The calculation of the full line is based on the assumption of thermal equilibrium, a condition which is fulfilled in experiment at $T=110\,\mathrm{K}$ only up to pressures of 150 MPa. The arrow denotes the zero-pressure bulk modulus calculated from the phonon dispersion determined at $T=200\,\mathrm{K}$ (Ref. 27).

$$B_0(T)=B_0(70\ K)-0.006\cdot(T-70)\cdot\mathrm{GPa}. \tag{5}$$

Our assumption on $B_0(T)$ is supported by a calculation of $B(150\,\mathrm{K})$ from the elastic constants evaluated from phonon data[26,27] (see the arrow in Fig. 8), which are not influenced by reorientational motions.

As can be seen from Fig. 8, the model describes the data very well. For $T=110\,\mathrm{K}$, the model applies, of course, only to the pressure region where the structure is in thermal equilibrium. For $p>300\,\mathrm{MPa}$, the orientations are clearly frozen in. The undershoot of the data around 200 MPa on releasing the pressure is typical of relaxation effects when coming from the glass phase.

The model predicts a 50:50 ratio of the two orientations at $p=164\,\mathrm{Mpa}$ (Fig. 9), in very good agreement with the cross over of the (10,2,2)-intensity curves observed at $T=110\,\mathrm{K}$ and 150 K, respectively, see Fig. 10. With increasing pressure, n_h increases rapidly, reaching $n_h\sim0.9$ at $T=130\,\mathrm{K}$ and $p=500\,\mathrm{MPa}$. Therefore, we assumed that cooling the sample under a pressure of 500 MPa will lead to a phase with about 90% of the molecules in the hexagon orientation. This value does not depend strongly on details of the model, because n_h is already rather close to unity. Further, it does not depend very much on the glass transition temperature T_g at $p=500\,\mathrm{MPa}$ assuming $T_g=120\,\mathrm{K}$ (as proposed in Ref. 18) leads to $n_h=0.92$. In this context, we would like to add that we made attempts to derive T_g at $p=500\,\mathrm{MPa}$ from our cooling curves of the lattice parameter a_0 or the (10,2,2)-Bragg peak intensity (10,2,2) vs temperature. However, the

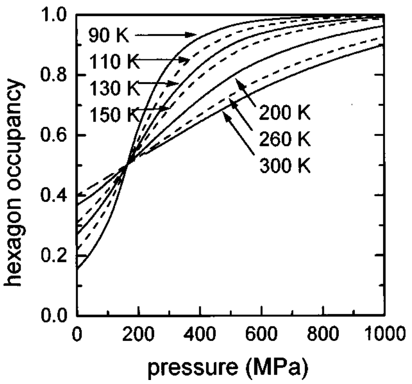

FIG. 9. Hexagon occupancy versus pressure as calculated from the model explained in the text assuming thermal equilibrium.

signature of the glass transition was rather weakly pronounced in these curves and therefore did not allow us a precise determination of T_g.

We note that the rapid increase of n_h from 0.5 to 0.9 between $p = 160$ MPa and 500 MPa at $T = 130$ K is a consequence of a drastic change of ΔG for two reasons: firstly, the contribution $p\Delta V$ to ΔG increases more than linearly with p because of the increasing ΔV, and secondly, driving the structure towards a hexagon phase will reinforce itself due to the change of ΔG with n_h as depicted in Fig. 7.

IV. DISCUSSION

The results on the compressibility of solid C_{60} published in the literature[1–10] show considerable scatter, and so one might ask for the reasons of this scatter and whether we might claim that the results presented in this paper are more reliable than those of previous investigations. The experimental techniques used so far were powder diffraction,[1,2,4–6,9,10] piston and cylinder techniques,[3,7,8,29] and high-resolution dilatometry.[12,28] In these experiments, either gas[4,9,12,28] or NaCl (Refs. 5 and 6) or ethanol-methanol[2] or glycerol[29] was used as a pressure transmitting medium, or the loading force was applied directly onto a C_{60} pellet without any pressure transmitting medium.[3,5,7,8,10] Because Schirber *et al.*[9] and Grube *et al.*[28] have shown that rare-gas intercalation of C_{60} leads to significant changes of the compressibility as well as of the fcc-to-sc transition pressure, we leave results for intercalated C_{60} out of consideration. Further, we leave those results out of account that were obtained by increasing the pressure in large steps as was done in Refs. 1, 2, 5, and 10: these studies were unable to separate the volume change associated with the fcc-to-sc phase transition from the total volume change, and therefore cannot be expected to yield a correct value for the zero-pressure room-temperature compressibility. Representative room-temperature results are displayed in Fig. 11. There is obviously very good agreement between our results and those of recent dilatometric measurements.[28] We note that both experiments show a very sharp phase transition at practically the same pressure. In contrast, the data of Lundin and Sundqvist[7] show a very smeared transition which indicates that the pressure in the cylinder is very inhomogeneous. It appears that the phase transition occurs in some grains already at very low nominal pressure, and, as a consequence, the low values of the bulk modulus for $0 \leqslant p \leqslant 300$ MPa reported in[7] do not reflect the intrinsic properties of C_{60}. For large pressures, when all the grains have been driven into the sc phase, there is good agreement between the results of Ref. 7 and ours. The low value of the zero pressure bulk modulus found by Lundin and Sundqvist[7] motivated Simu and Soldatov[29] to repeat the experiment with the same apparatus, but using a sublimated sample and, most importantly, glycerol as a pressure transmitting medium leading to purely hydrostatic conditions. In fact, the phase transition sharpened up substantially (see Fig. 11). The general tendency to underestimate the volume change with pressure is probably a calibration problem related to the large contribution of the pressure transmitting medium to the gross effect.

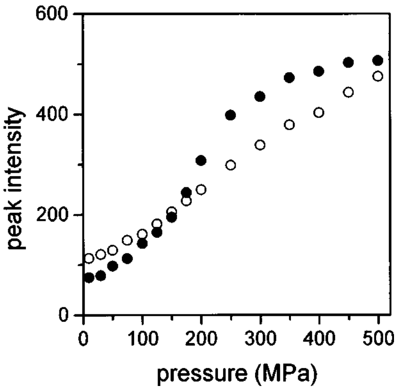

FIG. 10. Pressure dependence of the (10,2,2)-Bragg peak intensity observed at $T = 150$ K (open dots) and $T = 110$ K (full dots), respectively. The 150 K data have been multiplied by a factor 1.1 to account for the increase in the Debye-Waller factor between 110 and 150 K.

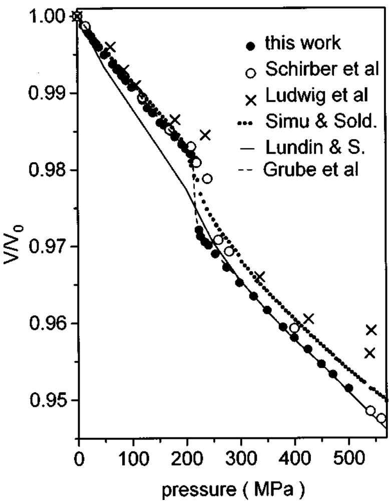

FIG. 11. Compilation of room-temperature compressibility data as reported by Schirber *et al.*,[9] Ludwig *et al.*,[6] Lundin and Sundqvist,[7] Grube *et al.*,[28] Simu and Soldatov[29] and this work.

We consider the agreement between our results and those of Schirber *et al.*[9] as very satisfactory except for the somewhat broadened transition in the data of Ref. 9. Since Schirber *et al.*[9] used gas as a pressure-transmitting medium, pressure conditions were certainly purely hydrostatic. Possibly, crystal perfection of the powder sample was less than that of the large single crystals used in our work and that of Ref. 28

leading to a smearing of the transition.

The data of Ludwig *et al.*[6] are too sparse to see how sharp the phase transition was in this experiment. In any case, the discrepancies between the results of Ref. 6 and ours and those of Refs. 9 and 28 cannot be explained by a smearing of the phase transition. Whatever the reason for the systematic deviations might be, we think that we have good reasons to believe that the excellent agreement between our data and those of Ref. 28 and—for large pressures—also Refs. 7 and 9 is not accidental and that our data and those of Ref. 28 settle the issue of the room-temperature compressibility of C_{60}.

The low-temperature compressibility of C_{60} has been studied in Refs. 4, 6, 7, and 12. David and Ibberson[4] studied the compressibility in the temperature range 150–200 K up to pressures of 2.8 kbar. The equation of state reported in Ref. 6 is not in full agreement with our 150 K data, but a nearly perfect agreement is achieved after omitting the relatively inaccurate p-T cross term $3(3)\times 10^{-5}\,\mathrm{pT}$.

According to our results, the 152 K data of Ref. 7 obtained with a piston and cylinder technique underestimate the compressibility of C_{60} at $p=500\,\mathrm{MPa}$ by about 10%. Surprisingly, the 236 K data of Ref. 7 fit very well to our 150 K data. We note that we found much smaller differences between the compressibilities at 150 and 262 K than Lundin and Sundqvist[7] found between 152 and 236 K.

There is good agreement between the 70 K data of Ref. 6 and ours and the 170 K data of Ref. 6 and our 150 K data, whereby only one data point of Ref. 6 for each temperature falls within the pressure range investigated in this work. There is less good agreement between the zero pressure bulk moduli given in Ref. 6 and obtained in this work (~10% deviations), which is understandable from the fact that Ludwig *et al.*[6] had made their measurements with large increments of pressure and therefore had to rely on an equation of state supposed to be valid over a very large pressure range. Finally, we note that there is satisfactory agreement between the dilatometric data of Grube[12] for $T=110\,\mathrm{K}$ and ours, although the agreement is not as good as found for room temperature.

As to the zero pressure volume difference between the hexagon and the pentagon phases, our value agrees within experimental error with those derived from the lattice constant as a function of temperature at ambient pressure by David, Ibberson, and Matsuo[20] or Gugenberger *et al.*,[21] whereas David and Ibberson[4] had found a value some 50% larger from the pressure variation of the free energy. This discrepancy reduces to ~30% when considering the pressure dependence of the volume difference discussed above. The remaining difference can be attributed to the neglect of the variation of ΔG with the hexagon occupancy in the evaluation of ΔV by David and Ibberson.

V. CONCLUSIONS

We have shown that it is essential to use gas as a pressure transmitting medium to obtain reliable values of the compressibility of solid C_{60}, at least in the pressure range accessible in our experiment. In particular, the fcc-sc phase transition remains very sharp, which allowed us to identify fluctuation effects as predicted by theory. At low temperatures, we were able to separate the contribution of pressure-induced molecular reorientations to the bulk modulus. In an attempt to understand these effects quantitatively, we were led to an extension of the commonly considered two-state model, in that the energy difference between the pentagon and the hexagon orientation is assumed to be dependent on the hexagon occupancy, and that the volume difference between the two orientations increases with pressure due to the larger compressibility of the hexagon phase as compared to that of the pentagon phase.

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[26] The elastic constants c_{11} and c_{12} were evaluated from the three parameter force constant modes listed in Table I of Ref. 27, from which the bulk modulus was obtained as $B=\frac{1}{3}(c_{11}+2c_{12})$. As the model was fitted to 200 K data and not to 150 K data, the B value was subsequently corrected for the general hardening of the phonon frequencies between 200 and 150 K as shown in Fig. 13 of Ref. 27.

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