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## Neutron scattering study of a high-pressure polymeric C<sub>60</sub> phase

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**Abstract.** The vibrational spectrum of a high-pressure phase of C<sub>60</sub> prepared at 21 kbar and 620 K was studied by inelastic neutron scattering and compared with the spectrum of the simple cubic phase restored in the same sample by vacuum annealing at 620 K. The intermolecular band of the restored cubic phase is between 2 and 7 meV and resembles that of pristine C<sub>60</sub>. The spectrum of the high-pressure phase shows a strong band with maxima at 12.8 and 16.6 meV and a minor peak around 5.2 meV, and, thus, demonstrates new interball modes at higher energies than the intermolecular vibrations in pristine C<sub>60</sub>. Only minor energy shifts and splitting of some vibrational bands were observed in the high-pressure phase in the energy range of 25–110 meV, corresponding to the radial intramolecular modes, but the measured spectra markedly differed in the range of the tangential intramolecular modes, 110–220 meV. The experimental data for the high-pressure phase are in reasonable agreement with the infinite-chain polymerization model.

### 1. Introduction

The C<sub>60</sub> fullerite normally forms in the face-centred cubic (fcc) phase at ambient pressure, which transforms to the simple cubic (sc) phase on cooling below 260 K [1–3]. The phonon spectrum of C<sub>60</sub> has been extensively studied by means of infrared (IR) and Raman spectroscopy [4–9] and inelastic neutron scattering (INS) [10–17]. The experimental spectra have formed the basis for numerous model simulations [16–22]. Characteristic features of the spectra are the bands of intermolecular and intramolecular vibrations. The former band involves librational and translational modes in the energy range 0–8 meV, the latter one represents radial and tangential modes in the energy ranges 30–110 and 120–200 meV, respectively. The bands are separated by a gap between 8 and 30 meV.

Other phases have recently been observed in C<sub>60</sub> after photon [23–27] and electron [28] irradiation or thermal treatment under high pressure [29–39]. The new high-pressure phases are assumed to originate from various kinds of C<sub>60</sub> polymerization. Raman, IR, x-ray, mass spectral and toluene solubility data have been presented to support this idea.

The lowest reported pressure for the occurrence of C<sub>60</sub> polymerization is about 7 kbar (at 620 K) [33]. The density of the phase recovered from these conditions was by ~9% higher than that of pristine C<sub>60</sub>. The x-ray diffraction pattern of this phase was simulated

most accurately on the basis of a monoclinic structure which was, in fact, very close to an orthorhombic one [34]. Rather similar x-ray patterns have also been reported in other works [29,35,38] where  $C_{60}$  was treated at  $P = 25\text{--}95$  kbar and  $T = 470\text{--}670$  K, but the patterns were discussed in terms of cubic [29], orthorhombic [38] or monoclinic [35] structures. INS or neutron diffraction data from the polymerized high-pressure phases have not been available until recently.

This work presents the vibrational spectra obtained in an INS study of the polymerized  $C_{60}$  phase prepared at 21 kbar and 620 K and the cubic  $C_{60}$  phase restored in the same sample by vacuum annealing at 620 K.

## 2. Experimental details

Preparation of the high-purity  $C_{60}$  powder has been described earlier [33,40]. The final stage of preparation was sublimation of the powder at 870 K in a vacuum of  $10^{-5}$  Torr.

The  $C_{60}$  powder was compacted into pellets of 12 mm diameter and about 2.5 mm thick. Their total weight was 3.2 g. The pellets were mounted between thin plates of rolled molybdenum inside Teflon ampoules. Precautions were taken to avoid contamination of the sample, but the process of compacting took about 3 h, when  $C_{60}$  could absorb gases from the ambient atmosphere. Therefore, each assembled ampoule was heated to 600 K in a vacuum of  $10^{-5}$  Torr for 1 h or more. This is enough to remove gaseous impurities from  $C_{60}$  [41]. Then the ampoule was rapidly closed and placed into the high-pressure cell.

To produce the high-pressure phase, the pellets were heat-treated at  $T = 620$  K for 40 min under a quasi-hydrostatic pressure of  $P = 21 \pm 1$  kbar generated between profiled anvils made of tungsten carbide. The pressure was released after cooling to room temperature, then the sample was stored in a small light-proof container evacuated to less than  $10^{-1}$  Torr until the start of the INS measurements.

In order to restore the fcc phase for the control INS experiment, the pressure-treated sample was annealed at  $T = 620 \pm 20$  K and  $P \leq 10^{-5}$  Torr for 12 h, then stored as above. The lattice parameter of this sample at room temperature,  $a = 14.11$  Å, was small compared to the value for as-prepared pristine  $C_{60}$  before the thermobaric treatment,  $a = 14.17$  Å, therefore we refer to this phase from now on as *restored*  $C_{60}$ .

To characterize the crystal structure of the high-pressure  $C_{60}$  phase (hpp- $C_{60}$ ), a neutron diffraction pattern was measured at room temperature on the POLARIS diffractometer at the spallation neutron source, ISIS, Rutherford Appleton Laboratory, UK [42]. The diffraction pattern revealed that the range of large interplane spaces,  $d = 2.5\text{--}15$  Å, could be described within a structure close to fcc with  $a \simeq 13.85$  Å, but the data fit was rather poor at small  $d$ -values, 0.1–2.5 Å. The interatomic radial distribution function (RDF) of hpp- $C_{60}$  in the range 0–15 Å was obtained by Fourier transformation of the experimental structure factor at neutron momentum transfers up to  $50$  Å<sup>-1</sup>. Simulating the fullerite RDF for different  $C_{60}$ – $C_{60}$  distances, we found that the experimental data were best described if the nearest intermolecular distance was approximately 9.2 Å. Similar intermolecular distances have been reported for the high-pressure  $C_{60}$  phases (9.22 and 9.62 Å) [29] and for the polymeric fullerite chains in  $RbC_{60}$  and  $KC_{60}$  (9.14 and 9.11 Å, respectively) [43]. Further analysis is under way.

Rotational diffusion in hpp- $C_{60}$  was studied by quasielastic neutron scattering using the IRIS spectrometer [42] at ISIS. It is well known that heating of the sc ordered  $C_{60}$  phase results in a broad quasielastic component near 255 K when the sample transforms to the fcc phase, in which molecules are able to undergo free rotations on their lattice sites [44]. No broadening of this kind was observed in our experiment on hpp- $C_{60}$  in the temperature range

4.2–315 K. Therefore, free molecular rotation does not occur in hpp- $C_{60}$  in this temperature interval. This result supports the idea that hpp- $C_{60}$  studied is polymeric in nature.

The INS spectrum of the high-pressure  $C_{60}$  phase was measured at 25 K using the time-focused crystal analyser spectrometer, TFXA, at ISIS [42]. The spectrometer has an excellent resolution,  $\Delta\omega/\omega \leq 2\%$ , in the experimental range between 2 and 200 meV. The measured data were transformed to the dynamic structure factor  $S(Q, \omega)$  versus energy transfer using standard programs. Here  $\omega$  and  $Q$  are the neutron energy transfer and neutron momentum transfer, respectively.

The INS experiment on the restored  $C_{60}$  phase was carried out at 77 K using the inverted geometry time-of-flight spectrometer KDSOG-M [45] installed at the IBR-2 pulsed reactor in Dubna, Russia. The spectrometer has a medium resolution,  $\Delta\omega/\omega \simeq 4\text{--}10\%$ , in the energy transfer range 1–200 meV. The data were transformed to the generalized vibrational density of states,  $G(\omega)$ , which is a standard procedure for data taken on the KDSOG-M spectrometer.

The background spectra in both experiments were determined from empty-can measurements under the same conditions and subtracted from the experimental data.

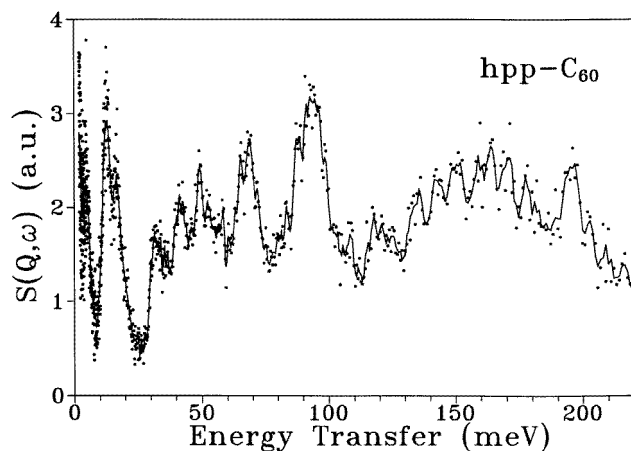
Both spectrometers used, TFXA and KDSOG-M, provide similar geometric conditions. A white incident neutron beam scattered at the sample, and neutrons with the final energy of  $E_r \simeq 4$  meV passed through the analysing system composed of a PG crystal and a cold polycrystalline beryllium filter, then they were recorded. Neutron momentum transfer and neutron energy loss are related by the following expression:  $(\hbar Q)^2/2m = 2E_r + \omega - 2\sqrt{E_r(E_r + \omega)} \cos(\phi)$ , where  $m$  is the neutron mass and  $\phi$  is the neutron scattering angle. The TFXA measurements were carried out at  $\phi = 135^\circ$ . The neutron scattering angles in the experiment at KDSOG-M were 80, 100, 120 and  $140^\circ$ , the spectra collected at each angle were transformed to  $G(\omega)$  and summed up. Since the final energy of scattered neutrons was small, the trajectories/volumes in the  $(Q, \omega)$  space covered by two spectrometers were very close.

Carbon atoms scatter neutrons only coherently, therefore neutron scattering had to be averaged over a large region of neutron momentum transfer in order to obtain the vibrational density of states of a polycrystalline  $C_{60}$  sample. The quality of the average is determined by the ratio  $R$  of the volume of the reciprocal space covered in the INS experiments,  $V_{Q^3}$ , to the volume of the Brillouin zone,  $V_{BZ}$  [46]. In the case of a  $C_{60}$  crystal  $V_{BZ} \simeq 0.087 \text{ \AA}^{-3}$ , and the ratio  $R$  is very large. For energy resolution  $\text{res} = \Delta\omega/\omega = 0.02$  (spectrometer TFXA) and energy transfer 2 meV, this ratio is  $R = 2\pi Q^3 \text{res}/V_{BZ} \simeq 30$ . The  $R$ -value becomes larger at higher energy transfer and lower resolution, i.e. the condition of averaging was valid in the whole range of energy transfer studied at both spectrometers, 2–220 meV.

There were no corrections for multiple or multiphonon scattering. The neutron transmission through the sample was high, more than 90%, and multiple neutron scattering was negligible. At low temperatures, multiphonon contributions were negligible in the energy range of main interest, 2–30 meV. They became comparable to one-phonon scattering at higher energies. However, in the case of polymeric  $C_{60}$ , which has a broad dispersed one-phonon part of the vibrational spectrum (see below), the multiphonon contributions should look like some structureless background and should not result in sharp features.

### 3. Results and discussion

The  $S(Q, \omega)$ -INS spectrum of the hpp- $C_{60}$  is shown in figure 1, and the  $G(\omega)$ -spectrum for the restored  $C_{60}$  phase is presented in figure 2(a) (at the top). For comparison, the  $S(Q, \omega)$ -



**Figure 1.** The INS spectrum,  $S(Q, \omega)$ , of the hpp- $C_{60}$  (prepared at 21 kbar and 620 K) as measured on TFXA at 25 K. The smoothed spectrum is shown as a solid curve.

spectrum of the high-pressure phase was transformed to the generalized vibrational density of states,  $G(\omega)$ , using

$$G(\omega) = S(Q, \omega) 2m\omega / \hbar^2 Q^2 [n(\omega) + 1] \quad (1)$$

where  $n(\omega)$  is the Bose factor. The result is shown in figure 2(a) (at the bottom). The spectra in figure 2(a) are normalized to the same area under the  $G(\omega)$  curves in the energy range 0–110 meV where the counting statistics was high in both experiments. The smoothed data given as solid lines in figure 2(a) are directly compared in figure 2(b) where the superimposed spectra of the high-pressure and restored phases are plotted as solid and dashed curves, respectively.

The positions of the peaks in the  $G(\omega)$ -spectra of hpp- $C_{60}$  and restored  $C_{60}$  are presented in table 1 together with the available INS data for the sc  $C_{60}$  phase [10–13]. Assignment of the  $C_{60}$  vibrations in table 1 is given after [10] and [47]. Some minor features were observed in the spectrum of restored  $C_{60}$  in addition to the data in table 1, i.e., shoulders at 30.1, 36.3 and 85.0 meV and, probably, a peak at 130 meV (see figure 2(a) at the top).

The experimental spectra can be divided into three parts: the low-energy range of 0–25 meV where pristine  $C_{60}$  is assumed to have intermolecular modes below 8 meV and no phonon states between 8 and 25 meV, the medium-energy range of the radial intramolecular modes, 25–110 meV, and the high-energy range of the tangential intramolecular modes, 110–200 meV.

### 3.1. Intermolecular vibrations

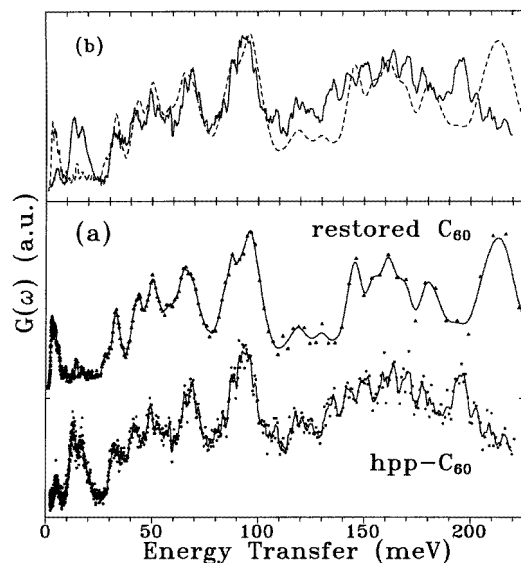
The difference between the spectra is very prominent in the low-energy range. The spectrum of the restored  $C_{60}$  phase shown in figure 3(a) exhibits an intense band between 2 and 7 meV and is very similar to the well known vibrational spectrum of pristine  $C_{60}$  in this range. The intermolecular vibrations in the sc phase of pristine  $C_{60}$  cover the range 0–8 meV and include a strong librational peak around 2.6 meV and two librational peaks at 3.5 and 5.0 meV, which overlap with the translational peaks at 4 and 6 meV due to TA and LA phonon branches [14–17]. Corresponding peaks in the spectrum from the restored cubic

**Table 1.** Peak positions in the INS spectra of hpp-C<sub>60</sub> and restored C<sub>60</sub> compared to the available data for pristine sc C<sub>60</sub>. All values are in millielectron volts.

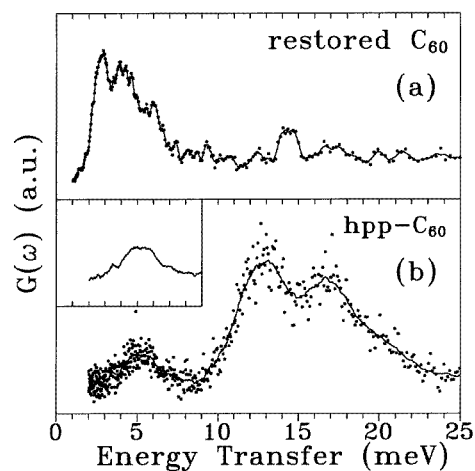
Assignment [10, 46]	sc, 10 K [11]	sc, 20 K [10]	sc, 25 K [12]	sc, 30 K [13] <sup>a</sup>	Restored 77 K	hpp 25 K
				2.2 sh <sup>b</sup>		
				2.7	2.8	
				3.8		
				4.4	4.2	5.2
				5.9	6.0	
			9.9			
		12	12.6		14.4 sm <sup>c</sup>	12.8
		18	17.0			16.6
—		29 sh			27.9 sm	
H <sub>g</sub>		33	32.7		32.9	33.0 <sup>d</sup>
—	34		33.6			
T <sub>2u</sub> , G <sub>u</sub>		43, 44	42.7		43.2 <sup>d</sup>	41.7 <sup>d</sup>
—	44		44.0			45.8 sm
H <sub>u</sub>	50	50	50.1		50.2	49.2
H <sub>g</sub>	54	54	53.6			52.6 sm
G <sub>g</sub> , A <sub>g</sub>	61	60	60.5		57.8 sm	58.2 sm
—			65.2			65.4
T <sub>1u</sub>	66 sh	66	66.5		66.5 <sup>d</sup>	
—	70		69.8			68.8
T <sub>1u</sub>		71	71.4			71.7 sm
—	79	77				
—	82–103	83	83.4	83.5		83.6 sm
H <sub>g</sub>		88	88.7	89.0	87.6	88.0
—		92		92.5		93.7
H <sub>g</sub>		96	94.9	94.5	95.9	
—			100.8	96.5		98.6
—		104	104.2	99.5		
G <sub>g</sub>	108	109		104.0		108.2 sm
—		114				
T <sub>2g</sub> , G <sub>u</sub>	120	119	120.4		118.9 sm	121.5 <sup>d</sup>
T <sub>2g</sub> , G <sub>u</sub> , T <sub>1g</sub>		124	129.4	127.5		
—		132				
H <sub>g</sub>	136	136	135.0	134.5		134.2 <sup>d</sup>
—	143–161	139	139.1	137.5		142.9
T <sub>1u</sub>		147		148.5	145.8	
—		149	150.9	154.5		150.3
H <sub>g</sub> , H <sub>u</sub>		156		158.5		158.9
—			164.5	163.5	161.0 <sup>d</sup>	163.7
—	167–199	168		168.5		169.9
H <sub>g</sub> , T <sub>1u</sub>		176	179.5	178.5	180.7	177.5
—				182.5		
A <sub>g</sub>		184	188.5	187.0		
—			193.8	190.0		195.1
H <sub>g</sub>		196	198.8	196.0		202.6 sm
—						208.8 sm
H <sub>g</sub> , H <sub>g</sub>			211.0		213	215.8 sm

<sup>a</sup> The energy range 9–80 meV was not presented in [13].<sup>b</sup> Shoulders.<sup>c</sup> Small peaks.<sup>d</sup> Split peaks whose maxima are listed below:

restored C <sub>60</sub>	hpp-C <sub>60</sub>
43.2 ⇒ 42.0 + 43.8	33.0 ⇒ 30.2 + 31.6 + 33.8 + 35.4 + 36.7
66.5 ⇒ 65.2 + 68.2	41.7 ⇒ 39.9 + 41.3 + 42.5 + 43.5
161.0 ⇒ 155.4 + 161.2 + 168.0	121.5 ⇒ 117.4 + 120.8 + 124.9
	134.2 ⇒ 132.6 + 135.5.



**Figure 2.** (a) The  $G(\omega)$ -vibrational spectra of hpp- $C_{60}$  (TFXA, 25 K) and the restored cubic  $C_{60}$  phase (KDSOG-M, 77 K). (b) The smoothed spectra shown in (a) as solid curves presented as a superposition of the solid and dashed curves for the high-pressure and restored phases, respectively.



**Figure 3.** Low-energy parts of the  $G(\omega)$ -spectra of (a) the restored cubic  $C_{60}$  phase (KDSOG-M, 77 K) and (b) and hpp- $C_{60}$  phase (TFXA, 25 K). The curves are polynomial-spline fits of the experimental points. For clarity, the fitting curve for hpp- $C_{60}$  is plotted to 9 meV in the inset.

$C_{60}$  phase are observed at 2.8 meV (strong), around 4.3 meV (maxima at 3.9, 4.3 and 4.6 meV) and at 6.0 meV. The energy of the first peak, 2.8 meV, is large compared to the published data for the sc  $C_{60}$  phase at 77 K. Therefore, the interaction between the fullerene molecules in the restored cubic phase is stronger than in pristine  $C_{60}$ . This is consistent with the reduced lattice parameter measured in the restored  $C_{60}$ .

The low-energy vibrations of hpp- $C_{60}$  are completely different from those of restored  $C_{60}$ , as seen in figure 3(b). Only a minor peak is found below 8 meV with a maximum around 5.2 meV and a slight shoulder at 3.5 meV (see inset), but there is a very strong band at higher energies with two maxima at 12.8 and 16.6 meV. All the peaks are rather broad compared to the instrumental resolution. A three-Gaussian fit gives full widths at half-maximum of 2.6, 3.1 and 6.1 meV, respectively. The intensity ratio of the new bands around 5.2, 12.8 and 16.6 meV is 1 : 3.8 : 7.3. Thus, the first peak at 5.2 meV contributes only about 8% to the integrated intensity of the low-energy range. This dramatic re-distribution of intensity in the interball vibrational region of the spectrum can be attributed to formation of polymeric  $C_{60}$ , and the degree of polymerization must be rather high.

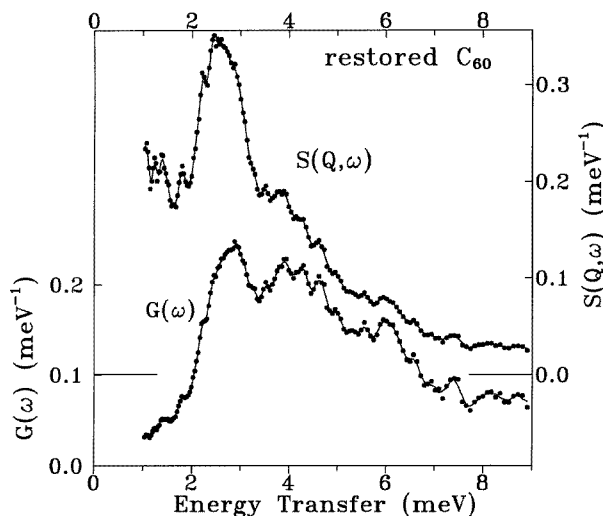
When polymerization of  $M$  molecules occurs,  $6(M - 1)$  intermolecular librational and translational modes transform to new low-energy intramolecular modes of the polymer. The INS intensities are directly proportional to the density of vibrational states weighted on the squared amplitudes of the atomic oscillations. If the observed re-distribution of intensity were due to the formation of dimers, for example, the intermolecular band of dimeric  $C_{60}$  (similar to that in the sc phase) should show an approximate decrease in intensity by only a factor of two, providing the force constants between carbons in different dimers are the same as in pristine  $C_{60}$ . On the other hand, one can roughly estimate from the INS spectra that the effective interaction between the  $C_{60}$  cages in the hpp- $C_{60}$  is at least ten times stronger than in pristine or restored  $C_{60}$  (the ratio of force constants is about the squared ratio of the ‘average’ energies of the bands, which is more than three).

There were several calculations of the new interball modes to appear in the vibrational spectrum of polymeric  $C_{60}$  at low energies [48–50]. Adams *et al* [48] predicted peaks at 8.6, 13.8 and 15.2 meV in the dimer model or peaks at 9.9, 11.3, 14.8 and 20.0 meV in the case of infinite-chain polymerization. Porezag *et al* [49] calculated the odd-parity librational modes at 2.7 and 4.3 meV and a torsion mode at 2.9 meV due to ball twisting around the molecular axis of a dimer. A dimer interball mode analogous to the stretching mode in a diatomic molecule and two even-parity librations were also predicted at 11.0, 16.1 and 18.1 meV, respectively [49].

The model of infinite-chain polymerization seems to describe the experimental data for hpp- $C_{60}$  more adequately. Strong dispersion of the interball modes is very likely, and this might be the cause of the width of the band which covers the energy range 9–24 meV. The peak observed at 5.2 meV could also represent the external intermolecular modes due to translational motions and librations of infinite chains around their polymerization axes.

It is worth noting that the  $S(Q, \omega)$ - and  $G(\omega)$ -spectra of the same sample differ at low phonon energies because the Bose factor in (1) is energy dependent and  $Q^2$  is not a linear function of  $\omega$ . However, the spectra are very similar at higher energy transfers,  $\omega > 30$  meV, where  $n(\omega) \ll 1$  and  $Q^2(\omega) \sim \omega$ . Earlier INS data on sc  $C_{60}$  measured on different spectrometers and at different temperatures were presented either as  $S(Q, \omega)$ - or as  $G(\omega)$ -spectra. For the sake of comparison, both representations of the intermolecular part of our restored  $C_{60}$  INS spectrum are given in figure 4. It is seen from the figure that peaks of the  $S(Q, \omega)$ - and  $G(\omega)$ -functions differ both in intensity and in position. The  $G(\omega)$ -spectrum is approximately temperature independent. In the harmonic approximation, the only temperature dependent contribution to  $G(\omega)$  is the Debye–Waller factor,  $\exp(-2W) = \exp(-Q^2\langle u^2 \rangle)$ , which is close to unity at the neutron momentum transfers corresponding to this energy range (here  $\langle u^2 \rangle$  is the mean square displacement of a carbon atom). Therefore, it seems more appropriate to compare the INS peak positions observed at different temperatures using the  $G(\omega)$ -spectrum.





**Figure 4.** The INS spectrum of the restored cubic  $C_{60}$  phase (KDSOG-M, 77 K) shown as  $S(Q, \omega)$ - and  $G(\omega)$ -representations.

The  $G(\omega)$ -spectrum in figure 4 is in good agreement with the earlier data [14–17] except for the position of the first peak. The  $S(Q, \omega)$ -spectrum in figure 4 looks similar to that observed by Coulombeau *et al* [13] apart from higher intensity at low energies due to the higher temperature of the sample in the present experiment.

It is pertinent to note here that an intense band between 10 and 20 meV was observed in the earlier INS experiments on the sc  $C_{60}$  phase [10, 12]. There is obvious coincidence between the energy of this band and the range of the new modes found in the present pressure-polymerized fullerite. Renker *et al* [16] studied INS on  $C_{60}$  purified by vacuum sublimation and proposed that no vibrations occurred in high-purity sc  $C_{60}$  in this energy interval. We assume now that the band at 10–20 meV in the spectra of pristine  $C_{60}$  could be either due to solvent impurities in the samples or due to photopolymerization, which could occur during sample storage. The latter effect was eliminated in [16] due to the high-temperature purification procedure. Recently Coulombeau *et al* [13] have renewed their earlier INS data for pristine  $C_{60}$  [12] using another sample and spectrometer (see table 1). They did not plot the energy range 9–80 meV but confirmed that the intermolecular vibrations in pristine  $C_{60}$  had energies less than 7 meV and related the peaks earlier observed at 10 to 20 meV [12] to inaccurate background subtraction. The origin of an ambiguous weak peak at 14.4 meV in the present spectrum of the restored fullerite is therefore unclear but may be due to a small admixture of polymerized  $C_{60}$ , which may be still present within the restored  $C_{60}$  as a product of an incomplete reversion from the high-pressure phase.

The present INS data should be compared to the available Raman scattering spectra of polymerized  $C_{60}$ . Davydov *et al* [35] observed a Raman peak at 14.7 meV after a high-pressure treatment at 3.0 GPa and 473 K, which was caused by formation of the same high-pressure  $C_{60}$  phase. The peak was not detected, however, after a treatment at a lower temperature of 373 K [35]. The Raman spectra of photopolymerized  $C_{60}$  films showed either a peak at the same energy, 14.4 meV, [24] or one strong mode at 14.3 meV and two minor ones at 10.5 and 17.4 meV [25]. Comparison of the optical and INS spectra gives another argument for conspicuous dispersion of the interball modes over the Brillouin zone.

### 3.2. Intramolecular vibrations

In spite of drastic modification of the low-energy range of the  $C_{60}$  vibrational spectrum upon polymerization, figure 2 shows that changes are modest at intermediate energies and involve mainly the vibrational bands over 110 meV. The  $G(\omega)$ -curves of hpp- $C_{60}$  and restored  $C_{60}$  are very similar in the range of the radial intramolecular excitations, 25–110 meV. This fact is rather surprising because the molecule structure is anticipated to be modified by polymerization. There are two peaks in the range of the radial vibrations which look rather different in the measured spectra. The first one has two maxima at 27.9 and 32.9 meV in the restored cubic  $C_{60}$  phase. A corresponding peak in the high-pressure phase is rather broad and has five maxima which are listed in the footnote under table 1. Similar results were calculated in [48] and [49], where these modes were explained by splitting of the  $H_g$  mode. For a dimer, the calculated energies were 30.0, 31.5 and 34.1 [48] or 32.5, 34.2 and 37.9 meV [49]. The calculated splitting of this mode is much larger for infinite polymeric chains.

The peak at 108.2 meV in the  $G(\omega)$ -spectrum of hpp- $C_{60}$  was not observed in the spectrum of the restored fullerite. This suggests that its occurrence could also be due to the effect of polymerization. However, this peak has also been reported to occur in pristine  $C_{60}$  [10, 11].

In the range of the tangential modes, 110–220 meV, the resolution of the KDSOG-M spectrometer is not so good, and the statistics of the experimental data is rather poor. Nevertheless, it is worth noting the observed large difference between the measured spectra in this range. A characteristic feature of the hpp- $C_{60}$  spectrum is the reduced scattering intensity above 200 meV. Instead, two peaks appear at 134.2 and 195.1 meV, which are absent from the spectrum of restored  $C_{60}$ . As a result, the intensity distribution over the range of the tangential modes is smoother in the hpp- $C_{60}$  spectrum than in restored  $C_{60}$ .

## 4. Conclusions

The high-pressure and high-temperature treatment of pure  $C_{60}$  (21 kbar and 620 K) resulted in a considerable change of the fullerite vibrational spectrum. The low-energy vibrations in the high-pressure phase consist of a peak at 5.2 meV and a very strong two-peaked band between 9 and 25 meV with maxima at 12.8 and 16.6 meV (pristine  $C_{60}$  has no vibrations in the energy range 8–30 meV). The changes were minimal in the range of the radial intramolecular modes, 25–110 meV, but several vibrational bands in the spectrum from the high-pressure phase were split. A more noticeable re-distribution of the scattering intensity occurred in the range of the tangential modes, 110–220 meV. Calculations using infinite-chain polymerization models give a better correspondence with the experimental data than do calculations involving dimer models.

Vacuum annealing at 620 K restored the cubic  $C_{60}$  phase. Its vibrational spectrum is essentially the same as that of pristine  $C_{60}$  except for a somewhat higher energy of the first librational peak, 2.8 meV.

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