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Neutron spectroscopy of fullerite hydrogenated under high pressures

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Abstract

A new hydrofullerite was synthesized when the C_{60} fullerite was treated under a hydrogen gas pressure of 30 kbar at 620 K for 24 h and quenched. The inelastic neutron scattering spectra of the as-prepared sample and that after annealing at 300 K showed that the as-prepared hydrofullerite consisted of $C_{60}H_x$ molecules and interstitially dissolved molecular hydrogen. Both spectra exhibited peaks at 13 meV characteristic of polymeric fullerites. © 1999 Elsevier Science B.V. All rights reserved.

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A recent inelastic neutron scattering (INS) study of the C_{60} hydrofullerite synthesized at 620 K under a hydrogen pressure of 6 kbar and quenched to liquid nitrogen was undertaken on the KDSOG-M spectrometer, at IBR-2, Dubna, Russia. This showed that the quenched sample consisted of $C_{60}H_x$ molecules, $x \approx 24$, packed as the BCC lattice and interstitial H_2 molecules, dissolved in the ratio of 1.4 H_2 mol/$C_{60}H_x$ mol [1]. The $C_{60}H_x$ molecules were stable under normal conditions whereas the interstitial hydrogen left the sample upon annealing at 300 K.

This report presents the INS data from hydrofullerite prepared and quenched under a higher hydrogen pressure, of 30 kbar. The spectra were measured at 24 K in the range of the energy transfer 2–500 meV using the high-resolution time-of-flight spectrometer TFXA at ISIS (RAL, UK). Both the as-prepared (quenched) state and the final state (after annealing for 3 h at room temperature in vacuum) were studied. Fig. 1 shows that the spectra of both samples are equivalent up to 6 meV energy transfer, within the experimental accuracy. The INS spectrum of pristine C_{60} at energies below 8 meV was assigned to the intermolecular translational and librational vibrations (see e.g. Ref. [2]).

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We believe that the bands observed in our spectra below 6 meV are of the same nature. The large peak at about 156 meV (which shows structure at 147.5, 154.0, 160.0 and 166.5 meV) and the small peak at 357.5 meV are similar to those observed in the spectrum of hydrogenated amorphous carbon [3]. These peaks are immediately assigned to the C–H bending and stretching modes, respectively. The peak at 312 meV is at twice the energy transfer of the C–H bending and can be assigned to its first overtone. These INS features, which involve the intermolecular bands and the intramolecular C–H bending and stretching modes of the $C_{60}H_x$, remain essentially the same for both the quenched and annealed hydrofullerite states. The difference between these two spectra (curve 3 in Fig. 1) shares none of the features of the original curves. This difference curve represents the INS spectrum from molecular hydrogen trapped in quenched hydrofullerite, which left the sample upon annealing.

The main features in the INS spectra and their behaviour upon annealing are similar to those found previously for hydrofullerite prepared at 6 kbar [1]. We interpret this to mean that the 30 kbar as-prepared hydrofullerite consists of $C_{60}H_{32}$ molecules[1] with molecular hydrogen dissolved on interstitial sites. However, the spectral features of interstitial molecular hydrogen in the new 30-kbar-hydrofullerite differ markedly from those of the 6-kbar-hydrofullerite. Two peaks observed at about 15.3 and 29.7 meV (Fig. 2) are close to energies of the first transitions between the rotational states of the 3-D free hydrogen molecule, $E_{0\to1} = 14.7$ meV and $E_{1\to2} = 29.4$ meV [5]. The peak at 8.9 meV is rather close to the first transition between the states of 2-D free molecular hydrogen, $E_{0\to1} = 7.35$ meV [5]. This indicates that, at least some of, the H_2 molecules occupy interstitial sites in the $C_{60}H_{32}$ unit cell which strongly affect the rotational behaviour of hydrogen.

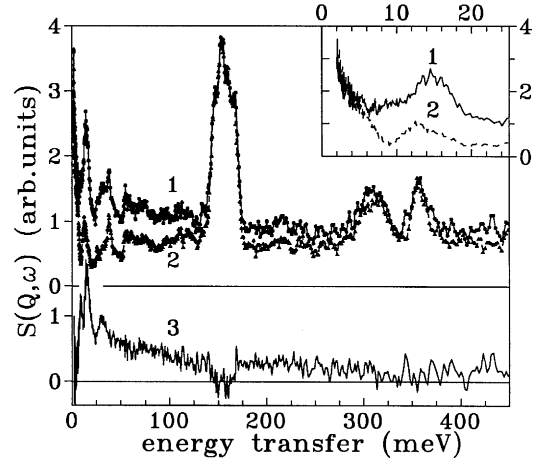

Fig. 1. The INS spectra of hydrofullerite synthesized at 30 kbar and quenched to liquid N_2 (curve 1), then annealed at 300 K (curve 2), both at 24 K. The difference between these spectra (curve 3) represents vibrations of interstitial molecular hydrogen in the quenched hydrofullerite. The inset shows curves1 and 2 at low energies on a larger scale.

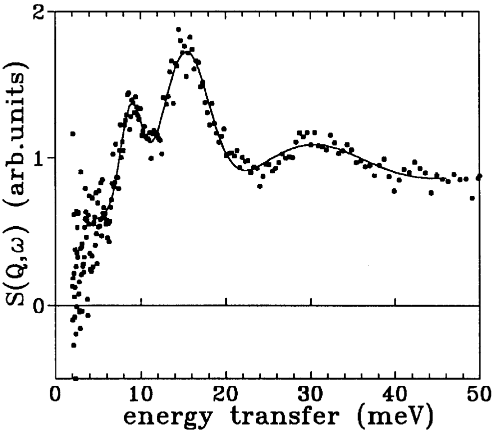

Fig. 2. The difference INS spectrum (curve 3 from Fig. 1) on a larger scale. The solid curve is a three-Gaussian fit.

Other features in the present INS spectra of hydrofullerites are peaks at 13, 25.8 and 38 meV (Fig. 3) as well as two broad, slightly structured features, which extend up to the C–H bending mode region. There is a sharp low-energy cut-off at 53 meV, the intensity minimum between the features occurs at 86 meV. Peaks in the INS spectrum of pristine C_{60} above 30 meV are due to intramolecular vibrations [1,6]. Therefore, the spectral features presently observed above 30 meV also

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[1] The recent measurement on the eVS spectrometer at ISIS performed on the annealed state of hydrofullerite $C_{60}H_x$ prepared at 30 kbar has shown that the content of bound hydrogen was $x = 31.6 \pm 1.0$ [4].

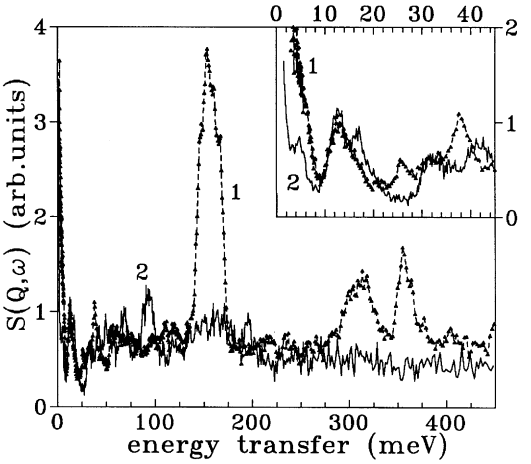

Fig. 3. Comparison of the INS spectra of hydrofullerite synthesized at 30 kbar after final annealing (curve 1) and polymeric C_{60} prepared at 21 kbar (curve 2) [6], both at 24 K. The inset shows the curves in the range upto 45 meV on a larger scale.

represent intramolecular vibrations of the carbon atoms. Here, however, the strong spectral response occurs because of the involvement of the hydrogen atoms of $C_{60}H_{32}$.

The peak near 13 meV is a notable feature of the INS spectra of 30-kbar-hydrofullerite, it was not observed in the spectra of 6-kbar-hydrofullerite [1]. This feature is very close to the vibrational modes characteristic of polymeric C_{60} [6]. The C_{60} polymerization occurs at 620 K on compression over 7 kbar [7]. Comparison of the INS spectrum of the annealed $C_{60}H_{32}$ prepared at 30 kbar with the recent data for C_{60} polymerized at $P = 21$ kbar [6] (Fig. 3) strongly suggests polymeric binding of $C_{60}H_{32}$ in the present hydrofullerite.

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