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Abstract
The dielectric properties of C_{60} have been measured as functions of temperature
and hydrostatic pressure in the ranges 80–370 K and 0–0.8 GPa. The
results show sharp anomalies at the rotational transition above 260 K and
large relaxation peaks associated with the rotational 'glass transition'. From
the measured frequencies of the loss peaks we calculate the energy barrier
for molecular jumping between the 'pentagon' and 'hexagon' molecular
orientations. The energy barrier increases by 13% GPa^{-1}.

1. Introduction

Fullerenes, such as C_{60}, have been much studied under pressure [1, 2]. The molecules in solid
C_{60} rotate almost freely in the rotationally disordered high-temperature face-centred cubic (fcc)
phase (above 260 K at atmospheric pressure), but on cooling this motion slows down and is
transformed to a ratcheting or rocking motion in the orientationally ordered simple cubic (sc)
phase at low temperature or under high pressure.

In the sc phase, there are two possible molecular orientations. At zero pressure, molecules
are nominally oriented with a double C=C bond on one molecule facing the centres of carbon
atom pentagons on its neighbours ('P' or 'pentagon' orientation). In the other 'H' or 'hexagon'
orientation, where the molecules are oriented with a double bond facing instead the centre of a
hexagon. However, the energy difference between the orientations is very small and there is a
strong temperature dependence of the fraction of molecules that is 'P' (or 'H') oriented [1, 3].
Under pressure the relative energies of the two phases changes rapidly and above 200 MPa
the 'H' orientation is preferred [4]. The energy barrier between the two states is very much
higher than the energy difference, and below 90 K the molecular reorientation stops and the
structure 'freezes' into an orientational glass [1–3]. Because the orientational state depends
on pressure many interesting relaxation phenomena can be observed if the pressure is changed
in this glassy state and the material is allowed to relax on heating at a new pressure [5, 6].

Dielectric measurements on C_{60} show relaxation peaks connected with the rotational or
ratcheting motion of the molecules. The results can therefore be analysed to find the energy
barrier between the two states. In theory, no strong dielectric effects should be observed in

C_{60} because of the symmetry of the molecules, but in practice, oxygen diffuses rapidly into the lattice. Charge transfer from the oxygen molecules to neighbouring C_{60} molecules leads to large dipole moments which couple strongly to ac electric fields [7]. Dielectric studies at atmospheric pressure showed that the characteristic energy barrier between different molecular orientations is about 350 meV [7], very similar to values obtained by other methods.

Although there have been many investigations of the dielectric properties of C_{60}, we are aware of only one study under high pressure [8]. This study was only concerned with finding the slope of the fcc–sc phase transition under pressure up to 0.5 GPa, and no information was obtained on the dielectric loss and thus on the reorientational dynamics. We have therefore measured the dielectric properties of C_{60} over wide ranges in frequency, pressure, and temperature, to obtain further information.

2. Experimental details

Nominally 99.98% pure, sublimed C_{60} in the form of a course powder was obtained from Term USA, Berkeley, CA. 300 mg was placed between two stainless steel plates, 23 mm in diameter, forming a capacitor. The upper plate was perforated to allow the pressure medium free access and the distance between the plates was kept at 0.4 mm by ceramic spacers. The capacitance of the empty device was about 6 pF. The capacitor was inserted into a piston-and-cylinder pressure vessel which could be heated electrically or cooled using liquid nitrogen. Temperature T and pressure p were measured *in situ* using a type K thermocouple and a manganin gauge, respectively. A 50/50 mixture of *n*- and *iso*-pentane hydrostatic to below 150 K in the pressure range used [9], was used as a pressure medium. The capacitance and loss tangent of the filled capacitor were measured using a four-probe method with a HP 4192 impedance bridge, with resolutions of 10^{-14} F and 0.0001, respectively. Measurements were carried out over the ranges 100 Hz–1 MHz, 80–370 K, and up to 0.8 GPa.

3. Experimental results and discussion

Preliminary experiments were first carried out on pressed pellets of C_{60} using a solid pressure medium. These experiments were not very successful. The solid medium caused unpredictable changes in the capacitor geometry under pressure, and relaxation peaks were weak and not easily analysed. No systematic analysis could be carried out. Probably pressed C_{60} pellets contain such large numbers of lattice defects that 'normal' molecular motion is no longer possible.

In later experiments hydrostatic conditions were used, with a pentane mixture as pressure medium. In these experiments we measured the capacitance C and the loss tangent D as functions of T, p, and frequency, f. Because the data for D show the most interesting features we will concentrate our analysis on this quantity. Figure 1 shows a typical set of results, obtained at 400 MPa. The figure shows the measured loss tangent as a function of T at four different frequencies, from 100 Hz to 100 kHz.

The curves show several types of anomalies as functions of temperature and frequency. Starting from the high-temperature side, there is first a sharp, frequency-independent anomaly near 340 K, with sudden jumps or steps in the curves. This anomaly is connected with the rotational transition from the high-T fcc rotationally disordered phase into the partly orientationally ordered, low-temperature sc phase. Below this, there is a combined peak and step decrease structure in D over a fairly wide range in frequency. These anomalies are strongly
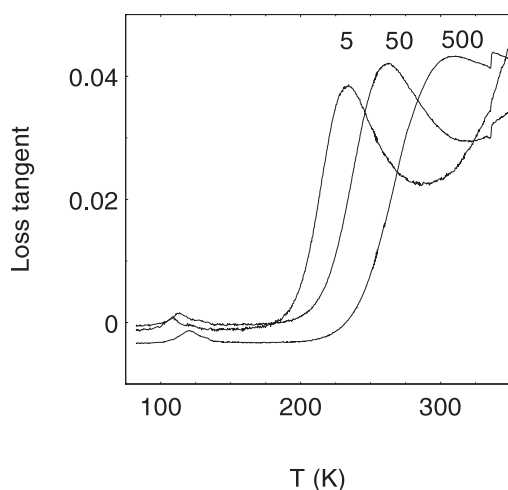
Figure 1. Loss tangent D as a function of T, at the frequencies 5, 50, and 500 kHz.
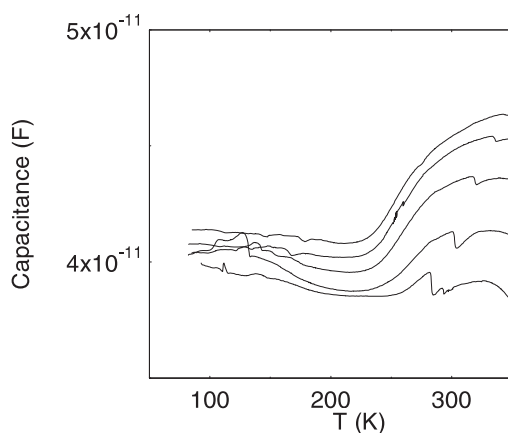

Figure 2. Total measured capacitance as a function of T at 0.1, 0.2, 0.3, 0.4, and 0.5 GPa (from bottom up).

frequency dependent and are connected with molecular relaxation in the low-temperature phase. Finally, near 100 K, there is another small frequency-dependent peak-type anomaly which is not yet completely understood but seems to be related to a further low-temperature degree of freedom in the lattice.

From the high-temperature anomalies, the phase boundary between the fcc and the sc phases can be deduced. Figure 2 shows the total measured capacitance at 50 kHz at several pressures, showing that the temperature of the anomaly shifts with pressure in a systematic way. From the observed anomalies we deduce the slope of the phase line to be $dT/dp = 170$ K GPa^{-1}, in good agreement with literature data [1, 2].

The large loss peaks in figure 1 are connected with molecular relaxation in the partially orientationally ordered phase, and the peak temperatures are very strongly T-dependent. Such a behaviour is well known in many glass-forming materials and the 'glass transition temperature' T_g is often calculated by extrapolating the loss behaviour to some low frequency, usually 1 mHz (corresponding to a characteristic experimental duration of 1000 s). Applying this model to our data we obtain values for the glass transition temperature T_g between 125 and 130 K. Direct measurements by other methods give values between 80 and 90 K, with a significant increase with increasing pressure [5]. We do not know the reason for these discrepancies.
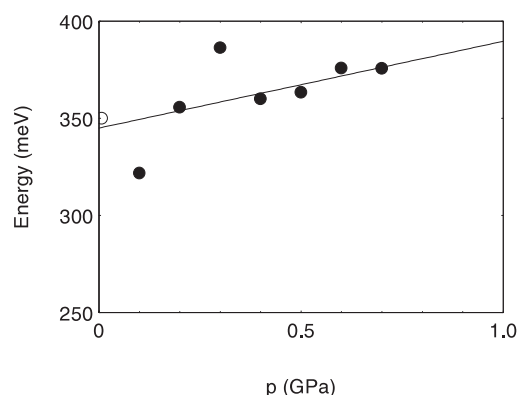
Figure 3. The calculated energy threshold for molecular reorientation in the sc phase.

In a two-state model, the energy barrier between the two states is usually calculated by assuming an Arrhenius model. In such a model we assume that motion between these states is thermally activated, such that the typical jump frequency f_0 can be written

$$f_0 = f_{00} \exp(-E_0/k_B T),$$

where f_{00} is an intrinsic constant and E_0 a characteristic threshold energy. In the present case we assume that molecules jump between the two orientational states, the 'P' and 'H' orientations. At each pressure, the energy barrier E_0 can be found from the slope of $\log f$ versus the inverse of the temperature at which the maximum loss occurs at this f.

The results of these calculations are shown in figure 3. In a first experiment, measurements on a pressed sample gave a value for E_0 of 350 meV, in excellent agreement with the value found by Pevzner *et al* [7]. The high-pressure experiments under hydrostatic conditions give a rather large scatter in the data below 400 MPa but a good fit to a straight line can still be found. This line extrapolates to 345 meV at zero pressure, in excellent agreement with both our own zero-pressure data and those of Pevzner *et al* [7], and has a slope of $+44.7$ meV GPa^{-1} corresponding to a pressure coefficient of 0.13 GPa^{-1}.

Acknowledgment

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