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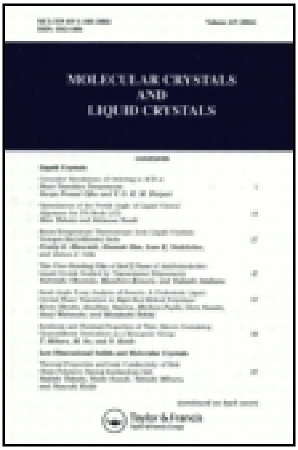

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Elastic Properties of Fullerenes

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ELASTIC PROPERTIES OF FULLERENES

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Abstract We report on ultrasonic investigations of the frequency dependent and temperature dependent sound velocity in pure C_{60} and in C_{60}/C_{70}-compounds. For both compositions of pressed bulk samples used here elastic anomalies owing to the wellknown transitions at about 260 K and 160 K are observed. Concerning the absolute values of the elastic stiffness our results differ markedly from those found by means of low frequency vibrating reed techniques on C_{60} single crystals.

Bearing in mind the potential applicability of bulk materials for manufacture and development we concentrated our activities on investigations of the elastic properties of moderately pressed (0.2-0.4 GPa) fullerene compounds. Conventional powder consisting of a mixture of C_{60}- and ≈15% C_{70}-molecules as well as purified C_{60} (ratio:99.99%) was used as starting material. The powder was pressed at ambient temperature into cylindrical samples (diameter:≈5mm, thickness:≈3mm), which subsequently were goldplated in order to avoid chemical reactions with air and the ultrasonic bonding agent used. After carefully polishing, the compact samples were bonded to a piezoelectric quartz transducer.

Although the samples obtained are of fair mechanical strength, the ultrasonic investigations are restricted to frequencies up to about 30 MHz because of an only moderate acoustic quality factor for longitudinal ultrasound. Fig.1 shows the relation between the excited ultrasonic frequency and the wavenumber (reciprocal wavelength) obtained for a C_{60}/C_{70}-compound and a specimen consisting of pure C_{60} respectively. The remarkable linearity observed for each sample demonstrates an ideal dispersionless behaviour at least in the frequency range investigated here. Consequently the longitudinal sound velocity v_L directly obtained from the diagram is independent of frequency and amounts to about 6 600 m/s for pure C_{60} and to about 12 900 m/s for the C_{60}/C_{70}-compound respectively, which is unexpectedly high. Accordingly the elastic moduli derived from the relationship $C_L = \rho\, v_L^2$ and the experimentally obtained mean mass density $\rho \approx 1.5$ g/cm^3 characterize materials of fairly high stiffness.

For the pure C_{60}-sample one obtains a mean elastic modulus $C_L = 65$ GPa but for the C_{60}/C_{70}-compound $C_L = 245$ GPa. These values are quite high in comparison with the elastic moduli usually determined for solid fullerenes by means of low frequency vibrating reed techniques[1] or pressure dependent volume dilatation measurements[2] . In particular the elastic behaviour of the pressed C_{60}/C_{70} - compound found here is not very reminiscent of a solid cohered primarily by van der Waals forces .

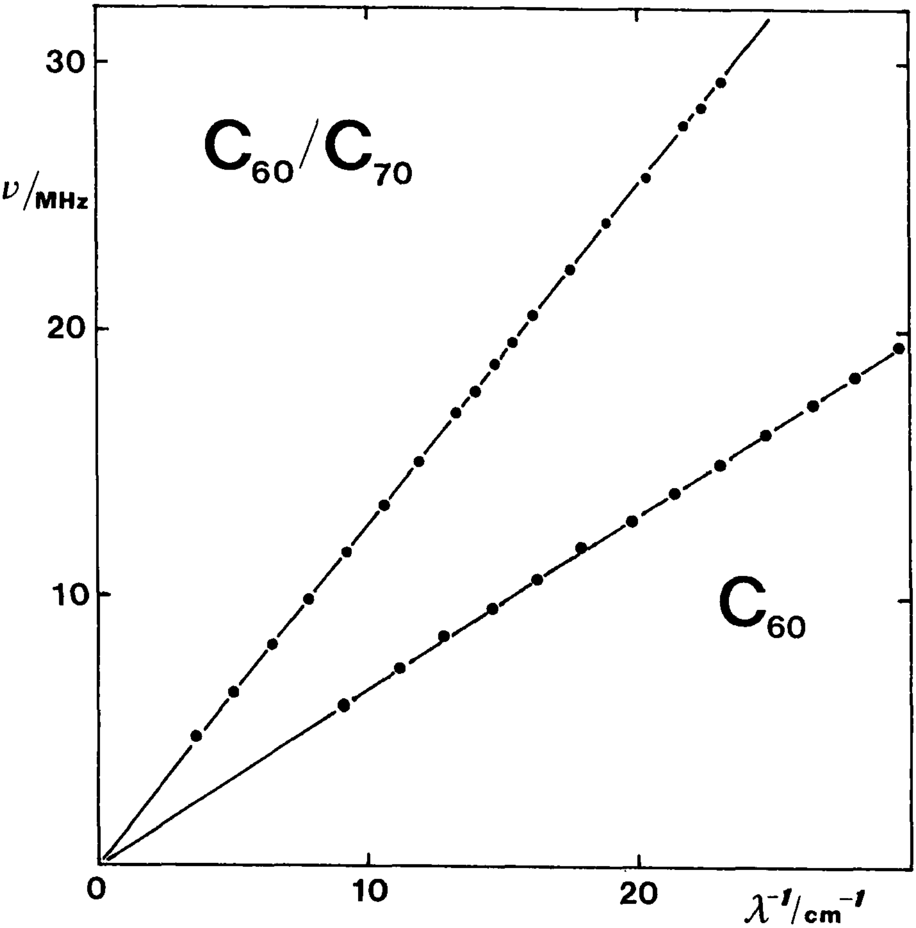

Fig.1 Elastic dispersion behaviour of pressed fullerene compounds for longitudinal ultrasound at room temperature.

The latter conclusion is corroborated by a comparison of the wellknown elastic coefficients obtained for different carbon allotropes[3] .This demonstrates that the moduli of pressed fullerenes have to be placed between those of diamond (≈ 1100 GPa) and the modulus of the interplanar bonding in graphite (≈ 40 GPa) as well as the intermolecular

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bonding in single crystalline fullerene ($\approx$ 20 GPa). Since the elasticity range covered by all carbon allotropes refers to chemical bonding from van der Waals to a purely covalent type, the tendency towards covalent bonding especially of pressed C_{60}/C_{70} seems obvious. At present it is essentially unclear where the observed stiffening arises from. One might speculate, however, that this behaviour mainly originates in a mesoscopic superstructure built up by a covalent network, which extends all over the bulk and is probably developed when preparing compact samples by means of external pressure. In particular the occurence of nonhydrostatic conditions during pressing the fullerene powder may resemble a high-temperature regime permitting a degree of structural fluidity. This is corroborated by some experiments, which focused on irreversible changes due to nonhydrostatic compression[4] and to longtime conserving at high pressure[5]. Furthermore, it was shown recently that even for single crystals the formation of an additional polymerized C_{60}-phase can be observed[6] , which seems to be quite stable.

Concerning the temperature dependence of the elastic moduli at ambient temperature a coefficient of about 30 MPa/K is determined for the C_{60}/C_{70}-compound but only of about 5 MPa/K for the pure C_{60} specimen, which is rather low compared to the one of graphite and diamond. Unlike these classical carbon allotropes the elastic behaviour of single crystalline C_{60} is strongly influenced by several phase transitions and ordering effects when cooling down below room temperature. Although the magnitude of the elastic coefficients differs considerably for both pressed compounds, their temperature dependent sound velocities (Fig. 2 and 3) show anomalies just at the temperatures where the critical behaviour is observed in C_{60} single crystals. It is remarkable that the elastic stiffening of the C_{60}/C_{70}-compound reflected by a steeper increase in sound velocity at about 260 K - here observed at several MHz - is comparable with the stiffening obtained for single crystalline C_{60} by means of low frequency vibrating reed techniques corresponding to a structural (fcc-sc) phase transition. On the other hand the temperature dependent sound velocity in the pure C_{60} specimen is only little, though visibly influenced by stiffening effects at the transition temperature.

Anomalies sometimes observed in single crystalline C_{60} between 155 K and 170 K are commonly associated with some type of orientational ordering of the C_{60} molecules in the sc-lattice. Although far from welldefined lattice symmetry these ordering processes seem to be effective in pressed C_{60} as well as C_{60}/C_{70} too. For both a significant change in the elastic behaviour with respect to temperature is detectable by the temperature dependent sound velocity measurements performed. As can be seen in Fig.2 when cooling down below a characteristic temperature ($\approx$ 155 K) a quite strange behaviour is observed especially for the C_{60}/C_{70} - compound. In particular the formerly very smooth temperature dependence of the sound velocity becomes "noisy" when passing T ≈155 K. Furthermore, below this temperature the velocity data are not fully reproducible in this compound, which is a signature of irreversible processes probably triggered by the molecular ordering expected in C_{60} single crystals. Since with further temperature cycling the acoustic quality factor successively decreased, especially when cooling below 155 K, it seems obvious that these irreversibilities are accompanied by some destructive mechanism as e.g. the formation of microcracks in the interior of the bulk. Such crack formation is further supported by the appearance of thermal stress in bulk fullerenes during temperature sweeps. These stresses, however, are easily obtained by non negligible temperature gradients already at low sweeprates arising from the very low temperature conductivity of these materials comparable with the one of insulating glasses. This property in conjunction with the structural stability however is of great importance concerning the technical applicability of these materials.

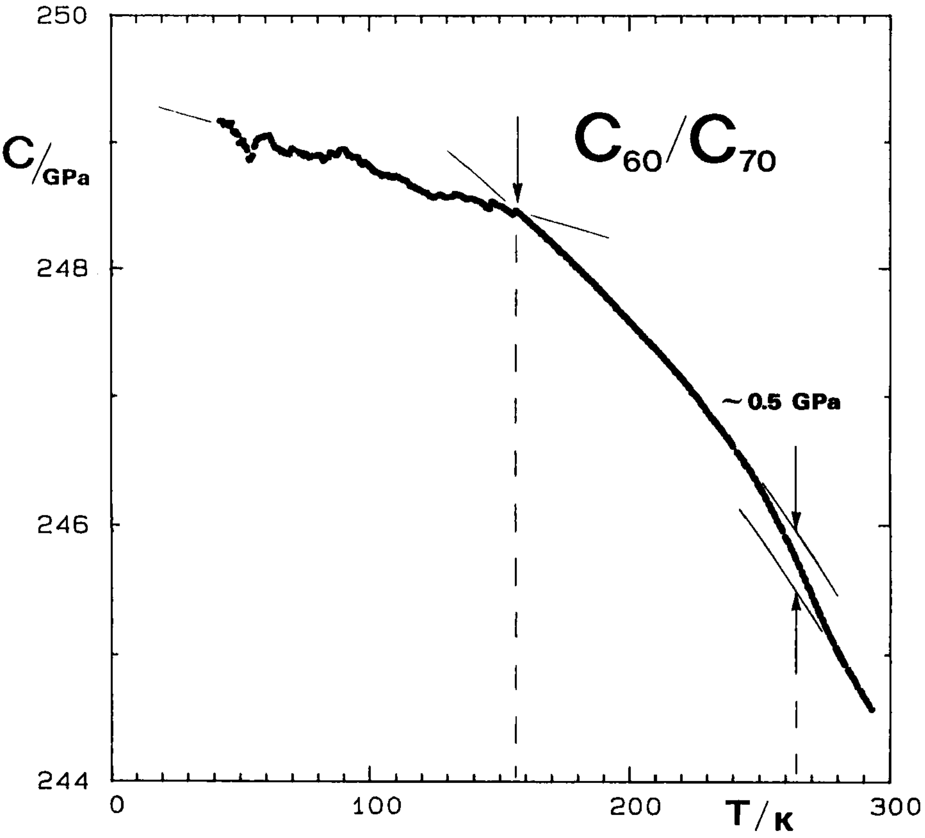

Fig.2 Temperature dependence of the elastic modulus of pressed C_{60}/C_{70} obtained from longitudinal sound velocity data at 18 MHz.

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Surprisingly, aging effects seem to be of minor importance for the sample made of pure C_{60}, although the conditions of sample preparation should not differ very much. As shown in Fig.3, a non monotonous behaviour of the temperature dependent sound velocity could be revealed below about 100 K only, possibly also arising from irreversible processes which however did not affect the acoustic quality factor markedly. The shallow steplike increase below 170 K must be identified with the expected molecular ordering mentioned earlier but it is commonly believed that the elastic response due to time dependent stress relaxation is strongly frequency dependent and therefore also temperature dependent. In contrast to this idea our findings clearly indicate that the characteristic temperature remains nearly unchanged although the excited sound frequency is at least three orders of magnitude higher than in vibrating reed measurements, which is in apparent contradiction to the mechanism suggested[1,7,8].

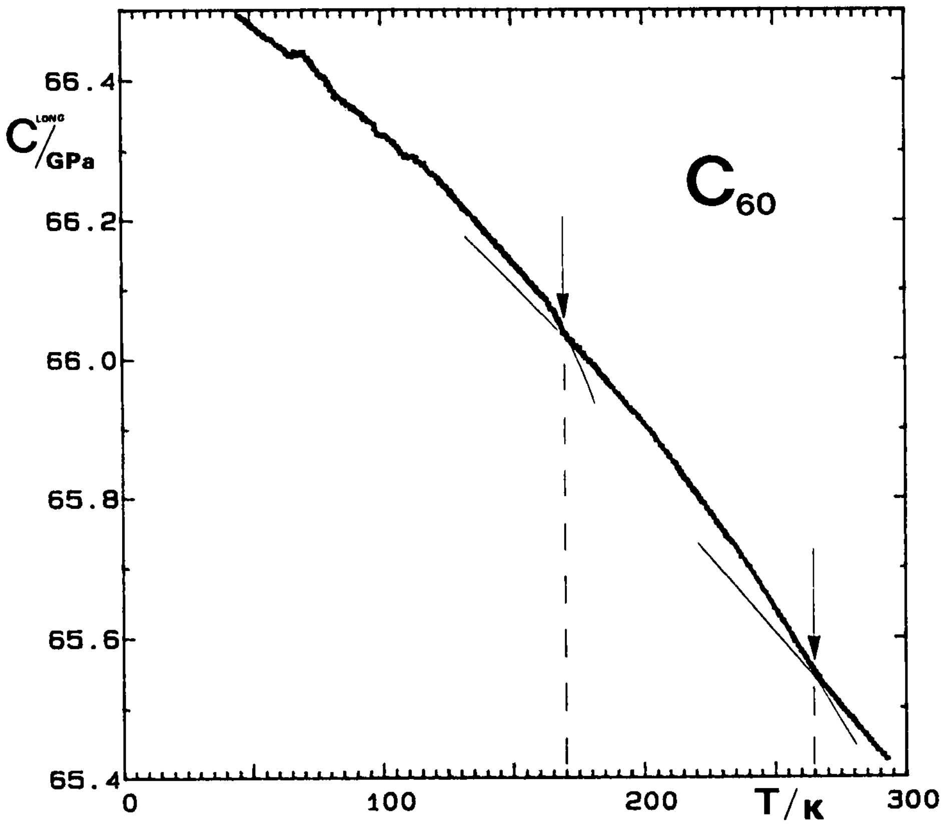

Fig.3 Temperature dependence of the elastic modulus of pressed C_{60} obtained from longitudinal sound velocity data at 18 MHz.

Quite similar difficulties in the interpretation of our results arise, concerning the origin of the relatively sharp transition observed at 260 K in both pressed fullerene compounds. Since it is wellknown that the critical temperature of the fcc-sc transition is very pressure dependent ($\partial T_c/\partial p \approx 110$ K/GPa), it seems rather unlikely that pressing fullerene powder into compact samples should not have any influence on the transition temperature. Such peculiarities, however, might be explained most simply by the assumption that pressed fullerenes are more suitable considered as mixed phases than e.g. as homogeneous glasses. This interpretation seems obvious regarding the elastic coefficients obtained, which on average are fairly large but are only little affected when passing the critical temperature. Though the associated mean bonding strength in the pure C_{60}-sample turns out to be much more van der Waals like compared to C_{60}/C_{70} , nevertheless the elastic stiffness determined is at least three times larger than that of C_{60} single crystals.

The mechanical stability of pressed fullerene compounds investigated here is partly influenced by structural phase transitions and molecular ordering effects also known from single crystals when cooling down to lower temperatures. This gives rise to irreversibilities especially after temperature cycling and limits the application potential of these systems for practical use. On the other hand, since the fatigue resistance of the pressed fullerenes seems to be very dependent on composition, detailed informations about this topic are highly important. Consequently investigations concerning the influence of the fullerene stochiometry on the thermal stability of pressed fullerene compounds are very desirable.

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