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Acoustic phonon dispersion in single-crystal C₆₀

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Abstract. The longitudinal elastic constants of C₆₀ single crystals were measured in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions near $T_c = 260$ K by an ultrasonic CW resonance technique in the MHz region. The comparison with previous low-frequency ($f = 1$ Hz) elastic measurements yields a huge acoustic phonon dispersion near T_c . We show that the dispersion is due to the crossover from isothermal to adiabatic behaviour.

1. Introduction

Since the discovery of a method for producing bulk quantities of C₆₀—the most prominent fullerene—fullerene science has spread out rapidly into solid-state and molecular physics, chemistry, and materials science, etc. In the short period since the discovery of C₆₀, an amazing variety of compounds have been found, which show all sorts of interesting material properties. Examples include the metal–insulator transitions in the alkali-metal fullerenes AC₆₀, the superconductivity of A₃C₆₀, and the magnetic ordering of the organic material TDAE-C₆₀, to name but a few.

Even pure C₆₀ has very interesting properties: it is a model plastic molecular crystal. At room temperature, the molecules are orientationally disordered and perform hindered rotations at their lattice sites, resulting in an $Fm\bar{3}m$ structure. Upon cooling, certain molecular reorientations freeze out, leading via an order–disorder phase transition to a $Pa\bar{3}$ structure at $T_c = 260$ K. Below T_c the molecules perform reorientational jumps between various nearly degenerate sites. This motion dies out on further cooling below the freezing temperature, which depends on the measurement timescale.

Several attempts have been made to measure the elastic properties of C₆₀. There were some measurements of the elastic properties for compacted C₆₀ specimens [1, 2] (all ultrasonic measurements, at $f = 5$ MHz in [1] and $f = 18$ MHz in [2]), and polycrystalline films [3]. There have also been measurements made of Young's modulus on small single crystals, using vibrating-reed techniques [4, 5], performed in the 10 kHz to ~ 80 kHz region. Very recently, Kobelev *et al* [6] succeeded in determining the whole elastic stiffness matrix of C₆₀ single crystals at room temperature by means of sound velocity measurements.

A few years ago, we measured the temperature dependence of the elastic constants of C₆₀ single crystals at very low frequencies ($f = 0.1$ Hz–50 Hz) [7], using a 'Dynamic Mechanical Analyzer' (Perkin–Elmer). We found a rather large negative dip anomaly in the elastic constant of about 30% at $T_c = 260$ K for a measurement frequency of 1 Hz. All of the

above mentioned elastic constant measurements indicate that this large anomaly is drastically reduced at higher measurement frequencies. However, these results are not conclusive, since they were performed either on polycrystalline or on solution-grown samples. To study the acoustic phonon dispersion for the same samples, i.e. to test whether the strong dispersion is present in pure C_{60} , we have performed continuous-wave resonance measurements on sublimation-grown C_{60} single crystals.

2. Experimental details

The C_{60} single crystals were grown by a sublimation–condensation method in a closed evacuated glass tube [8]. High-performance liquid chromatography (sensitivity $\leq 0.2\%$) measurements on crystals prepared in the same way [15] show no signs of impurities. Also Raman and IR spectroscopy measurements did not show any signs of the higher fullerenes.

The temperature dependences of the elastic constants were measured with the continuous-wave (cw) resonance technique [9]. In this technique, standing waves are set up in a composite oscillator consisting of a transducer, a coupling film, and a sample by applying the sinusoidally varying voltage over the transducer. The sound velocity v_s is obtained in terms of sample length l_s , density ρ , and frequency f_n as $v_s = 2l_s(f_{n+1} - f_n)$ where f_n is the n th resonance frequency of the specimen. The elastic stiffness constants can be determined from the sound velocity as $C = \rho v_s^2$.

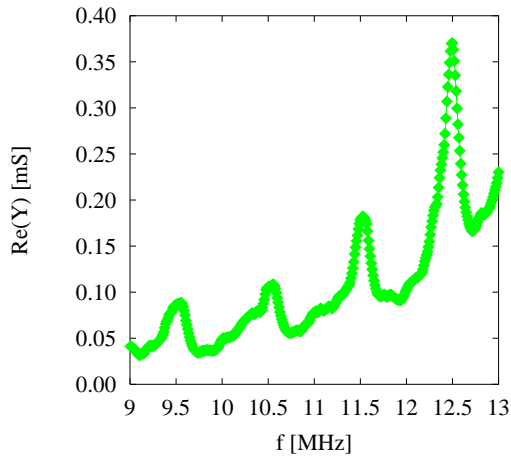


Figure 1. The impedance of the composite oscillator as a function of the frequency.

Since the resonance frequencies of the composite oscillator correspond to the maxima of the impedance, the sound velocity in the probe can be determined by measuring the impedance as a function of the frequency. Figure 1 shows a typical frequency spectrum of the composite oscillator at room temperature using C_{60} as the sample. In our experimental set-up, lithium niobate transducers with resonance frequency of 15 MHz were coupled to C_{60} samples with a thin film of glycerol. The impedance of the composite oscillator was measured with an HP 4192A LF impedance analyser and the temperature was controlled with a He closed-cycle cryostat.

The measurements were performed on two different sets of crystals:

- Measurements in the $\langle 111 \rangle$ direction were made on crystals which have been grown in the form of a plate, with two large (111) faces. These samples were used without any mechanical polishing.

- Since no crystals with two large (100) faces were available, for measurement in the $\langle 100 \rangle$ direction, samples with one dominant (100) face were selected, and a $(\bar{1}00)$ face was created by polishing.

The typical thickness of the samples used for the cw measurements was ≈ 1 mm, with an area of ≈ 10 mm².

3. Experimental results

From the cw measurements on the C_{60} single crystals, we have determined the temperature dependences of the sound velocities and the elastic constants for longitudinal modes in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. The corresponding elastic constants are C_{11} and

$$C^{(111)} = \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})$$

respectively. The measured sound velocities at 262 K were $v_L^{(100)} = 3030$ m s⁻¹ and $v_L^{(111)} = 3615$ m s⁻¹. This agrees quite well with recent ultrasonic measurements on C_{60} single crystals [6].

Figures 2 and 3 show the temperature dependences of the sound velocities and elastic constants for $\langle 100 \rangle$ and $\langle 111 \rangle$ longitudinal modes.

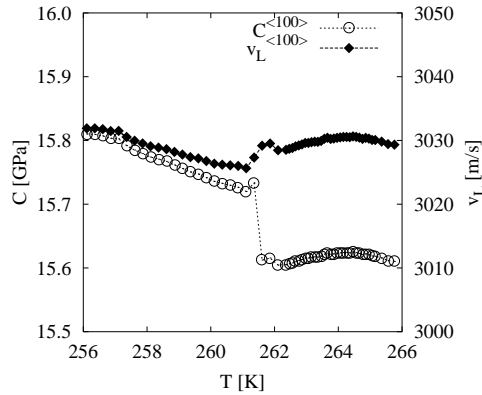


Figure 2. Continuous-wave measurements in the $\langle 100 \rangle$ crystallographic direction.

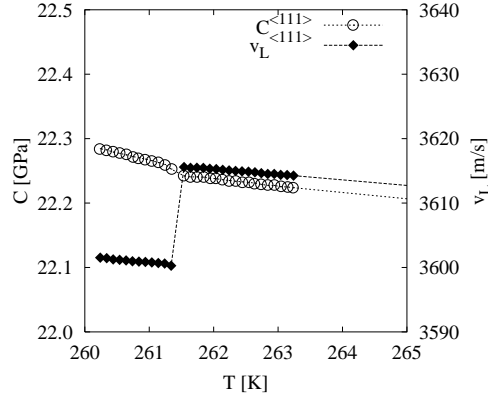


Figure 3. Continuous-wave measurements in the $\langle 111 \rangle$ crystallographic direction.

It should be noticed that the sound velocities and elastic constants show quite different temperature behaviours. The sound velocities exhibit a small negative discontinuity at T_c , whereas the corresponding elastic constants show a positive jump at the phase transition. This unusual behaviour is due to the fact that the discontinuity in the thermal expansion of C_{60} at T_c (see figure 4) prevails over the discontinuity in v_L . Figure 5 shows the low-frequency ($f = 1$ Hz) Young's modulus $Y^{(111)}$ of C_{60} [7] in the vicinity of the phase transition. One clearly observes that the negative-dip anomaly which appears at low frequencies (figure 5) is completely absent at high measurement frequencies (figures 2 and 3). Instead a positive anomaly appears. In the next section we will discuss this behaviour in more detail.

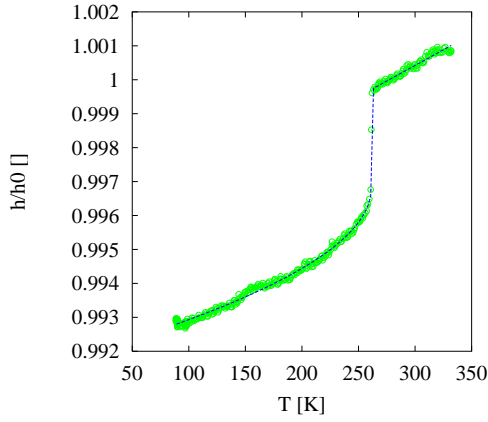


Figure 4. Thermal expansion of C_{60} crystal.

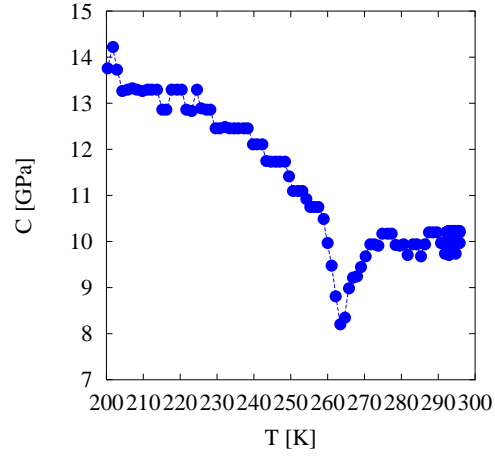


Figure 5. The Young's modulus of C_{60} measured at $f = 1$ Hz in the $\langle 111 \rangle$ direction.

4. Discussion

It is well known that the phase transition from the orientationally disordered phase with space group $Fm\bar{3}m$ to the ordered phase $Pa\bar{3}$ involves a six-component order parameter [10]. The Landau free energy includes a cubic invariant, which implies that the phase transition is of first order. For a qualitative description of our experimental results we use a simplified model, with a one-component order parameter η and a scalar strain variable ϵ . To describe the elastic properties, we have to include the coupling between the order parameter and the strain. The lowest order coupling term in the free-energy expansion is of the type $\eta^2\epsilon$ [11]. At least two different mechanisms could be responsible for the observed acoustic dispersion: one is connected with the crossover from isothermal to adiabatic elastic behaviour (temperature fluctuations) and the other is due to the order parameter relaxation (the Landau–Khalatnikov mechanism). The corresponding theory was already worked out in [12], and we will here only summarize the main results. To include the effects of heat diffusion we use the following free energy:

$$F = \frac{A}{2}(T - T_0)\eta^2 + \frac{B}{3}\eta^3 + \frac{D}{3}\eta^4 + a\eta^2\epsilon + \frac{b}{2}\eta^2\epsilon^2 + \frac{C^0}{2}\epsilon^2 - C^0\alpha^0(T - T_*)\epsilon - S_0T \quad (1)$$

where α^0 and S^0 are the thermal expansivity and the entropy, respectively, above T_c , and C^0 is the background part of the elastic constant.

Dynamic elastic constants close to a phase transition can be derived from the equations of motion for a system of coupled strain ϵ , order parameter η , and temperature T . These are obtained from Lagrange's equations for continuous systems by taking the Landau free energy (1) as the potential energy in the Lagrangian. By solving the linearized equations for $\delta\epsilon$, $\delta\eta$, and δT —which are the fluctuations of the corresponding quantities—in the Fourier-transformed space one obtains the dynamic elastic constant as [12]

$$C(q, \omega) = C^0 - \frac{4a^2\eta_0^2\chi_\eta(T)}{1 - i\omega\tau_\eta} - \frac{(C^0)^2\alpha^2T}{C_V} \frac{i\omega\tau_{th}}{1 - i\omega\tau_{th}} \quad (2)$$

where χ_η is the order parameter susceptibility, C_V the isochoric specific heat, and α the thermal expansivity.

The second term in equation (2) is the well known Landau–Khalatnikov contribution, and is frequency dependent due to the order parameter relaxation. The third term—we call it the thermal diffusion term—describes the crossover between the isothermal and adiabatic limit, when going from $\omega\tau_{th} \ll 1$ to $\omega\tau_{th} \gg 1$. The thermal relaxation time τ_{th} is given by

$$\tau_{th}(T, q) = \frac{C_V(T)}{\kappa(T)q^2} \quad (3)$$

where κ is the thermal conductivity and q is the wave vector of the applied strain field, i.e. $q = 2\pi/\lambda$ ($\lambda \approx 100 \times 10^{-6}$ m) in ultrasonic experiments. In a three-point-bending experiment, $\lambda = 2d$, where d is the thickness of the sample. Using typical values for $C_V/\kappa = 10^3$ s cm⁻² one obtains $\tau_{th} = 2 \times 10^{-3}$ s for ultrasonic waves and $\tau_{th} = 10^{-1}$ s for DMA measurements with samples of about 0.3 mm thickness. Therefore $\omega_{US}\tau_{th}(q) \gg 1$, implying that with ultrasonic measurements the adiabatic elastic constants are probed. In a DMA experiment, one can vary $\tau_{th}(q)$ by varying the sample size, and one can measure the crossover from isothermal to adiabatic behaviour by varying the measurement frequency or the sample size.

The difference between the isothermal (C^T) and the adiabatic (C^S) elastic constants is

$$(C^S - C^T)(T) = \frac{(C^0)^2\alpha^2(T)T}{C_V(T)} \quad (4)$$

which is a well known thermodynamic relation [13].

In fact the temperature dependences of the thermal expansivity [14] and the specific heat have been measured [15] by several authors. Using these values we have calculated the difference between the isothermal and the adiabatic elastic constant at various temperatures near T_c [12]. It turns out that the adiabatic correction displays a divergent behaviour as T_c is approached due to the large transition anomaly of the thermal expansivity. This value is of the order of the negative elastic anomaly measured at low frequencies (1 Hz). This implies that the strong acoustic dispersion observed in C_{60} near T_c is due to the isothermal–adiabatic crossover.

These results show that at transitions which exhibit large anomalies in the thermal expansivity (e.g. near a λ -type phase transition), the elastic anomaly due to the $\eta^2\epsilon$ -coupling can be fully suppressed in the adiabatic limit. The fact that the isothermal elastic constants show pronounced anomalies while the adiabatic ones exhibit no anomalies has an important implication. According to thermodynamics, the ratio of the adiabatic compressibility and the isothermal compressibility is related to the ratio between the specific heat at constant volume C_V and the specific heat at constant pressure C_p . This implies for C_{60} that C_V exhibits almost no anomaly at T_c in contrast to the large λ -anomaly of C_p . This means that if the free thermal expansion of C_{60} single crystals is inhibited, the features of the phase transition are dramatically changed. Thus, the coupling between the order parameter and the strain plays the decisive role in the phase transition of C_{60} .

Moreover, from the present investigation we have learned that, especially in cases for which large thermal expansivity is exhibited near T_c (e.g. near λ -type transitions), high-frequency elastic measurements may not be adequate for studying the nature of the elastic coupling, phase transition mechanisms, critical behaviour, etc.

There are not many cases for which the isothermal–adiabatic crossover has been studied experimentally. One is that of NaNO_2 [16]. It undergoes two order–disorder phase transitions to an antiferroelectric and to a ferroelectric phase. The adiabatic elastic compliances were measured by a composite-oscillator method at about 100 kHz. They showed only small anomalies at the transition points. The isothermal elastic constants were calculated from the adiabatic ones and the data on the specific heat and the thermal expansivity. The authors

have shown that there is a large difference between the adiabatic and the isothermal elastic compliances. In particular, near the antiferroelectric phase transition the isothermal elastic compliances tend to diverge toward T_c , while the adiabatic ones exhibit only small cusps at this temperature.

Another example—KSCN—was recently studied by us. KSCN undergoes an order-disorder phase transition to an antiferrodistortive phase at $T_c = 415$ K [17]. We succeeded in measuring the frequency dependence of the elastic constants over a wide frequency range ($f = 0.1$ Hz–50 Hz using a ‘Dynamic Mechanical Analyzer’ (Perkin–Elmer), and $f = 10$ MHz using ultrasonic techniques) [18]. In this case we found two acoustic phonon dispersions: the low-frequency one (between 0.1 Hz and 50 Hz with characteristic time $\tau \approx 0.1$ s) was due to the crossover from isothermal to adiabatic behaviour, and the second one (between $f = 50$ Hz and $f = 10$ MHz) was due to the order parameter relaxation.

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