

Soft phonons and phase transition in amorphous carbon

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The temperature and pressure dependencies of the elasticity of amorphous carbon (a-C) have been measured using an ultrasonic technique. The microstructure and properties of a-C are found to be very sensitive to pressure and temperature. A striking softening of the long-wavelength acoustic phonons relative to the carbon crystals is observed in a-C. The pressure-volume hysteresis loop indicates that a first-order amorphous-to-amorphous phase transition occurs in a-C under high pressure.

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Amorphous carbon (a-C) is of considerable interest because of its hardness, chemical inertness, infrared transparency, and biocompatibility.¹⁻⁴ Despite the intense investigations over the last 15 years, however, a fundamental understanding of the microstructure and properties as well as their relationship of the simple glass is still lacking. Some of the existing knowledge is strongly debated. Some theoretical models have been proposed about the detailed structure of a-C,^{5,6} but there has been much controversy. Therefore, the study of the microstructure and physical properties of a-C is of both fundamental and technological interest.

Ferraz and March⁷ have suggested the existence of a liquid-liquid phase transition for carbon in 1979. Until 1997 the first experimental, though indirect, evidence for the transition was reported.⁸ It suggested that an amorphous-to-amorphous transition occurs in a-C. However, to our knowledge, no direct experimental evidence about the transition induced by pressure P and/or temperature T has been reported thus far.

Ultrasonic technique provides a powerful tool for studying the elastic properties of solid matter, which are of central importance in understanding the vibrational properties and the shift of the mode energies.⁹ Since the acoustic properties are particularly sensitive to microstructural changes, the ultrasonic method is useful for probing subtle structural changes in a solid as a function of pressure and temperature. In this letter, the acoustic velocities and the volume of a-C were measured *in situ* as functions of T (down to 2 K) and P (up to 4.5 GPa). A super softening of long-wavelength acoustic phonons in a-C relative to its crystalline states is observed. Evidence of amorphous-to-amorphous phase transition under pressure and low temperature in a-C is found.

The sample of a-C with a high-purity mass spectrum was purchased from a commercial company. The a-C consists predominantly of a short-range order of strained graphitelike layers. The glass was cut to a cuboid $14 \times 15 \times 6.158$ mm for ultrasonic measurements. The acoustic velocities and their P dependence were measured at room temperature using a pulse echo overlap method with a frequency of 10 MHz.¹⁰ The travel time of ultrasonic waves propagating through the sample was measured using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. The measuring sensitivity for the acoustic velocities was ± 10 m/s. The ultrasonic velocity and attenuation coefficient on T were measured simultaneously at various frequencies from

2 to 300 K. The measurements were performed several times under cyclic load and unload to examine the reproducibility. The measuring sensitivity for the attenuation was ± 1.5 dB/cm.

The ultrasonic velocities under pressure were determined *in situ* on a piston-cylinder high-pressure apparatus, and electric insulation oil was used for the pressure-transmitting medium.¹⁰ Density ρ was determined by the Archimedean principle, and its accuracy is within 0.1%. The elastic constants (e.g., the bulk modulus K , Young's modulus E , shear modulus G , and Poisson's ratio σ) are derived from the acoustic velocities and density.⁹ The Debye temperature θ_D was calculated using the equation.⁹ $\theta_D = h/k_B(4\pi/9)^{-1/3}\rho^{1/3}(1/v_l^3 + 2/v_t^3)^{-1/3}$, where v_l, v_t , h , and k_B are the longitudinal and transverse velocities, the Planck constant, and the Boltzmann constant, respectively.

The a-C rod was machined down into 4.13 mm in diameter and cut to a length of 7 mm to fit the tungsten carbide pressure cell. The pressure and volume (P - V) relation of a-C was measured by a piston-displacement technique originally developed by Bridgman at room temperature up to 4.5 GPa.¹¹ The volume change of the sample under high pressure was determined by the linear compressibility of the solid, and from this the change of the volume was calculated. The linear change of dimension of the glass sample was measured by a digital displacement meter, and the pressure was monitored by a pressure meter with accuracy better than ± 0.5 μ m. The volume change of the sample as well as the piston and pressure cell, and the pressure measurements were calibrated by the known P - V relation of pure Bi and Fe metals. Corrections were applied to remove the frictional effects and the distortion of the vessel in which the sample was contained according to Refs. 11 and 12. The sample was first precompressed to 1.0 GPa to eliminate the gap between the sample and pressure cell. The precompression has no obvious effect on the volume change of the sample. The P - V measurements were performed on several samples cut from the same a-C plate. For each sample, four pressure load and unload cycles were performed to examine the reproducibility and minimize errors. A diagram of the P - V measuring system and the details of the measurement procedure can be seen in.¹¹ X-ray-diffraction experiments indicate that no crystallization of any kind was observed for the sample after compression.

TABLE I. Various parameters (ρ , B , G , E , σ , and θ_D) for a-C, graphite, and diamond.²¹

Sample	ρ (g/cm ³)	K (GPa)	G (GPa)	E (GPa)	σ	C_{11} (GPa)	C_{12} (GPa)	θ_D (K)
a-C	1.557	11.29	9.02	21.38	0.184	23.4	5.40	337.2
Graphite	2.26	20.1 ^a	4.5 ^a	1060 ^a	0.16 ^a			2500 ^a
		5.5 ^b	440 ^b	36.5 ^b	0.34 ^b			950 ^b
Diamond	3.515	400–550	534.3	1144.6				1860

^aMeasured along close-packed plane.

^bMeasured along c axis.

The v_l , v_s , and ρ of a-C under ambient conditions (measured at 10 MHz) are 3.870 km/s, 2.408 km/s, and 1.5569 g/cm³, respectively. Table I presents the elastic constants and θ_D of a-C. For comparison the elastic constants and θ_D of the graphite and diamond are also given in Table I.¹³ The G , E , and θ_D of a-C are far smaller than those of diamond and graphite. (The elastic constants and θ_D of graphite have two values depending on orientation; its average values are much larger than those of a-C.) This result means there is striking phonon softening in a-C relative to its crystals. The softening is much larger compared to metallic and oxide glasses.¹⁴ In metallic glasses, the softening is in the range of 20–60%.¹⁴ For a-C, the C-C linkage has covalent bonds as well as van der Waals bonds as has the graphite crystal. The dominant covalent-bonded structure gives the glass a significant spread in bond angles. The larger V change (or density difference) between a-C and its crystals contributes to the softening. The large V -change can also sensitively induce the changes of electron configuration, atomic interaction force, and the relative flow between atoms. Therefore, a-C has large modulus changes (phonons softening) relative to its crystals. For metallic glasses, however, the nature of the metallic bond is retained even though atomic long-range order is lacking. After crystallization, there is no large change of the number of nearest-neighbor atoms and the distance between atoms. So the metallic glasses have less acoustic phonon softening.

Figure 1 shows temperature dependence of v_l of a-C at 7, 21, and 35 MHz, and the inset shows the attenuation α_l at 35 MHz. Because of the low acoustic attenuation

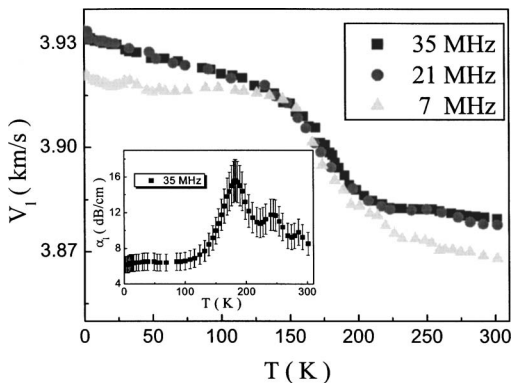


FIG. 1. The temperature dependence of the longitudinal velocity of a-C at 7, 21, and 35 MHz. The inset shows the ultrasonic attenuation (35 MHz) as a function of temperature.

(<4.0 dB/cm at room temperature for a-C) and low measuring sensitivity for the attenuation, we can get reasonable data only at high frequencies. At low frequencies, such as 7, 10, and even 21 MHz, scattering of the data allows hardly any reasonable data. Therefore, we measured the T -dependent attenuation α_l at 35 MHz. Even though the temperature variation of v_l measured at 7 MHz deviates from that at higher frequencies (in fact, the relative deviation <0.3% is either because the acoustic velocities are frequency dependent or because of measurement error), v_l changes rapidly around 135 K, independent of frequency. Correspondingly, a sudden change of the attenuation occurs at 135 K as shown in the inset (α_l shows other maxima near room temperature, which is possibly due to measurement error). The abnormal changes in both v_l and α_l indicate a relaxation process takes place that could be caused by a structural transition onset around 135 K. The changes of v_l and α_l when T is in the range from 135 to 220 K can be explained on the basis of the interaction between the acoustic wave and a broadly distributed two-level system. Anderson *et al.* explained their ultrasonic attenuation data on fused quartz based on such a model.¹⁵ According to the double-well potential model,¹⁵ there should be a certain number of atoms that can sit more or less equally in two equilibrium positions in a-C. The different configuration may be a result of a small variation of bond angle or the physical equivalence of bond lengths. The tunneling of atoms or groups of atoms between two nearly degenerate local energy minima leads to a peak in absorption.¹⁵ The very broad absorption peak indicates the effect of a distribution of the activation energies. The T -dependent attenuation behavior indicates the occurrence of a T -activated structural relaxation in a-C.¹⁵ Based on limited experimental data presented here and limited available similar results in literatures on the attenuation of the glassy carbon, we can draw no definite conclusions on the mechanism of attenuation. The origin of the phenomenon needs to be clarified.

The P dependence of v_l and v_s of a-C are shown in the inset of Fig. 2. The v_l increases roughly linearly with increasing P , whereas v_s decreases. Some silicate glasses with similar covalent network structures have similar profiles,¹⁰ while both v_l and v_s of metallic glasses increase with increasing P .¹⁴ The slopes for v_l and v_s of a-C with respect to pressure are 0.149 and -0.152 km (s GPa)⁻¹, respectively. The negative pressure dependence of v_s is attributed to the bonding structure of the a-C.¹⁰ The relative variations of E , G , K , and σ as a function of P are shown in Fig. 3. Based on the values of K and its P derivative, the equation

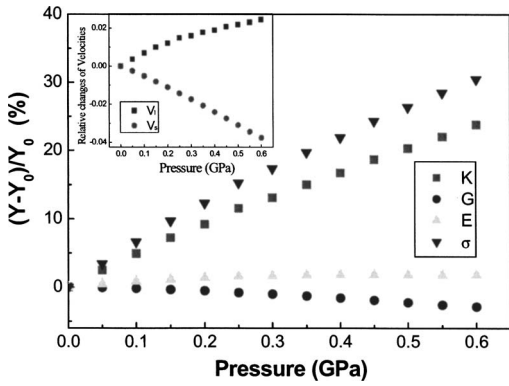


FIG. 2. Variations of elastic constants Y ($Y=E, G, K$, and σ) of a-C as a function of P . Y is normalized using $(Y-Y_0)/Y_0$, where Y_0 is a normal modulus at ambient pressure. The inset is the variation of longitudinal and transverse acoustic velocities v_l and v_s as functions of pressure.

of state (EOS) of a-C is obtained in the Murnaghan form:¹⁶ $P=2.52[(V_0/V(P))^{4.48}-1]$ (GPa), where V_0 is the volume under ambient conditions. The obtained EOS curves of a-C and a typical $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass (vit1) are presented in Fig. 3. The a-C exhibits a much larger volume change than that of metallic glasses.

For a-C, the dE/dP , dK/dP , and $d\sigma/dP$ are 0.62, 4.48, and 0.09, respectively, whereas dG/dP is negative (-0.03)—a situation related to the decrease of v_s with increasing pressure—further confirming the existence of mode softening in a-C. The P dependencies of the second-order elastic constants provide a measure of the vibrational anharmonicity of acoustic modes, which can be expressed by the Grueneisen constant (defined as volume dependence of the mode frequency ω_i): $\gamma_i=-d \ln \omega_i/d \ln V$. For an isotropic solid, such as a-C, γ_i has only two components: γ_l and γ_s , which refer to the longitudinal and shear waves, respectively, and are given as⁹ $\gamma_l=-(K/C_{11})[3-(2C_{12}/K)-3(dK/dP)-4(dG/dP)]$ and $\gamma_s=-(1/6G)[2G-3K(2G/dP)-\frac{3}{2}K+\frac{3}{2}C_{12}]$. From the measurement of elastic constants and their P derivatives, we get $\gamma_l=1.25$ and $\gamma_s=-0.27$. The mean acoustic Grueneisen constant $\bar{\gamma}=(\gamma_l+2\gamma_s)/3=0.24$. The anharmonicity of the acoustic mode in a-C is small but $\gamma_s < 0$,

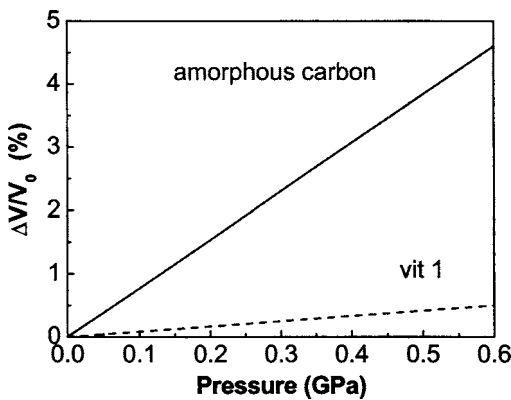


FIG. 3. Volume compression curves of a-C and vit1 up to 0.6 GPa, V_0 is the volume under ambient pressure.

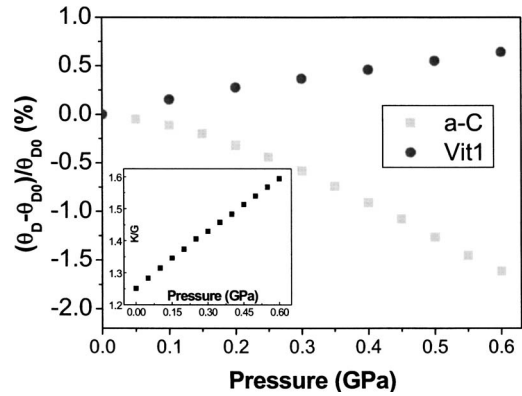


FIG. 4. The relative variations of the Debye temperature of a-C and vit1 with pressure, θ_{D0} is a normal Debye temperature under ambient conditions. The inset is the P -dependent K/G for a-C.

indicating transverse phonon softening under pressure.⁹

The pressure dependence of θ_D is shown in Fig. 4. Note that θ_D decreases monotonously with increasing P . The inset in Fig. 5 shows that the ratio of K/G decreases linearly with pressure, further confirming P -induced mode softening in a-C. For comparison, the P -dependent θ_D for vit1 is also plotted in Fig. 4. For vit1, θ_D increases monotonically with increasing P , implying an increase in rigidity upon pressure. Demarest¹⁷ predicted that that pressure could induce a phase transition in mode softening solids, i.e., when the K/G reduces to a value between 5 and 7, a phase transition would occur. The possible transition pressure for a-C, estimated according to Ref. 17, is $\sim 2.3-2.6$ GPa.

A way to obtain direct evidence for phase transition is to measure the V change of a solid as a function of pressure. The knowledge of the P - V relation is of central importance for the general identification of phase transition in condensed matter.¹⁸ Figure 5 shows *in situ* P - V curves of a-C in load and unload processes up to 4.5 GPa. The P - V curve agrees well with the EOS determined by the acoustic method from 0 to 0.6 GPa. However, with increasing P , an obvious hysteresis effect for the load and unload cycle appears. X-ray-diffraction examinations (not show here) before and after the dilatometric measurement show no crystallization after the

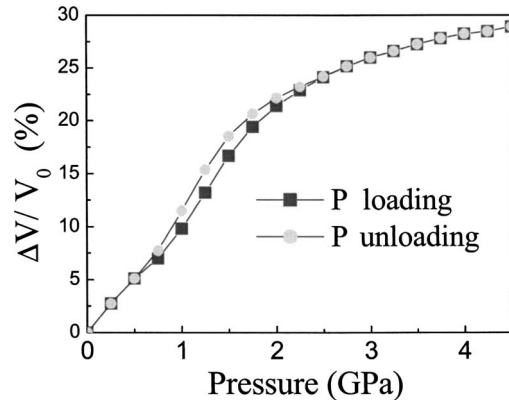


FIG. 5. The relative volume change $\Delta V/V_0$ of a-C during compression and decompression at room temperature. A hysteresis loop can be seen (Ref. 24).

P - V measurements. The result is strongly suggestive of a P -induced phase transition in a-C.¹⁸ The transition occurs over a pressure range of 1.75 GPa (the onset and ending pressures are 0.75 and 2.5 GPa, respectively—lower than predicted), and the relative V change in the transition range is $\sim 5\%$ and much larger than the measurement error ($\sim 0.5\%$) indicating that the observed hysteresis is intrinsic and not due to experimental artifacts. The transition between amorphous phases has been observed in a number of nonmetallic amorphous systems, such as amorphous ice,¹⁹ silica glass,²⁰ and polymer,²¹ where an amorphous solid can exist in two distinct amorphous forms: low- and high-density amorphous phases. This is the first evidence of an apparent transition between amorphous phases in a-C. The first-order phase transition was also found in liquid carbon,⁸ and it was attributed to density changes. A two-phase model, which consists of a mixture of sp^2 -bonded graphitic clusters embedded in a sp^3 -bonded matrix,² has been proposed in a-C. The mixture of C-C bonds in a-C is typical of the bonding seen in graphite and diamond. The bonds in graphite have sp^2 hybridization, which leads to three-fold coordination at each C atom. The bonds in diamond have sp^3 hybridization, which is characterized by four-fold (tetragonal or tetrahedral) bonding coordination. The variation of sp^3 fraction is found to be linear over the whole possible range of densities.²² The pressure effect is a compressive influence on the activation process. From the point of view of energy, pressure in 10–15 GPa can supply additional energy only about 10^{-1} eV per atom according to the stored energy calculation on a-C, due to hydrostatic deformation (the temperature effect is ob-

vious, and 100 K can supply an additional energy of $\sim 10^{-2}$ eV per atom).²³ The additional energy that results from applied pressure is much smaller compared to the activation energy of crystallization of 1–3 eV; therefore, crystallization cannot be induced by such external compression. However, high pressure promotes low-activation energy processes in glasses, such as relaxation and local atomic movement, and it affects the bonding energies of sp^2 and sp^3 sites depending on bond length and angle. Therefore, high pressure may change the microscopic configuration of a-C. Since pressure modifies the short-range order, the P -induced transition from one amorphous form to another in a-C appears to arise from microstructural modifications due to higher density. We note that applied pressure of 1.0 GPa is roughly equivalent to a 100–150 K temperature decrease, with regard to stored energy,²³ and the process of exerting pressure is generally equivalent to decreasing temperature. Thus, the transition observed at 135 K may correspond to the transition observed around 0.75 GPa.

In summary, our results confirm that the microstructure and properties of a-C are very sensitive to pressure and temperature. The a-C can exist in two distinct amorphous phases, i.e., low- and high-density amorphous phases. Our results present an indication of phase transition between these two phases in a-C under high pressure.

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