Anisotropy in the Structure of Pressure-Induced Disordered Solids

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(Received 2 November 1992)

Molecular dynamics calculations revealed that a pressure-induced "amorphized" solid is disordered and anisotropic but not structurally related to an isotropic quenched melt. The results reproduce and explain the anomalous elastic behavior observed via Brillouin scattering on α quartz [L. E. McNeil and M. Grimsditch, Phys. Rev. Lett. **68**, 83 (1991)]. The reversal in frequency shifts for sound propagation in the perpendicular and parallel directions is due to the unequal densification in the a and c directions. The helical chains are found to recover upon depressurizing. Anisotropy of pressure amorphized solids is thus a general property, and pressure-induced amorphization is not related to melting.

PACS numbers: 61.50.Ks, 64.60.Cn, 81.30.Hd

The discovery of a pressure-induced crystalline-to-disordered phase transition under hydrostatic conditions has led to a very active search for this phenomenon in a variety of materials. This method is now described as one of the standard preparative techniques for glasses [1]. A general mechanism was first suggested [2] in the initial work on ice I_h, that the transformation was related to thermodynamic melting and the recovered phase is isotropic analogous to glass prepared from a quenched liquid. This conjecture was further encouraged by results obtained from neutron diffraction which indicated that the high density ice recovered at ambient pressure had a structure apparently resembling that of the liquid at similar density [3]. Recently, there have been several significant experimental and theoretical studies which offered new insights into the transformation mechanism. The first [4] is that a single crystal of α-berlinite ($AlPO_4$) undergoes a pressure-induced transition to a phase which appears to be disordered by x-ray diffraction, that is, there is a loss of translational periodicity, but it reverts back to a single crystal with the same orientation when the pressure is released. This behavior is contrary to that observed in the isostructural α-quartz where the densified phase is found to be disordered and is metastable at ambient conditions [5]. In a related Brillouin scattering study [6], it was shown that α-quartz subjected to sufficient pressure and then recovered at ambient pressure is considerably anisotropic as reflected in the longitudinal acoustic velocities. The most unusual observation is that the acoustic wave velocity of the recovered sample parallel to the original crystalline c axis was found to be remarkably similar to the original value and it is *smaller* than that of the acoustic velocity in the perpendicular direction. In addition, there is a sudden reversal in the decreasing trend of the frequency shift perpendicular to the original c direction when the pressure is reduced below 2.5 GPa. This observation has raised the speculation that the helical structure along the c direction may have recovered. A partial understanding of these experimental reports has been provided by a series of theoretical studies on ice I_h [7], α-quartz [8,9], and $AlPO_4$ [10]. It was shown, through molecular dynamics (MD) [8] and total-energy calculations [9], that pressure amorphization in α-quartz is mechanical in nature and is due to a weakening of a shear modulus as indicated by a violation of one of the Born stability conditions $(C_{11}-C_{12})C_{44}-2C_{14}^2>0$, which leads to a collapse in the crystalline structure bulk modulus as reflected by a dramatic decrease in the quantity $(C_{11}+C_{12})C_{33}-2C_{13}^2>0$. More significantly, MD calculations also reproduced the memory effect observed in $AlPO_4$ [10]. It was shown that the necessary requirement for the memory effect is dependent on the existence of a component in the solid which is relatively undeformable and therefore retains its identity and coordination geometry well past the order-disorder transition pressure. An important outstanding problem is, therefore, to resolve the dichotomy [6] that there is a large anisotropy in the acoustic wave velocities in the recovered compressed phase of α-quartz parallel and perpendicular to the c direction as observed in the Brillouin scattering experiment and also a reversal in the sign of the elastic anisotropy compared with the original crystalline phase. The close resemblance of the acoustic wave velocities in the recovered phase and the crystalline phase along the c axis does not necessarily yield unambiguous information on the possible structure of the recovered sample since it is clearly much denser than the original material. In this Letter, new theoretical results on the structural and elastic properties of α-quartz with the application of pressure through the order-disorder transformation and as the pressure is released will be presented. The underlying reasons for the apparent anomalous elastic behavior are discussed.

The constant stress and constant enthalpy (S,H,N) MD method [11] using a semiempirical potential for SiO_2 developed by van Beest, Kramer, and van Santen [12] was employed in this study. The calculations were performed on 192 SiO_2 molecules held at 300 K. The size and shape of the simulation cell are allowed to change subject to an external stress. The details of the computational procedure have been reported previously [8,13]. The elastic moduli are calculated from the strain fluctuations [14]. In the crystalline phase, the elastic moduli can be converted into acoustic wave velocities or frequency shifts [15], which are the observables in the Brillouin scattering experiments using the calculated densities and refractive indices computed from the Lorentz equation [16]. In the transformed disordered phase, there is no simple relationship between elastic moduli and acoustic velocities [15]. Exceedingly long calculations with 10^5 time steps of 0.5 fs are usually required to achieve a convergence in the elastic moduli of several percent [14]. The rate of convergence was found to improve with increasing pressure. According to previous experience [13], the calculated elastic moduli are expected to be accurate to within 10%–20% of the actual values. The calculated parallel and perpendicular components of the frequency shifts for crystalline quartz as a function of pressure are shown in Fig. 1. The agreement is reasonable up to the phase transition at 23 GPa except that the last calculated parallel component at 22.5 GPa is considerably higher than the observed value. This discrepancy may be due to the uncertainties in the experimental measurement as the scattering peaks become indistinct above 15 GPa [6]. After pressurizing the sample beyond the phase transformation, the magnitude of the three principal components C_{11}, C_{22}, and C_{33} of the elastic tensor are equivalent within 10% but the other elements are still fairly large. This indicates that the sample is not isotropic, even at high pressures.

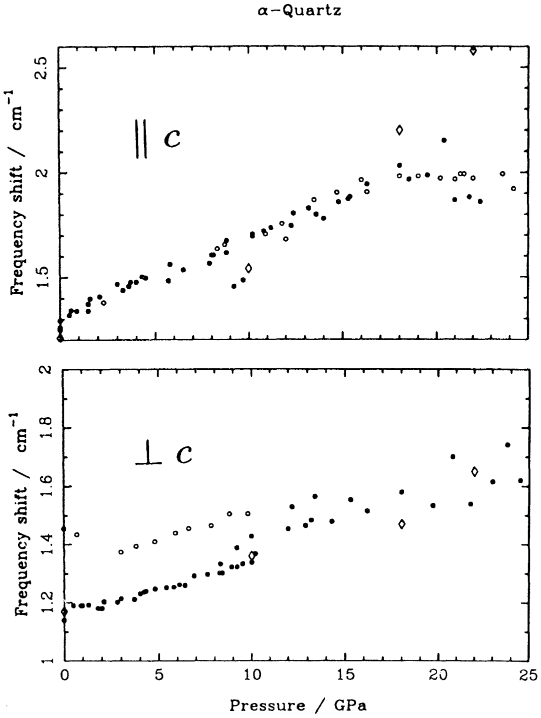

FIG. 1. The experimental (solid circles for compression and open circles for decompression) and calculated (diamonds) frequency shifts upon increasing pressure for α-quartz. The upper frame is for longitudinal sound waves parallel to the crystalline axis and the lower frame is for sound waves perpendicular to the crystalline *c* axis.

The pressure was removed in steps of 5 GPa with annealing at each step at least for 50 ps. The material recovered at ambient pressure lacks long-range order as indicated by the calculated radial distribution functions. The calculated density of 3.07 g/cm^3 is 21% greater than that of the starting crystalline phase [13]. An experimental value for this important quantity is not yet available. A comparison with the closely related densification of amorphous SiO_2 [17] where the calculated increase in density of 20% agrees well with the 18%–20% observed experimentally indicates that the present value for the recovered α-quartz should also be reliable. Two important features were exhibited in the decompression of the material (Fig. 2). As the pressure is lowered, the sample density decreased steadily from 4.20 to 3.56 g cm^{-3} from 25 to 2.5 GPa. An abrupt increase in the volume of 16% occurs between 2.5 to 0 GPa leading to a sudden change in density from 3.56 to 3.07 g cm^{-3}. This structural relaxation is accompanied by a change in the coordination number of nearest oxygen neighbors located within 2.2 Å of a Si atom which encompasses the first coordination shell for all the pressures studied here. The coordination number is about 5.3 immediately above the transition and it decreases gradually to 4.7 at 2.5 GPa. Then, the coordination number decreases rapidly to 4.3 at ambient pressure. As explained previously, the high density disordered phase is stabilized by increased coordination [8,9]. The fivefold coordination helps to crosslink the adjacent helical chains. At 25 GPa the structure is dominated by

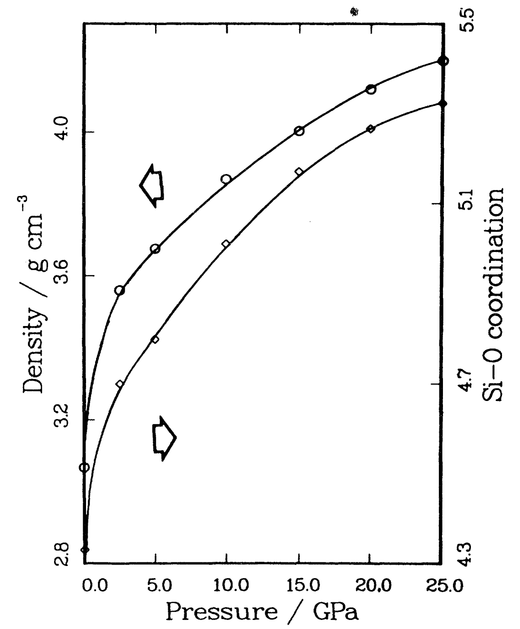

FIG. 2. The calculated density and Si-O coordination number vs pressure upon lowering the pressure on the disordered material made from α-quartz at 25 GPa.

fivefold coordinated silicon atoms with a significant population of sixfold coordination. Upon the release of pressure to 2.5 GPa, the coordination changes from 5.3 to 4.7 indicating that there is still a substantial fraction of fivefold coordinated silicon atoms present. At ambient pressure the coordination number decreased to 4.3 which is clearly higher than the ideal coordination of 4. The remnants of 5 coordinations maintain the disordered structure. The recovered phase is kinetically stable even after annealing at 1000 K for 5 ps. Upon inspection of the dimensions of the simulation box, it was found that the length dimension of the *c* axis recovered to within 1% of its original value whereas the *a* and *b* dimensions remain smaller by about 9% and 12%, respectively. This observation indicates that in the recovered solid the packing in the original *a*-*b* planes is denser than along the *c* direction. Selected helical chains parallel to the *c* axis are shown in Fig. 3. Apart from occasional crosslinkage through fivefold coordinations, the helical network is largely preserved in the recovered material. The calculated structural changes parallel the behavior of the frequency shifts observed in the acoustic wave measurements [6]. In the experiment, upon decompression the frequency shifts of the acoustic waves propagating parallel to the original crystalline *c* axis decrease and closely retrace the path for compression. In contrast, the frequency shifts in the perpendicular direction initially decrease with pressure and the magnitudes are slightly higher than for the compression. Below 2.5 GPa, the frequency shift increases suddenly and at ambient pressure the relative magnitude of the parallel and perpendicular components of the frequency shifts have reversed.

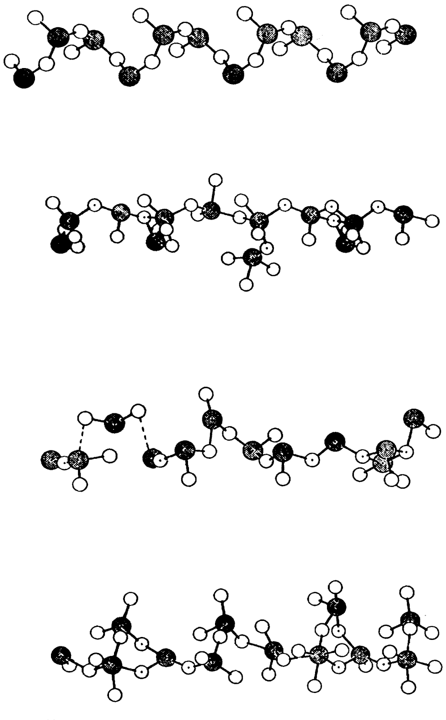

FIG. 3. Helices taken from different regions of the MD sample after recovery at ambient pressure as compared with a helix (left-hand side of figure) from crystalline α-quartz. The open and shaded circles represent oxygen and silicon atoms, respectively.

This curious behavior can now be interpreted. Even in a disordered phase, the velocity of acoustic waves propagating parallel to a principle axis is expected to be proportional to the square root of the ratio of principal components of the elastic moduli and the density [15]. The reason for the apparent similarity in the frequency shift of the acoustic waves parallel to the original *c* direction is because of a cancellation effect. In comparison to the crystalline phase at the same pressure, both the density and elastic moduli of the transformed sample are higher and the ratio of these quantities remains similar. Knowing the fact that the relationship is not exact in the disordered phase, nevertheless at 10 GPa the calculated square root of the ratio of the relevant elastic moduli (C_{11}) and the densities (d) for both the crystalline ($C_{11}=1.3$ Mbar, $d=3.0\ \mathrm{g\,cm^{-3}}$) and disordered ($C_{11}=1.89$ Mbar, $d=3.9\ \mathrm{g\,cm^{-3}}$) phase are approximately 2. Moreover, this ratio is not affected by the sudden decrease in density at 2.5 GPa since the MD cell dimension along the *c* direction has also recovered to within 1% of the original value (*vide infra*). A somewhat different situation is observed in the perpendicular directions. As noted above, the crystal packing in the recovered sample is *anisotropic* and is denser in these directions indicating that the lattice effectively becomes more rigid and the moduli relevant to the propagation of acoustic waves in this direction should also be larger. Therefore the frequency shift of the acoustic waves in the perpendicular direction is higher than that in the crystalline phase. As the pressure is decreased from 2.5 GPa to ambient pressure the Si-O nearest-neighbor coordination number decreases by about 8% (Fig. 2) compared with a density reduction of 16% over this pressure range. However, the higher coordination and therefore the rigidity of the lattice and the high elastic moduli in the original *a*-*b* planes is basically maintained. Therefore the sudden decrease in the density is the primary cause for the increase in the sound velocity or frequency shift due to the acoustic waves. The conclusion reached here is consistent with the remark that it is highly unlikely that the changes in refractive index alone cause the observed anomalous behavior [6]. In addition, the calculations provide a detailed atomic description of the structural changes which confirms the speculation that a closer packing of helical chains perpendicular to the *c* axis leads to an increase in acoustic velocities along this direction. The close agreement between experiment and theory shows that the recovered material is disordered and anisotropic and is not related to a glass.

Brillouin scattering data on pressured-induced order-disorder transformations are presently only available for α-quartz. However, a theoretical study [7] of ice I_h when it is compressed shows that a similar mechanism is also responsible for the transformation. More importantly, compressed ice retains the basic structural features of the starting material [7]. This strongly suggests that pressurized ice would also be disordered and anisotropic with respect to its elastic properties. Although pressure-induced disorder has now been observed in a wide variety of materials, the properties of the recovered phases remain largely unexplored. Structure factors obtained in diffraction experiments only indicate the loss of long-range order but not necessarily the existence of an isotropic random network.

We wish to thank Professor H. Kiefte for a critical reading of the manuscript.

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