

Observation and explanation of the reversible pressure-induced amorphization of $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$

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(Received 18 November 1991)

X-ray and Raman measurements show that crystalline $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ becomes amorphous above a pressure of 9.4 GPa. Upon release of the pressure, the crystalline state returns. We report *reversible* pressure-induced amorphization for a substance that can be prepared as a melt-quenched glass at ambient pressure. We suggest a mechanism for the amorphization based on the formation of a noncrystallographic packing of polytetrahedral units. A consideration of several pressure-induced amorphizations indicates that polytetrahedral amorphization mechanisms are appropriate for nondirectionally bonded materials, but are not appropriate for solids where covalent and hydrogen bonding predominates. Polytetrahedral ordering provides a link between amorphous states formed by compression and those formed by more conventional methods at ambient pressure (e.g., melt quenching).

I. INTRODUCTION

The phenomenon of *reversible* pressure-induced amorphization has been observed for several substances: SnI_4 , AlPO_4 , LiKSO_4 , $\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4$, and $\text{Ca}(\text{OH})_2$.¹⁻⁷ We report in this paper x-ray and Raman measurements which show that crystalline $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ becomes amorphous when compressed above 9.4 GPa. Unlike the previously observed *reversible* amorphizations, this material can be prepared, at ambient pressure, as both a glass and a crystalline solid. The reversibility of the transformations indicates that the pressure-induced amorphization is caused by a small perturbation of the atoms from their positions in the crystalline state; this suggests a close relationship between the ordering in crystalline and amorphous solids. The reported observations motivated us to investigate why certain solids, when pressurized, amorphize reversibly, while others either transform irreversibly or remain crystalline.

A crystalline solid is distinguished from other states of matter by having periodic translational order, i.e., the solid can be obtained by the repetition of a single motif consisting of an atom or an atomic cluster. As Gaskell has pointed out, a noncrystalline solid is characterized by what it is not: it is *disordered* or *amorphous* or *a*periodic.⁸ The emerging viewpoint is that noncrystalline materials are not simply a random arrangement of atoms, but that they have a defective order.^{9,10} The discovery of quasicrystalline metal alloys, for example, has highlighted this fact and caused a minor revolution in crystallography and the solid-state sciences.¹¹ Also, extended domains of order were recently found in glassy CaSiO_3 .¹² A powerful unifying concept in the study of quasicrystals and amorphous solids is the idea of polytetrahedral order (*vide infra*).^{13,14} We propose that polytetrahedrality is equally important in describing the phenomenon of pressure-induced amorphization for certain types of materials. The viewpoint advocated teaches us to visualize nondirectionally bonded amorphous solids as packings of certain structures or atoms rather than as discrete local units exhibiting only short-range order.

We propose, in this paper, a structural model for the pressure-induced amorphization of $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ involving the formation of a noncrystallographic packing of polytetrahedral units. We then examine whether or not the model applies to other pressure-induced amorphizations. We conclude that polytetrahedral ordering plays a role in understanding the amorphization of solids which have only nondirectional bonding among their basic structural units. It is not immediately evident how to extend the ideas to compounds with directional bonding, e.g., covalent and hydrogen bonding.

II. EXPERIMENTAL METHODS

The crystalline $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ sample was prepared as follows: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Aldrich) was heated at 200 °C for 2 h to remove the water; equal molar amounts of $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 (Baker) were then placed in a platinum crucible in a dry box and melted by heating at 450 °C for 20 min. The crystalline sample was prepared by quenching from the melt. Differential thermal analysis (DTA) experiments and density measurements (2.03 g/ml, less than either of the pure components) indicate that the sample is not a simple physical mixture of sodium and calcium nitrates. The density was measured by Quantachrome Corporation with a pycnometer. The DTA and density measurements suggest that a nonequilibrium solid solution has been formed.¹⁵

The experimental techniques used to measure Raman spectra at high pressures have been discussed in detail elsewhere.¹⁶ We discuss them briefly here. A modified Merrill-Bassett style diamond anvil cell was used to generate high pressures.¹⁷ Inconel gaskets, with a 0.3-mm hole, were used to contain the samples (used as powders < 100 mesh); 4:1 methanol:ethanol was used to transmit the pressure. The same results were obtained when the experiments were performed with no pressure transmitting medium. The 514.5-nm line of a Spectra-Physics model 2020-5W argon laser was used for the excitation of Raman effects; the scattered light is gathered at 160° to the incident exciting beam by a Spex 1403 double

monochromator. Approximately 500 mW of power was incident on the sample for all experiments. All high-pressure Raman measurements reported in this paper were reproducible. The National Bureau of Standards ruby calibration method was used to monitor the pressure in the diamond cell.¹⁸

The x-ray diffraction patterns were measured by EDXD (energy-dispersive x-ray diffraction) at CHESS (the Cornell High Energy Synchrotron Source) using a Ge solid-state detector.¹⁹ *Ed* for all measurements was determined, with a piece of gold foil, to be 89.34 keV Å. The same high-pressure cells and experimental protocol were used as for the Raman measurements, except that no pressure transmitting fluid was used. The pressure was monitored by mixing 10% by volume gold powder (Alpha, 99.95%, grain size 1–3 μm) with the sample. The change in the (111) diffraction line of gold was monitored; the pressure was then calculated using an equation of state.²⁰ We mixed the gold homogeneously throughout the sample. The gold also served to indicate that we had truly lost the diffraction patterns of the samples and had not erred in aligning the cell with the synchrotron beam.

III. EXPERIMENTAL RESULTS

We measured the effect of compression on the Raman spectra and the x-ray-diffraction pattern of a crystalline $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ sample. The major result is that the calcium-sodium sample becomes amorphous when compressed above 9.4 GPa and that the crystallinity of the sample returns upon release of the pressure.

The ambient pressure Raman spectrum of the calcium-sodium sample is a superposition of the spectra of $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 . (See Fig. 1.) Specifically, there are two vibrational modes of the NO_3 ion, which are monitored: a symmetric stretch ($1050\text{--}1070\text{ cm}^{-1}$) and an out-of-plane bending mode ($700\text{--}750\text{ cm}^{-1}$).^{21,22} The nitrate symmetric stretch for calcium and sodium nitrate appears at the same energy, hence there is a single peak at $\sim 1067\text{ cm}^{-1}$; the lowest-energy feature is associated with sodium, the higher with calcium. As the sample is compressed, the Raman features broaden and shift to higher energy, the symmetric stretches split apart and then recombine, and the signal weakens and begins to decay until the spectral features resemble those of the melt-quenched glass formed at ambient pressure.²² Upon release of the pressure the Raman signal characteristic of the crystalline state returns with some decline in the Raman intensity from the prepressurization spectrum. (Typically the pressure is released from the sample over the course of 4 h. At the end of this period the crystalline Raman spectrum returned. We did not monitor the spectrum during the decompression.) The precipitous decline in the vibrational intensity and the broadening of spectral features is a hallmark of the noncrystalline state because of the loss of translational periodicity;²³ this behavior has been observed for other materials that amorphize with pressure.^{5,6} Raman measurements alone, though, cannot determine conclusively that complete amorphization has occurred.

We measured the powder x-ray-diffraction patterns of

the sample under compression to determine whether complete amorphization occurred. The intensity of the diffraction pattern of the $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ sample (Fig. 2) declines continuously with pressure until all the diffraction peaks vanish at a pressure of 9.4 GPa; upon release of the pressure, the major crystalline diffraction peaks return but with a loss of intensity.

Shear and fracture of the sample could produce the phenomena observed in the Raman and x-ray-diffraction patterns. We consider this unlikely since (i) the pressure indicators used in the Raman and x-ray measurements show a uniform pressure environment where the transitions take place, (ii) the transformation is reversible, (iii) the changes in the Raman spectrum are the same with and without pressurizing fluid, and (iv) it is observed by both Raman and x-ray measurements, which probe different length scales ($\sim 10\text{ Å}$ and $\sim 1000\text{ Å}$, respectively).

IV. DISCUSSION

We outline below the concepts of polytetrahedral ordering and propose a mechanism for the amorphization of crystalline $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$. We then examine the

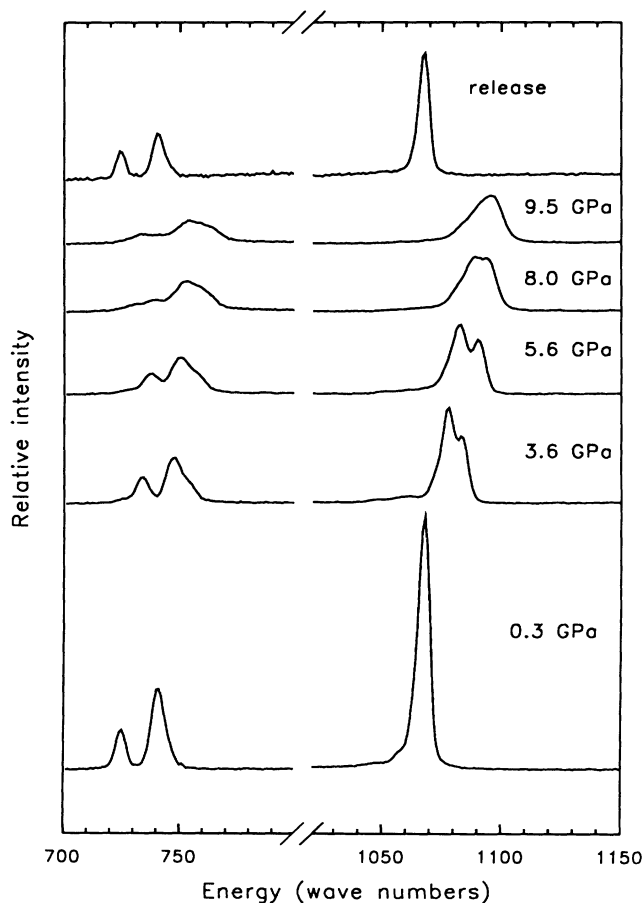


FIG. 1. Raman spectra of the crystalline $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ sample at pressures of 0.3, 3.6, 5.6, 8.0, and 9.5 GPa, and after releasing the pressure.

application of the ideas to other pressure-induced amorphizations.

A. Polytetrahedral ordering

The key concept in polytetrahedral ordering, as discussed in great detail by Nelson and Spaepen, is as follows.¹⁴ The lowest-energy configuration of four atoms interacting by a pairwise central potential is a tetrahedron. Tetrahedra, though, cannot be packed together to form a crystalline solid; i.e., tetrahedra are not space-filling objects. In order to overcome this so-called topological frustration, nature produces crystals containing very distorted tetrahedra as the basic building blocks, or mixtures of tetrahedra and octahedra. Due to the inability of tetrahedra to fill space, structural units built from

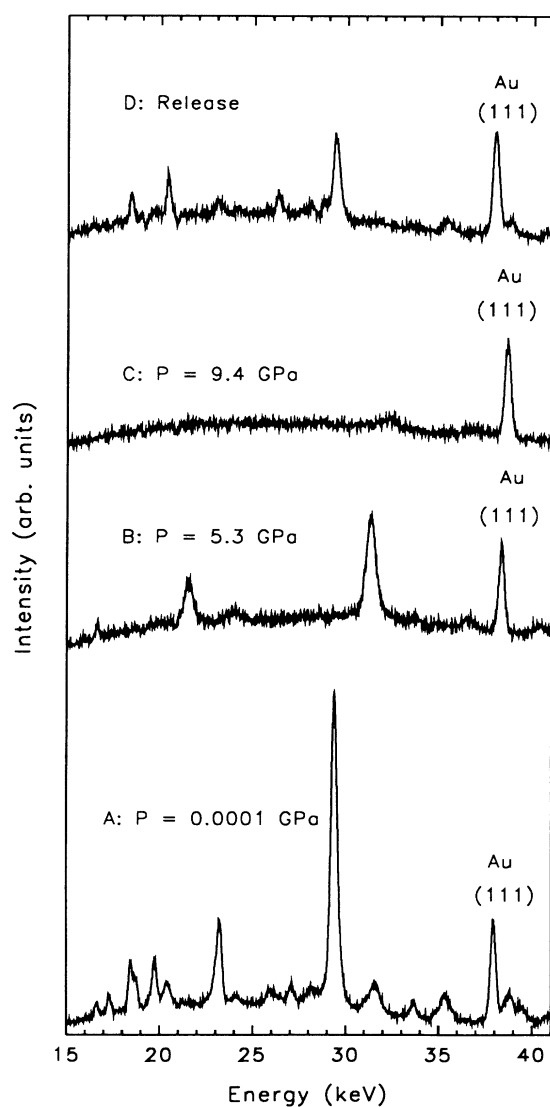


FIG. 2. Energy-dispersive x-ray-diffraction patterns of the crystalline $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ sample at pressures of 0.0001 (A), 5.3 (B), 9.4 GPa (C), and after releasing the pressure (D). The spectra have been normalized to the intensity of the Au (111) peak.

tetrahedra have been used to describe clusters of atoms, glasses, certain metal alloys, and quasicrystals.^{24–26} Using a central potential Hoare and Pal have shown that polytetrahedral arrangements of atoms are more stable than corresponding face-centered-cubic (fcc) clusters; McAdon and Goddard have extended these ideas beyond pair potentials by using a valence bond method to demonstrate that the most stable neutral seven-atom cluster of lithium atoms is a polytetrahedral unit.^{27,28} This led Hoare to suggest that one can think of an amorphous material as composed of polytetrahedral groupings of atoms.²⁹ This general viewpoint is adopted below. Although tetrahedra can combine to produce many types of building blocks, prominent in this discussion is the icosahedron, which is formed by packing together 20 slightly distorted tetrahedra.

Any mechanism for pressure-induced amorphization must be consistent with a decreased intensity in the Raman and x-ray data when compared before and after pressurization, an increase in sample density, and the reversibility of the transformations—specifically, the crystallinity of the sample must be lost, but with coordination numbers intact and atomic distances perturbed only modestly. These criteria imply that the topology of the crystalline state remains largely intact throughout the pressurization. Polytetrahedral packings are consistent with these criteria (*vide infra*). This leads us to look for polytetrahedral packings that are topologically accessible from the crystalline state.

B. A mechanism for the amorphization of $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$

Consider the environment of the cations in the calcium-sodium sample. The solid contains calcium and sodium coordination polyhedra: calcium in $\text{Ca}(\text{NO}_3)_2$ is surrounded by a slightly distorted cuboctahedron of oxygen atoms (see Fig. 3); sodium in NaNO_3 is coordinated by six oxygens in the shape of an octahedron.³⁰ A simple way for crystalline calcium-sodium nitrate to become amorphous would be *via* a transformation of the cuboctahedron to an icosahedron. Mackay has pointed out that a cuboctahedron can be transformed into an icosahedron by a twist of its triangular faces or by a uniform contraction of the 12 vertices (see Fig. 3).³¹ This transformation results in a noncrystallographic mixture of octahedra and icosahedra with a density higher than the crystalline packing.

Contrast the behavior of the calcium-sodium nitrate sample with that of pure sodium and cesium nitrates. X-ray studies indicate that these samples remain crystalline to the highest pressures attained: 10.0–13.0 GPa.³² The crystalline structure of these materials is based on a packing of tetrahedra and octahedra, which cannot be transformed by a displacive mechanism into polytetrahedral units. The tetrahedra in these crystals are “virtual”; they are formed from the interstitial sites of the octahedrally coordinated cesium and sodium ions. It is difficult to divide the crystals into somewhat distorted polytetrahedral units without large changes in the coordination shells of the octahedrally coordinated atoms.

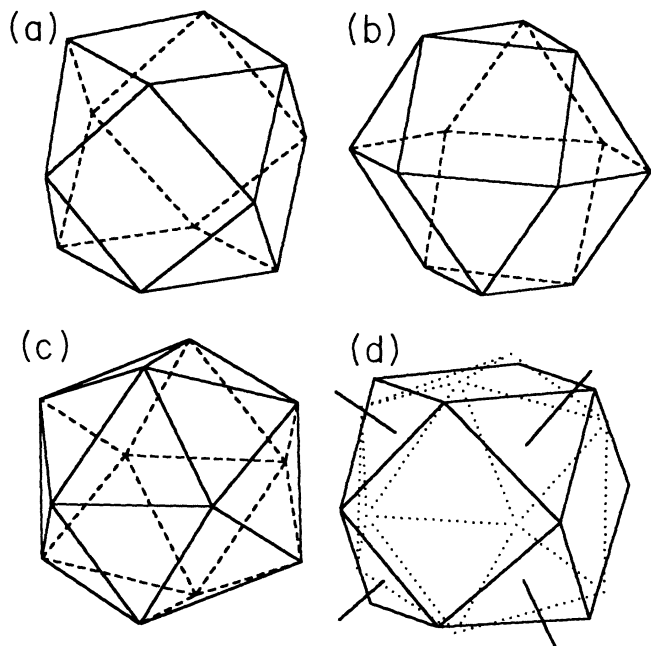


FIG. 3. The oxygen atoms in $\text{Ca}(\text{NO}_3)_2$ are arranged around calcium in the shape of (a) a cuboctahedron; the iodine atoms in SnI_4 are arranged in a cuboctahedron and also in the shape of (b) a twinned cuboctahedron. These polyhedra can be transformed into (c) an icosahedron by a rotation of the triangular faces or a uniform contraction of the center-vertex distances; (d) shows the transformation of a cuboctahedron via the rotation of its faces around the axes shown. (Adapted from Ref. 31.)

C. Application of polytetrahedral ordering to other pressure-induced amorphizations

Consider another solid, which has been observed to amorphize reversibly under pressure: SnI_4 .² Tin tetraiodide is a molecular solid: tin is surrounded by a tetrahedron of iodine atoms; these units are held together by van der Waals forces.³³ The tetrahedral units are rigid, yet mobile; since the SnI_4 tetrahedra are held together by weak nondirectional forces, the units can rearrange into noncrystallographic packings based on the tetrahedron. We propose that this repacking occurs by a largely displacive rather than a thermally activated mechanism; this displacive mechanism leaves the topology of the crystal substantially intact (*vide infra*).

A polytetrahedral mechanism for the transformation of SnI_4 is as follows. Mackay has shown that a packing of spheres in the shape of a cuboctahedron can be surrounded by a large number of shells of spheres also arranged in the form of a cuboctahedron. The n th shell will contain $10n^2 + 2$ spheres. This arrangement of atoms is that of cubic close packing (ccp); note, though, a crucial point: SnI_4 is *not* close-packed, the "spheres" can be compressed closer together. This cuboctahedral grouping of atoms can be transformed into a noncrystallographic icosahedral sphere packing (isp) by the same rotation or compression mechanism that transforms the cuboctahedron into a icosahedron. This mechanism can also turn

the twinned cuboctahedron (TCO) coordination shell found in a hexagonal close packing (hcp) into an icosahedron (see Fig. 3). The central unit of the icosahedral sphere packing is a tetrahedron; also, each atom in an isp is surrounded by 12 other atoms. Iodine atoms in SnI_4 are packed in the shape of slightly distorted cuboctahedra or twinned cuboctahedra; there are three cuboctahedra for every TCO.²⁷ (All coordination numbers reported in this paper are calculated using a Voronoi construction.³⁴) This suggests that large clusters of icosahedral symmetry could be formed by the rotation and compression of the tetrahedral building blocks found in SnI_4 . The result of this transformation would be an amorphous solid. This transformation fulfills the criteria outlined above: it (1) is displacive, (2) is consistent with the Raman and x-ray data in that the crystallinity of the sample is lost, (3) results in an increased density, (4) is reversible, and (5) preserves the local tetrahedral arrangement of atoms. This last point is consistent with x-ray and Mössbauer measurements, which show that the tetrahedral symmetry of the SnI_4 molecules is well preserved at high pressures.^{2,35} The mechanism provides an explanation for the small degree of irreversibility evident in the Raman and x-ray results since noncrystallographic packings cannot be continued indefinitely without a large degree of bond strain.^{14,25-27} Sadoc and Mosseri show that polytetrahedral packings are perfect in a three-dimensional curved space, but that "defects" must occur when the structure is projected onto Euclidean three-dimensional space.²⁵ These defects are regions where the connectivity is altered or a "disclination line" is formed—i.e., a wedge of material inserted or removed from the structure. Our view, then, of pressure-induced amorphizations is that a polytetrahedral packing is formed through a topologically invariant transformation, with some reconstructive formation of defects occurring at the edges of the packing to accommodate bond strain. It is this reconstruction that gives rise to the small extent of irreversibility observed experimentally.

Polytetrahedral ordering explains why elemental metals do not become amorphous when compressed.³⁶ Based on our model one would expect, at first glance, that metals would become amorphous since their bonding is nondirectional and cuboctahedral atomic arrangements exist in these materials (i.e., fcc and hcp lattices). It is their close packing that prevents a pressure-induced amorphization. To rearrange a close-packed structure into a noncrystallographic packing requires a completely reconstructive transformation—a close-packed structure cannot be turned into a noncrystallographic packing through an increase in density.³⁷ Thus, with compression one would not expect an isp to form.

Consider now the application of the polytetrahedral packing mechanism to other solids that undergo pressure-induced amorphization. As noted above, polytetrahedral packings are the lowest-energy packing only for nondirectional potentials; when directional bonding becomes important, then the stable structure, unlike ionic solids, is determined by more than just the packing of atoms—the discreteness and spatial direction of the covalent bond, for example, must be taken into ac-

count. Contrast the compounds $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$: the former amorphizes reversibly when compressed, the latter does not amorphize.^{6,7} Since the substances are isostructural a model based purely on packing considerations is not reasonable. The different behaviors when compressed may lie in the directional bonding in the materials: the high-pressure vibrational data of Kruger, Williams, and Jeanloz indicate clearly that hydrogen bonding is significant and also different for $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$.⁶ Also, the single-crystal diffraction studies of α -quartz at high pressures indicates that a simple polytetrahedral packing model is not applicable. As SiO_2 is compressed, the SiO_4 tetrahedra become very distorted.³⁸ Most solids that amorphize (either reversibly or irreversibly) have directional bonding and are not described by simple polytetrahedral packing arguments; for example: coesite, ice, $\text{CaAlSi}_2\text{O}_8$, Fe_2SiO_4 , and AlPO_4 .^{1,39}

Last, we consider the questions, "Why do crystal-to-amorphous transformations occur and what 'kind' of transitions are they?" Kruger and Jeanloz have suggested that pressure-induced amorphization could result from a kinetically impeded phase transition between crystalline states.¹ Similarly, Adams, Haines, and Leonard have suggested that a pressure-induced disordered phase results because a high-pressure crystalline phase is kinetically inaccessible at room temperature.⁴⁰ The same type of driving forces has been suggested for other solid-solid amorphizations.⁴¹

The use of polytetrahedral ordering in describing pressure-induced amorphizations suggests that there is a "geometrical instability" that impedes the phase transition. This is similar to the idea of Hazen and Finger, who suggested that an important factor in crystal-crystal phase transitions is a "geometrical instability which arises from the misfit of adjacent structural elements."⁴² When a crystalline solid is stressed beyond its stability field, the atoms attempt to rearrange into a new crystalline structure. Since the phase transition is kinetically impeded, the atoms are unable to move enough to rearrange into a new crystalline state. The atoms then search for the nearest low-energy state. For a nondirectionally bonded solid, the atoms will find a polytetrahedral packing since the lowest free-energy grouping of atoms is polytetrahedral.^{14,27} This packing is a trade-off between lattice energy and minimization of the free energy locally around polytetrahedral units. Since polytetrahedral units cannot form a crystalline lattice, nature gives up some of the free energy of the local packing to form a crystalline lattice, which results in an overall lowering of the free energy. When a solid is pressurized, energy is imparted to

it. This suggests that with pressure we supply the free energy due to the crystallinity of the lattice *via* pressure-volume work, allowing the atoms to slip into their polytetrahedral arrangements.

V. CONCLUSIONS

We presented above x-ray and Raman measurements that indicate that crystalline $\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3$ becomes amorphous at pressures greater than 9.4 GPa. The crystalline state returns when the pressure is released. The suggestion was made that the amorphization occurs *via* the displacive formation of a noncrystallographic packing based on polytetrahedral units. A consideration of several pressure-induced amorphizations indicates that the polytetrahedral ordering is applicable to nondirectionally bonded materials; its application to solids with covalent and hydrogen bonding is not immediately evident. Polytetrahedral ordering does explain, though, why elemental metals do not become amorphous when compressed.

More generally, this work suggests that a certain class of amorphous solids should be viewed as a packing of certain ions rather than in terms of discrete local units exhibiting only short-range order. While amorphous materials do not have order in the sense of translational periodicity, certain pressure-induced amorphous materials have a molecular arrangement that exhibits elements of medium-range order.

Establishing the relationship between pressure-induced amorphous states and amorphous materials prepared by more conventional methods (e.g., melt quenching) will be very fruitful in understanding the detailed structural principles involved in *all* amorphous materials.⁴³ Our suggestion that polytetrahedral ordering is present in a class of pressure-induced amorphous solids is one such link between compression-amorphized materials and those prepared at ambient pressure.

ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of the Petroleum Research Fund administered by the American Chemical Society, for partial support of this research and to the Department of Chemical Engineering, Carnegie-Mellon University for financial support. The authors wish to thank Dr. K. Brister and the staff at CHESS for their assistance with the high-pressure EDXD experiments. One of us (W.S.H.) wishes to thank Professor E. I. Ko for many enlightening discussions.

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