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Pressure-induced crystallization of vitreous $ZnCl_2$

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In situ Raman scattering measurements have been obtained for vitreous $ZnCl_2$ compressed isothermally to 25 GPa. The Raman spectra indicate that, in contrast to other tetrahedral framework glasses, when compressed at room temperature glassy $ZnCl_2$ crystallizes to the high-pressure $CdCl_2$-structured phase between 2.3 and 3.0 GPa; on decompression, the high-pressure phase remains until 1.1 GPa, where it then reverts to γ-$ZnCl_2$. On recompression the γ-$ZnCl_2$ phase converts to the $CdCl_2$ phase at 2.5 GPa and backtransforms at 1.1 GPa upon decompression. We suggest that a density-driven phase separation in the supercooled liquid regime underlies the amorphous-to-crystalline transition of $ZnCl_2$ and other glassy materials.

I. INTRODUCTION

The numerous investigations of the high-pressure behavior of tetrahedral framework glasses have provided a unique perspective on the response of metastable phases to isothermal compression. Most intriguing, when compressed isothermally at 77 K, glassy water undergoes a pseudo-first-order phase change from a low-density amorphous (LDA) phase to a high-density amorphous (HDA) phase.[1] This unusual ‘‘polyamorphic’’ transformation between two thermodynamically distinct amorphous phases has been rationalized as the nonergodic manifestation of a first-order transition between two *liquid* phases in the supercooled regime of water and provides evidence that in addition to the normal liquid-vapor critical point there exists a *second* critical point of water in its metastable supercooled region.[2–4] The existence of a second critical point in water in its metastable region reveals the thermodynamic basis for the highly anomalous physical behavior displayed by water both within and near its normal thermodynamic stability field. This includes the observed increase in the self-diffusion of water with increasing pressure,[5] the existence of a temperature of maximum density,[6] and the divergence in the thermal expansivity[7] and heat capacity[8] of water on cooling below its thermodynamic melting point.

Liquid silicates display many ‘‘waterlike’’ anomalies, including an initial decrease in viscosity and increase in diffusivity of network-forming ions with increasing pressure.[9,10] Although recent computer simulations on liquid silica show that, as with water, the compressibility becomes increasingly divergent with decreasing temperature, indicative of an approach to a critical point (here, the terminus of a coexistence line between two liquid silica phases),[11] an abrupt transition between two amorphous phases of silica does not occur. Instead, when compressed at room temperature, a gradual transition from a ‘‘low-density’’ silica structure to a ‘‘high-density’’ silica structure takes place over a pressure interval of more than 20 GPa.[12–14] Undoubtedly, in a glass as deeply undercooled as silica ($T_g \sim 1430\,\mathrm{K}$) kinetic barriers to transformation most likely obscure any first-order type transition.

In order to make the polyamorphic transition of a tetrahedral framework glass more kinetically accessible, we selected a glass with a glass transition temperature T_g closer to ambient temperature. Zinc chloride is unusual among the halides for its high viscosity at its melting point ($T_m = 593\,\mathrm{K}$) and consequently its ability to supercool into a glass at a relatively low glass transition temperature ($T_g = 375\,\mathrm{K}$). A thorough investigation of the glass structure by neutron diffraction revealed vitreous zinc chloride to consist of a distorted close-packed array of chloride ions in which zinc cations are randomly distributed in the tetrahedral sites,[15] producing a three-dimensional network of predominantly corner-linked tetrahedra, but with a reduced average intertetrahedral bond angle of 109.5° compared to 145° for silica glass. The more ionic, less directional bonding than that of silica makes structural rearrangement in zinc chloride considerably easier, resulting in the lower cohesive energy of the solid reflected in the relatively low melting point and glass transition temperature of zinc chloride and the non-Arrhenius viscosity curve of liquid $ZnCl_2$ as a function of T_g/T. Hence, $ZnCl_2$ has been termed a ‘‘weakened’’ analog of the network-forming liquid silica.[16]

High-pressure studies of SiO_2, GeO_2, and BeF_2 glasses found that the initial compression mechanism of these glasses relies on the narrowing of the rather large distribution of intertetrahedral angles before the onset of a gradual fourfold to sixfold coordination change of the metal atom and the simultaneous two-fold to threefold coordination change of the anion.[13,17,18] In contrast, glassy H_2O has a very narrow distribution of intertetrahedral angles ($\pm 5°$) much like that of zinc chloride; compression of amorphous water produces an abrupt transition at 6.0 kbars to the high-pressure amorphous phase. Thus, we suspected vitreous zinc chloride would display a similar cooperative transition between two polyamorphs. However, as our studies bore out, a polyamorphic transition to a high-density glass is not directly observed; instead, the high-pressure phase of layered $ZnCl_6$ octahedra ($CdCl_2$-type structure) crystallizes from the glass under compression. From our results we infer that the pressure-induced crystallization of vitreous $ZnCl_2$ and other glassy materials results from an intrinsic instability in the liquid phase regime.

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II. EXPERIMENT

The method of synthesis employed here is similar to that used in the production of high-purity vitreous zinc chloride developed for materials used in quantum electronics.[19] Reagent-grade zinc chloride was dried overnight in an oven. The dried reagent was melted and chlorine gas, dried over phosphorus pentoxide, was bubbled through the melt followed by a dry nitrogen flush. The melt was drawn into a Pyrex® ampoule, quenched in a liquid nitrogen bath, and flame sealed under vacuum. Due to the extreme hygroscopicity of the glass and subsequent devitrification to the cristobalite-type α-$ZnCl_2$ in the presence of minute amounts of water, the sample remained under vacuum in a sealed ampoule until the day of use. All manipulation of the material took place in an argon-filled drybox. The glass was gently crushed to a powder and then loaded without a pressure medium in the 125-μm-diameter sample chamber of a preindented T301 stainless steel gasket. The sample and fine ruby chips were compressed between two type-Ia low-fluorescence diamonds mounted in a Mao-Bell type diamond anvil cell. Pressure measurements were made from the calibrated shift of the ruby R_1 phosphorescence line.[20] At least three rubies were measured to gauge pressure gradients, which remained less than 10% of the pressure.

In situ Raman measurements were made at room temperature (298 ± 3 K) on an Instruments S. A. triple spectrometer (S3000) using 200-mW power of the 488.0-nm line of an Ar^+ laser as the excitation source focused to a ~5 μm spot at the sample. A liquid-nitrogen-cooled charge-coupled device (CCD) detector (PI-1100) collected the signal. The spectra were collected in both parallel polarized (HH) and crossed polarized (VH) configurations using 180° backscattering geometry.

III. RESULTS AND DISCUSSION

Several crystalline polymorphs of $ZnCl_2$ have been reported at ambient conditions.[21] Prior to 1961, it was widely accepted that the ambient stable phase had a layered structure in which each zinc was coordinated to six chloride ions to form regular octahedra with van der Waals bonding between the layers.[22] Later investigations proved that zinc chloride and beryllium fluoride, unusual in halides for their glass-forming abilities, have bonding based on a tetrahedral framework. Although not isostructural to SiO_2 polymorphs, the α- and β-polymorphs of $ZnCl_2$ crystallize to a cristobalite-type three-dimensional network of corner-linked tetrahedra,[23] while γ-$ZnCl_2$ crystallizes to a layered structure of cross-linking tetrahedra in the red-HgI_2 structure.[24] Subsequent synthesis investigations revealed that in the scrupulous absence of water and impurities an orthorhombic structure containing corner-linked $ZnCl_4$ tetrahedra is the only phase of $ZnCl_2$ obtained at ambient conditions.[25] This orthorhombic phase has been referred to as δ-$ZnCl_2$ in recent literature.[12,26]

A comparison of the Raman spectra of the α-polymorph and the glass shows that the spectrum of the glass is clearly similar to that of the cristobalite-type α-phase (Fig. 1). Although little work has been done on the assignment of the Raman features, it can be surmised that the intense mode at 233 cm^{-1} of α-$ZnCl_2$ [Fig. 1(a)] corresponds to the 410-cm^{-1} symmetric Si-O stretch in cristobalite SiO_2. The ambient Raman spectrum of vitreous $ZnCl_2$ is dominated by the highly polarized vibrational mode at 235 cm^{-1} [Fig. 1(b)]. In analogy to the silica glass, we interpret this mode to correspond to the symmetric stretch of the Zn-Cl-Zn linkages involving the motion of the Cl atom in the plane bisecting the Zn···Zn line. The narrow spectral width of this mode (full width at half maximum of ~50 cm^{-1}) attests to the relatively tight distribution of the intertetrahedral angle θ, which is estimated to be 10°. The low-frequency mode or ‘‘boson peak’’ near 75 cm^{-1}, attributed to the anomalous low-energy excitation present in glasses, is also evident. In the diamond anvil cell, difficulty resolving this peak from the laser line precluded an accurate measurement of the boson peak shift with pressure.

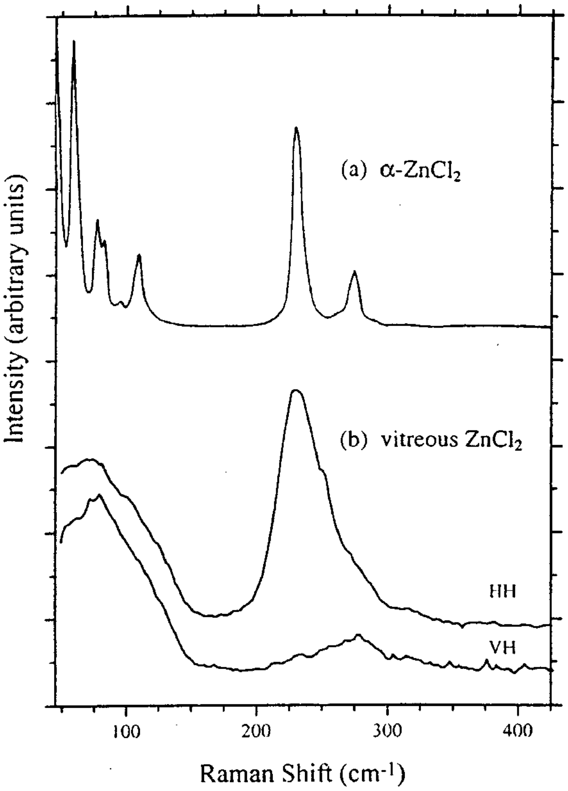

FIG. 1. Raman spectra of (a) crystalline α-$ZnCl_2$ and (b) vitreous $ZnCl_2$ collected in parallel (HH) and crossed (VH) polarizations.

Upon initial compression, the peak shape of the main symmetric stretching mode remains relatively unchanged (Fig. 2); a slight shift to higher frequency of the center of the band indicates tighter packing of the anions with compression. The pressure dependence of the main band closely follows that of the symmetric stretching peak of cristobalite-type α-$ZnCl_2$.[27] We note that, unlike the high-pressure spectra of silica and germania glasses, which show a dramatic decrease in intensity corresponding to the onset of the coordination change,[13,17,28] only a very minor premonitory change in intensity of this mode takes place upon compression prior to the substantial changes in the glass structure (i.e., coordination change).

Between 2.3 and 3.0 GPa, an abrupt change occurs in the Raman pattern, as well as visually in the sample. As the

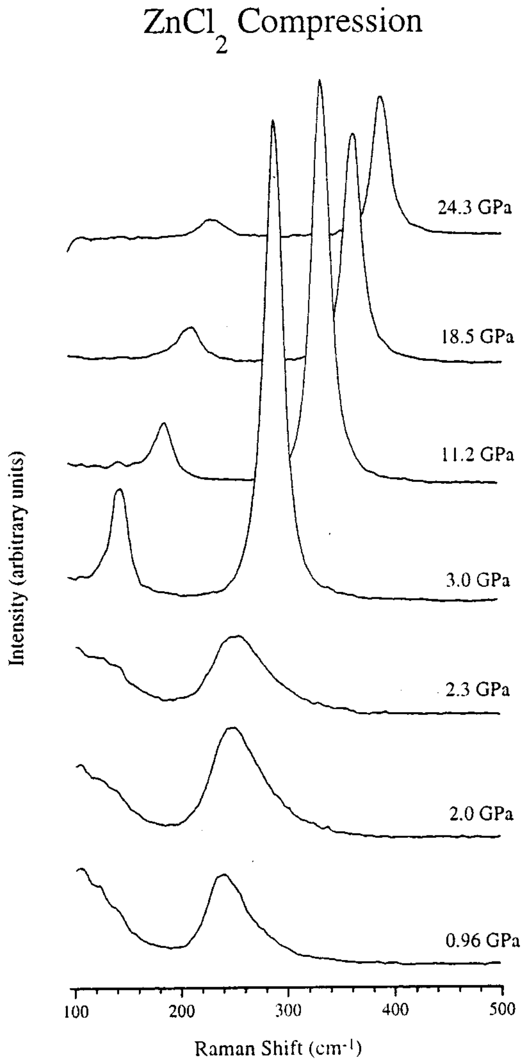

FIG. 2. *In situ* Raman spectra during isothermal compression of vitreous $ZnCl_2$. At 3.0 GPa the spectra change drastically upon crystallization of the $CdCl_2$-structured high-pressure phase.

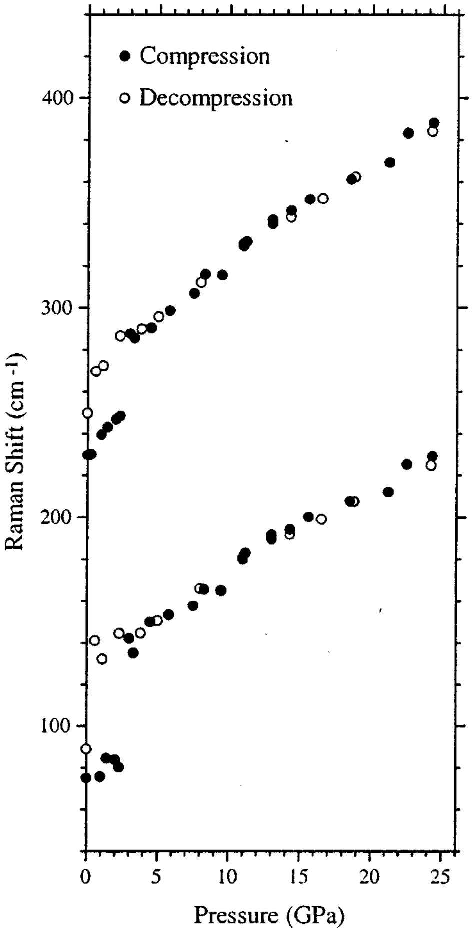

FIG. 3. Frequency shifts during compression (filled circles) and decompression (open circles) of $ZnCl_2$ clearly indicating the pressure-induced crystallization at 3.0 GPa on compression and pressure quench of γ-$ZnCl_2$ on decompression.

sample became optically microcrystalline, all modes associated with the vibrations of the tetrahedral glass network were replaced by an intense mode at 290 cm^{-1} and a much weaker band at 140 cm^{-1}. The new Raman pattern and the glass spectra were not observed to coexist at any time. The Raman spectrum at 3.0 GPa closely resembles that of the *in situ* high-pressure $ZnCl_2$ phase observed by Sakai *et al.*[27] produced by the compression of α-$ZnCl_2$ above 2.7 GPa. Based on *in situ* x-ray diffraction of the high-pressure phase, Sakai and co-workers assigned the structure to a $CdCl_2$-type hexagonal unit cell. We observed the high-pressure $CdCl_2$-structured phase to pressures as high as 25 GPa without evidence of further transformation.

Factor group analysis of a $CdCl_2$-type structure with space group $D_3^7(R32)$ and $Z^B=1$ yields the irreducible representation of the optical normal modes of vibration

$$\Gamma_{\text{vib}}=A_1(\text{R})+A_2(\text{ir})+2E(\text{R,ir}).$$

The intense band at 290 cm^{-1} is assigned to the Raman-active A_1 mode and the 140-cm^{-1} band to an E mode. An additional interlayer shear E mode may lie at lower frequencies unresolved in this experiment. The pressure dependencies for the A_1 and E modes of the $CdCl_2$ phase (Fig. 3) agree with those previously reported[27] as well as with values obtained for the pressure dependencies of cadmium halides.[29]

On decompression (Fig. 4), the high-pressure phase remains until 1.1 GPa, where it reverts to another crystalline phase which remains stable to ambient conditions. The Raman pattern of the recovered phase closely matches that of γ-$ZnCl_2$.[21,27] This assignment was confirmed by the powder x-ray diffraction pattern of a sample recovered from compression to 9 GPa in a multiple-anvil apparatus. We also found, as previously reported, that γ-$ZnCl_2$ converts to the high-pressure phase at 2.5 GPa if recompressed, and back-transforms at 1.1 GPa upon decompression.

In situ compression studies of α-$ZnCl_2$ showed a first-order phase transition to the unquenchable high-pressure $CdCl_2$-type phase, referred to by Sakai *et al.* as δ-$ZnCl_2$.[27] (To avoid possible confusion with the orthorhombic phase mentioned above, in this work we refer to the high-pressure phase as the $CdCl_2$-phase.) The pressure-induced transformation of the low-pressure α-$ZnCl_2$ phase of corner-linked $ZnCl_4$ tetrahedra to the high-pressure $CdCl_2$ phase of layered $ZnCl_6$ octahedra requires a low activation energy for the

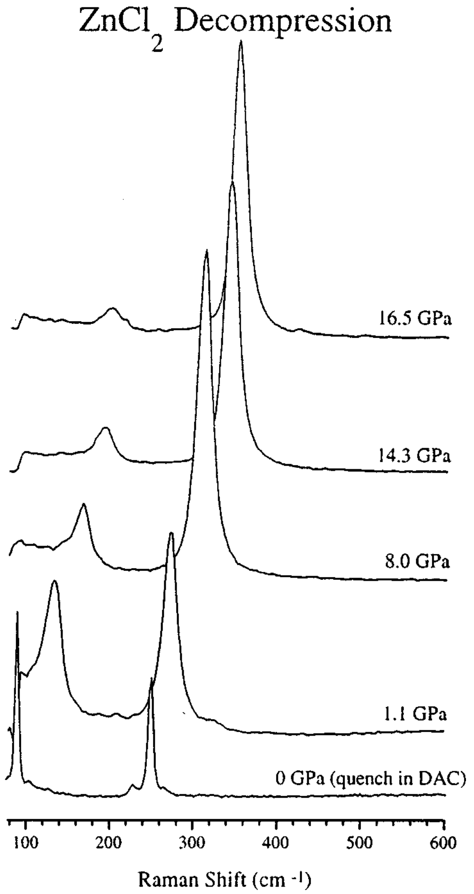

FIG. 4. *In situ* decompression and pressure quench of $ZnCl_2$. The Raman spectrum and x-ray pattern of the quenched phase are consistent with γ-$ZnCl_2$.

nucleation of the high-pressure phase in order for it to be accessible at room temperature. Even with such a low activation energy, in the glassy state long-range cooperative motions of the crystal are replaced by short-range structural relaxations; consequently, crystallization from compression alone is unlikely, especially in light of measurements of the glass transition temperature T_g, which show a steady increase with pressure up to 2 kbars.[30] We suggest that mechanical instability at the spinodal of the low-pressure glass phase results in the catastrophic crystallization of vitreous zinc chloride at pressure.

At ambient pressure, zinc chloride is an ''intermediate'' glass-forming liquid in Angell's classification.[31] In analogy to $CdCl_2$ which melts to a liquid containing $CdCl_4$ tetrahedra,[32] we propose that at pressures near 3.0 GPa the structure of the zinc chloride above the melting temperature T_m still resembles the low-pressure structure, with Zn in tetrahedral coordination, while a glass quenched from a melt held at that pressure is likely to resemble the thermodynamically stable $CdCl_2$ structure with Zn in octahedral coordination. The large configurational difference between the liquid and glass phases at that pressure would result in an extremely fragile glass transition. At temperatures above T_m, increasing pressure gradually transforms the tetrahedrally bonded liquid to an octahedrally bonded liquid; recent experiments support the idea that at elevated temperatures and pressures configurational differences between the liquid and high-density glass phases disappear and result in accessible glass-forming regions for high-pressure glass phases.[33] As temperatures drop into the supercooled regime, the pressure-induced transition between the ''low-density'' and ''high-density'' liquid may become more apparent, until below some critical temperature T_C the drastic configurational difference results in the isochemical density-driven separation of two thermodynamically distinct liquid phases.

In the case of zinc chloride and the several amorphous semiconductors that crystallize under pressure,[34–37] we conjecture that at the pressure of the transition (near 2.3 GPa) the extremely ''fragile'' liquid is not glass-forming; i.e., the glass transition is superseded by homogeneous nucleation, reflected in the fact that $CdCl_2$-structured compounds are not typically glass-forming at ambient pressure. Thus, as in water, a liquid-liquid transition in the supercooled regime may be precluded by the homogeneous nucleation of the thermodynamically stable phase. In light of a density-driven phase transition in the liquid free energy surface, in the nonergodic regime below T_g the tetrahedral framework glass may be compressed beyond the liquid-liquid equilibrium until the mechanical limit of metastability, the spinodal, of the low-density glass is reached. At the spinodal, thermodynamic barriers to transformation vanish; however, the low kinetic requirements of the high-pressure crystalline phase allows for nucleation and growth of the $CdCl_2$ phase. Our observations predict that a polyamorphic transition from a low-density glass phase to a high-density glass phase would be directly observed in vitreous $ZnCl_2$ at lower temperatures where nucleation of the high-pressure crystalline phase would be suppressed. Recent experiments in our laboratory indicate that at low temperature there is a transition to a high-density amorphous phase which at room temperature is masked by the crystallization phenomenon.[38]

The high-pressure behavior of vitreous $ZnCl_2$ demonstrates an important link between tetrahedral network oxide glasses, which undergo a gradual densification via a coordination change of the metal atom, and chalcogenide glasses, which often abruptly crystallize accompanied by a semiconductor-to-metal transition. For glasses such as SiO_2 and GeO_2, the formation of the high-coordinate metal atom is thermally activated and, therefore, is kinetically hindered at temperatures well below T_g, resulting in the densification of the glass over several to tens of gigapascals. Volume measurements obtained as a function of pressure for amorphous germanium, on the other hand, show a discrete volume change for the pressure-induced semiconductor-to-metal transition upon crystallization of the β-Sn phase.[32] Although the density increase on crystallizing has been suggested as a driving force for pressure-induced crystallization,[39] our results for vitreous zinc chloride suggest that it may be the underlying free energy surface of the liquid that controls the high-pressure behavior of these metastable materials, and that isochemical liquid-liquid phase transitions may be common in the supercooled regime of materials that have competing structural configurations at high pressure.

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[1] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **314**, 76 (1985).

[2] R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).

[3] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) **360**, 324 (1992).

[4] P. H. Poole, U. Essmann, F. Sciortino, and H. E. Stanley, Phys. Rev. E **48**, 4605 (1993).

[5] C. A. Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1982), Vol. 7, pp. 1–81.

[6] A. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, London, 1969).

[7] D. E. Hare and C. M. Sorensen, J. Chem. Phys. **84**, 5085 (1986).

[8] C. A. Angell, M. Ogani, and W. J. Sichina, J. Phys. Chem. **86**, 998 (1982).

[9] I. Kushiro, J. Geophys. Res. **81**, 6347 (1976).

[10] B. T. Poe, P. F. McMillan, D. C. Rubie, S. Chakraborty, J. Yarger, and J. Diefenbacher, Science **276**, 1245 (1997).

[11] P. H. Poole, M. Hemmati, and C. A. Angell, Phys. Rev. Lett. **79**, 2281 (1997).

[12] Q. Williams and R. Jeanloz, Science **239**, 902 (1988).

[13] R. J. Hemley, H. K. Mao, P. M. Bell, and B. O. Mysen, Phys. Rev. Lett. **57**, 747 (1986).

[14] C. Meade, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **69**, 1387 (1992).

[15] J. A. E. Desa, A. C. Wright, J. Wong, and R. N. Sinclair, J. Non-Cryst. Solids **51**, 57 (1982).

[16] L. V. Woodcock, C. A. Angell, and P. Cheeseman, J. Chem. Phys. **65**, 1565 (1976).

[17] D. J. Durben and G. H. Wolf, Phys. Rev. B **43**, 2355 (1991).

[18] J. L. Yarger, Ph.D. dissertation, Arizona State University, 1996.

[19] I. M. Batyaev and M. A. Solov'ev, Zh. Prikl. Kim. **66**, 492 (1993) (in Russian).

[20] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

[21] D. W. James, R. M. Parry, and W. H. Leong, J. Raman Spectrosc. **7**, 71 (1978).

[22] L. Pauling, Proc. Natl. Acad. Sci. USA **15**, 709 (1929).

[23] B. Brehler, Z. Kristallogr. **115**, 373 (1961).

[24] H. R. Oswald and H. Jaggi, Helv. Chim Acta **43**, 72 (1960).

[25] J. Brynestad and H. L. Yakel, Inorg. Chem. **17**, 1376 (1978).

[26] M. Wilson and P. A. Madden, Phys. Rev. Lett. **80**, 532 (1998).

[27] M. Sakai, N. Kuroda, and Y. Nishina, J. Phys. Soc. Jpn. **54**, 4081 (1985).

[28] C. H. Polsky, K. H. Smith, and G. H. Wolf, J. Non-Cryst. Solids **248**, 159 (1999).

[29] D. M. Adams and T. K. Tan, J. Phys. Chem. Solids **42**, 559 (1981).

[30] C. A. Angell, E. Williams, K. J. Rao, and J. C. Tucker, J. Phys. Chem. **81**, 238 (1977).

[31] C. A. Angell, J. Non-Cryst. Solids **102**, 205 (1988).

[32] Y. Takagi, N. Itoh, and T. Nakamura, J. Chem. Soc., Faraday Trans. 1 **85**, 493 (1989).

[33] K. Leinenweber and C. A. Angell (unpublished).

[34] K. Tanaka, Phys. Rev. B **42**, 11 245 (1990).

[35] K. Tanaka, Phys. Rev. B **43**, 4302 (1991).

[36] G. Parthasapathy and E. S. R. Gopal, Bull. Mater. Sci. **6**, 231 (1984).

[37] S. Asokan, G. Parthasarathy, and E. S. R. Gopal, J. Mater. Sci. Lett. **4**, 502 (1985).

[38] C. H. Polsky, K. Leinenweber, L. M. Martinez, C. A. Angell, and G. H. Wolf (unpublished).

[39] R. J. Hemley, L. C. Chen, and H. K. Mao, Nature (London) **338**, 638 (1989).