

**Pressure-Induced Coordination Changes in Crystalline and Vitreous GeO<sub>2</sub>**J. P. Itie,<sup>(1)</sup> A. Polian,<sup>(1)</sup> G. Calas,<sup>(2)</sup> J. Petiau,<sup>(2)</sup> A. Fontaine,<sup>(3)</sup> and H. Tolentino<sup>(3)</sup><sup>(1)</sup>Laboratoire de Physique des Milieux Condensés, Université de Paris 6, 75252 Paris, France<sup>(2)</sup>Laboratoire de Minéralogie-Cristallographie, Universités de Paris 6 et 7  
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*In situ* high-pressure x-ray-absorption spectra have been performed on amorphous and crystalline GeO<sub>2</sub> using a diamond-anvil cell adapted to an energy-dispersive spectrometer. The coordination of Ge changes from fourfold to sixfold at pressures between 7 and 9 GPa. The progressive evolution of the measured Ge-O distances as well as the modification in the x-ray-absorption near-edge structure indicate two different sites rather than a progressive site modification. The phase transition observed in the amorphous phase is reversible in contrast to that observed in the crystalline form.

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Phase transitions in minerals under high pressure are known to govern some of the major geophysical properties of the Earth's interior.<sup>1</sup> Similar behavior has been suspected to occur in silicate melts, causing strong density modifications due to a coordination change of the network-forming cations (aluminum and silicon) from fourfold to sixfold.<sup>2</sup> Some evidence for coordination changes of silicon in silicate glasses has been recently obtained from high-pressure infrared spectroscopy.<sup>3</sup> However, the structural mechanisms are still unclear owing to the lack of knowledge of the variation of interatomic distances with increasing pressure. Germanates are structural analogs of silicates: As the former exhibit phase transitions at lower pressure than the latter, they can serve as model compounds which are more accessible to experiment. Germanium is also an element which can be conveniently studied with x-ray-absorption spectroscopy (XAS), as the silicon *K* edge occurs in the soft-x-ray domain, which hinders observations in such devices as diamond-anvil cells. GeO<sub>2</sub> is structurally related to SiO<sub>2</sub>, a compound of considerable interest in either its crystalline or amorphous form. Densification of vitreous silica under pressure has been reported and structural modifications have been determined with Raman, Brillouin, and NMR spectroscopy.<sup>4,5</sup> Similarly, vitreous GeO<sub>2</sub> (*a*-GeO<sub>2</sub>) and *a*-quartz GeO<sub>2</sub> (*q*-GeO<sub>2</sub>) have been studied at high pressure using Raman, Brillouin, and XAS.<sup>6-8</sup> However, no major coordination changes have been found to occur, partly because the pressures attained were not high enough. The present study reports the first direct evidence of complete coordination change of germanium in both *q*-GeO<sub>2</sub> and *a*-GeO<sub>2</sub>. XAS spectra were measured *in situ* at various pressures up to 29 GPa and the derived interatomic distances give important insight into the structural transformation process. The transformation is found to be reversible in *a*-GeO<sub>2</sub> while the compressed crystal does not recover its original

structure.

X-ray-absorption spectra have been recorded at the DCI storage ring at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique using the dispersive XAS station which permits data collection of a full spectrum at once. A Si(111) ellipsoidally bent crystal was used as the dispersive optics. The energy band pass was 450 eV wide. All the Bragg-reflected photons were focused through the image of the source which is 500 μm wide. High-resolution x-ray-absorption near-edge structure (XANES) data were recorded using a Si(311) crystal. Details on the spectrometer have been given elsewhere.<sup>9</sup> The samples were compressed in a diamond-anvil cell<sup>10</sup> and the pressure was measured using the linear ruby fluorescence calibration with  $d\lambda/dP = 3.65$  Å/GPa. The gasket was drilled to 200 μm and placed at the polychromatic focus. The x-ray beam goes through the diamond anvils. The two major drawbacks of this geometry are (i) the weak beam transmission which restricts their use to photons above 9 keV, and (ii) the spurious Bragg reflections due to the diamond single crystals. By adjusting the cell orientation relative to the incident beam, these reflection-induced "glitches" are rejected from the studied energy range (300 eV above the edge in this experiment). Two advantages of the present configuration deserve to be pointed out. First, analog spectra are visible on an oscilloscope so that Bragg-peak rejection can be performed before data collection begins. Second, the focusing optics allows a high flux to pass through the 200-μm-wide sample, which represents an intensity gain of 50 over a step-by-step scanning spectrometer. The pressure-transmitting medium was silicone oil to avoid chemical interaction with the samples as would occur if ethanol-methanol were used. Three kinds of samples were studied: *q*-GeO<sub>2</sub> up to 29.1 GPa, rutile-type GeO<sub>2</sub> (*r*-GeO<sub>2</sub>) up to 24.7 GPa, and vitreous (unannealed) GeO<sub>2</sub> up to 23.2 GPa. The XANES at the

Ge  $K$  edge in  $r$ -GeO<sub>2</sub> is not strongly modified with pressure, the most notable feature being the progressive splitting of the edge crest with increasing pressures, indicating a deformation of the octahedron. Since the sixfold-coordination is maintained,  $r$ -GeO<sub>2</sub> XANES serves as a reference of sixfold-coordinated germanium at high pressure.

Near-edge spectra of fourfold-coordinated Ge in  $q$ -GeO<sub>2</sub> are characterized by well-defined features<sup>8,11</sup> which undergo strong modifications in their relative intensities and positions with increasing pressure [Fig. 1(a)]. Below 6.9 GPa the low-energy peak  $A$  loses inten-

sity, but does not shift, whereas the two higher-energy peaks  $B$  and  $C$  progressively move 2 eV to higher energies. Distances derived from extended x-ray-absorption fine-structure (EXAFS) confirm the published data.<sup>8,12</sup> Both XANES and EXAFS show drastic changes between 6.9 and 7.4 GPa and the overall features become very similar to those of sixfold-coordinated Ge. It looks like a smoothed rutile XANES, reflecting a local disorder. EXAFS spectra have been fitted using experimental phase-shift and amplitude functions extracted using zero-pressure  $q$ - and  $r$ -GeO<sub>2</sub> for fourfold and sixfold coordination, respectively. In these conditions interatomic distances are accurate to 0.015 Å. A one-shell model has been chosen in all cases. Measured Ge-O dis-

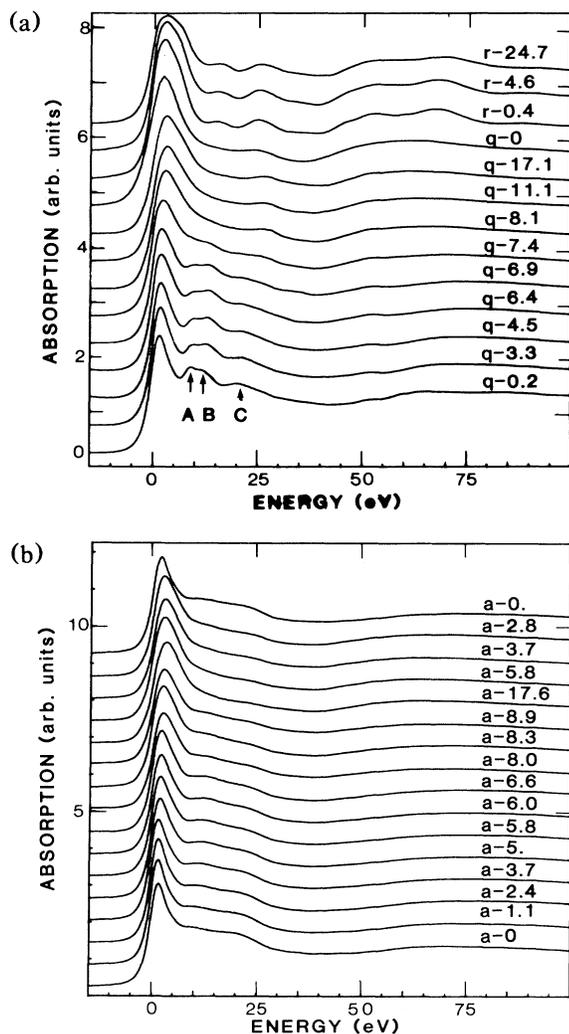


FIG. 1. XANES spectra at the Ge  $K$  edge at various pressures. (a) In  $q$ -GeO<sub>2</sub> and  $r$ -GeO<sub>2</sub> at increasing pressures from bottom to top.  $q$ -0 is a sample quenched from 17.1 GPa to 0 pressure. The arrows indicate the peaks  $A$ ,  $B$ , and  $C$  as discussed in the text. (b) In  $a$ -GeO<sub>2</sub> at pressures increasing up to 17.6 GPa and then decreasing down to 0 pressure from bottom to top.

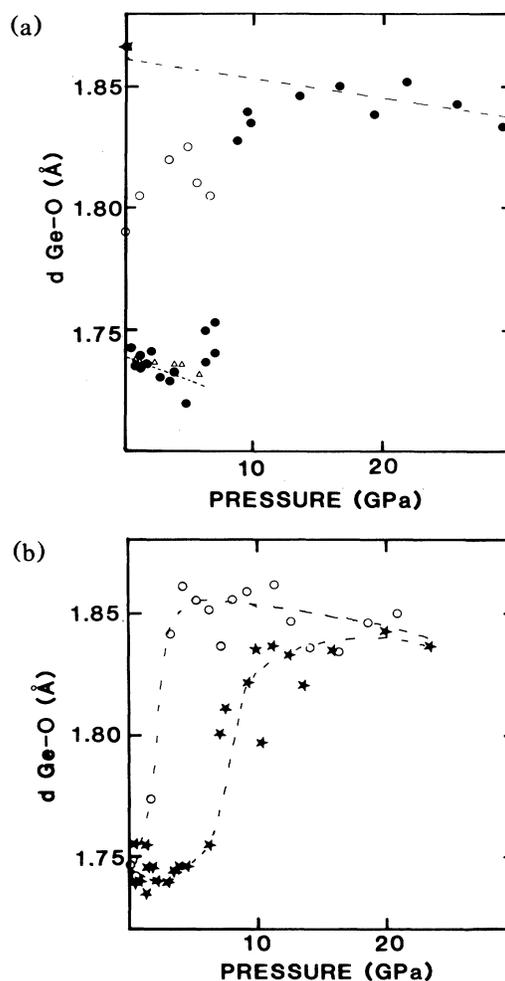


FIG. 2. Evolution of Ge-O distances as a function of pressure. (a)  $q$ -GeO<sub>2</sub>: full circles, at increasing pressure; open circles, decreasing pressure after a run up to 9.7 GPa; arrow, quenched sample after a run up to 29.1 GPa; open triangles, from Houser *et al.* (Ref. 8). Dashed line is only a guide for the eye. (b)  $a$ -GeO<sub>2</sub>: stars, increasing pressure; open circles, decreasing pressure. Dashed line is only a guide for the eye.

tances increase from 1.73 to 1.85 Å between 7 and 12 GPa, respectively [Fig. 2(a)]. The high-pressure Ge-O distance is close to the expected value in octahedral coordination (e.g., the Ge-O average distance of 1.89 Å in *r*-GeO<sub>2</sub> at zero pressure). The wide range of pressure where both coordinations coexist indicates that the coordination change is sluggish and the variation in the apparent Ge-O distance shows the presence of two sites. This leads to an increase of the apparent Debye-Waller factor  $\sigma$ . This is confirmed by XANES data in this "transition zone": The spectra are a weighted sum of the spectra of low- and high-pressure *q*-GeO<sub>2</sub> (Fig. 3), which evidences again a mixing of both coordination numbers. In the high-pressure phase, two and eight germanium second neighbors are found at 2.8 and 3.3 Å, respectively, at significantly shorter distances than in *r*-GeO<sub>2</sub> at ambient pressure (Ge-Ge = 2.86 and 3.42 Å). The Ge-O-Ge angle corresponds to the values found in zero-pressure *r*-GeO<sub>2</sub> (98° and 130°, respectively). In the high-pressure phase, XANES structures are less pronounced and the Debye-Waller-type parameter  $\sigma$  found for Ge-Ge distances is significantly higher.

*a*-GeO<sub>2</sub> shows a local structure similar to that of *q*-GeO<sub>2</sub>, i.e., corner sharing tetrahedra, but with a distribution of Ge-O-Ge angles which is consistent with the absence of long-range ordering.<sup>13</sup> These structural properties are exemplified by XANES spectra which show smoothed features as compared to *q*-GeO<sub>2</sub> [Fig. 1(b)]. With increasing pressure, both the shift of the edge crest and the relative intensity of edge features are restored

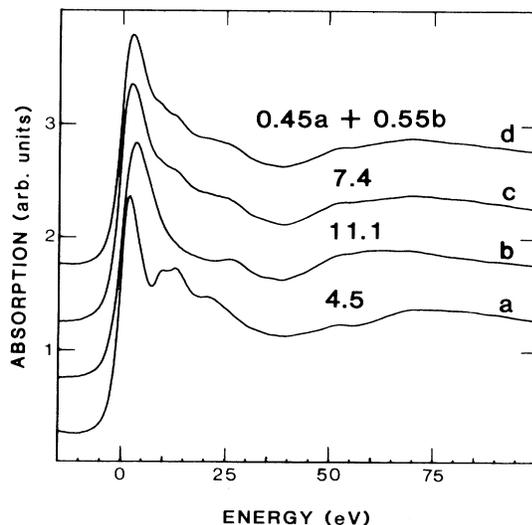


FIG. 3. Evidence for the coexistence of two different sites in *q*-GeO<sub>2</sub> in the pressure range of the phase transition. XANES spectrum of *c* (7.4 GPa) is well reproduced in *d* by a weighted addition of XANES spectra in the low- and high-pressure phases (*a* and *b*, respectively).

and look like those of *q*-GeO<sub>2</sub>. The major transformation occurs between 6.6 and 8.0 GPa, with some evidence from the edge shape (i.e., broadening) for the presence of two sites up to 10 GPa. The presence of sixfold-coordinated Ge shows a first-order phase transition. The evolution of the Ge-O distances is shown in Fig. 2(b): Ge-O distances in the range of 1.84 Å are observed above 10 GPa instead of 1.74 Å at lower pressure. As pointed out above, the XANES spectra change in a transition zone between 6.6 and 10 GPa. Ge-O distances are indeed similar in amorphous and crystalline forms at all pressures. Owing to the static disorder in *a*-GeO<sub>2</sub>, the Ge-Ge distances are difficult to ascertain.

Experiments on decreasing the pressure are important for the insight they give on the structural processes involved during the transformation. The coordination change in *q*-GeO<sub>2</sub> is irreversible, as it is not possible to recover the fourfold coordination of the nondensified phase. The sample quenched from 29.1 GPa remains in the high-pressure phase, as shown by XANES and by EXAFS. The large Ge-O distances measured, 1.87 Å instead of 1.84 Å at 29.1 GPa, may be interpreted as a relaxation of GeO<sub>6</sub> octahedra while releasing pressure, a process compatible with the molar volume change of  $\approx 6\%$  between 30 GPa and zero pressure.<sup>14</sup> The non-reversible character of the coordination change is related to the metastability of *q*-GeO<sub>2</sub> at ambient *P-T* conditions.<sup>1</sup> The coordination change is related to a transition from corner- to edge-sharing polyhedra. Because of the stoichiometry of the compound, this process is only compatible with higher coordination numbers. When quenching the densified *q*-GeO<sub>2</sub> from above the transition zone defined above, an intermediate state is retained, with a decrease of the average Ge-O distances down to approximately 1.8 Å [Fig. 2(a)]. In contrast to the transformation of the crystalline phase, the coordination change observed in *a*-GeO<sub>2</sub> is reversible. When pressure is released from 23.2 GPa, Ge-O distances are first found to increase up to 1.86 Å, as already observed in the crystalline form. However, at 2 GPa, there is a sudden decrease down to 1.74 Å [Fig. 2(b)], the value corresponding to that measured in the starting material. Although a large hysteresis is observed, the transformation is fully reversible at room temperature. Hysteresis may be related to transformation kinetics which is slow when building a low-efficiency oxygen packing from a densely packed high-pressure form. Reversibility in coordination changes has been inferred from infrared spectra of silicate glasses at high pressures, although hysteresis is not easy to detect in the broadened absorption bands of these glasses.<sup>2</sup> The wide distribution of Ge-Ge distances and bonding angles implies a different ring statistics in amorphous and crystalline GeO<sub>2</sub> which may be responsible for the full reversibility of the phase transformation in the former. Previous Brillouin scattering experiments<sup>7</sup> on *a*-GeO<sub>2</sub> have shown an irreversible

transformation in samples quenched from 20 GPa. In light of the results of the present study, this modification cannot be interpreted as arising from a permanent coordination change. This behavior has to be put together with structural data on densified silica: Although a permanent densification in  $\alpha$ -SiO<sub>2</sub> is attained after bringing samples to pressures above 10 GPa, the only major structural difference with the initial, undensified silica samples is a reduction of the average ring size.<sup>5,15</sup> The notion of "amorphous polymorphs" introduced by Grimsditch<sup>4</sup> may concern modifications of long-range order as well as coordination changes.

In light of the present results and by analogy between  $\alpha$ -SiO<sub>2</sub> and  $\alpha$ -GeO<sub>2</sub>, the coordination change of amorphous silica at pressures above 30 GPa is confirmed.<sup>2</sup> The similarity of the XAS results concerning the coordination change at high pressure in both  $\alpha$ -GeO<sub>2</sub> and  $q$ -GeO<sub>2</sub> shows that the transition is dominated by short-range order. This strongly suggests that similar coordination changes may occur in the melt. The reversibility of the transition observed in amorphous materials hinders the measurement on quenched samples: This transition must be investigated *in situ* at high pressures and temperatures.

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