

Pressure-induced elastic anomaly in a polyamorphous metallic glass

Qiaoshi Zeng,^{1,a)} Zhidan Zeng,¹ Hongbo Lou,¹ Yoshio Kono,² Bo Zhang,³ Curtis Kenney-Benson,² Changyong Park,² and Wendy L. Mao^{4,5}

¹Center for High Pressure Science and Technology Advanced Research (HPSTAR), 1690 Cailun Road, Pudong, Shanghai 201203, People's Republic of China

²HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

³Institute of Amorphous Matter Science, School of Materials Science and Engineering and Anhui Provincial Key Lab of Functional Materials and Devices, Hefei University of Technology, Hefei 230009, China ⁴Geological Sciences, Stanford University, Stanford, California 94305, USA ⁵Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

(Received 9 February 2017; accepted 18 May 2017; published online 31 May 2017)

The pressure-induced transitions discovered in metallic glasses (MGs) have attracted considerable research interest offering an exciting opportunity to study polyamorphism in densely packed systems. Despite the large body of work on these systems, the elastic properties of the MGs during polyamorphic transitions remain unclear. Here, using an *in situ* high-pressure ultrasonic sound velocity technique integrated with x-ray radiography and x-ray diffraction in a Paris-Edinburgh cell, we accurately determined both the compressional and shear wave velocities of a polyamorphous Ce₆₈Al₁₀Cu₂₀Co₂ MG up to 5.8 GPa. We observed elastic anomalies of a MG with minima (at ~1.5 GPa) in the sound velocities, bulk modulus, and Poisson's ratio during its polyamorphic transition. This behavior was discussed in comparison to the elastic anomalies of silica glass and crystalline Ce. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4984746]

A material can have multiple chemically identical but structurally distinct phases, which is a phenomenon called polymorphism. Polymorphism is common in crystalline solids and is often associated with symmetry breaking; diamond and graphite are well-known examples. For glasses, which are at the extreme end of structural disordering of solid materials, no identifiable structural symmetry exists. Is polymorphism in amorphous materials (i.e., polyamorphism) still possible? Surprisingly, over the last few decades, with the density change $\Delta \rho$ as the relevant order parameter, pressureinduced transitions between distinct amorphous states, namely, polyamorphic transitions,^{1,2} have been discovered in many network glass systems, e.g., in amorphous ice,³ oxides,^{4–6} chalcogenides,⁷ silicon,⁸ and germanium.⁹ All these systems have directional bonding and low coordination (<6) local environments under ambient pressure which can transform to more densely packed structures with an increase in atomic coordination under high pressure. These polyamorphic transitions from a low-density amorphous (LDA) state to a high-density amorphous (HDA) state have attracted intense research effort, which has improved our fundamental understanding of the disordered glasses and their corresponding liquids.¹ Moreover, the study of polyamorphism can also lead to the development of technologically useful glass materials with identical composition but dramatically different physical properties.¹⁰

Recently, polyamorphic transitions have also been observed in metallic glasses (MGs).^{11–18} This is interesting because polyamorphism was thought to be impossible in nondirectional, densely packed MGs that already have the maximum coordination number (12–14) of random nearest neighbors.¹⁹ These unusual phenomena in MGs are mainly

^{a)}Author to whom correspondence should be addressed: zengqs@hpstar.ac.cn

related to an electronic mechanism, such as the delocalization of the 4f electrons under high pressure, which leads to bond shortening.^{11–13} This type of polyamorphism is different from the conventional structural polyamorphism in network glasses that typically involves a coordination increase often coupled with bond lengthening (e.g., the Si-O and Ge-O bonds⁵) Although it shares the same mechanism of pressure-induced 4f delocalization, in contrast to the sharp volume collapse of the crystalline γ -to- α cerium transition at ~ 0.9 GPa, which occurs almost without hysteresis,²⁰ this type of electronic polyamorphism in MGs exhibits a continuous transition with a large hysteresis loop upon releasing pressure.¹¹ In this respect, it is similar to the structural polyamorphism in network glasses, which involves the coordination rearrangement that characteristically occurs over a wide pressure range and shows considerable hysteresis.^{4,5,21}

The polyamorphism in MGs has been studied by various techniques, such as *in situ* high-pressure x-ray diffraction (XRD),^{11–17} pair distribution function analysis,^{18,22} extended x-ray absorption fine structure,¹⁷ x-ray absorption near-edge spectroscopy,¹³ transmission x-ray microscopy (TXM),²¹ inelastic x-ray scattering (IXS),¹⁶ and resistivity measurements.^{15,23} Sound velocity as property sensitive to structure has been extensively used to study phase transitions in amorphous materials. For example, the polyamorphic transition in silica glass was found to exhibit an interesting elastic anomaly with sound velocities (both compressional and shear waves) and bulk modulus minima at ~2–3 GPa.^{24,25} Therefore, an interesting question is raised: Is there a similar elastic anomaly associated with polyamorphism in MGs?

Zhang *et al.*²⁶ observed a negative pressure dependence of both compressional and shear wave sound velocities up to 0.5 GPa in $\text{Ce}_{70}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{10}$ MGs using a pulse-echo



overlap ultrasonic technique in a piston-cylinder pressure apparatus. This result was surprising because the MGs typically show a positive pressure derivative of the sound velocities.²⁷ Further, Duarte et al.¹⁶ performed an in situ high-pressure XRD on the Ce70Al10Ni10Cu10 MG and confirmed that it has a pressure-induced polyamorphic transition starting at ~ 2 GPa similar to those observed in other Cebased MGs.¹³ Using an *in situ* high-pressure IXS technique in a diamond anvil cell, Duarte et al.¹⁶ revealed a linear positive pressure dependence of the compressional sound velocity in the Ce70Al10Ni10Cu10 MG from 5 GPa to 22 GPa and extrapolated the sound velocity to almost ambient pressure with another positive slope. Since the data points during the transition pressure range (~ 0.5 to ~ 5 GPa) are missing, the elastic properties associated with the polyamorphic transition in Ce-based MGs remains inexplicable, which hinders our comprehensive understanding of this type of polyamorphism and MGs themselves.

In the present work, the sound velocities as a function of pressure were accurately determined through the pressureinduced polyamorphic transition in a $Ce_{68}Al_{10}Cu_{20}Co_2$ MG. We revealed an anomalous sound velocity drop and then increase during the polyamorphic transition. Furthermore, the elastic moduli and Poisson's ratio were derived through the polyamorphic transition. Elastic anomalies with minima in the bulk modulus and Poisson's ratio under pressure were observed in a MG.

MG samples with a nominal composition of $Ce_{68}Al_{10}$ $Cu_{20}Co_2$ were prepared by copper mold casting into rods with a diameter of ~2 mm.²⁸ Master ingots were prepared by arcmelting a mixture of commercial-purity Ce (99.5 wt. %) with high-purity Al (99.99%), Cu (99.99%), and Co (99.99%) in a zirconium-gettered high-purity argon atmosphere. They were all remelted five times to ensure a homogenous composition. The glass nature of the prepared samples was confirmed by XRD and differential scanning calorimetry (DSC). The mass density $\rho = 6.79$ g/cm³ at ambient conditions was determined by the Archimedes principle on an analytical balance (Mettler Toledo-XS205DU). Recently, phase separation was reported in Ce-Al-Ga ternary MGs;²⁹ however, no evidence to show similar phase separation in this Ce₆₈Al₁₀Cu₂₀Co₂ MG by previous studies.^{28,30}

To determine both the compressional $(V_{\rm P})$ and shear $(V_{\rm S})$ wave velocities as a function of pressure through the polyamorphic transition of the Ce₆₈Al₁₀Cu₂₀Co₂ MG, we employed an *in situ* high-pressure ultrasonic technique integrated with synchrotron radiation x-ray radiography and energy-dispersive XRD in a Paris-Edinburgh (PE) cell at the beamline 16-BM-B of HPCAT at the Advanced Photon Source (APS), Argonne National Laboratory (ANL).³¹ The as-prepared rod sample was carefully machined down to a disk with a $\sim 900 \,\mu m$ thickness and a diameter of $\sim 2 \, mm$. Both ends of the rod were polished flat and parallel (final thickness of 604 μ m) using 1 μ m diamond paste to maximize the mechanical contact for elastic wave propagation. Then, the sample was loaded into an x-ray transparent hexagonal BN chamber in the PE cell.³² The sample assembly is shown in Fig. 1(a). It should be noted that all the quantities needed to calculate the sound velocities were directly measured without any assumptions. The acoustic wave travel time (t)



FIG. 1. Sample assembly for the *in situ* high-pressure ultrasonic sound velocity measurements. (a) A schematic illustration of the high-pressure cell assembly. Different colors represent different materials used in the cell. All the materials of the cell are quite transparent to the x-ray beam. The scale bar represents 1 mm. The two-dimensional x-ray radiography image of the MG sample loaded in the PE cell at 0.3 GPa (b) and at 5.8 GPa (c) with a spatial resolution of $0.95 \,\mu$ m/pixel. The black scale bar represents 200 μ m. The sample with heavy elements shows sharp contrast to the Al₂O₃ (top) and NaC1 (bottom). The sample length along ultrasonic wave travel path can be directly obtained by fitting the interfaces between sample/Al₂O₃ and sample/NaCl in the radiography images.

for the compressional wave (30 MHz) and shear wave (20 MHz) and the sample length (*L*) were measured simultaneously by the integrated ultrasonic (pulse overlap method²⁵) and x-ray radiography [Figs. 1(b) and 1(c)] techniques. Then, the sound velocity *V* was calculated from the equation V = 2L/t. The structure evolution of the sample was monitored by the energy-dispersive XRD. We did not observe any sign of crystallization during compression. The pressure was directly determined from the energy-dispersive XRD of the standard NaCl.³³

Figures 1(b) and 1(c) show the x-ray radiography images of the Ce₆₈Al₁₀Cu₂₀Co₂ MG sample at 0.4 GPa and 5.8 GPa, respectively. The sample length shrunk significantly during compression, but the top and bottom surfaces of the rod sample remained parallel, which is critical for the precise determination of V_P and V_S over the entire pressure range in this work. Figure 2(a) presents V_P and V_S as a function of pressure up to 5.8 GPa. V_P was approximate twice of V_S , and V_P was more sensitive to pressure change than V_S . These features are normal for solids and consistent with previous reports on MGs under high pressure.^{26,34} However, we observed that V_P and V_S both decreased with pressure below \sim 1.5 GPa. This is unusual when compared to the typical behavior of MGs, which show positive pressure derivatives for both V_P and V_S^{26} However, it agrees with the results from the in situ high-pressure ultrasonic study on another Ce-based MG (Ce₇₀Al₁₀Ni₁₀Cu₁₀) below 0.5 GPa by Zhang et al.²⁶ Nevertheless, above 1.5 GPa, both V_P and V_S returned to a normal stiffening behavior with positive pressure



FIG. 2. Ultrasonic sound velocities and the sample density of $Ce_{68}Al_{10}$ $Cu_{20}Co_2$ MG versus pressure. (a) The compression wave (V_p) and shear wave (V_s) velocities as a function of pressure were measured up to 5.8 GPa. Minima is observed in both V_p and V_s at ~1.5 GPa. Error bars are smaller than the symbol size. (b) The density of $Ce_{68}Al_{10}Cu_{20}Co_2$ MG through its polyamorphic transition obtained by calculations from sound velocities (open black circles) and by the direct TXM measurement (solid blue diamonds). The dashed lines are the Birch–Murnaghan isothermal equation of state of the LDA (black dashed line) and HDA (blue dashed line) from Ref. 21. Arrows indicate the critical pressures of the polyamorphic transition.

derivatives, which agrees with the *in situ* high-pressure IXS measurement on the Ce₇₀Al₁₀Ni₁₀Cu₁₀ MG above 5 GPa by Duarte et al.¹⁶ Therefore, we observed both sound waves in a MG showing anomalous velocity minima (at ~ 1.5 GPa). In addition, V_P displays another weak kink at ~4.5 GPa which, in contrast, is not obvious in V_S . This means V_P may be more sensitive to polyamorphic transition than V_S in MGs. With a linear approximation, the pressure derivatives of both V_P (dV_P/dP) and V_S (dV_S/dP) are $-0.118 \text{ km s}^{-1} \text{ GPa}^{-1}$ and $-0.008 \text{ km s}^{-1} \text{GPa}^{-1}$ below 1.5 GPa, respectively. These values are close to the pressure derivatives $(dV_P/dP = -0.133)$ km s⁻¹ GPa⁻¹ and $dV_s/dP = -0.007$ km s⁻¹ GPa⁻¹) determined by Zhang *et al.*²⁶ on the $Ce_{70}Al_{10}Ni_{10}Cu_{10}$ MG below 0.5 GPa. Above 1.5 GPa, both sound velocities V_P and V_S change much faster with pressure, $dV_P/dP = 0.201 \text{ km s}^{-1} \text{GPa}^{-1}$ and $dV_S/$ $dP = 0.031 \,\mathrm{km \, s^{-1} \, GPa^{-1}}.$

Sound velocities are determined as a function of pressure, so the density of a statistically isotropic material can be derived from the density-sound velocity relationship³²

$$\rho_{P_{n+1}} = \rho_{P_n} + \int_{P_n}^{P_{n+1}} (1 + \alpha \gamma T) / (V_P^2 - 4V_S^2/3) dP, \quad (1)$$

where ρ_{P_n} is the density at pressure P_n , T is the temperature, α is the thermal expansion coefficient, and γ is the Grüneisen parameter. P_0 (n=0) is the ambient pressure. $(1 + \alpha \gamma T)$ $=C_{\rm P}/C_{\rm V}\approx 1$ is the ratio of the specific heat at constant pressure and volume. Figure 2(b) presents the sample density calculated using relationship (1) as a function of pressure up to 5.8 GPa and the density measured previously by the in situ high-pressure TXM and XRD techniques.²¹ Both sets of density data show similar trends versus pressure demonstrating an obvious polymorphic transition from LDA to HDA states starting at \sim 1.5 GPa and ending at \sim 4.5 GPa. These critical pressures of the polyamorphic transition coincide with the critical pressures of sound velocities indicated by arrows in Fig. 2(a). Hence, it suggests that the anomalous behaviors of sound velocities in Ce68Al10Cu20Co2 MG are closely with associated the pressure-induced polyamorphic transition.

In a previous study of MGs without polyamorphic transitions, the density data calculated from ultrasonic sound velocities using relationship (1) and directly measured by TXM measurements agreed with each other very well.²¹ However, as shown in Fig. 2(b), the density data from ultrasonic sound velocity calculations are obviously underestimated compared to the direct density measurement data from TXM (smaller by $\sim 3\%$ at 5.8 GPa), two sets of data started to diverge above 1.5 GPa. Relationship (1) actually is only valid with an assumption that a sample does not have structural transformation and irreversible densifications during compression.³¹ Through the polyamorphic transition of the Ce₆₈Al₁₀Cu₂₀Co₂ MG, although the transition is continuous, the sound velocities are changing sharply. With discrete data points rather than continuous curves measured, considerable errors could be accumulated in the integration of sound velocities using relationship (1) through the transition region. This can be evidenced by the density discrepancy emerging at ~ 1.5 GPa and saturating at ~ 4.5 GPa when the transition is almost completed. Therefore, it means that we should be very careful to calculate density from the ultrasonic data using relationship (1) if a polyamorphic transition exists in MGs.

With both the density (from TXM) and sound velocities as a function of pressure obtained, for an isotropic homogenous material such as a MG, bulk modulus *K*, shear modulus *G*, Young's modulus *E*, and Poisson's ratio σ of the Ce₆₈Al₁₀Cu₂₀Co₂ MG under pressures can be derived using the following equations:³⁵

$$K = \rho \left(V_p^2 - \frac{4}{3} V_s^2 \right),\tag{2}$$

$$G = \rho V_s^2, \tag{3}$$

$$\sigma = \frac{\left(V_p^2 - 2V_s^2\right)}{2\left(V_p^2 - V_s^2\right)},$$
(4)

$$E = 2G(1+\sigma). \tag{5}$$

Figure 3 shows the elastic moduli and Poisson's ratio as a function of pressure up to 5.8 GPa covering the pressure range for the polyamorphic transition in $Ce_{68}Al_{10}Cu_{20}Co_2$ MG.



FIG. 3. Elastic moduli and Poisson's ratio of the Ce₆₈Al₁₀Cu₂₀Co₂ MG as a function of pressure. Minima at ~1.5 GPa and weak kinks at ~4.5 GPa are observed in both the bulk modulus (*K*) and Poisson's ratio (σ). A change in slope occurs at ~1.5 GPa in the shear (*G*) and Young's (*E*) moduli. Arrows indicate the critical pressures of the polyamorphic transition.

The bulk modulus and Poisson's ratio both decrease initially with pressure and then increase, showing minima at ~ 1.5 GPa and a weak kink at ~ 4.5 GPa. In contrast, the shear and Young's modulus increase over the entire range of compression but only show a substantial slope change at \sim 1.5 GPa. These critical pressures [as indicated by the arrows in Fig. 3] in the elastic moduli and Poisson's ratio are consistent with the transition pressures of the polyamorphic transition in the Ce₆₈Al₁₀Cu₂₀Co₂ MG [Fig. 2(a)]. These results below 0.5 GPa agree with those reported previously by Zhang *et al.*,²⁶ showing the negative pressure dependence in K and σ but the positive pressure dependence in G and E. The Poisson's ratio σ as a density-independent parameter is believed to be sensitive to atomic structure.³⁶ The similarity between the bulk modulus and Poisson's ratio curves in Fig. 3 indicates their anomalous behavior is mostly caused by the structural softening rather than density change below \sim 1.5 GPa, which, in contrast, does not induce an anomaly in shear modulus and Young's modulus.

The minimum observed in the bulk modulus K of the Ce₆₈Al₁₀Cu₂₀Co₂ MG is analogous to the elastic anomaly extensively discovered in the silica glass with minima at \sim 2–3 GPa.³⁷ Most materials become stiffer under pressure as a result of the constituent atoms being squeezed together. Therefore, it is surprising that silica glass and the Ce₆₈Al₁₀ Cu₂₀Co₂ MG both soften under compression at low pressures (below \sim 2 GPa). Theoretical³⁷ and experimental³⁸ studies interpreted the sound velocity and bulk modulus anomaly in the silica glass as a localized reversible structural polyamorphic

transition, which is similar to the transition in β -to- α cristobalite. During compression of silica glass, an abrupt rotation of the Si-O-Si bonds occurs, affecting the network ring geometry and thereby the elastic response of the structure to imposed mechanical constraints.³⁷ For Ce₆₈Al₁₀Cu₂₀Co₂ MG, it also has a polyamorphic transition. It has been reported that the 4felectrons of Ce in the Ce-based MG can inherit the pressureinduced delocalization transition from crystalline Ce, which causes bond shortening, volume collapse, and structural softening during compression.¹³ Regarding the transition process, the γ -to- α phase transition caused by the 4f electron delocalization in crystalline Ce is an abrupt iso-structural transition,²⁰ but due to the fluctuations in the local stress fields, the 4f electron of each Ce atom in the MG matrix may delocalize sporadically at different pressures even starting at very low pressures. Consequently, the global properties of the glass structure only change gradually over a wide range of pressure. During the γ -to- α phase transition in crystalline Ce, anomalous minima in both V_p and bulk modulus K were also observed at ~ 0.75 GPa. The V_p and K curves versus pressure of the crystalline Ce even exhibit highly similar shapes with those of Ce₆₈Al₁₀Cu₂₀Co₂ MG.³⁹ These results suggest that the elastic anomaly of the Ce68Al10Cu20Co2 MG originates from the pressure-induced transition.

In contrast to the similarity of V_p , K, and σ between the Ce₆₈Al₁₀Cu₂₀Co₂ MG, crystalline Ce, or silica glass, their V_S and G show remarkably different behaviors during compression. For example, in the Ce₆₈Al₁₀Cu₂₀Co₂ MG, its shear wave velocity V_s decreases initially with pressure until reaching a minimum at ~1.5 GPa and then increases almost linearly. In crystalline Ce, its V_s remains almost constant below and above the phase transition pressure of 0.75 GPa with a sudden jump in between of them. This indicates that V_s may be more sensitive to structural difference in terms of ordering/disordering between the crystalline and corresponding amorphous forms. On the other hand, V_P of the Ce₆₈Al₁₀Cu₂₀Co₂ MG could exactly inherit the behavior of crystalline Ce regardless of their structural difference.

In silica glass, the sound velocities V_P and V_S change with the close rate $(dV_P/dP = -0.48 \text{ km s}^{-1} \text{ GPa}^{-1}$ and $dV_S/dP = -0.25 \text{ km s}^{-1} \text{ GPa}^{-1}$ below 2 GPa);²⁵ however, V_P changes much faster than V_S during compression in the Ce₆₈Al₁₀Cu₂₀Co₂ MG $(dV_P/dP \approx 15 \ dV_S/dP)$ below 1.5 GPa). Consequently, the shear modulus *K* in silica glass also decreases with increasing pressure; in contrast, the shear modulus *K* in the Ce₆₈Al₁₀Cu₂₀Co₂ MG shows positive pressure dependence. These differences could be caused by the different types of bonding and packing between the silica glass and MG.

In summary, using the *in situ* high-pressure ultrasonic sound velocity techniques integrated with synchrotron radiation x-ray radiography and XRD, we precisely determined the sound velocities during the compression of a $Ce_{68}Al_{10}Cu_{20}Co_2$ MG through its polyamorphic transition. Combining the sound velocity data with previous density data obtained by TXM, the elastic anomalies with minima at ~1.5 GPa in compressional and shear wave sound velocities, the bulk modulus and Poisson's ratio were observed in a MG. Compared with the compression behaviors of the silica glass and crystalline Ce, we conclude that the elastic anomaly is closely associated with the pressure-induced polymorphic transitions, and the shear sound velocities are very sensitive to the bonding/structural difference between these materials. Moreover, compared to kinks in diffraction peak position versus pressure in XRD studies,^{11–17} the elastic anomalies obtained by sound velocity measurements can also be another powerful and sensitive indicator to search for and study more polyamorphism in MGs.

We thank Dr. Ho-kwang Mao, Dr. Weihua Wang, Dr. Guoyin Shen, and Dr. John Tse for helpful discussions. This research was supported by the National Natural Science Foundation of China (Grant No. U1530402) and the National Thousand Youth Talents Program in China. W.L.M. was supported by NSF-EAR-1055454. B.Z. was supported by the Fundamental Research Funds for the Central Universities in China (Grant No. JZ2016HGPB0671). Use of the HPCAT facility was supported by DOE-NNSA (Grant No. DE-NA0001974) with partial instrumentation funding by NSF. Y.K., C.K.B, and C.P. acknowledge the support of DOE-BES/DMSE under Award DE-FG02-99ER45775. A.P.S. was supported by DOE-BES, under Contract No. DE-AC02-06CH11357.

¹P. F. McMillan, J. Mater. Chem. 14, 1506 (2004).

- ²D. Machon, F. Meersman, M. C. Wilding, M. Wilson, and P. F. McMillan, Prog. Mater. Sci. **61**, 216 (2014).
- ³O. Mishima and Y. Suzuki, Nature **419**, 599 (2002); C. A. Tulk, C. J. Benmore, J. Urquidi, D. D. Klug, J. Neuefeind, B. Tomberli, and P. Egelstaff, Science **297**, 1320 (2002); C. A. Tulk, R. Hart, D. D. Klug, C. J. Benmore, and J. Neuefeind, Phys. Rev. Lett. **97**, 115503 (2006).
- ⁴J.-P. Itié, A. Polian, G. Calas, J. Petiau, A. Fontaine, and H. Tolentino, Phys. Rev. Lett. **63**, 398 (1989).
- ⁵C. Meade, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. 69, 1387 (1992);
 M. Guthrie, C. A. Tulk, C. J. Benmore, J. Xu, J. L. Yarger, D. D. Klug,
 J. S. Tse, H. K. Mao, and R. J. Hemley, *ibid.* 93, 115502 (2004).
- ⁶S. K. Lee, P. J. Eng, H. K. Mao, Y. Meng, and J. Shu, Phys. Rev. Lett. 98,
- 105502 (2007); E. Soignard, S. A. Amin, Q. Mei, C. J. Benmore, and J. L. Yarger, Phys. Rev. B 77, 144113 (2008).
- ⁷W. A. Crichton, M. Mezouar, T. Grande, S. Stolen, and A. Grzechnik, Nature 414, 622 (2001); Q. Mei, C. J. Benmore, R. T. Hart, E. Bychkov, P. S. Salmon, C. D. Martin, F. M. Michel, S. M. Antao, P. J. Chupas, P. L. Lee, S. D. Shastri, J. B. Parise, K. Leinenweber, S. Amin, and J. L. Yarger, Phys. Rev. B 74, 014203 (2006).
- ⁸P. F. McMillan, M. Wilson, D. Daisenberger, and D. Machon, Nat. Mater. 4, 680 (2005).
- ⁹M. H. Bhat, V. Molinero, E. Soignard, V. C. Solomon, S. Sastry, J. L. Yarger, and C. A. Angell, Nature **448**, 787 (2007); O. I. Barkalov, V. G. Tissen, P. F. McMillan, M. Wilson, A. Sella, and M. V. Nefedova, Phys. Rev. B **82**, 020507 (2010).
- ¹⁰P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan, Science 275, 322 (1997).
- ¹¹H. W. Sheng, H. Z. Liu, Y. Q. Cheng, J. Wen, P. L. Lee, W. K. Luo, S. D. Shastri, and E. Ma, Nat. Mater. 6, 192 (2007).
- ¹²Q. S. Zeng, Y. C. Li, C. M. Feng, P. Liermann, M. Somayazulu, G. Y. Shen, H. K. Mao, R. Yang, J. Liu, T. D. Hu, and J. Z. Jiang, Proc. Natl. Acad. Sci. U. S. A. **104**, 13565 (2007).
- ¹³Q. S. Zeng, Y. Ding, W. L. Mao, W. G. Yang, S. V. Sinogeikin, J. F. Shu, H. K. Mao, and J. Z. Jiang, Phys. Rev. Lett. **104**, 105702 (2010).
- ¹⁴Q. S. Zeng, Y. Z. Fang, H. B. Lou, Y. Gong, X. D. Wang, K. Yang, A. G. Li, S. Yan, C. Lathe, F. M. Wu, X. H. Yu, and J. Z. Jiang,

- J. Phys.: Condens. Matter 22, 375404 (2010); G. Li, Y. Y. Wang, P. K. Liaw, Y. C. Li, and R. P. Liu, Phys. Rev. Lett. 109, 125501 (2012); W. Zhao, Y. Y. Wang, R. P. Liu, and G. Li, Appl. Phys. Lett. 102, 031903 (2013); C. L. Lin, A. S. Ahmad, H. B. Lou, X. D. Wang, Q. P. Cao, Y. C. Li, J. Liu, T. D. Hu, D. X. Zhang, and J. Z. Jiang, J. Appl. Phys. 114, 213516 (2013); Y. Y. Wang, W. Zhao, G. Li, Y. C. Li, and R. P. Liu, Mater. Lett. 110, 184 (2013); Q. Luo, G. Garbarino, B. Sun, D. Fan, Y. Zhang, Z. Wang, Y. Sun, J. Jiao, X. Li, P. Li, N. Mattern, J. Eckert, and J. Shen, Nat. Commun. 6, 5703 (2015).
- ¹⁵Q. S. Zeng, V. V. Struzhkin, Y. Z. Fang, C. X. Gao, H. B. Luo, X. D. Wang, C. Lathe, W. L. Mao, F. M. Wu, H. K. Mao, and J. Z. Jiang, Phys. Rev. B 82, 054111 (2010).
- ¹⁶M. J. Duarte, P. Bruna, E. Pineda, D. Crespo, G. Garbarino, R. Verbeni, K. Zhao, W. H. Wang, A. H. Romero, and J. Serrano, Phys. Rev. B 84, 224116 (2011).
- ¹⁷L. Belhadi, F. Decremps, S. Pascarelli, L. Cormier, Y. Le Godec, S. Gorsse, F. Baudelet, C. Marini, and G. Garbarino, Appl. Phys. Lett. **103**, 111905 (2013).
- ¹⁸F. Decremps, G. Morard, G. Garbarino, and M. Casula, Phys. Rev. B 93, 054209 (2016).
- ¹⁹H. W. Sheng, W. K. Luo, F. M. Alamgir, J. M. Bai, and E. Ma, Nature 439, 419 (2006); D. B. Miracle, Nat. Mater. 3, 697 (2004).
- ²⁰M. J. Lipp, D. Jackson, H. Cynn, C. Aracne, W. J. Evans, and A. K. McMahan, Phys. Rev. Lett. **101**, 165703 (2008).
- ²¹Q. S. Zeng, Y. Lin, Y. J. Liu, Z. D. Zeng, C. Y. Shi, B. Zhang, H. B. Lou, S. V. Sinogeikin, Y. Kono, C. Kenney-Benson, C. Y. Park, W. G. Yang, W. H. Wang, H. W. Sheng, H. K. Mao, and W. L. Mao, Proc. Natl. Acad. Sci. U. S. A. **113**, 1714 (2016).
- ²²L. Zhang, F. Sun, X. Hong, J. Wang, G. Liu, L. Kong, H. Yang, X. Liu, Y. Zhao, and W. Yang, J. Alloy. Compd. 695, 1180 (2017).
- ²³L. Zhang, J. Wang, F. Tang, H. Yang, X. Liu, Y. Zhao, and W. Yang, High Pressure Res. **37**, 11 (2017); X. R. Liu and S. M. Hong, Appl. Phys. Lett. **90**, 251903 (2007).
- ²⁴K. i. Kondo, S. Iio, and A. Sawaoka, J. Appl. Phys. **52**, 2826 (1981); C.-S. Zha, R. J. Hemley, H-k. Mao, T. S. Duffy, and C. Meade, Phys. Rev. B **50**, 13105 (1994).
- ²⁵Y. Kono, A. Yamada, Y. Wang, T. Yu, and T. Inoue, Rev. Sci. Instrum. 82, 023906 (2011).
- ²⁶B. Zhang, R. J. Wang, and W. H. Wang, Phys. Rev. B **72**, 104205 (2005).
- ²⁷W. H. Wang, Prog. Mater. Sci. **57**, 487 (2012).
- ²⁸P. Yu, R. J. Wang, D. Q. Zhao, and H. Y. Bai, Appl. Phys. Lett. **91**, 201911 (2007).
- ²⁹D. Singh, S. Basu, R. K. Mandal, O. N. Srivastava, and R. S. Tiwari, Intermetallics **67**, 87 (2015); D. Singh, D. Singh, R. K. Mandal, O. N. Srivastava, and R. S. Tiwari, J. Alloy. Compd. **590**, 15 (2014).
- ³⁰P. Yu, K. C. Chan, W. Chen, and L. Xia, Philos. Mag. Lett. **91**, 70 (2011).
- ³¹Y. Kono, C. Park, T. Sakamaki, C. Kenny-Benson, G. Y. Shen, and Y. B. Wang, Rev. Sci. Instrum. 83, 033905 (2012).
- ³²Q. Zeng, Y. Kono, Y. Lin, Z. Zeng, J. Wang, S. V. Sinogeikin, C. Park, Y. Meng, W. Yang, H.-K. Mao, and W. L. Mao, Phys. Rev. Lett. **112**, 185502 (2014).
- ³³F. Birch, J. Geophys. Res. **91**, 4949, doi:10.1029/JB091iB05p04949 (1986).
- ³⁴W. Liu, Q. S. Zeng, Q. K. Jiang, L. P. Wang, and B. S. Li, Scr. Mater. 65, 497 (2011).
- ³⁵E. Schreiber, O. L. Anderson, and N. Soga, *Elastic Constants and their Measurements* (Mcgraw-Hill Education, 1974).
- ³⁶G. N. Greaves, A. L. Greer, R. S. Lakes, and T. Rouxel, Nat. Mater. 10, 823 (2011).
- ³⁷L. Huang and J. Kieffer, Phys. Rev. B 69, 224203 (2004).
- ³⁸C. Sonneville, T. Deschamps, C. Martinet, D. de Ligny, A. Mermet, and B. Champagnon, J. Non-Cryst. Solids. 382, 133 (2013).
- ³⁹M. J. Lipp, Y. Kono, J. Zs, H. Cynn, C. Aracne-Ruddle, C. Park, C. Kenney-Benson, and W. J. Evans, J. Phys.: Condens. Matter 25, 345401 (2013).