Local structure of molten AuGa$_2$ under pressure: Evidence for coordination change and planetary implications

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In situ x-ray diffraction measurements and inverse Monte Carlo simulations of pair distribution functions were used to characterize the local structure of molten AuGa$_2$ up to 16 GPa and 940 K. Our results document systematic changes in liquid structure due to a combination of bond compression and coordination increase. Empirical potential structure refinement shows the first-neighbor coordination of Ga around Au and of Au around Ga to increase from about 8 to 10 and 4 to 5, respectively between 0 and 16 GPa, and the inferred changes in liquid structure can explain the observed melting-point depression of AuGa$_2$ up to 5 GPa. As intermetallic AuGa$_2$ is an analogue for metallic SiO$_2$ at much higher pressures, our results imply that structural changes documented for non-metallic silicate melts below 100 GPa are followed by additional coordination changes in the metallic state at pressures in the 0.2–1 TPa range achieved inside large planets.

The study of densified liquid structures provides fundamental information for understanding thermodynamic phase diagrams, including the effects of distinct crystalline phases on melting at various pressures and temperatures. The intermetallic compound AuGa$_2$ exhibits rich polymorphism in the solid state$^{1,3}$, transforming from 8- to 10-coordinated crystal structures (Ga around Au) at pressures below 30 GPa. We present high-pressure x-ray diffraction measurements in order to determine whether analogous structural changes take place in the liquid. The melting temperature of AuGa$_2$ is known to go through a minimum around 5.5 GPa$^3$, presumably because of competing structural changes in the crystalline and liquid phases, but this interpretation needs verification through measurements on the melt under pressure. Developments in experimental techniques over recent years are providing rich information about liquid structures over a much wider range of pressures than heretofore possible, complementing the vast amount of data available for crystal-structural transformations under pressure$^{4-6}$. Moreover, there is only limited understanding of the local structure of solid amorphous AuGa$_2$, with the available information amounting to the total structure factor obtained from electron diffraction$^7$, which does not provide such detail as pair distribution functions from experiment or modelling (e.g., Monte-Carlo modelling).

Results from Experiments and Modeling

Data were obtained by heating each of the crystalline phases of AuGa$_2$ to temperatures slightly above melting (Table 1), the two-dimensional diffraction patterns recorded by image plate confirming the absence of any crystalline phase after melting$^1$. In spite of our limited Q range, which constrains the simulation of measurements to low magnitudes of the scattering vector Q, we were able to observe distinct features in the diffraction patterns for liquid AuGa$_2$ at pressures at which different sub-solidus crystal structures are stable (Table 2, Fig. 1a).

The most prominent peak (Peak 3, Fig. 1c) in the structure factor S(Q) at temperatures above the melting temperatures of cubic and orthorhombic phases (P ≤ 11 GPa) has a clear shoulder on the low-Q side (Peak 2, Fig. 1c). This is distinct from the result for the monoclinic-to-melt pattern (P = 16 GPa, Fig. 1a), which shows a broad peak at Q = 2.62(5) Å$^{-1}$ attributable to overlapping of the prominent peak and shoulder. Peak 3 for the liquid S(Q) is in the range of 2.87–2.95 Å$^{-1}$ at 11 GPa and below, matching the highest peaks in the diffraction patterns of the
Table 1. Pressures measured during heating for individual experimental runs, with C, O and M representing cubic (fluorite), orthorhombic (cotunnite) and monoclinic ("post-cotunnite") phases. Uncertainties in pressure and temperature are up to ±2 GPa and ±5 K.

| Run #1 | Run #2 | Run #7 | Run #8 | Run #9 |
|--------|--------|--------|--------|--------|
| P(GPa) | T(K)   | Phase  | P(GPa) | T(K)   | Phase  | P(GPa) | T(K)   | Phase  | P(GPa) | T(K)   | Phase  |
| 0      | 295    | C      | 0      | 295    | C      | 0      | 295    | C      | 0      | 295    | C      |
| 1.5    | 295    | C      | 7.7    | 295    | C, O   | 8.8    | 295    | O      | 10.7   | 295    | C, O   | 16.2   | 295    | C, M   |
| 1.5    | 473    | C      | 6.3    | 673    | O, C   | 8      | 395    | O      | 11     | 723    | O, C   | 16.2   | 673    | M      |
| 1.65   | 743    | C      | 6.3    | 723    | O      | 5.5    | 763    | Melt, C| 11     | 803    | Melt, O, C | 16.2   | 773    | M      |
| 1.5    | 763    | C      | 6.3    | 773    | Melt, C| 5.5    | 773    | Melt   | 11     | 863    | Melt   | 16.2   | 930    | Melt   |
| 1.5    | 783    | C      | 6.3    | 783    | Melt   | 11     | 863    | Melt   | 16.2   | 930    | Melt   |
| 1.5    | 803    | Melt   | 11     | 803    | Melt   | 16.2   | 930    | Melt   |

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which is consistent with the calculated average value of $n_{\text{GaAu}}$ that increases from 3.9(4) to 4.9(5) at 16.2 GPa (Fig. 6b). The presence of GaAu$_4$ structural units in the melt at low pressure is also in line with the ratio of second to first neighbor distances observed in $G(r)$, $r_2/r_1 \approx 1.63$ for tetrahedra (Fig. 4)\textsuperscript{8,9}. Integration of the broad peak in the Au-Au pair distribution function ($3 < r < 6$ Å) gives a coordination number $n_{\text{AuAu}} = 12.1(8)$ at ambient conditions and rising to 14.5(9) by 16 GPa, confirming that liquid AuGa$_2$ densifies via collapse of the second- and higher-coordination shells under pressure. We find that the average coordination number calculated over the

Figure 1. (a) Experimental (thick grey lines) and EPSR simulated (thin black lines) total structure factors, $S(Q)$, for liquid AuGa$_2$ at different pressures. (b) Diffraction patterns for crystalline phases at corresponding pressures. (c) Pressure dependence of the liquid $S(Q)$ peaks for $1.5 < Q < 3.5$ Å$^{-1}$, with Peaks 2 and 3 merging to form a broad peak (BP) at 16 GPa.
range $1.0 < r < 3.8\,\text{Å}$, rises from $n_{\text{average}} = 10.8(6)$ at ambient conditions to $13.3(7)$ 16 GPa based on the fits to our experimental data, and this compares well with $n_{\text{average}}$ calculated by integrating the intensity under the peak in $g(r)$, $\rho_0 4\pi r^2 g(r)$ (Fig. 6b and see Supplementary Figure S12).
Ga-Au-Ga and Au-Ga-Au bond-angle distributions were calculated for neighbors separated by less than 3.3 Å. The bond-angle distributions obtained from amorphous-AuGa2 at ambient conditions are characterized by peaks at ∼68° and 108° for Ga-Au-Ga and Au-Ga-Au, close to the ideal values for 8-fold and tetrahedral (109°) coordination and consistent with our estimates for $n_{AuGa}$ and $n_{GaAu}$, respectively (Fig. 7). With increasing pressure, the Au-Ga-Au angle distribution forms a broad peak centered near 86° that accords with fivefold coordination. The main Ga-Au-Ga distribution peak broadens and becomes asymmetric with pressure, indicating coordination change toward a distribution of first-neighbor configurations ranging from 7.9 to 9.4 (Fig. 8).

Silica is the archetypal rock-forming compound making up terrestrial planets, and it is expected to take on the cotunnite structures and to become metallic at multi-Mbar (~200–500 GPa) pressures1,10–16. Therefore, we expect that fluid AuGa2 may serve as an analog of the liquid metallic silicates present at the high pressures relevant to the interiors of large planets, such as super-Earths and other extrasolar planets17. Moreover, it has been found that silicate melts (magmas) undergo structural transformations, with increasing first-neighbor coordination reducing the volume difference between crystal and melt, such that magmas can sink at depth rather than being buoyant as observed at the surface (e.g., causing volcanic eruptions)17,18. These conclusions have been documented through high-pressure spectroscopy and x-ray diffraction on silicate (and analogue) melts and glasses, documenting Si-O coordination increasing from 4 to 6 by about 35 GPa19–24; recent diffraction results show no significant coordination increase beyond 6–6.8 to nearly 200 GPa25, however. Along with flattening of the melting curve, $T_m(P)$, atomistic models predict that the adiabatic temperature gradient (or Grüneisen parameter, $\gamma = (\partial \ln T/\partial \ln \rho)_S$) of the melt exhibits the unusual tendency of increasing over a range of depths due to increasing coordination26,27 ($T$, $P$ and $\rho$ are temperature, pressure and density; subscripts $m$ and $S$ refer to melting and constant entropy).

Our results provide evidence for pressure-induced coordination change in intermetallic AuGa3, a potential analogue for the liquid metallic state of SiO2 that is stable at pressure relevant to large planetary interiors. Thus, based on our measurements we expect that the Si–O coordination in silicate melts increases beyond the 4- to 6-fold range documented by experiments to date up to 100–200 GPa, and toward 10-fold at pressures above 500 GPa where the cotunnite phase of SiO2 is predicted to be stable. Such changes in liquid structure are expected to affect planetary evolution by influencing the buoyancy of magmas relative to coexisting crystals over specific depth ranges within a planet, with element partitioning between liquid and crystals potentially determining whether melts sink or rise, and the Grüneisen parameter exhibiting anomalous pressure dependencies as at lower pressures.

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### Table 2. Pressures, temperatures and initial atomic number densities used for EPSR simulations. "Amorphous (glass) state at ambient conditions: data from literature".

| P (GPa) | T(K)  | Crystal phase-to-melt       | Au Coordination ($n_{AuGa}$) | Atomic number density (atoms/Å³) |
|--------|-------|-----------------------------|-------------------------------|---------------------------------|
| 0      | 300   | Cubic fluorite-type         | 8                             | 0.0535*                         |
| 1.5    | 803   | Cubic fluorite-type         | 8                             | 0.0547                          |
| 6.3    | 823   | Orthorhombic+Cubic          | 8–9                           | 0.0577                          |
| 5.5    | 863   | Orthorhombic cotunnite      | 9                             | 0.0571                          |
| 11     | 863   | Orthorhombic cotunnite      | 9                             | 0.0595                          |
| 16.2   | 938   | Monoclinic "post-cotunnite"| ~10                           | 0.0615                          |

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Figure 4. Positions of the first peak in the reduced pair distribution functions, $G(r)$, for liquid AuGa2 (squares) and ratio of the second to first peak positions (circles). The dashed lines indicate the ideal ratio determined for a simple close-packed hard sphere-like structures ($r_2/r_1 \approx 1.91$) and for an ideal tetrahedral structural unit ($r_2/r_1 \approx 1.63$). The errors in peak positions are in the range of ±0.002–0.018, smaller than the corresponding symbols.
Methods

Experimental study. AuGa₂ was prepared by arc melting the elements under an Ar atmosphere, and x-ray diffraction confirms the expected cubic fluorite-type structure (Fm3m) with lattice parameter, \(a = 6.079(3) \text{ Å}\) \(^{28}\). We used a resistively heated diamond-anvil cell (DAC) driven by a gas membrane for the present experiments \(^{29}\). A 10 × 10 \(\mu\text{m}\) beam of 25 keV energy (0.4959 Å wavelength) x-rays, as selected by a Si(111) double-crystal monochromator at the Advanced Light Source beamline 12.2.2, was used to collect diffraction patterns; the beam was focused at the sample position \(^{30}\). We used BN backing plates with different opening angles on the detector side, which allowed diffraction data to be collected up to a maximum scattering vector-magnitude of \(Q = 7 \text{ Å}^{-1}\), corresponding to a resolution in radial distribution functions \(\Delta r \sim 0.740 (\pm 0.045) \text{ Å}\). Diffraction patterns were obtained using a Mar345 image plate located 290.0 (\pm 0.1) mm from the sample, and processed with fit2d and Celref \(^{31,32}\). On-line ruby (Al₂O₃:Cr³⁺) and samarium-doped strontium tetra-borate (SrB₄O₇:Sm²⁺) fluorescence were used to determine pressure of the hot sample (stimulated with an in-line 200 mW blue diode laser to increase the photon counts at high temperatures). Temperature was measured to an accuracy of \(\pm 5 \text{ K}\) up to 900 K, using a K-type thermocouple next to the diamond culet \(^{3,29}\). Rhenium was the gasket material, and liquefied argon served as the pressure-transmitting medium \(^{3}\).

For each of our experiments, the sample was taken to the desired pressure and then put through a heating and cooling cycle; we observed consistent pressure drifts during each cycle, caused by thermal expansion of the diamond-cell components (pressure-temperature paths for five runs are given in Table 1). Complete melting of AuGa₂ is identified by loss of long-range order, indicated by disappearance of x-ray diffraction peaks of the crystalline phase and a simultaneous increase in diffuse scattering over the entire 2\(\theta\) range (raw melt data collected by heating various AuGa₂ phases are shown in Supplementary Figs S1–S5) \(^{3}\). A new sample was reloaded after each thermal cycle, and diffraction patterns from melting various AuGa₂ phases are illustrated in Fig. 1a. The experimental melt patterns shown in Fig. 1a were collected separately on a region free of gasket peaks, with longer exposure time in order to get good peak intensity relative to background.

EPSR method to refine 3D structural model. McGreevy \(^{33}\) reviews a wide range of issues relating to the inversion of diffraction data to derive real-space functions. Although emphasizing reverse Monte Carlo methods, McGreevy also discusses empirical structure refinement (EPSR), and Soper \(^{34}\) provides further details. We use the EPSR method to fit and extrapolate to high \(Q\) the total structure factor \(S(Q)\) derived from each diffraction pattern (Fig. 1a), using 1000 Au and 2000 Ga atoms in the simulation box at conditions summarized in Table 2. The \(S(Q)\) data are then Fourier transformed to get radial distribution functions (see Supplementary Figure S6a). Application of EPSR requires that the sample density is known, which makes characterizing the liquid structures challenging. The density of molten AuGa₂ was determined using two different methods: (i) from the slope of the reduced pair distribution functions, \(G(r)\), below 2.2 Å (see Supplementary Figure S6b); and (ii) from experimental measurements of the unit-cell volumes of the crystalline phases just below the melting temperature (Supplementary Figure S6c). The former includes truncation errors, so here we present results based

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**Figure 5.** Au-Au, Au-Ga, and Ga-Ga partial pair distribution functions calculated from the EPSR simulations for (a) amorphous AuGa₂ at \(P = 0\) and \(T = 300\) K, and (b, c, d) liquid AuGa₂ under pressure.

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on using the latter method (Table 2). Storm \textit{et al.}\textsuperscript{35} have estimated the volume changes occurring on melting of AuGa\textsubscript{2} by making use of low-pressure \(dT/dP\) data, and evaluated entropies of fusion based on the assumption that the addition of the entropies of fusion for the elements along with the entropy of mixing gives a reasonable estimate for the entropy of fusion of the compound. The decrease in volume on melting of AuGa\textsubscript{2} is estimated to be \(0.5 \text{ cc/mole}\). This results in approximately \(\leq 1\%\) change in volume on melting up to about 10 GPa, and justifies the use of crystalline-phase density just before melting to estimate the liquid density. Atomic number densities calculated using the two methods are compared in Supplementary Table S1.

The Lennard-Jones potential-well depth and range for Au (Ga) were set to 0.1632 (0.1750) kJ/mol and 2.93 (1.60) Å, with initial parameters perturbed until we obtained a satisfactory fit to the diffraction data. Minimum approach distances of 2.77, 2.30 and 2.70 Å for, respectively, Au-Au, Au-Ga and Ga-Ga pairs are calculated using atomic radii of Au and Ga, and served as constraints in carrying out Monte Carlo simulations of the experimental S(Q). Corrections for background and Compton scattering, as well as normalization by the atomic form factors (Supplementary Figure S7) are applied.

**Table 3.** The details of integrating procedure at coordination numbers calculation. *\(n_{\text{avg}} (\text{calculated}) = C_{\text{Au}} [n_{\text{AuGa}} + n_{\text{AuAu}}] + C_{\text{Ga}} [n_{\text{GaAu}} + n_{\text{GaGa}}]\), \(C_{\text{Au}} \approx 0.33\) (Atomic concentration of Au) and \(C_{\text{Ga}} \approx 0.67\) (Atomic concentration of Ga). **See Supplementary Figure S12.

**Figure 6.** (a) Pressure dependence of Au-Ga (nearest-neighbor) and Ga-Ga bond distances determined from partial pair distribution functions (Fig. 5). (b) Coordination numbers around Au- and Ga-atoms, \(n_{\text{AuGa}}\), \(n_{\text{GaAu}}\), \(n_{\text{AuAu}}\) and \(n_{\text{GaGa}}\) and experimental and calculated average coordination numbers.
used to obtain the structure factor from the diffraction data\textsuperscript{36}. The EPSR simulations show good agreement with zero-pressure diffraction data for amorphous AuGa\textsubscript{2} (Supplementary Figure S8).

Our fits to experimental $S(Q)$ yield chi-square values in the range $\chi^2 = 0.002$–$0.016$ (Supplementary Figure S9), with convergence in $\sim$2600 iterations and best fits achieved after $\sim$8000 iterations of the EPSR steps.

**Figure 7.** Au-Ga-Au (a) and Ga-Au-Ga (b) bond-angle distributions as functions of pressure, and structural motifs at zero pressure (c,d) captured from EPSR.

**Figure 8.** Schematic representation of densification mechanism and corresponding structural moieties in liquid AuGa\textsubscript{2}. Amorphous solid (a) includes GaAu\textsubscript{4} tetrahedral units connected to each other via Au-Au bonding and to AuGa\textsubscript{8} polyhedral units via Au-Ga bonding. Densification is dominated by large inward shifting of the second- and higher coordination shells under pressure (b). Melt-AuGa\textsubscript{2}, obtained at highest pressure shows higher order polyhedral units, 5 and 9 coordination around Ga and Au atoms, respectively (c).
(Supplementary Figure S10). There remain issues about the reliability of the simulations, but EPSR uses reasonable assumptions to produce close fits to the experimental diffraction data, and the results can be Fourier transformed to obtain the radial distribution functions. The derived structural information (e.g., coordination numbers and bond angle distributions) provides one means of assessing the quality of the results.

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Author Contributions
B.K.G., S.V.R. and R.J. devised the project, B.K.G. and S.V.R. performed the experiments. B.K. and S.V.R. analyzed the experimental data. B.K. carried out EPSR analysis of diffraction data. All authors contributed in writing the manuscript.
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