

## Structural Complexity in Gallium under High Pressure: Relation to Alkali Elements

O. Degtyareva,\* M. I. McMahon, D. R. Allan, and R. J. Nelmes

*School of Physics and Centre for Science at Extreme Conditions, The University of Edinburgh,  
Mayfield Road, Edinburgh, EH9 3JZ, United Kingdom*

(Received 8 April 2004; published 11 November 2004; publisher error corrected 6 December 2004)

Ga-II, the stable phase of Ga between 2 and 10 GPa at room temperature, is shown to have a complex 104-atom orthorhombic structure. A new phase, Ga-V, is found between 10 and 14 GPa, with a rhombohedral  $hR6$  structure. Ga-II has a modulated layer structure like those recently reported for Rb-III and Cs-III, with similar 8- and 10-atom  $a$ - $b$  layers stacked along the  $c$  axis in the sequence 8-10-8-8-10-8-8-10-8-8-10-8. The  $cI16$  structure of Li and Na can be understood as a stacking of very similar 8-atom layers. It is suggested that a Hume-Rothery mechanism contributes to the occurrence of these complex structures in such different metals.

DOI: 10.1103/PhysRevLett.93.205502

PACS numbers: 61.50.Ks, 62.50.+p

Among the elements, gallium exhibits unusual complexity in its crystal structures, phase transitions, and phase diagram [1]. The ambient pressure (AP) phase, Ga-I, has a unique orthorhombic crystal structure with eight atoms in the unit cell [1], Pearson notation  $oC8$ , that has a partially covalent bonding character. Gallium has an unusually low melting temperature of 303 K at AP [it melts at room temperature (RT) under a pressure of only 0.5 GPa], and the liquid phase is known to be anomalous [2]. On further compression, liquid Ga crystallizes at 2 GPa and RT. The result is not the stable Ga-II phase, but metastable Ga-III [3,4], which has a simple body-centered-tetragonal  $tI2$  structure [5,6], like that of the neighboring group-III element indium at AP. Ga-II is obtained if Ga-I is instead compressed through the solid-solid transition below the minimum in the melting temperature at 273 K [3,4], or if metastable Ga-III is supercooled down to 200 K at pressures around 3 GPa [6]. In this Letter, we show that the true structure of Ga-II is a remarkably complex orthorhombic structure with 104 atoms in the unit cell, closely related to complex structures recently reported for alkali elements [7–10]. We suggest that this surprising relationship between elements with very different electronic configurations may be understood in terms of a Hume-Rothery mechanism that opens a pseudogap in the electronic density of states at the Fermi level. We also report the identification of a new phase, Ga-V, stable between Ga-II and Ga-III.

The structure of Ga-II has previously been reported to be body-centered cubic with only 12 atoms in the unit cell, from single-crystal diffraction data collected at 313 K and 2.6 GPa [6]. But subsequent powder diffraction studies found a series of complex diffraction patterns on pressure decrease from Ga-III (the stable phase above 15 GPa [11]) to Ga-II, none of which could be explained by the  $cI12$  structure alone [13]. Thus, the  $cI12$  structure proposed for Ga-II in Ref. [6] was not confirmed, and there was possible evidence for an additional phase.

Theoretical calculations of the electronic structure of Ga-II (in the  $cI12$  structure) and Ga-III indicate a nearly free electron behavior, in contrast to the partially covalent character of Ga-I [14]. Ga is superconducting at AP with a transition temperature  $T_c$  of 0.85 K that rises significantly (to 6.38 K) at the transition to Ga-II [15]. This adds further interest to determining the nature of Ga-II.

We used a sample of 99.999% purity from Strem Chemicals to collect x-ray angle-dispersive powder diffraction data ( $\lambda = 0.4654 \text{ \AA}$ ) and single-crystal data ( $\lambda = 0.4765 \text{ \AA}$ ) at the Synchrotron Radiation Source, Daresbury Laboratory, and on laboratory facilities. The experimental procedures were as reported recently in Refs. [7,8].

On pressure increase at RT, our data showed Ga transforming from the  $oC8$  structure of Ga-I [1] into the liquid phase, and then recrystallizing into a single-crystal of Ga-III. The  $oC8$  powder patterns were entirely free from contaminant. We collected single-crystal data from the Ga-III sample and confirmed the  $tI2$  structure [5,6], with lattice parameters of  $a = 2.798(1) \text{ \AA}$  and  $c = 4.419(2) \text{ \AA}$  at 4.0(1) GPa. On further slow pressure increase, we found a phase transition at 10.5(5) GPa into Ga-V, a previously unknown phase, with a textured diffraction pattern like that reported at 15.2 GPa in Ref. [13]. Above 14.0(5) GPa a further phase appeared with a smooth powder pattern. This could be fitted to the  $tI2$  structure (Fig. 1), showing that Ga-III reappeared at higher pressure at RT, as also reported in Ref. [13].

At 13.5(2) GPa on pressure decrease, Ga-III transformed back to Ga-V, which then transformed to another phase with a complex and highly textured pattern at 10.0(2) GPa. This phase, preliminarily assigned as Ga-II, was retained on pressure decrease down to the melting pressure of 2 GPa. Figure 1 shows powder patterns obtained on pressure decrease, and they are essentially the same as those reported in Fig. 1 of Ref. [13]. (Our pressures are a little lower than those reported in Ref. [13].)

The integrated profile of the Ga-V phase at 12.2 GPa was indexed on the basis of a cell with lattice parameters  $a = 5.0588 \text{ \AA}$  and  $\alpha = 110.78^\circ$ . The atomic volume of  $15.76 \text{ \AA}^3$  at 12.2 GPa and RT, estimated from the metastable Ga-III phase at these conditions, gave 6 atoms in this cell (Pearson notation  $hR6$ ). Systematic absences in the observed reflections were consistent with space groups  $R3c$  and  $R\bar{3}c$ . But Rietveld refinement yielded a unique solution with  $R\bar{3}c$ , and atoms in the  $(6e)$  position  $(x, \frac{1}{2} - x, \frac{1}{4})$  with  $x = 0.437(2)$ . The final fit to this structure is shown in inset (i) of Fig. 1.

By contrast, the strongly recrystallized nature of Ga-II and the apparent complexity of its crystal structure prevented solution of the structure from powder diffraction data. Instead, by cooling Ga-III down to 200 K at 3 GPa as in Ref. [6], we obtained a single-crystal sample of Ga-II that gave sharp diffraction reflections with FWHM of  $\omega = 0.5^\circ$ . The 2D diffraction images revealed groups of closely spaced reflections, indicating a large lattice repeat in one direction. Indexing gave a  $C$ -face centered orthorhombic unit cell with lattice parameters  $a = 5.976 \text{ \AA}$ ,

$b = 8.576 \text{ \AA}$ , and  $c = 35.758 \text{ \AA}$  at 2.8(1) GPa and RT. A total of 919 reflections were collected to a resolution of  $0.6 \text{ \AA}$ , and averaged to give 418 unique reflections. Systematic absences determined the space group uniquely as  $C222_1$ .

The *ab initio* structure solution using direct methods (see Refs. [7,8]) yielded a structure with 104 atoms occupying 14 independent sites. The final fit gave a goodness of fit  $\chi^2$  of 1.170, and the refined atomic coordinates and lattice parameters are in Table I. The atomic volume of  $17.62(3) \text{ \AA}^3$  is the same within error as for Ga-III at the same pressure. Each atom is surrounded by ten others at distances between 2.65 and  $3.3 \text{ \AA}$  (Table I).

How is this complex solution for Ga-II to be reconciled with the much simpler  $cI12$  structure obtained by Bosio [6] using a sample obtained by following the same P-T path? Our data show diffraction intensities of the  $oC104$  structure to be strongly modulated along the  $l$  axis, and clusters of strong reflections can be “indexed” on a body-centered monoclinic cell with  $a = 5.951 \text{ \AA}$ ,  $b = 5.939 \text{ \AA}$ ,  $c = 5.944 \text{ \AA}$ , and  $\alpha = 91.7^\circ$  at 2.8 GPa, very close to the body-centered-cubic cell proposed by Bosio [6] with  $a = 5.951 \text{ \AA}$  at 2.6 GPa. And the apparent systematic absences in this pseudoindexing of the clusters are as reported by Bosio [6]. The data collection techniques available to Bosio would almost certainly not have detected the weak reflections between clusters, nor resolved the closely spaced strong reflections in the clusters. It is thus very probable that Bosio obtained the same complex

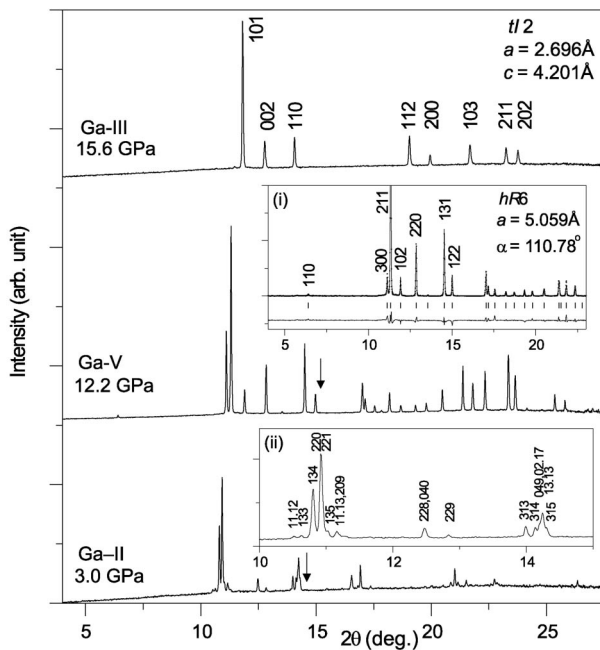


FIG. 1. Integrated angle-dispersive powder diffraction profiles of Ga on pressure decrease from 16 GPa.  $hkl$  indices are shown for Ga-III at 15.6 GPa. Arrows in the Ga-V and Ga-II profiles mark the position of  $2k_F$  (see text). Inset (i) shows a Rietveld refinement fit of Ga-V to the  $hR6$  structure at 12.2 GPa; some  $hkl$  indices are given. Tick marks below the profile indicate peak positions of the  $hR6$  structure. Below the tick marks is the difference between the observed and calculated profiles. Inset (ii) shows an expanded region of the Ga-II pattern at 3.0 GPa indexed on the  $oC104$  unit cell with lattice parameters  $a = 5.966 \text{ \AA}$ ,  $b = 8.557 \text{ \AA}$ , and  $c = 35.615 \text{ \AA}$ . The notation  $hkl$  is used for  $l \geq 10$ .

TABLE I. Refined atomic coordinates of Ga-II ( $oC104$ ) at 2.8(1) GPa and RT in space group  $C222_1$ . The refined lattice parameters are  $a = 5.976(1) \text{ \AA}$ ,  $b = 8.576(1) \text{ \AA}$ ,  $c = 35.758(3) \text{ \AA}$ . The number of nearest-neighbor (nn) distances is given in ranges (i) 2.65–2.7  $\text{\AA}$ , (ii) 2.7–3.1  $\text{\AA}$ , and (iii) 3.1–3.3  $\text{\AA}$ . These ranges are selected for comparison with Cs-III and Rb-III [7,8], and the upper bound of 3.3  $\text{\AA}$  is set at the first minimum in the distribution of contact distances.

Site	Atomic coordinates ( $\times 10^4$ )	No. of nn distances					
		$x$	$y$	$z$	(i)	(ii)	(iii)
Ga1	4b	5000	1802(9)	2500	2	8	0
Ga2	8c	6956(9)	4684(7)	2716(2)	2	8	0
Ga3	8c	5804(9)	7858(8)	2861(2)	0	10	0
Ga4	8c	2772(9)	5622(7)	3081(2)	0	10	0
Ga5	8c	-341(7)	7809(6)	3292(2)	1	9	0
Ga6	8c	8482(8)	4567(6)	3430(2)	1	9	0
Ga7	8c	5632(9)	6919(6)	3666(2)	0	10	0
Ga8	8c	2324(8)	4838(7)	3851(2)	0	9	1
Ga9	8c	6129(10)	2914(7)	4003(2)	1	9	0
Ga10	8c	8276(10)	5660(7)	4250(2)	1	8	1
Ga11	8c	-30(9)	2613(7)	4435(2)	1	7	2
Ga12	4a	2460(9)	0	5000	0	8	2
Ga13	8c	1052(10)	3090(7)	5170(2)	0	8	2
Ga14	8c	3574(8)	5518(7)	5409(2)	1	8	1

phase. Furthermore, powder diffraction patterns obtained on pressure decrease match those of Ref. [13] and can be fully indexed on the  $oC104$  unit cell as shown in inset (ii) of Fig. 1, thus accounting for the discrepancies from Bosio's  $cI12$  structure previously noted [13].

The structures of Ga-V and Ga-II are shown in Fig. 2, and compared with the  $cI12$  structure proposed by Bosio [6]. It is intriguing that the  $hR6$  structure is so similar to the  $cI12$  structure. Furthermore, the outlined volumes in the drawings of the  $cI12$  and  $oC104$  structures show a similarity between them too. The  $oC104$  structure cannot be constructed as a superstructure of  $cI12$ , and the relationship appears to be accidental—a similarity of spatial arrangement is likely in fitting the strong reflections of the true structure. Nevertheless, the relationship of  $cI12$  to both Ga-V and Ga-II is clearly interesting and will be explored further in a separate publication, along with a more detailed account of the Ga-V structure and the revised Ga phase diagram following this work.

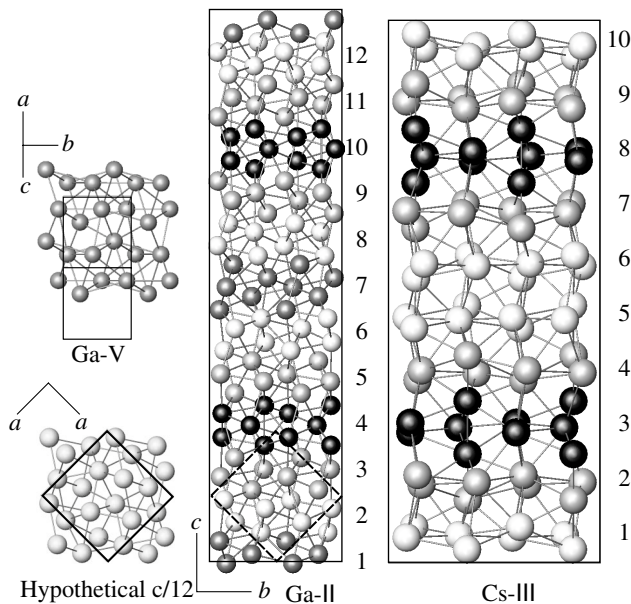


FIG. 2. Crystal structures of Ga-II at 2.8 GPa, Ga-V at 12.2 GPa, and Cs-III at 4.3 GPa [7] shown on the same scale. The Ga-V structure and axes are viewed along a  $[101]$  direction to aid comparison with the hypothetical  $cI12$  structure. The latter is shown with the same density as Ga-II, and corresponding volumes are marked in both of these structures. Cs-III and Ga-II are viewed along the  $a$  axis of the  $C222_1$  unit cell. The Ga-II cell origin is at  $x = 1/4$ ,  $y = -1/8$  relative to the standard space group origin, to allow direct comparison. The 8- and 10-atom  $a$ - $b$  layers in the two structures are numbered. Nonequivalent 8-atom layers are in two different shades of light gray. The 10-atom layers common to Ga-II and Cs-III are shown in black. The 10-atom layers 1 and 7, peculiar to Ga-II, are shown in dark gray. Contact distances up to 2.9 Å for Ga-V, 3.3 Å for Ga-II and  $cI12$ , and 4.7 Å for Cs-III are shown as solid lines.

Figures 2 and 3 display the key structural findings of this study that (i) the structure of Ga-II is strikingly related to the layer-stacking structures of Cs-III (shown here) and Rb-III, and (ii) the recently discovered  $cI16$  structures of Li and Na are also part of this family. The Cs-III and Rb-III structures have the same  $C222_1$  space group as Ga-II, and have been interpreted as comprising a sequence of 8- and 10-atom  $a$ - $b$  layers stacked along the  $c$  axis [8]. Ga-II can be understood in terms of very similar 8- and 10-atom layers, but with an additional set of 10-atom layers (such as 7 in Figs. 2 and 3). Figure 3 shows that the 10-atom layer 7 of Ga-II has essentially the same arrangement as its Cs-III-like layer 3, but rotated 90° around the  $c$  axis and then compressed along  $a$  and stretched along  $b$ .

The Ga-II structure can thus be understood as an 8-10-8-8-10-8-8-10-8-8-10-8-8-10-8 stacking of the same 8- and 10-atom layers as in Cs-III (sequence 8-8-10-8-8-8-8-10-8-8) and Rb-III (sequence 8-10-8-8-10-8). And the high-pressure  $cI16$  structure of Li [9] and Na [10] can be regarded as a simple end member of this series, with Cs-III-like 8-atom layers (only) stacked along a  $[110]$  direction of the  $cI16$  unit cell (Fig. 3). The  $cI16$  structure is a simple distortion of body-centered cubic (bcc) in which each atom is shifted  $\sim 0.05$  in fractional coordinates along one of the bcc  $\langle 111 \rangle$  directions [9]. The 8-atom layers in  $oC84$  Cs-III and  $oC52$  Rb-III have arrangements remarkably close to the same distortion from bcc. The 10-atom layers are similar but more complex and accommodate an additional 2 atoms [8].

Theorists have generally attributed structural changes and complexity under pressure in the heavier alkali metals to the effects of  $s$  to  $d$  transitions in the electronic structure [16]. However, this cannot apply to Li and Na, where an  $s$ - $p$  orbital mixing has been shown for the  $cI16$  structure [9,17], nor to the group-III element Ga which has a very different electronic configuration and valency

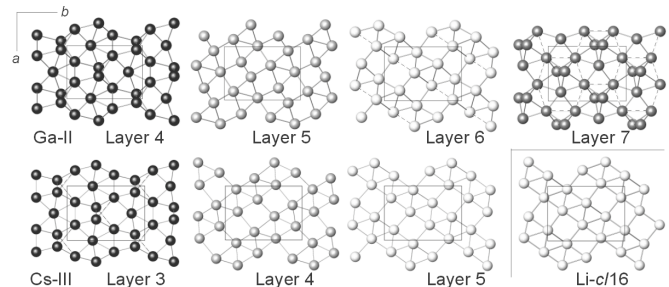


FIG. 3.  $a$ - $b$  layers of Ga-II and Cs-III viewed down the  $c$  axis, and an 8-atom layer of Li- $cI16$  viewed along a  $[110]$  direction (Ref. [9]), are all shown the same size for clarity. Unit cells are marked by solid lines. Origins used and contact distances marked by solid lines are as in Fig. 2 for Ga-II and Cs-III. For Li, contact distances  $< 2.5$  Å are shown. Dashed lines show longer nearest-neighbor distances in the range 3.3–3.6 Å (Ga-II) and 4.7–5.0 Å (Cs-III).

from the alkali elements. Recent calculations of the band structure of Ga [18] show that  $s$ - $p$  mixing is far more likely than any  $s$  to  $d$  transfer in the relevant pressure range. These complex phases in Ga and the alkali metals thus appear to require a different explanation, in terms of a mechanism that can be common to them all.

The stability of the  $cI16$ ,  $oC52$ , and  $oC84$  structures in the alkali elements has recently been analyzed within the Hume-Rothery mechanism [19]. It is proposed that the structural distortions from bcc give rise to new diffraction planes forming a Brillouin zone (BZ) boundary close to the Fermi surface (FS) [19]; interaction between the BZ boundary and the FS can then open a pseudogap and reduce the overall electronic energy. This mechanism is used to account for intermetallic phases [20], complex phases of elemental metals [21], and another type of complex structure, quasicrystals (e.g., Ref. [22]). The additional atoms in the 10-atom layers may play the role of tuning the electron count or density [19]. Figure 1 shows that the BZ-FS picture can indeed also be applied to Ga-II (and also Ga-V), despite a large difference from the alkali metals in the radius of the FS,  $k_F$  [23]. The diffraction patterns of these phases reveal groups of relatively strong diffraction peaks (around  $14.2^\circ$  for Ga-II and  $14.8^\circ$  for Ga-V) with wave vectors close to  $2k_F$ , as required to define a BZ boundary close to  $k_F$ . The resulting (extended) BZs for the Ga structures are nearly filled ( $\sim 90\%$ ), and an increased electronic density of states near the BZ boundaries is expected, similar to the situation in Li- $cI16$  [9,19].  $\gamma$ -brass is a system known to be stabilized by the Hume-Rothery mechanism, and the zone filling is  $\sim 90\%$  in that case also [20].

The Hume-Rothery mechanism also provides a plausible explanation for known correlations between the appearance of these complex structures and changes in conductivity. Increases in resistivity have been reported at the transitions to Ga-II [4], Cs-III [24], and Li- $cI16$  [25], and a pseudogap arising from a BZ-FS interaction would give a reduced density of states at the Fermi level, as shown for Li in Ref. [9]. The known increases in superconducting  $T_c$  for Ga-II [15] (see above) and Li- $cI16$  [26] may be correlated with the increase in the density of states just below the Fermi level implied by the proposed pseudogap. However, calculations of electron-phonon coupling in these complex structures are needed to test this possibility.

It is interesting to note that theoretical calculations show the Hume-Rothery effect to be enhanced under pressure [27], essentially because the electronic kinetic energy contribution increases more rapidly with increasing density (pressure) than do the electrostatic terms. These complex structures may thus be an intrinsically high-pressure phenomenon in the elemental metals.

This work was supported by grants from EPSRC, funding from CCLRC, and facilities provided by

Daresbury Laboratory. M. I. M. acknowledges support from the Royal Society. We thank V. Degtyareva for valuable discussions, and M. Roberts and S. Teat of Daresbury Laboratory for setting up the 9.1 and 9.8 beamlines.

---

\*Present address: Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road N.W., Washington, DC 20015, USA.

- [1] J. Donohue, *The Structure of the Elements* (Robert E. Krieger Publishing Company, Malabar, FL, 1982).
- [2] S. Tsay and S. Wang, Phys. Rev. B **50**, 108 (1994), and references therein.
- [3] P.W. Bridgman, Phys. Rev. **48**, 893 (1935).
- [4] A. Jayaraman *et al.*, J. Phys. Chem. Solids **24**, 7 (1963).
- [5] C. E. Weir, G. J. Piermarini, and S. Block, J. Chem. Phys. **54**, 2768 (1971).
- [6] L. Bosio, J. Chem. Phys. **68**, 1221 (1978).
- [7] M. I. McMahon, R. J. Nelmes, and S. Rekhi, Phys. Rev. Lett. **87**, 255502 (2001).
- [8] R. J. Nelmes *et al.*, Phys. Rev. Lett. **88**, 155503 (2002).
- [9] M. Hanfland *et al.*, Nature (London) **408**, 174 (2000).
- [10] M. Hanfland *et al.*, ESRF Annual report, 2000.
- [11] Ga-III has been shown to be stable up to 120 GPa where it transforms to a Ga-IV phase with an fcc structure [12].
- [12] K. Takemura, K. Kobayashi, and M. Arai, Phys. Rev. B **58**, 2482 (1998).
- [13] O. Schulte and W. B. Holzapfel, Phys. Rev. B **55**, 8122 (1997).
- [14] M. Bernasconi, G. L. Chiarotti, and E. Tosatti, Phys. Rev. B **52**, 9988 (1995).
- [15] W. Buckel and W. Gey, Z. Phys. **176**, 336 (1963).
- [16] G. J. Ackland and S. K. Reed, Phys. Rev. B **67**, 174108 (2003), and references therein.
- [17] N. E. Christensen and D. L. Novikov, Solid State Commun. **119**, 477 (2001).
- [18] S. I. Simak *et al.*, Phys. Rev. Lett. **85**, 142 (2000).
- [19] V. F. Degtyareva, in *High-Pressure Crystallography*, edited by A. Katrusiak and P. McMillan (Kluwer Academic Publishers, Dordrecht, 2004), pp. 447–456; G. J. Ackland and I. D. Macleod, New J. Phys. (to be published).
- [20] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936).
- [21] N. W. Ashcroft, Phys. Rev. B **39**, 10552 (1989).
- [22] A. P. Smith and N. W. Ashcroft, Phys. Rev. Lett. **59**, 1365 (1987); A.-P. Tsai, J. Non-Cryst. Solids **334–335**, 317 (2004).
- [23] The Fermi radius is  $k_F = (3\pi^2 z/V_{at})^{1/3}$ , where  $z$  is the number of valence electrons ( $z = 3$  for Ga), and  $V_{at}$  is the atomic volume determined from crystal structure.
- [24] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 165 (1952).
- [25] V. E. Fortov *et al.*, JETP Lett. **70**, 628 (1999).
- [26] K. Shimizu *et al.*, Nature (London) **419**, 597 (2002).
- [27] N. W. Ashcroft (private communication).