Evidence for superconductivity in Rb metal above 55 GPa pressure

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The only alkali metal known to be superconducting at ambient pressure is Li at 0.4 mK. Under 30 GPa pressure T_c for Li rises to 14 K. In addition, nearly 50 years ago the heavy alkali metal Cs was reported to become superconducting near 1.3 K at 12 GPa. In the present experiment the superconductivity of Cs under pressure is confirmed. In addition, strong evidence is presented in electrical resistivity measurements that neighboring Rb also becomes superconducting near 2 K at 55 GPa as it enters the $oC16$ phase, as for Cs, where T_c decreases under the application of pressure. It would seem likely that under the right temperature/pressure conditions all alkali metals, including metallic hydrogen, will join the ranks of the superconducting elements. With the addition of Rb, 55 of the 92 naturally occurring elements are superconducting at ambient or high pressure.

At first glance the alkali metals would appear to be rather mundane compared to the other elemental solids in the periodic table: None of the alkali metals are magnetic and only one, Li, is known to be superconducting at ambient pressure, but then only at the exceedingly low temperature of $T_c \simeq 0.4$ mK [1]. Their simple bcc structure and free-electron character make the alkali metals ideal simple metals with very nearly spherical Fermi surfaces. As for all monovalent metals, their low electronic density of states favors weak electron-phonon interactions that are insufficient, except for Li, to support superconductivity [2].

The large atomic volume and very high compressibility of all alkali metals lead to significant changes in their properties under the application of very high pressures. The atomic volume of Cs metal shrinks fivefold under $\sim$50 GPa [3]. As a result, the once free-electron alkali metals with a cubic bcc crystal structure become *electrides* under sufficient pressure where the conduction electrons no longer surround each cation but are forced into interstitial lattice sites [4], becoming *de facto* anions [5]. In addition, the marked pressure-induced changes in the character of the conduction electrons through s-p transfer in Li and Na and s-d transfer in K, Rb, and Cs are believed to destabilize the highly symmetric low-pressure structures (bcc, fcc) and favor complex, lower-symmetry structures [6]. Another result of the marked change in conduction electron character is that the superconducting transition temperature of Li soars from 0.4 mK at ambient pressure to 14 K at 30 GPa [7], an increase of over four orders of magnitude.

Superconductivity in Cs near 1.3 K was reported many years ago by Wittig [8] for pressures near 12 GPa, close to the pressure where Cs enters the orthorhombic $oC16$ phase [9]. In the Supplemental Material [10] very recent experiments are presented that confirm these early results. It would seem likely that all alkali metals will become superconducting under pressure, yet no superconductivity has been found for the following: Na in the pressure/temperature ranges to 58 GPa above 4 K [2]; K to 17 GPa above 1.5 K or to 44 GPa above 4 K [2], as well as to 94 GPa above 1.35 K [13]; and Rb to

21 GPa above 50 mK [14]. Schwarz *et al.* [15] have suggested that a search for Rb should be carried out for pressures of 50 GPa and above since this is the pressure where Rb takes on the same $oC16$ phase where Cs becomes superconducting.

In the present electrical resistivity studies on Rb the pressure range of previous work has been extended to $\sim$80 GPa for temperatures above 1.3 K. Strong evidence is given for the appearance of superconductivity in Rb near 2 K following a sluggish phase transition at 50 GPa from the tetragonal $tI4$ to the orthorhombic $oC16$ phase. Rb thus becomes the 55th elemental superconductor in the periodic table.

Polycrystalline Cs (99.98 % pure) and Rb (99.75 % pure) samples were obtained in sealed glass ampoules from Alfa Aesar. A diamond anvil cell (DAC) made of conventional and binary CuBe [16] was used to generate pressures to $\sim$80 GPa between two opposed diamond anvils (1/6 carat, type Ia) with 0.5-mm-diam culets. The force applied to the anvils was generated by a stainless-steel diaphragm filled with He gas [17]. The Re gasket (250 μm thick) was preindented to 80 μm and a 250-μm-diam hole drilled through the center of the preindentation area. A cubic boron nitride (cBN)-epoxy insulation layer was compressed onto the surface of the gasket (see Fig. 1). Four Pt strips (4 μm thick) were then placed on the insulation layer, acting as electrical leads for the four-point resistivity measurement. Further details are published elsewhere [18,19].

Whereas a small, thin lanthanide sample was normally placed on top of the four Pt strips (see Fig. 1 in Ref. [19]), the extreme softness of the alkali metals led to large sample extrusion out of the cell, necessitating shaping a bowl in the cBN-epoxy cell to contain the alkali metals, as illustrated in Fig. 1. Because of their extreme air sensitivity, the Cs and Rb samples were loaded into the bowl-shaped chamber inside a glove box filled with ultrahigh-purity Ar gas.

The DAC was inserted into an Oxford flow cryostat capable of varying temperature from ambient to 1.3 K. Pressure was determined at room temperature using the diamond vibron [20]. With a ruby manometer the pressure can normally be measured *in situ* over the entire temperature range [21].
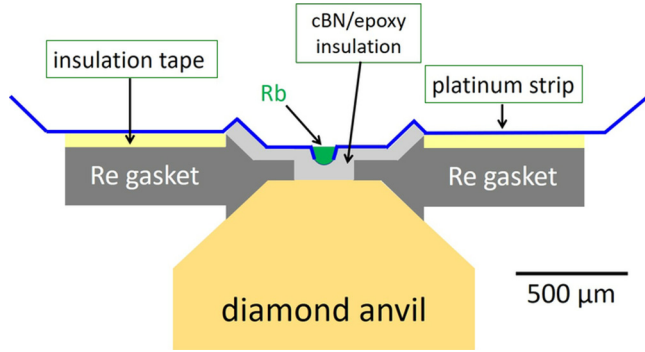
FIG. 1. Schematic drawing of pressure cell with Re gasket used in the present four-point electrical resistivity experiments on pure Cs and Rb. Unlike the standard configuration (see Fig. 1 in Ref. [19]), here a bowl is formed in the central cBN/epoxy section to contain the soft alkali metals. The opposing diamond anvil presses downward from above generating pressures to ∼80 GPa.

Unfortunately, the ruby sphere would normally sink into the soft alkali metal, the $R1$ fluorescence being lost. However, in one experiment to 14 GPa on Cs the ruby fluorescence could be detected to low temperatures, revealing a pressure increase of ∼17% on cooling from 295 to 4 K. This pressure increase
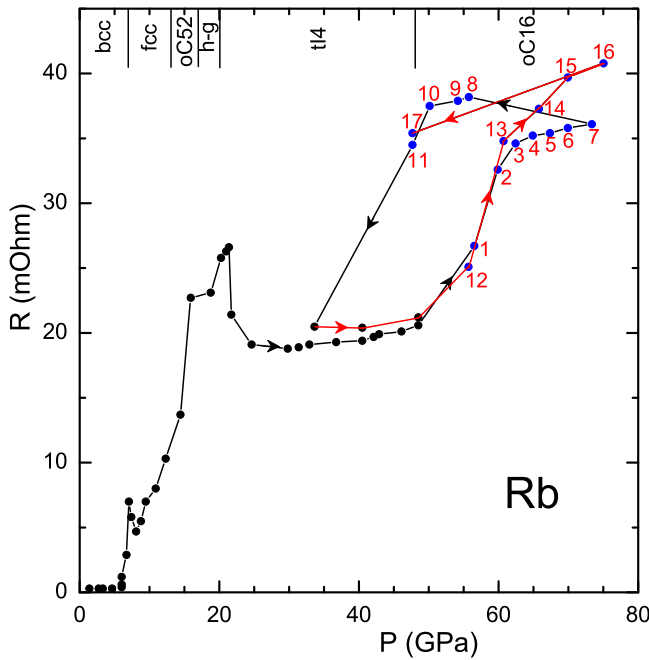

FIG. 2. Dependence of room-temperature resistance of Rb on pressure to 75 GPa. The arrows give the direction of pressure change. Beginning at the lowest pressure, data are taken along the black line to point 7, followed by a pressure decrease to 34 GPa. The red line then tracks a second increase in pressure to point 16, followed by a decrease to point 17. Beginning with data point 1 on the black line, all further data points $R(T)$ were measured between 295 and 1.3 K. For blue data points superconductivity was observed near 2 K; for black data points no evidence for superconductivity was found above 1.3 K. Numbers give the order of measurement for blue data points first on the black line, then on the red line. Crystal structures at the top of graph are from Ref. [22].
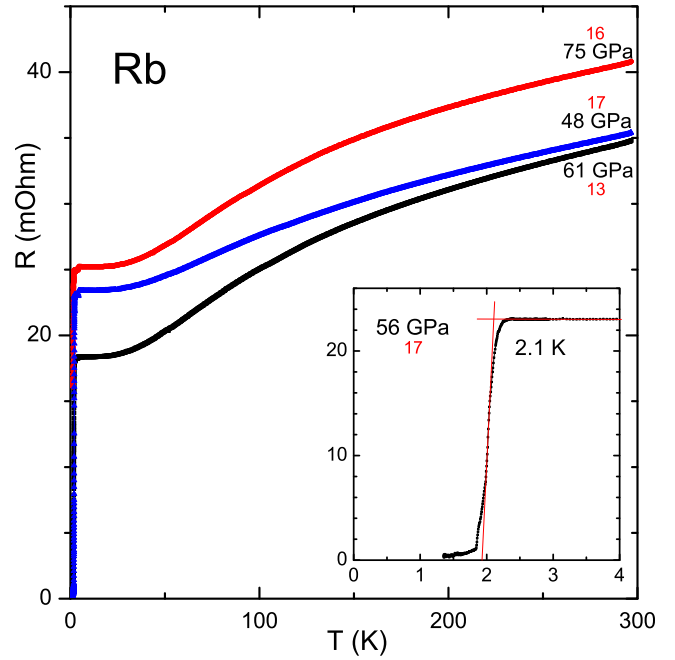

FIG. 3. Resistance of Rb vs temperature at three different pressures where a superconducting transition is seen at low temperature. Red numbers give the order of measurement from Fig. 2. The inset shows a transition at 2.1 K for 56 GPa. The value of the transition temperature is determined by the intersection point of two straight lines.

was used in experiments on both Cs and Rb to estimate the pressure at low temperatures from the measured vibron pressure at ambient temperature.

In Fig. 2 the resistance of Rb at ambient temperature (295 K) is plotted versus both increasing and decreasing pressure. Initially the pressure was slowly increased along the black line to 73 GPa, then decreased to 34 GPa, followed by an increase along the red line to 75 GPa, then decreased to 48 GPa. The many structural phase transitions that occur in pure Rb over this pressure range are shown at the top of the graph [22]. A small peak in $R(P)$ marks the bcc → fcc transition 7 GPa with a much more prominent structure in $R(P)$ for the next transitions. In the tetragonal $tI4$ phase the resistance changes little with pressure, but begins to increase sharply after passing the $tI4 \rightarrow oC16$ phase boundary at 48 GPa. The sizable hysteresis in $R(P)$ reveals the first-order nature of this transition that is reportedly very sluggish at ambient temperature [15]. The $R(P)$ dependence and structural phase diagrams at ambient temperature for Cs bear a marked similarity to those for Rb in Fig. 2 if the differences in the transition pressures are taken into account, as seen in the Supplemental Material [10].

In Fig. 3 the temperature-dependent resistance of Rb is displayed for 61, 75, and 48 GPa, measured in that order, as seen by comparing the order of measurement numbers to those in Fig. 2. At all three pressures a sharp drop in the resistance is observed near 2 K (see the inset in Fig. 3 for 56 GPa), as would be expected for a superconducting transition. As discussed below, it is common in superconducting alkali metals that the resistivity fails to disappear completely
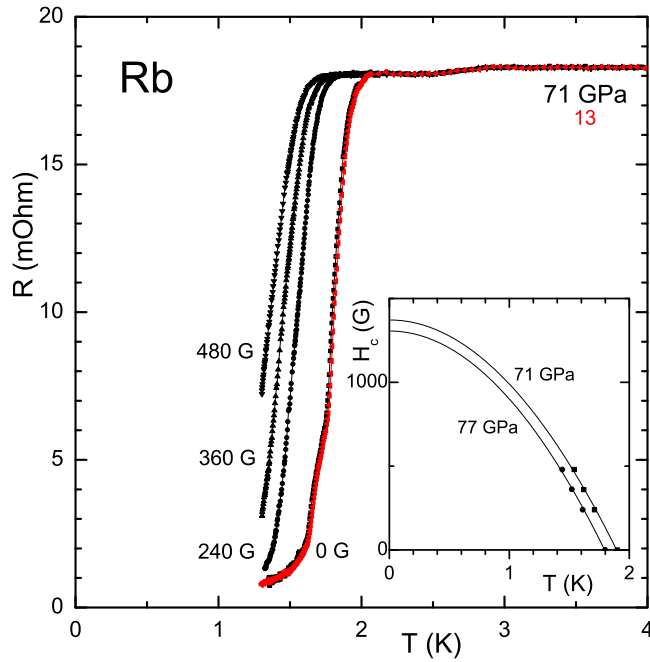
FIG. 4. Resistance Rb vs temperature to 4 K at 71 GPa for four different values of magnetic field 0, 240, 360, and 480 G. The superconducting transition shifts to lower temperatures with increasing magnetic field. The inset shows the dependence of the transition temperature on magnetic field at 71 and 77 GPa pressure. The fit of the data allows an estimate of critical field H_0 at 0 K (see text). The number "13" gives the order of data points from Fig. 2.
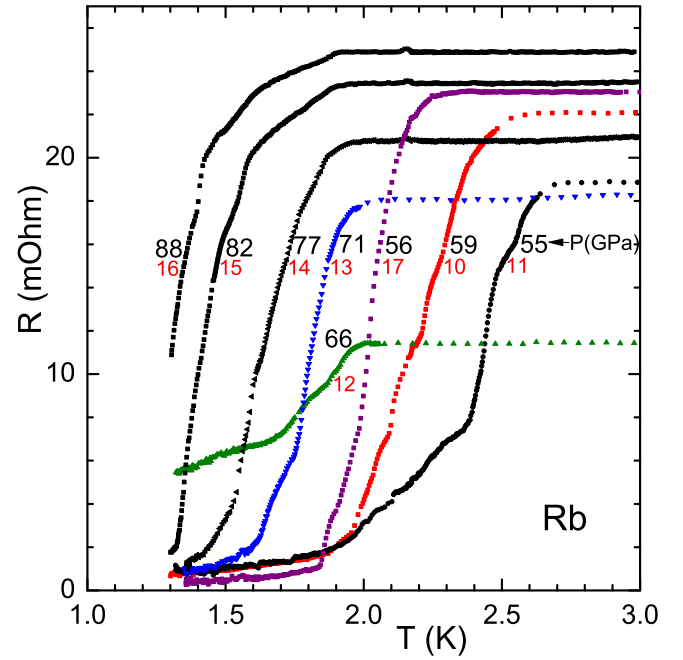

FIG. 5. Resistance of Rb vs temperature to 3 K showing superconducting transitions at various pressures. Black numbers give the value of pressure for each transition. Red numbers give the order of measurement from Fig. 2. The smaller size of the transition at 66 GPa gives evidence the sample is in a mixed phase.

in high-pressure experiments. A marked negative curvature is evident in the temperature dependence of the resistance, a hallmark of transition metals. This is clear evidence for strong d character in the conduction electrons of Rb at these very high pressures arising from s-d electron transfer.

In Fig. 4 a sharp drop in the resistance is also observed for Rb at 71 GPa. As the magnet field is increased to 480 G, the sharp drop is seen to shift to progressively lower temperatures at the rate $\sim$1 mK/G. The sharp resistance drop plus the shift of the transition to lower temperatures in a magnetic field give strong evidence that Rb metal becomes superconducting for pressures above 56 GPa.

In the inset in Fig. 4 the dependence of the critical temperature on magnetic field is plotted at both 71 and 77 GPa. From a fit to these data using the standard expression $H_c(T) = H_0[1 - (T/T_c)^2]$ [23], the critical field at 0 K, H_0, can be estimated for Rb to be $H_0 \approx 1370$ and 1310 G at 71 and 77 GPa, respectively. In the Supplemental Material [10] it is pointed out that for Cs, $H_0 \approx 270$ G at 15.1 GPa. For Li from Ref. [7], $H_0 \approx 800$ and 1000 G at 22 and 24 GPa, respectively.

In Fig. 5 the dependence of the resistance of Rb on temperature is plotted to 3 K at various pressures. Except for the data at 56 GPa, the transition temperature T_c is seen to decrease monotonically with increasing pressure. Interestingly, the resistance at 3 K shows a nonmonotonic pressure dependence that reflects that shown in Fig. 2 for the resistance at room temperature. The dependences of T_c on pressure from Fig. 5 and a second experiment are shown in Fig. 6, yielding from the straight-line fit the value $dT_c/dP \simeq -39$ mK/GPa.

From the above results it is clear that superconductivity in Rb above 1.3 K only occurs in its $oC16$ phase, but not in the $tI4$ phase. As this sluggish phase transition begins with increasing pressure, the resistivity starts to rise, as seen in Fig. 2. At 48 GPa the sample is still in the $tI4$ structure and no superconductivity is observed. However, upon increasing pressure to 56 GPa (points 1 or 12) the resistance has clearly increased, indicating that at least some of the $tI4$ phase has transitioned to $oC16$. That only a partial superconducting transition is seen for points 1 and 12 (see Fig. 5 for point 12) shows that at 56 GPa the sample is still in a mixed phase region. As the pressure is increased further to 75 GPa (points 12–16 or 1–7 in Fig. 2), the resistivity begins to saturate, possibly indicating the phase transition to $oC16$ is nearing completion. At the same time the superconducting transition becomes more complete. At no pressure does the resistance get closer than 98% to zero. This effect of nonzero resistance observed here for Rb as well as for Cs in the Supplemental Material [10] and earlier by Ullrich [24,25], arises from the nonideal geometry in the resistivity experiment and the inhomogeneous pressure distribution across the sample. Studies of the ac susceptibility and resistivity on Rb and Cs to temperatures well below 1.3 K are recommended.

Since the superconducting transition temperature T_c for Rb decreases monotonically with increasing pressure, the highest value of T_c would occur at the lowest pressure, as long as the sample remains in the high-pressure $oC16$ phase. These facts were used to maximize the value of T_c by decreasing pressure from point 16 to 17 (or from point 7 to points 10 or 11) in Fig. 2 where Rb is still mainly in the $oC16$ phase on unloading due to the large $\sim$15 GPa hysteresis in $R(P)$.
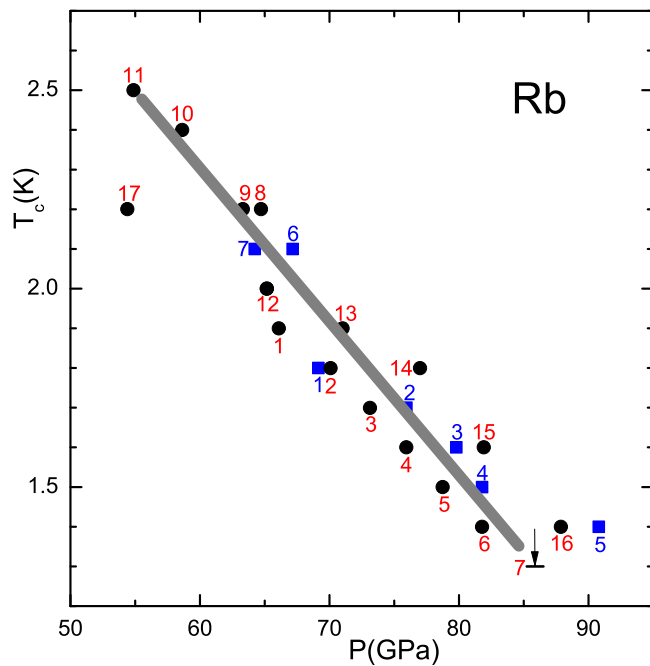
FIG. 6. Dependence of transition temperature T_c of Rb on pressure to 88 GPa in two separate experiments (black ●, blue ■). The broad gray straight line gives a rough fit to the data with slope $dT_c/dP \simeq -39$ mK/GPa.

Indeed, the $R(T)$ data in Fig. 5 for points 10, 11, and 17 place T_c in the range 2.2–2.5 K, the highest values measured in the present experiment.

The importance of the $oC16$ phase for the appearance of superconductivity above 1.3 K is not restricted to Rb but also applies to neighboring Cs, as emphasized by Schwarz *et al.* [15]. Once in the $oC16$ phase, the transition temperature T_c for both Rb and Cs is observed to decrease with increasing pressure. In addition, for Cs the transition between the same two phases $tI4 \rightarrow oC16$ is accompanied by a marked increase in the resistivity, as seen in the Supplemental Material [10]. In electronic structure calculations on Rb by Fabbris *et al.* [26],

a prominent peak structure already appears in the density of states near the Fermi level for pressure near 16 GPa, the conduction electrons taking on a significant d character. At the fcc $\rightarrow oC52$ phase transition a sizable enhancement in the density of states occurs. Perhaps the sudden appearance of superconductivity in Rb near 55 GPa is the result of a similar enhancement at the $tI4 \rightarrow oC16$ phase transition.

In the next lighter alkali metal K the $tI4 \rightarrow oC16$ transition also occurs, but not until the much higher pressure of 96 GPa [27]. Debessai [13] found no superconductivity in K above 1.35 K to 94 GPa pressure. A search for superconductivity in K to pressures higher than 1 Mbar would thus seem warranted.

In all three heavy alkali metals Cs, Rb, and K the importance of the pressure-induced s-d electron transfer has been emphasized. It is likely responsible for the transition from tetragonal $tI4$ to the lower-symmetry orthorhombic $oC16$ structure. McMahan [28] has calculated the completion pressure for the s-d transfer in Cs and Rb to be 15 and 53 GPa, respectively, near the pressures where the $tI4 \rightarrow oC16$ transition in both cases begins, but also where the resistivity rises steeply and superconductivity appears. A parallel calculation [28] for K finds its s-d transfer to complete at ~60 GPa, a lower pressure than that for the $tI4 \rightarrow oC16$ transition.

In summary, a superconducting transition T_c near 2 K has been observed in four-point electrical resistivity measurements on Rb for pressures above 55 GPa. The transition only occurs after Rb enters the orthorhombic $oC16$ phase which is marked by a sharp increase in the resistivity. T_c decreases under pressure at the rate −39 mK/GPa. In all respects these results parallel those found for Cs near 12 GPa pressure. Based on these results it is predicted that K will become superconducting near 1 Mbar pressure when it enters the same $oC16$ phase.

[1] J. Tuoriniemi, K. Juntunen-Nurmilaukas, J. Uusvuori, E. Pentti, A. Salmela, and A. Sebedash, Nature (London) **447**, 187 (2007).

[2] J. S. Schilling, High Press. Res. **26**, 145 (2006).

[3] K. Takemura, N. E. Christensen, D. L. Novikov, K. Syassen, U. Schwarz, and M. Hanfland, Phys. Rev. B **61**, 14399 (2000).

[4] J. B. Neaton and N. W. Ashcroft, Nature (London) **400**, 141 (1999); J. Feng, R. G. Hennig, N. W. Ashcroft, and R. Hoffmann, *ibid.* **451**, 445 (2008); P. Söderlind, O. Erikson, B. Johansson, J. M. Wills, and A. M. Boring, *ibid.* **374**, 524 (1995).

[5] J. L. Dye, Science **301**, 607 (2003).

[6] D. A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).

[7] S. Deemyad and J. S. Schilling, Phys. Rev. Lett. **91**, 167001 (2003).

[8] J. Wittig, Phys. Rev. Lett. **24**, 812 (1970).

[9] U. Schwarz, K. Takemura, M. Hanfland, and K. Syassen, Phys. Rev. Lett. **81**, 2711 (1998).

[10] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.100.041109 for results of the present high-pressure resistivity studies on Cs metal, which includes Refs. [11, 12].

[11] M. I. McMahon, R. J. Nelmes, and S. Rekhi, Phys. Rev. Lett. **87**, 255502 (2001).

[12] Y. Ma, M. Eremets, A. R. Oganov, Y. Xie, I. Trojan, S. Medvedev, A. O. Lynkhov, M. Valle, and V. Prakapenka, Nature (London) **458**, 182 (2009).

[13] M. T. Debessai, Ph.D. thesis, Washington University in St. Louis, 2004.

[14] K. Ullrich, C. Probst and J. Wittig, J. Phys., Colloq. **6**, 463 (1978).

[15] U. Schwarz, K. Syassen, A. Grzechnik, and M. Hanfland, Solid State Commun. **112**, 319 (1999).

[16] J. S. Schilling, in *Proceedings of the 9th AIRAPT International High Pressure Conference, Albany, New York, July 24-29, 1983*, edited by C. Homan, R. K. MacCrone, and E. Whalley (North-Holland, New York, 1984); J. S. Schilling, Mater. Res. Soc. Symp. Proc. **22**, 79 (1984).

[17] W. B. Daniels and W. Ryschkewitsch, Rev. Sci. Instrum. **54**, 115 (1983).

[18] K. Shimizu, K. Amaya, and N. Suzuki, J. Phys. Soc. Jpn. **74**, 1345 (2005).

[19] J. Lim, G. Fabbris, D. Haskel, and J. S. Schilling, Phys. Rev. B **91**, 045116 (2015).

[20] Y. Akahama and H. Kawamura, J. Appl. Phys. **100**, 043516 (2006).

[21] A. D. Chijioke, W. J. Nellis, A. Soldatov, and I. F. Silvera, J. Appl. Phys. **98**, 114905 (2005).

[22] R. J. Nelmes, M. I. McMahon, J. S. Loveday, and S. Rekhi, Phys. Rev. Lett. **88**, 155503 (2002).

[23] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Thomson Learning, Boston, 1976), p. 745.

[24] K. Ullrich, Ph.D. thesis, University of Cologne, 1980.

[25] J. Wittig, in *Superconductivity in d- and f-Band Metals*, edited by W. Buckel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982), p. 321.

[26] G. Fabbris, J. Lim, L. S. I. Veiga, D. Haskel, and J. S. Schilling, Phys. Rev. B **91**, 085111 (2015).

[27] L. F. Lundegaard, M. Marques, G. Stinton, G. J. Ackland, R. J. Nelmes, and M. I. McMahon, Phys. Rev. B **80**, 020101(R) (2009).

[28] A. K. McMahan, Phys. Rev. B **29**, 5982 (1984).