

Structural and electrical properties of beryllium metal to 66 GPa studied using designer diamond anvils

Nenad Velisavljevic, Gary N. Chesnut, and Yogesh K. Vohra

Department of Physics, University of Alabama at Birmingham (UAB), Birmingham, Alabama 35294-1170

Samuel T. Weir, Vincent Malba, and Jagannadham Akella

Lawrence Livermore National Laboratory, Livermore, California 94550

(Received 24 September 2001; revised manuscript received 22 January 2002; published 8 May 2002)

The structural and electrical properties of alkaline-earth metal beryllium were studied to 66 GPa using designer diamond anvils. The ambient pressure hexagonal close-packed phase was found to be stable to the highest pressure of 66 GPa and the measured static equation of state differs substantially from the one derived from the existing shock wave data. The electrical resistance data at high pressure shows a gradual decrease in resistance to pressure up to 25 GPa followed by a slight increase to 53 GPa. The axial ratio (c/a) remains strongly nonideal with $c/a = 1.562$ at $V/V_0 = 0.708$, indicating that deviations from nearly free electron behavior are still dominant at high compressions.

DOI: 10.1103/PhysRevB.65.172107

PACS number(s): 62.50.+p, 64.70.Kb, 61.66.Bi, 64.30.+t

The high-pressure behavior of alkaline-earth metals, beryllium, magnesium, calcium, strontium, and barium is of considerable interest because of their large compressibility, complex phase diagrams, and the proximity of empty d bands above the filled electronic states.^{1,2} In the heavy alkaline-earth metals like calcium, strontium, and barium, pressure induced phase transitions are strongly influenced by the electronic s - d transfer and its impact on the total energy of various competing phases (for a review see Ref. 3). In the light alkaline metals like beryllium and magnesium, application of high pressure can lead to increased hybridization between s and p electrons with consequent changes in electronic density of states and total energies of various competing phases. Beryllium (Be) metal is of considerable interest because of its simple atomic configuration and anomalous physical properties including a high Debye temperature of 1440 K and extraordinarily small Poisson's ratio of 0.05. The crystal structure is hexagonal close packed with two atoms/cell and with only two valence electrons per atom. The crystal structure is nonideal as the axial ratio (c/a) at room pressure is 1.568 and deviates considerably from an ideal close-packed value of 1.633. All these deviations from an ideal behavior are attributed to deviations from simple nearly free electron behavior with a large spatially anisotropic p -electron component in the valence band. The temperature and pressure induced phase transitions have been examined theoretically in Be.⁴⁻⁶ The hexagonal close-packed (hcp) phase is stable up to 1530 K; above this temperature a body centered cubic (bcc) phase is observed. There is an approximately 4% increase in density at the hcp-bcc phase transition. The stability of bcc phase at ambient pressure is extremely limited, as melting is known to occur at 1560 K. Since, the bcc phase is denser than the hcp phase, application of high pressure is expected to stabilize the bcc phase. It has been predicted that the hcp phase of Be metal would transform to either a face-centered cubic or a bcc phase in the pressure range of 100–200 GPa at room temperature.⁴⁻⁶

There have been several static high-pressure studies on

beryllium metal. Marder⁷ reported a discontinuity in the electrical resistance of Be at a pressure of 9.3 GPa indicative of a possible phase transition. This was followed by a study of the effect of high pressure on the Fermi surface of Be.⁸ The subsequent high-pressure electrical resistance measurement to 40 GPa by Reichlin⁹ did not show any discontinuity, instead, only gradual changes in electrical resistance were observed to the highest pressure. Ming *et al.*¹⁰ reported a possible distortion of hcp lattice in Be based on additional diffraction peaks in the pressure range of 8.6 to 14.5 GPa. The present high pressure experimental work on Be is motivated by two considerations: (a) nonideal behavior of hcp phase and its stability under high pressures and (b) extending four probe electrical transport measurements to higher pressures using newly available designer diamond technology.¹¹

From an experimental point of view, high pressure studies on Be are extremely challenging because of its low atomic number ($Z = 4$) which leads to extremely weak x-ray diffraction signals in a diamond-anvil cell. Electrorefined beryllium of 99.8% purity was used in all high-pressure experiments. The surface oxidation layer was removed prior to loading in a diamond-anvil cell. Four different high-pressure experiments were carried out on beryllium metal. Two high-pressure experiments were carried out using diamonds with a culet size of 600 μm and samples of 130 μm diam. These experiments employed copper as a pressure marker and medium, using x-ray diffraction for pressure calibration. In the third experiment, we employed a designer diamond anvil with a culet size of 300 μm for simultaneous x-ray measurements and four probe electrical resistance measurements. The ruby pressure sensor was employed in our experiments with designer diamond anvils. In the fourth experiment, the highest pressure of 66 GPa was achieved on a Be sample with a diamond culet size of 300 μm and a sample of 80 μm diam with ruby as a pressure sensor. The nonhydrostatic calibration of ruby pressure sensor carried out to 180 GPa was used in the current experiments.¹² In the last two experiments with a ruby pressure sensor, no pressure medium was employed.

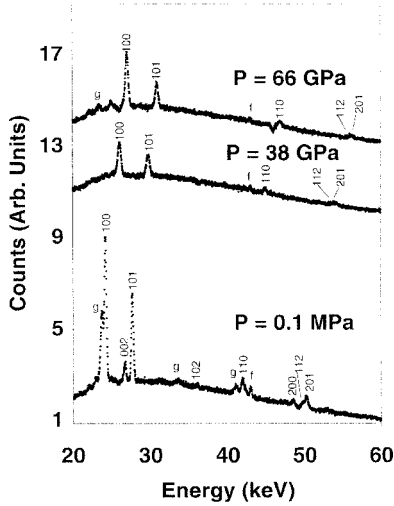


FIG. 1. Energy dispersive x-ray diffraction spectrum for beryllium metal at various pressures in a diamond-anvil cell. The diffraction angle $2\theta = 14.912^\circ$. The diffraction peaks are labeled by the (hkl) Miller indices for the hexagonal close-packed phase of beryllium. The weak peaks labeled g are from gasket material and peak labeled f is background fluorescence unaffected by pressure. The pressures indicated were measured by the ruby fluorescence technique.

Figure 1 shows the energy dispersive x-ray diffraction spectra of beryllium in the pressure range of atmospheric pressure (0.1 MPa) to the highest pressure of 66 GPa. These spectra were recorded at the superconducting wiggler beamline X-17C at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. An x-ray collimated beam of $50 \mu\text{m} \times 50 \mu\text{m}$ was used in all diffraction experiments. The ambient pressure phase for Be is hcp as it is evident by the observations of (100), (002), (101), (110), (200), (112), and (201) diffraction peaks and the measured lattice parameters at ambient pressure (0.1 MPa) are $a = 2.286 \pm 0.003 \text{ \AA}$ and $c = 3.58 \pm 0.01 \text{ \AA}$ with $c/a = 1.568$. At high pressures, we observe the loss of (002) reflection of the hcp phase due to basal-plane texture. This texture phenomenon is well documented in other hcp metals, most notably in iron under high pressures,¹³ with c axes parallel to the axis of the diamond-anvil cell. The (100), (101), (110), (112), and (201) peaks from the hcp phase are observed and could be fitted to the highest pressure indicating that there is no phase transformation to the highest pressure. The (200) diffraction peak is barely discernible in the spectra at high pressures and was not included in structural fits. The comparison between the observed and calculated interplanar spacings at 66 GPa is shown in Table I indicating a good fit to the hcp lattice with a mean error in d spacings of only 0.16%. The measured lattice parameter at 66 GPa are $a = 2.040 \pm 0.002 \text{ \AA}$ and $c = 3.19 \pm 0.02 \text{ \AA}$ with $c/a = 1.562$. The measured volume compression at 66 GPa is $V/V_0 = 0.708$.

Figure 2 shows the variation of the axial ratio, c/a , as a function of pressure to 66 GPa. The c/a ratio is nearly independent of pressure with an extremely small negative slope. All the experimental c/a data on beryllium can be fitted to the following equation:

TABLE I. The comparison between the observed and calculated interplanar spacings for the hcp phase of beryllium at 66 GPa. The calculated interplanar spacings for the hcp phase are based on lattice parameters $a = 2.040 \pm 0.002 \text{ \AA}$ and $c = 3.19 \pm 0.02 \text{ \AA}$.

Diffraction peaks Miller indices (hkl)	Observed interplanar spacings (d_{obs} \AA)	Calculated interplanar spacings (d_{calc} \AA)	%error ($d_{\text{obs}} - d_{\text{calc}}$ \AA) $100/d_{\text{obs}}$
(100)	1.767	1.767	0.0
(101)	1.545	1.545	0.0
(110)	1.021	1.020	0.1
(112)	0.864	0.859	0.6
(201)	0.852	0.851	0.1

$$c/a = 1.568 - 6 \times 10^{-5} P, \text{ where } P \text{ is in GPa,}$$

$$\text{and } 0.1 \text{ MPa} \leq P \leq 66 \text{ GPa.}$$

Figure 3 shows the measured pressure-volume (P - V) curve or equation of state for Be to 66 GPa at room temperature obtained in diamond-anvil cells. The equation of state employed in the present work is the adapted polynomial equation of state (AP2-EOS)^{14,15} and is shown below. The P is the pressure in GPa and $x^3 = V/V_0$ is the volume compression. The V_0 , B_0 , and B'_0 are the atomic volume, isothermal bulk modulus, and the first pressure derivative of the bulk modulus at ambient pressure.

$$P = 3B_0x^{-5}(1-x)\exp[C_0(1-x)][1 + C_2x(1-x)]$$

$$\text{(AP2-EOS).}$$

AP2 represents a second-order equation of state with the two free parameters B_0 and B'_0 . The parameter $B'_0 = 3 + 2/3(C_0 + C_2)$ and $C_0 = -\ln(3B_0/p_{FGO})$. The C_0 value is constrained by B_0 , V_0 , and atomic number Z .¹⁴ The shock data for copper^{16,17} when fitted to AP2-EOS gives $B_0 = 133 \text{ GPa}$ and $B'_0 = 5.4$. These parameters were employed in our pressure calculations based on a copper standard.

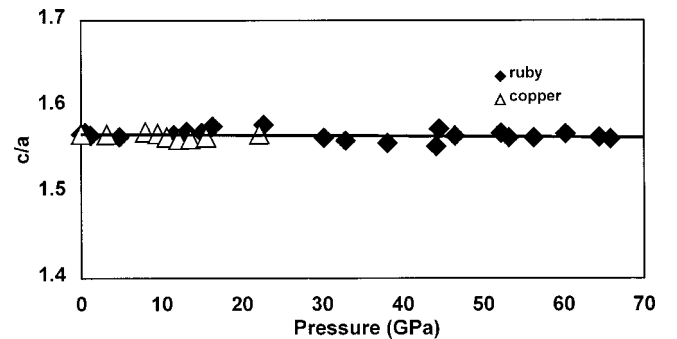


FIG. 2. The measured value of axial ratio (c/a) as a function of pressure for beryllium. The c/a data is shown for all experiments, some of them using a copper pressure marker, and others using a ruby pressure sensor. The solid line is the fit to all data and is described in the text.

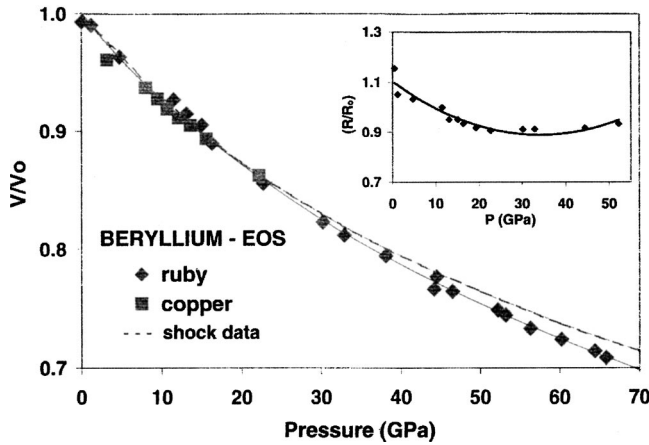


FIG. 3. The measured equation of state of beryllium at room temperature to 66 GPa. The equation of state data is shown for all experiments, some of them using a copper pressure marker, and others using a ruby pressure sensor. The solid curve is the AP2-EOS fit to the measured static equation of state and is described in the text. The dashed curve is the AP2-EOS fit to the isothermal shock equation of state (Ref. 17) and is described in the text. The inset shows the four-probe resistance measurements on beryllium sample as a function of pressure. The resistance data shown has been normalized to R_0 (the value at 11.5 GPa).

The static equation of state of Be between ambient pressure and 66 GPa was fitted to the following equation of state parameters. The least-square fit is displayed in Fig. 3 by a solid curve indicating that a AP2-EOS is sufficient to describe the static compression of beryllium metal to this pressure

$$B_0 = 106.5 \text{ GPa}, \quad B'_0 = 3.541, \quad \text{with}$$

$$C_0 = 0.8123 \quad (\text{AP2 fit to static data}).$$

The measured shock Hugoniot data on Be has been reduced to obtain an equation of state of Be to 90 GPa at room temperature.¹⁷ This reduced shock equation-of-state data for Be between ambient pressure and 70 GPa was fitted to the following equation-of-state parameters. The least-square AP2-EOS fit to the shock data is displayed by a dashed curve in Fig. 3

$$B_0 = 125.7 \text{ GPa}, \quad B'_0 = 2.921, \quad \text{with}$$

$$C_0 = 0.6465 \quad (\text{AP2 fit to shock data}).$$

It is to be noted that the values of bulk modulus obtained by the fits to static and shock data are close to the range of experimental values of 110 GPa to 127 GPa reported in the literature and with the theoretically calculated value of 131 GPa.⁵ The static and shock equation of state agree to 20 GPa, but show significant differences above this pressure. This

points to a need for reevaluation of the shock Hugoniot data with more reasonable assumptions on the Gruniesen parameter.

The rest of experiments on Be were performed using designer diamond anvils where tungsten metal probes were patterned using lithographic techniques at the Lawrence Livermore National Laboratory and encapsulated within a chemical vapor deposited diamond layer at the University of Alabama at Birmingham.¹¹ The electrical probes are only exposed near the center of the diamond for making contact with the sample and elsewhere they are completely insulated within a single crystalline diamond layer. This designer diamond anvil allows us to use a metallic gasket for sample containment and for a precise four-probe electrical resistance measurement. Furthermore, having eight electrical probes gives us the flexibility to measure four-probe resistance in various regions of the sample for any nonuniformity across the sample. The Fig. 3 inset shows the four-probe electrical resistance data to 53 GPa. The electrical resistance values have been normalized to the resistance value at 11.5 GPa. The electrical resistance of Be shows a gradual decrease with increasing pressure to 25 GPa and this is followed by a slight increase to 53 GPa. Our results are consistent with those reported by Reichlin.⁹ It should be added that no abrupt change in electrical resistance was observed in the present experiment that is consistent with the x-ray diffraction studies in this report. Previous electrical resistance measurements indicated a sharp discontinuity at 9.3 GPa (Ref. 7) that has not been reproduced in later studies.

In conclusion, our x-ray diffraction studies on beryllium under high pressures to 66 GPa indicate no evidence of a transition in the hexagonal close-packed phase to volume compression $V/V_0 = 0.708$. The static equation of state differs from the shock equation of state above 20 GPa. The four-probe electrical resistance measurements using designer diamond anvils show only gradual changes with pressure. The hcp structure remains nonideal with $c/a = 1.562$ at 66 GPa indicating that deviation from nearly free electron behavior is still observed up to high compressions.

We acknowledge support from the National Science Foundation (NSF) under Grant No. 9704428 and support by the B-Division at the Lawrence Livermore National Laboratory (LLNL) under the auspices of the U.S. Department of Energy by the University of California under Contract No. W-7405-ENG-48. We thank Dr. James E. Hanafee of LLNL for supplying the beryllium sample. We also thank Dino Ciarlo and Ron Lee for helpful discussions, and Steve Falabella for technical assistance. Research carried out (in part) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

- ¹D. A. Young, *Phase Diagrams of the Elements* (University of California, 1991), p. 78.
- ²J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974), Chap. 4.
- ³H. L. Skiver, Phys. Rev. B **31**, 1909 (1985).
- ⁴A. K. McMahan, in *Shock Waves in Condensed Matter—1981*, edited by W. J. Nellis, L. Seaman, and R. A. Graham, AIP Conf. Proc. No. 78 (AIP, New York, 1981).
- ⁵P. K. Lam, M. Y. Chou, and M. L. Cohen, J. Phys. C **17**, 2065 (1984).
- ⁶J. Meyer-ter-Vehn and W. Zittel, Phys. Rev. B **37**, 8674 (1988).
- ⁷A. R. Marder, Science **142**, 664 (1963).
- ⁸J. E. Schirber and W. J. O'Sullivan, Phys. Rev. **184**, 628 (1969).
- ⁹R. L. Reichlin, Rev. Sci. Instrum. **54**, 1674 (1983).
- ¹⁰L. C. Ming and M. H. Manghnani, J. Phys. F: Met. Phys. **14**, L1 (1984).
- ¹¹S. T. Weir, J. Akella, C. A. Ruddle, Y. K. Vohra, and S. A. Catledge, Appl. Phys. Lett. **77**, 3400 (2000).
- ¹²H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).
- ¹³H. R. Wenk, S. Matthies, R. J. Hemley, H. J. Mao, and J. Shu, Nature (London) **405**, 1044 (2000).
- ¹⁴W. B. Holzapfel, High Press. Res. **16**, 81 (1998).
- ¹⁵W. B. Holzapfel, M. Hartwig, and W. Sievers, J. Phys. Chem. Ref. Data **30**, 515 (2001).
- ¹⁶W. J. Nellis, J. A. Moriarty, A. C. Mitchell, M. Ross, R. G. Dandrea, N. W. Ashcroft, N. C. Holmes, and G. R. Gathers, Phys. Rev. Lett. **60**, 1414 (1988).
- ¹⁷R. G. McQueen, S. P. Marsh, J. W. Taylor, J. M. Fritz, and W. J. Carter, in *High Velocity Impact Phenomenon*, edited by R. Kinslow (Academic, NY, 1970), Chap. VII.