Static compression of metals Mo, Pb, and Pt to 272 GPa: Comparison with shock data

Yogesh K. Vohra and Arthur L. Ruoff

Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

Several metals, Mo, Pb, and Pt, have been compressed in a diamond anvil cell to 272 GPa and studied by energy-dispersive x-ray diffraction using a synchrotron source. The bcc phase of Mo was found to be stable to 272 GPa at 300 K, and the phase transition reported in shock compression at 210 GPa and 4100 K was not observed. This implies either a large hysteresis and/or significant vibrational and electronic contributions to the entropy change at the transition. The measured static equation of state of Pb to 272 GPa employing Pt and Mo as pressure standards shows stiffening as compared with shock data, and the reasons for this difference are discussed.

The issue of pressure standards is of immense technological and basic science importance in static and dynamic pressure research. The calibrated static pressures attainable in the diamond anvil cell have shown a steady increase in the past few years.[1-4] There have been parallel developments recently in identifying pressure standards derived from the shock equation of state. Nellis *et al.*[5] gave new absolute shock compression data for Al, Cu, and Pb and suggested the use of these metals as pressure standards for diamond anvil cell experiments to 1000 GPa. Holmes *et al.*[6] shock compressed Pt to 660 GPa using a two-stage gas gun to qualify this material as an ultra-high-pressure standard for both dynamic and static experiments. However, from the static-pressure x-ray-diffraction point of view, pressure standards should be stable in a particular crystallographic phase over an extended pressure range and preferably should have a high atomic number in order to get signals from sample volume of 10^{-10} cm^3. Also, the question of self-consistency among various pressure standards proposed in the literature remains an important issue and needs careful experimentation.

The calibrated static pressures of 364 GPa have now been achieved[4] in the diamond anvil cell and have lead to renewed interest in the phase transitions in the transition elements Cr, Mo, and W near the middle of the series.[3] Recently, acoustic velocity data under shock compression in Mo were interpreted as indicative of solid-solid phase transition[7] at 210 GPa and 4100 K. Also, the first-principles theoretical calculations based on linear muffin-tin orbital (LMTO) method predict a zero-temperature bcc to hcp transition at 320 GPa in Mo.[7] More recent shock experiments on W indicate similar solid-solid transition at 400 GPa.[8]

The motivation for the present series of experiments was twofold, the first being to look for the phase transition in Mo at static pressures above 200 GPa and the second being to compare the pressures obtained by different standards Mo, Pt, and Pb at extreme compressions. Three separate experiments were performed and the energy-dispersive x-ray-diffraction studies were carried out using the B1 white beam station at the Cornell High Energy Synchrotron Source (CHESS), Cornell University and the X-7A station at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The details of the x-ray-diffraction technique are given in Ref. 9. The first experiment employed diamonds with a flat diameter of 100-μm 5-degree level to a culet diameter of 300 μm; a mixture of Pb and Pt was studied to 124 GPa and resulted in a catastrophic failure of diamonds. The second experiment employed diamonds of 50-μm flat 7-degree bevel to 300-μm culet and a mixture of Pb and Pt was studied to 206 GPa and decompressed to study the reverse transitions in Pb.[10,11] The third experiment employed 25-μm flat diamond 7-degree bevel to 350-μm culet and a mixture of Mo and Pb was compressed to 272 GPa and is being held at this pressure for more studies. In an earlier work using the same diamond design as in the third experiment we had compressed Pt metal to 282 GPa.[3]

Figure 1 shows the energy-dispersive x-ray-diffraction (EDXD) pattern of the Mo and Pb mixture at a pressure
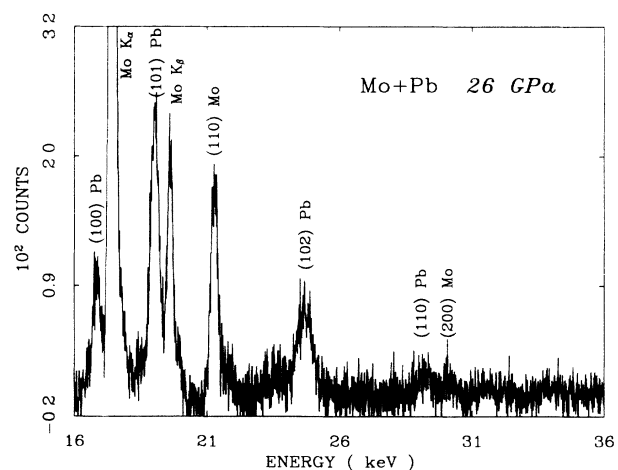

FIG. 1. Energy dispersive x-ray-diffraction spectrum (background subtracted) of Mo and Pb mixture at a pressure of 26 GPa calculated from Mo shock EOS. Pb is in the hcp phase and Mo is in the bcc phase at this pressure. The spectrum was taken at $Ed = 46.004$ keV Å at X-7a at NSLS in 20 min.

of 26.4 GPa. The Pb is in the hcp phase at this pressure and Mo is in the bcc phase. Pb has already undergone one phase transition from the fcc to the hcp phase around 13 GPa.[12] The pressure is calculated from the measured volume of Mo using the latest shock equation of state (EOS) of Mo from Los Alamos to 435 GPa (Ref. 8) fitted to the following Birch-Murnaghan EOS:[13]

$$P = \tfrac{3}{2}B_0(x^{7/3} - x^{5/3})[1 + \tfrac{3}{4}(B_0' - 4)(x^{2/3} - 1)] .$$

Here $x = V_N/V$, V is the volume per atom, and V_N is the extrapolated volume per atom of the phase under consideration at zero pressure. B_0 and B_0' are fitting parameters, and if the functional form of the EOS given above is exact for a given material, then they correspond to the isothermal bulk modulus and its pressure derivative evaluated at zero pressure. The Mo shock EOS is fitted with $B_0 = 262.8$ GPa, and $B_0' = 3.949$.

The shock EOS of Pb to 1000 GPa given by Nellis et al.[5] when fitted to the Birch-Murnaghan equation gives $B_0 = 38.98$ GPa and $B_0' = 5.037$. The measured volume of Pb in Fig. 1 when used with this Pb shock EOS gives a pressure of 27.5 GPa. In this compression range of Pb ($V/V_0 = 0.73$), the pressures calculated by different pressure standards only differ by 4%.

Figure 2 shows the EDXD spectrum of Mo and Pb mixture at a pressure of 267 GPa calculated from the Mo shock EOS. If we take the measured volume of Pb in Fig. 2 and use the Pb shock EOS then we get a pressure of only 238 GPa, about 29 GPa lower than the pressure obtained from Mo standard. Pb is in bcc phase at this pressure after undergoing a second sluggish hcp-bcc phase transition in the 100 GPa pressure range.[10,11] Mo retains its bcc phase up to this pressure, as can be seen by the presence of (110) and (200) diffraction peaks in Fig. 2 and the fact that no extra diffraction peaks were observed. It
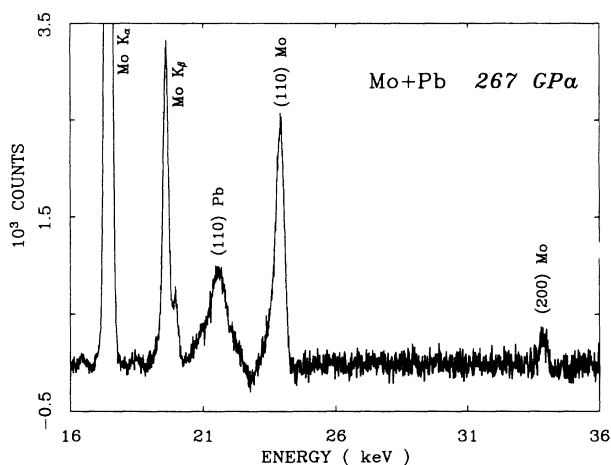
should be added that if Mo had transformed to the hcp phase as predicted by theory and supported by structural trends in transition metals, such a transition would be very clear in the diffraction pattern shown in Fig. 2. Further evidence that no phase transition has taken place is obtained from the plot of interplanar spacing of the strongest (110) diffraction peak of the bcc phase of Mo as a function of pressure measured by Pb shock EOS (Fig. 3). There is a continuous decrease with pressure and no abrupt changes are observed in the interplanar spacing around 210 GPa. The interplanar spacing of the strongest diffraction peak (101) for a hypothetical hcp phase of Mo is also indicated in Fig. 3 assuming no volume change at the phase transition.

The measured static EOS of Pb to 272 GPa using Mo and Pt as pressure standards is shown in Fig. 4. Most of the low-pressure fcc Pb data are from Mao et al.[14] using the ruby pressure scale which in turn was calibrated using shock data. It is to be emphasized that only single-phase data points are plotted in Fig. 4 and all the phase-mixture data points were omitted. This reduces the scatter in the measured EOS and distinctly shows the volume change at hcp-bcc transition. The static EOS of Pb obtained this way differs from the shock EOS (Ref. 5) as shown in Fig. 4. In particular, at a static compression of Pb $V/V_0 = 0.45$, Pb shock EOS underestimates pressure by as much as 10% in a systematic fashion. There is a good agreement between EOS data points of Pb obtained with Mo standard and those obtained with Pt standard in the overlap region of the data sets (Fig. 4). We believe, therefore, that the discrepancy between static and shock EOS for Pb is real and is not due to a particular choice of standard used to study Pb. The measured static EOS of fcc, hcp, and bcc phases of Pb are fitted to the Birch-Murnaghan EOS and the results are summarized in Table I.

FIG. 2. Energy dispersive x-ray-diffraction spectrum (background subtracted) of Mo and Pb mixture at a pressure of 267 GPa calculated from Mo shock EOS. Both Pb and Mo are in the bcc phase at this pressure. The (200) diffraction peak from bcc Pb is too weak to be observed at this pressure. The spectrum was taken at $Ed = 46.087$ keV Å at B1 station at CHESS in 300 min.
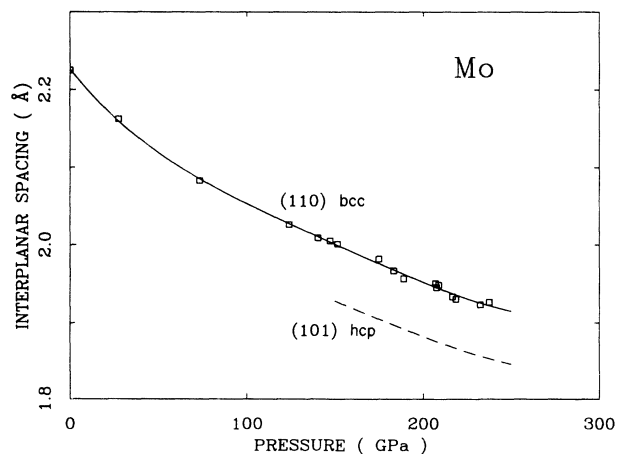

FIG. 3. The interplanar spacing for (110) diffraction planes of the bcc phase of Mo as a function of pressure measured by Pb shock EOS. The solid curve is only a guide to the eye and the dashed line indicates the (101) interplanar spacing for a hypothetical hcp phase.
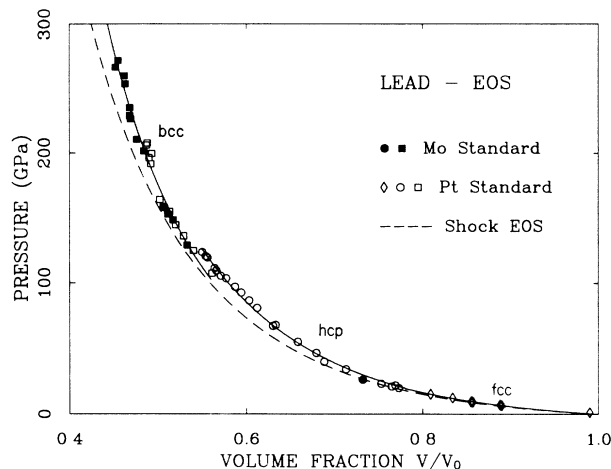
FIG. 4. The measured static EOS of Pb to 272 GPa using Mo and Pt pressure standards. The fcc, hcp, and bcc phases of Pb are plotted with different symbols. The solid curves are the fits to the Birch-Murnaghan EOS with parameters shown in Table I. The dashed curve is the shock EOS from Nellis *et al.* (Ref. 5).

It should be added that the 10% deviation of the static and shock EOS noted in the present work is within the upper-bound uncertainty of the 300 K isotherms for Al, Cu, and Pb given by Nellis *et al.*[5] However, the systematic deviation is interesting enough to reexamine the 300 K isotherm of Pb in light of the bcc high-pressure phase and possible errors due to large thermal correction to the Hugoniot in case of soft materials. It is interesting to point out that in shock compression of Pb to $V/V_0 = 0.45$, thermal pressure correction is around 240 GPa and corresponds to about 50% of the Hugoniot pressure. Measurements of melting temperature of Pb have been recently carried out to pressures of 100 GPa and temperature near 4000 K by Godwal *et al.*[15] in a laser heated diamond anvil cell. This recent study along with sound velocity measurements[16] in shock compressed Pb present strong evidence that Pb is molten at shock pressures higher than 50–60 GPa. This would indicate that the most of the shock Hugoniot data is in liquid phase and the liquid state models used in the reduction of Hugoniot to the isothermal EOS data should be reexamined.

The lack of a phase transition in Mo in static experiments to a volume compression V/V_0 of 0.646 (272 GPa) puts some important constraints on the phase transition

TABLE I. The parameters for the Birch-Murnaghan fits to the static equation of state for various phases of Pb. The V_0 for Pb is 30.326 Å^3/atom.

	fcc	hcp	bcc
B_0 (GPa)	43.20	46.63	29.02
B_0'	4.87	5.23	7.16
V_N/V_0	1.0	0.985	0.978

seen in shock waves at 210 GPa and 4100 K. There are two distinct possibilities for the phase diagram of Mo.

(1) The solid-solid phase boundary in Mo has a negative slope and from the present experiments $dT/dP > -60$ K/GPa. The negative slope of the bcc-hcp phase boundary has been suggested by Shaner[17] to owe its origin to the higher electronic entropy in the close packed structure relative to the bcc phase. It is of interest to point out that the molecular-dynamics simulations of hcp-bcc transition in Zr (Ref. 18) explicitly show the importance of electronic contribution to the entropy.

(2) The phase transition (bcc to hcp?) in Mo is sluggish and thermal activation or significant overpressure from equilibrium conditions may be needed to drive the transition in diamond anvil cell experiments.

In summary, we have compressed several metals Mo, Pb, and Pt to 272 GPa in the diamond anvil cell and structural studies were made using synchrotron sources. The ambient bcc phase of Mo was found stable to these pressures in static experiments and, when combined with shock data, has some interesting implications for the phase diagram of Mo. The pressure standards Mo and Pt were found to be consistent to 210 GPa, while the Pb pressure standard underestimates the pressure by about 10% at 270 GPa. The measured static equation of state of Pb should be used to refine the theoretical models used in the energetics of ion motion in both the solid and hot liquid metal.

ACKNOWLEDGMENTS

[1]Y. K. Vohra, S. J. Duclos, K. E. Brister, and A. L. Ruoff, Phys. Rev. Lett. **61**, 574 (1988).

[2]H. K. Mao, Y. Wu, R. J. Hemley, L. C. Chen, J. F. Shu, and L. W. Finger, Science **246**, 649 (1989).

[3]Y. K. Vohra and A. L. Ruoff, High Pressure Research **4**, 296 (1990).

[4]Y. K. Vohra, H. Xia, H. Luo, and A. L. Ruoff, Appl. Phys.

Lett. **57**, 1007 (1990).

[5]W. J. Nellis, J. A. Moriarty, A. C. Mitchell, M. Ross, R. G. Dandrea, N. W. Ashcroft, N. C. Holmes, and R. G. Gathers, Phys. Rev. Lett. **60**, 1414 (1988).

[6]N. C. Holmes, J. A. Moriarty, G. R. Gathers, and W. J. Nellis, J. Appl. Phys. **66**, 2962 (1989).

[7]R. S. Hixson, D. A. Boness, J. W. Shaner, and J. A. Moriarty,

Phys. Rev. Lett. **62**, 637 (1989).

[8]R. S. Hixson and J. W. Shaner (private communication).

[9]K. E. Brister, Y. K. Vohra, and A. L. Ruoff, Rev. Sci. Instrum. **57**, 2560 (1986).

[10]C. A. Vanderborgh, Y. K. Vohra, Hui Xia, and A. L. Ruoff, Phys. Rev. B **41**, 7338 (1990).

[11]J. Z. Hu, Y. Wu, J. F. Shu, R. J. Hemley, and H. K. Mao, Bull. Am. Phys. Soc. **35**, 285 (1990).

[12]T. Takahashi, H. K. Mao, and W. A. Bassett, Science **165**, 1352 (1969).

[13]F. Birch, J. Geophys. Res. **83**, 1257 (1978).

[14]H. K. Mao and P. M. Bell, Carnegie Inst. Washington Yearb.

77, 842 (1978).

[15]B. K. Godwal, C. Meade, R. Jeanloz, A. Garcia, A. Y. Liu, and M. L. Cohen, Science **248**, 462 (1990).

[16]D. A. Boness, J. M. Brown, and J. W. Shaner, in *Shock Waves in Condensed Matter 1987*, edited by S. C. Schmidt and N. C. Holmes (Elsevier, New York, 1988), p. 115.

[17]J. W. Shaner, in *Shock Compression of Condensed Matter-1989*, edited by S. C. Schmidt, J. N. Johnson, and L. W. Davidson (North-Holland, Amsterdam, 1990), p. 121.

[18]F. Williaime and C. Massobrio, Phys. Rev. Lett. **63**, 2244 (1990).