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# The crystal structure and stability of molybdenum at ultrahigh pressures

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## Abstract

Crystal structures and their stabilities for molybdenum under increasing hydrostatic pressures are investigated by first-principles calculations of the Gibbs free energy. Three structures are considered: body-centred cubic (bcc, the ground state at zero pressure), hexagonal close-packed (hcp) and face-centred cubic (fcc). For each structure and each pressure (up to 8 Mbar) the equilibrium states are found from minima of the Gibbs free energy at zero temperature. The stability is tested by calculating the elastic constants and checking whether they satisfy the appropriate stability conditions. The bcc structure is confirmed to be stable at zero pressure and at 6 Mbar. At and above 6.2 Mbar the ground-state structure changes to hcp, which is found to be stable at 7 Mbar. At 7.7 Mbar another transition occurs, and the ground-state structure changes from hcp to fcc. The fcc structure, which is unstable at zero pressure, becomes metastable over the range from 3 to 7.7 Mbar and becomes the ground state at higher pressures (at least up to 8 Mbar). Direct confirmation of these calculated transition pressures with experiment is not now possible, as the maximum static pressure currently reached experimentally is 5.6 Mbar, where Mo is found to be still in the bcc phase.

## 1. Introduction

Theoretical and experimental studies of phase stability in the transition metals over the past several years have confirmed that such phase stability is mostly controlled by the number  $Z_d$  of valence d electrons per atom [1]. The periodic table shows that  $Z_d$  increases with atomic number and produces the hcp–bcc–hcp–fcc sequence of structures found in the nonmagnetic 4d and 5d series. In general,  $Z_d$  also increases with increasing hydrostatic pressure because under compression the s and p energy bands, being spatially extended, rise in energy faster than the localized d bands. Thus compression favours the transfer of electrons from s- and p-like states into d-like states (the so-called s  $\rightarrow$  d transition) [1].

Based on this transfer Moriarty [1] made a number of interesting elementary structural predictions. If increasing pressure produces a positive s  $\rightarrow$  d electron transfer, then increasing

pressure for a given element corresponds structurally to moving to the right in the periodic table. Hence the effect of high pressure on the structure of most of the transition metals in the central rows can be inferred from the structures of the elements to the right of the one under consideration at zero pressure. Experimental confirmation of these predictions is hampered at least in part by the difficulty of reaching the multi-megabar pressures needed to drive the  $s \rightarrow d$  transitions. Hixson *et al* [2] made the first attempt at observing such a transition in Mo by measuring the acoustic velocity in compressed Mo using shock techniques.

Molybdenum is particularly interesting for high-pressure work because it is used in the calibration of the ruby fluorescence technique for ultrahigh-pressure static experiments [7], can be used as a gasket in experiments with the diamond-anvil cell (DAC) aimed at static pressures up to 6 Mbar [8], and finds applications in the nuclear-energy and aircraft industries. For Mo the elementary structural predictions mentioned above start from consideration of the zero-pressure structures of the sequence Mo–Tc–Ru–Rh in the periodic table and thus suggest that the structure sequence should be bcc–hcp–fcc with increasing pressure. Hixson *et al* [2] found a sharp break in the sound velocity in Mo against density at about 2.1 Mbar and 4000 K, which was interpreted to be indicative of a ‘solid–solid’ phase transition, but the structure of the final phase was not determined. However, more recent experiments in a laser-heated DAC up to 1 Mbar and 4100 K by Errandonea *et al* [3] suggested that the shock transition found by Hixson *et al* [2] may be due to melting.

A large number of theoretical studies of Mo under pressure [4–12] have been mostly qualitatively consistent with the elementary structural predictions mentioned above, but there is as yet no consensus about the magnitudes of the theoretical transition pressures and no direct experimental observation of any pressure-induced transition.

The theoretical studies were done almost exclusively with the linear muffin-tin orbital method, either nonrelativistic or/and relativistic [8], in the atomic-sphere approximation [1] or the local-density approximation [9]. The reported transition pressures vary widely in different calculations, from 3.2 to 6.2 Mbar for the bcc–hcp transition, from 4.7 to 7.4 Mbar for the hcp–fcc transition, and from 5.8 to 7.2 Mbar for the direct bcc–fcc transition. The experimental studies were done predominantly with the DAC technique, which was progressively improved to reach higher and higher pressures, from 2.72 Mbar [4] to 4.14 Mbar [5] and then to 5.60 Mbar [6]. All experimental studies consistently found the bcc structure to be stable up to the highest pressure reached, i.e., no phase transition was detected.

We present here the results of calculations done with the full-potential linearized augmented plane-wave (FPLAPW) method within the generalized gradient approximation (GGA). The procedures used in these calculations (to be described below) are different from those employed in all previous publications on Mo under pressure. The pressure is treated here as an independent variable, and equilibrium states for bcc Mo, hcp Mo and fcc Mo at any given pressure  $p$  are found from minima of the Gibbs free energy at  $T = 0$  K,  $G = E + pV$  ( $E$  and  $V$  are energy and volume per atom, respectively). The structural stability of these states is tested by evaluating the corresponding elastic constants from second strain derivatives of  $G$ . The results predict a transition from bcc to hcp Mo at about 6.2 Mbar (consistent with the negative experimental findings up to 5.6 Mbar), and a transition from hcp to fcc Mo at about 7.7 Mbar. The pressure dependence of the lattice parameters and the volume per atom of bcc, hcp and fcc Mo are obtained directly from the calculations.

## 2. Calculation procedures

For bcc, fcc, or in general any body-centred tetragonal (bct) structure, or for the hcp structure, all defined by a set of lattice parameters  $a$ ,  $b = a$ ,  $c$  and angles  $\alpha = \beta = 90^\circ$  and  $\gamma = 90^\circ$

or  $120^\circ$ , the total energy was calculated with the WIEN2k computer program developed by Blaha and co-workers [13]. This program uses the FPLAPW method for computation of the electronic structure of solids from the Kohn–Sham equations of density functional theory [14, 15], allowing the choice of either nonrelativistic or semi-relativistic calculations within either the local-density approximation (LDA) or the generalized gradient approximation (GGA). The calculations in this work were done with the semi-relativistic GGA and with the following parameters: muffin-tin radius of Mo  $R_{MT} = 2.0$  bohr; criterion for energy convergence  $1 \times 10^{-6}$  Ryd; plane-wave cutoff  $RK_{max} = 8$ ; largest vector in the charge-density Fourier expansion  $G_{MAX} = 16$  bohr $^{-1}$ ;  $k$ -point sampling in the Brillouin zone of 10 000 points, corresponding to 725, 560 and 785  $k$ -points for bcc, hcp and fcc Mo, respectively, in the irreducible wedge of the Brillouin zone. The 4s and 4p states are treated as band states throughout the pressure range.

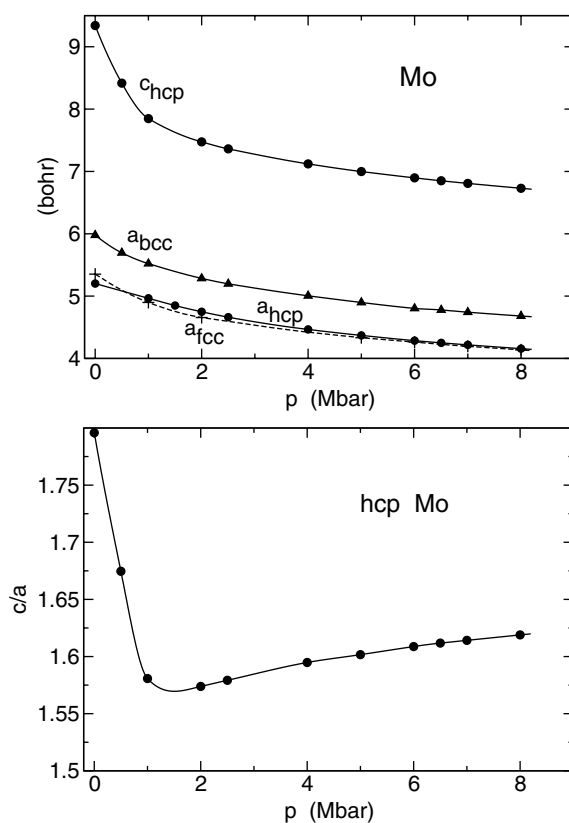
the determination of equilibrium states was done initially with the MNP procedure [16] and then with calculations of the epitaxial Bain path (EBP), which is a special path through tetragonal or hexagonal states that goes through *all* the equilibrium states. Those procedures are described in detail in previous publications [17, 18] and will only be briefly summarized here.

For any  $p \neq 0$  one chooses a value of  $a = a_1$  and varies the value of  $c$  until one finds the values  $c = c_1$  and  $E = E_1$  at which the slope of the energy  $E$  is  $(\partial E / \partial c)_a = -p a_1^2 \sin \gamma / 2$ , where  $\gamma$  is the angle between the  $a$  and  $b$  vectors ( $90^\circ$  for bcc structures,  $120^\circ$  or  $60^\circ$  for the hcp structures). This requirement for the slope of  $E$  arises from the condition that the stress  $\sigma_3$  in the  $c$  direction be equal to  $-p$  [17]. Then  $G_1 = E_1 + p V_1$  is the value of the free energy on the EBP at  $a_1$  and at pressure  $p$  ( $V_1$  is calculated from  $a_1$  and  $c_1$ ). The procedure is repeated for a sequence of choices of  $a$ , providing values of  $G$ , from which one can determine a minimum  $G_p$  which gives the Gibbs free energy at equilibrium at the chosen pressure  $p$ . Thus by choosing different values of  $p$  one determines an equilibrium path along which  $G(p)$ ,  $a(p)$ ,  $c(p)$  and  $V(p)$  are determined *directly*, i.e., avoiding constant-volume calculations to find equilibrium and evaluation of the pressure from  $-(dE/dV)$  along the equilibrium path.

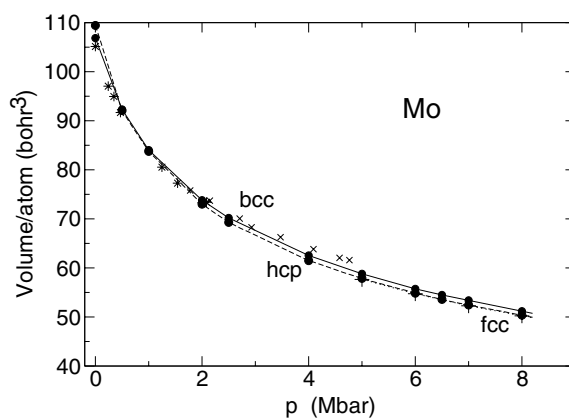
Investigations of the stability of the equilibrium states found at each  $p$  require evaluation of the elastic constants and tests that they satisfy the stability conditions for the crystal structure considered [19]. Procedures for the calculation of elastic constants involve applying appropriate strains to the unit cell, calculating the free energy of the strained cell and finally evaluating the curvature of  $G$  as a function of the strains [20] (the slope of  $G$  vanishes at equilibrium). For hcp structures one must also take into account internal relaxation, i.e., the fact that the nonequivalent atom in the hcp unit cell is free to move away from the position imposed by a homogeneous strain, thereby reducing the energy. Hence for hcp structures one distinguishes between approximate elastic constants determined with homogeneous strain, called *unrelaxed*, and elastic constants determined with inhomogeneous strain, called *relaxed*. In [20] a direct simple numerical procedure is given for calculating the relaxation effects.

### 3. Results and discussion

For each of the structures considered here (bcc, hcp and fcc) and for each pressure the calculations produce one value of the equilibrium free energy  $G$  and one value each for the lattice parameters  $a$ ,  $c$ ,  $c/a$  and  $V$ . We can therefore plot each of these quantities as a function of pressure. Figure 1 depicts the pressure dependence of the lattice parameters of the three structures. The behaviour is rather normal, except for the hcp  $c/a$  axial ratio, which drops linearly by about 10% within the first megabar, varying but little thereafter with increasing pressure. Figure 2 shows the equation of state for all three structures considered here, plus

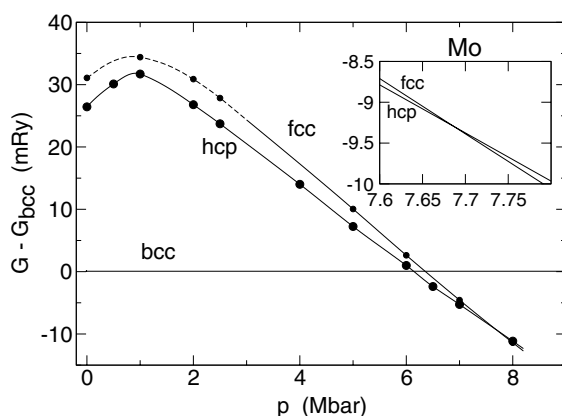


**Figure 1.** Calculated pressure dependence of the lattice parameters of bcc, hcp and fcc Mo (top panel) and of the axial ratio  $c/a$  of hcp Mo (bottom panel).



**Figure 2.** Theoretical pressure dependence of the atomic volume for bcc (full circles on solid curve), hcp (open circles on dashed curve), and fcc Mo (plus signs on dotted curve, from 5 to 8 Mbar only). The stars and crosses are experimental shock data from [17] and [18], respectively.

experimental shock data from McQueen *et al* [21] and Hixson and Fritz [22] for bcc Mo. The agreement of theory with experiment is good, being within 2%. In our results the volume difference  $V_{bcc} - V_{hcp}$  at the transition pressure of 6.2 Mbar is 0.9 bohr.



**Figure 3.** Free energy differences of hcp and fcc Mo with respect to bcc Mo. The dashed portion of the fcc curve indicates that fcc Mo is unstable in that region. The inset shows a magnified detail of the crossing between fcc and hcp free energies.

A plot of the free energies  $G$  of the three structures versus pressure shows small separation since all three have large values (from about  $-8099$  to  $-8095$  Ryd in the pressure range considered here), which differ from one another only by a few mRyd. More useful is a plot of the difference between the hcp and fcc  $G$  values and the bcc  $G$  value at the same pressure. Figure 3 shows the behaviour of these differences as a function of pressure. The bcc phase has the lowest free energy up to about 6.2 Mbar, where the hcp free energy crosses it. The hcp free energy in turn crosses the free energy of the fcc phase at about 7.7 Mbar (see the inset of figure 3). Above 7.7 Mbar, up to at least 8 Mbar, the fcc phase has the lowest  $G$  value and is the predicted ground state.

To establish the stability it is still necessary to test the stability conditions for each equilibrium state at least at some selected pressures. This test, as mentioned above, requires evaluation of all the elastic constants (six for tetragonal states, five for hexagonal states).

We first tested our procedures by calculating data for bcc Mo at zero pressure, for which experimental data are available, since that is the ground state. For the lattice parameter we find  $a = 3.1636$  Å, which compares favourably with the experimental value of 3.1468 Å [23] (0.5% difference). For the elastic constants  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ ,  $C' = (c_{11} - c_{12})/2$  and the bulk modulus  $B$  we find the results listed in the first row of table 1. The experimental data (at  $T = 0$  K) from [24] are given in parentheses in the second row: the differences amount to 0.3–1.5% for  $c_{11}$ ,  $c_{12}$ ,  $C'$  and  $B$ , and to about 14% for  $c_{44}$ ; hence the agreement is satisfactory,

We then calculated the elastic constants of bcc Mo at 6 Mbar, i.e., just before the  $G$  crossing with the hcp phase. These constants are listed in the third row of table 1: their values have increased, as expected, but the phase is still stable. It is interesting to compare our results with those of Christensen *et al* [9]. These authors presented a table of the pressure dependence of  $C'$ ,  $c_{44}$  and  $B$  for bcc Mo as calculated with the FP-LMTO method in the LDA approximation. Interpolating that table to about 6 Mbar we find  $C' = 4.07$  versus our 2.67,  $c_{44} = 6.8$  versus our 7.35, and  $B = 18.5$  versus our 20.5 (all in Mbar units). The agreement with our results is only fair; the differences are probably to be ascribed to the different calculation procedures adopted.

For the hcp phase we tested the stability at 7 Mbar, i.e., at a pressure at which its free energy is lower than that of the other two phases. We must evaluate all five elastic constants and take care of the internal relaxation for the shear constants  $c_{44}$  and  $c_{66}$ . The results are shown in rows 4 and 5 of table 1 (the numbers in square brackets are unrelaxed constants).

**Table 1.** Elastic constants of Mo structures at selected pressures. bcc = body-centred cubic; bct = body-centred tetragonal; fcc = face-centred cubic; hcp = hexagonal close-packed;  $p$  = hydrostatic pressure in Mbar;  $c_{ij}$  = elastic constants in Mbar;  $C' = (c_{11} - c_{12})/2$ ;  $B$  = bulk modulus. The numbers in parentheses in the bcc structure are experimental values at 0 K (from [24]). The numbers in square brackets in the hcp structure refer to unrelaxed constants. The \* in the fcc structure indicates that the elastic constants were not calculated, since the phase is unstable (energy maximum).

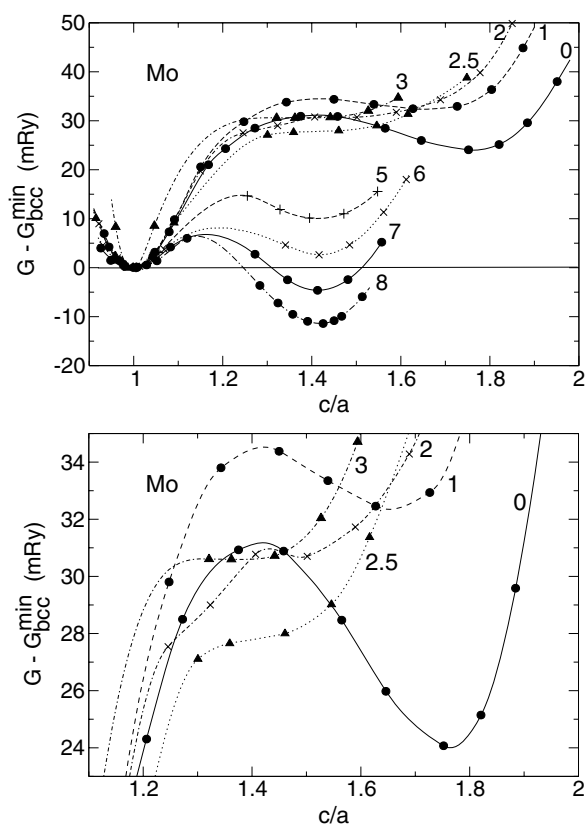
Structure	$p$	$c_{11}$	$c_{12}$	$C'$	$c_{13}$	$c_{33}$	$c_{44}$	$c_{66}$	$B$
bcc	0	4.5472 (4.5002)	1.7336 (1.7292)	1.4068 (1.3855)			1.0723 (1.2503)		2.6715 (2.6529)
	6	24.091	18.749	2.671			7.352		20.530
hcp	7	30.094	19.838	5.128	11.228	65.887	4.343	5.128	
	7						[4.356]	[6.759]	
bct	0	3.659	2.106	0.776	1.752	3.128	0.307	-1.491	
	1							-2.352	
	2							-0.656	
fcc	0 to 2	*	*	*	*	*	*	*	*
	3	12.706	11.312	0.606			4.668		11.777
	5	20.617	16.931	1.843			7.022		18.160
	8	32.040	23.073	4.483			9.608		26.062

Since relaxation always reduces  $c_{44}$  and  $c_{66}$ , relaxation is important for checking the stability. The stability conditions [19] are fulfilled, hence hcp Mo is stable at 7 Mbar.

The fcc phase requires a special discussion. At zero pressure we find fcc Mo to be unstable. This conclusion is immediately obvious from examination of the EBP for all tetragonal states of Mo in the form of energy versus axial ratio  $c/a$ . This EBP is the curve marked 0 (for  $p = 0$ ) in the top panel of figure 4, where the free energy is given in mRyd with respect to the bcc minimum at  $c/a = 1$ . At  $c/a = \sqrt{2}$ , the fcc phase, there is an energy maximum; hence the fcc phase is tetragonally unstable. There is also a higher-energy minimum at  $c/a = 1.76$ , a bct state of Mo which needs to be tested for metastability. The calculated elastic constants of this state are listed in row 6 of table 1, where  $c_{66}$  is negative; hence bct Mo is also unstable at zero pressure.

With increasing pressure the bct minimum moves left, towards smaller  $c/a$  values, as indicated by the curves marked 1, 2 and 2.5 (for  $p = 1, 2, 2.5$  Mbar, respectively). The evolution may be followed more easily in the magnified detail depicted in the bottom panel of figure 4. At 1 and 2 Mbar the bct state is still unstable, as shown by the negative values of  $c_{66}$  listed in table 1, and there is still an energy maximum at  $c/a = \sqrt{2}$ , i.e., the fcc phase is also still unstable. This situation is indicated by the \* listed in row 9 of table 1. At 2.5 Mbar the maximum and the minimum merge to give an inflection point, and at higher pressures they separate so that now there is a minimum at the fcc position (top panel of figure 4). We tested the stability of the fcc phase at 3, 5 and 8 Mbar—the corresponding elastic constants are listed in the bottom three rows of table 1, and they all satisfy the stability conditions. The conclusion is therefore that fcc Mo is unstable from 0 to about 2.5 Mbar, then becomes metastable up to about 7.7 Mbar, where its free energy crosses and becomes lower than that of the hcp phase, and at higher pressures (tested here only up to 8 Mbar) it becomes stable. We emphasize this conclusion in figure 3 by drawing the fcc curve dashed from 0 to 3 Mbar and solid at higher pressures.

The overall shapes of the free-energy difference curves in figure 3 resemble those presented in figure 1 of [9], but there is an important difference. Our figure 3 shows that the hcp-phase free energy lies below the fcc free energy at all pressures up to 7.7 Mbar (and becomes the ground state at 6.2 Mbar); at 7.7 Mbar the hcp free energy crosses the fcc free energy and fcc becomes the ground state. In figure 1 of [9] the hcp enthalpy (or free energy at 0 K) always



**Figure 4.** Epitaxial Bain paths of tetragonal Mo for several pressures. The ordinate is the difference between all free energies  $G$  and the minimum of the bcc structure  $G - G_{\text{bcc}}^{\text{min}}$ ; the abscissa is the axial ratio  $c/a$ . The numbers near each curve refer to the pressure in Mbar. The lower panel is a magnified detail of the region around  $c/a = \sqrt{2}$ .

lies above the fcc values and is never the ground state. This difference in the position of the fcc phase relative to the hcp phase may be due to our use of pressure as a basic variable so that the equation of state is not needed to find the equilibrium pressure. The necessity of differentiating  $E(V)$  to find the pressure loses accuracy compared to our direct procedure for determining the equilibrium state at a given pressure. Our procedure worked well in predicting the pressure of the hcp-to-bcc phase transition in Mg [18].

The result of the present study is therefore that the crystal structure of Mo changes from bcc to hcp at 6.2 Mbar and then from hcp to fcc at 7.7 Mbar. This result is in qualitative agreement with the elementary structural predictions of Moriarty [1] mentioned in the introduction, and illustrates the role played by the  $s \rightarrow d$  transition in this material. How this result compares with calculations by others and with experiment is shown in the summary of table 2. Three of those calculations do not result in the bcc–hcp–fcc sequence found in this work and by others, but find rather a direct transition from bcc to fcc. The experimental results, as mentioned above, are not relevant, as no transition was predicted by theory in the attainable range of pressures. The result of Ruoff *et al* [6] that bcc Mo is still stable at 5.6 Mbar is indeed consistent with our and Smirnova *et al*'s [11] result, but it would of course be desirable to have a positive confirmation. Unfortunately, the ultrahigh pressure range is still a very difficult range to



**Table 2.** Transition pressures for molybdenum. Summary of transition pressures (in Mbar) reported in the literature from theoretical and experimental studies of the crystal structures of Mo at ultrahigh pressures. The theoretical results apply to 0 K. The experimental results are given in the ‘shock data’ and ‘DAC data’ (diamond-anvil-cell data) lines.

Source	bcc $\rightarrow$ hcp	hcp $\rightarrow$ fcc	bcc $\rightarrow$ fcc
Hixson <i>et al</i> <sup>a</sup>	3.2	4.7	—
Moriarty <sup>b</sup>	4.2	6.2	—
Söderlind <i>et al</i> <sup>c</sup>	5.2	7.4	—
Christensen <i>et al</i> <sup>d</sup>	—	—	5.8
Boettger <sup>e</sup>	—	—	6.6
Smirnova <i>et al</i> <sup>f</sup>	6.2	—	—
Belonoshko <i>et al</i> <sup>g</sup>	—	—	7.2
This work	6.2	7.7	—
Shock data <sup>a</sup>	2.1	—	—
DAC data <sup>h</sup>	>5.6	—	—

<sup>a</sup> Reference [2]. Acoustic velocity data were interpreted to demonstrate a ‘solid–solid’ transition at about 2.1 Mbar and 4100 K, but no information was given about the structure of the final phase. The ‘solid–solid’ was tentatively identified with the bcc  $\rightarrow$  hcp transition.

<sup>b</sup> Reference [7].

<sup>c</sup> Reference [8].

<sup>d</sup> Reference [9]. The enthalpies of bcc and hcp Mo were found to cross at 6.5 Mbar, but the fcc phase has the lowest enthalpy above 5.8 Mbar.

<sup>e</sup> Reference [10]. The 6.6 Mbar result was obtained with a relativistic treatment; a nonrelativistic calculation yielded 4.7 Mbar.

<sup>f</sup> Reference [11]. The quoted result of 6.2 Mbar was found with the full-potential linear muffin-tin orbital (FP-LMTO) method. An LMTO Green function method within the coherent potential and atomic-sphere approximations (LMTO-GF-CPA-ASA) found 7.3 Mbar.

<sup>g</sup> Reference [12].

<sup>h</sup> Reference [6]. Room-temperature result.

attain reliably by static-pressure experiments. Despite the efforts of other experimentalists (Takemura and Nakano [25] reached 2.23 Mbar by using synthetic diamond as a backing plate in the DAC) the maximum pressure attained in a DAC remains 5.6 Mbar, as reached by Ruoff *et al* [5]. The calculations of Smirnova *et al* [11] indicate that alloys of Mo with Re and Os should have notably lower transition pressures, suggesting that x-ray experiments on such alloys may be useful to clarify the structural sequence of pure Mo. At ultrahigh pressures there is in addition the difficult problem of ensuring hydrostaticity [26, 27].

#### 4. Conclusion

Calculations with the FPLAPW-GGA method find pressure-induced transitions in Mo from bcc to hcp at 6.2 Mbar and from hcp to fcc at 7.7 Mbar. The stability of the structures is studied by evaluation of the corresponding elastic constants to pass the stability-conditions test. The fcc structure is found to be unstable from 0 to about 2.5 Mbar, then metastable up to 7.7 Mbar and finally stable at higher pressures. The bcc structure is confirmed to be stable at 6 Mbar, the hcp structure at 7 Mbar and the fcc structure at 8 Mbar.

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