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The phase diagram of molybdenum at extreme conditions and the role of local liquid structures

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Recent DAC measurements made of the Mo melting curve by the x-ray diffraction studies confirms that, up to at least 110 GPa (3300K) melting is directly from bcc to liquid, evidence that there is no basis for a speculated bcc-hcp or fcc transition. An examination of the Poisson Ratio, obtained from shock sound speed measurements, provides evidence that the 210 GPa (4100K) transition detected from shock experiments is a continuation of the bcc-liquid melting, but is from a bcc-to a solid-like mixed phase rather than to liquid. Calculations, modeled to include the free energy of liquid local structures, predict that the transition from the liquid to the mixed phase is near 150 GPa(3500K). The presence of local structures provides the simplest and most direct explanation for the Mo phase diagram, and the low melting slopes.

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I. Introduction

The phase diagram of molybdenum has become a controversial topic as the result of the conflicting interpretation of experimental shock melting measurements[1,2] and Diamond-anvil-cell(DAC)[3,4]. The relevant data is plotted in figure 1. Chronologically, it all begins with the shock experiments for Mo, made in 1989 by Hixson et al., in which two discontinuities in the longitudinal sound speed were detected[1]. One discontinuity is near 210 GPa (~4100K), and a second near 390 GPa (~10,000K). While the pressures

are measured, temperatures are calculated due to experimental limitations. Since the calculated temperatures vary considerably in accordance with the theoretical methods, for consistency we employ the temperatures first reported by Hixson et al, cited above. The shock discontinuity at 210 GPa has been interpreted as an bcc-hcp transition, and at 390 GPa as melting. Based on this interpretation a number of theoretical studies and computer simulations have predicted Lindemann-like melting curves (dashed line in figure 1) connecting from the normal melting point at 2860 K to 390 GPa.

Subsequent to the shockwave studies, in 2001, the Mo melting curve was measured statically to 90 GPa(3180 K) using a laser heated diamond anvil-cell(DAC)[3] and melting was detected by the observation of liquid motion upon heating the sample. Clearly, an extrapolation of the Mo DAC melting measurements points directly to the first shock discontinuity near 210 GPa, rather than the 390 GPa discontinuity. This suggests that the 210 GPa transition is an extension of the melting curve. Since the DAC melting slope is unusually small, ($dP/dT \sim 0$), this feature is at odds with the predictions of virtually all theoretical and computer simulations, and this has lead to a considerable degree of skepticism regarding the goodness of the data and whether the melting is actually a bcc-hcp transition[5]. In order to address these doubts, Santamaria-Perez et al.[4] employed the X-ray diffraction method at Grenoble, to detect melting that confirmed the earlier measurements, and extended the melting curve to 110 GPa(3300K). These data were included in figure 1. They found no evidence in their X-ray patterns to suggest the presence of a transition to higher temperature crystalline structure.

Low melting slopes have now been found in all seven of the early transition metals studied[3], Ta, W, Cr, Ti, V, Y, and Mo, indicating that the results for Mo and Ta are not unique, but are characteristic of this class of metals. In the case of Ta, just as in Mo, the melting measurements made by optically observing speckle motion in the liquid, have been confirmed by X-ray diffraction studies[6]. The origin of the low melting slopes have been attributed to Peierles/Jahn-Teller(P/JT) distortions of the *d*-electron bonding leading to the presence in the liquid of energetically preferred local structures with polytetrahedral and five-fold icosahedral short range order(ISRO)[7,8]. The presence of

such structures in transition metal liquids is now well documented, and a listing of experimental and theoretical references is included in two earlier reports [7,8].

Local liquid structures lower the melting temperature, by frustrating long-range ordering and crystal formation, and by increasing the communal entropy. Pressure induces an increase in their concentration maintaining a melting temperature lowering leading to low melting slopes (dT/dP). The P/JT distortion is optimal in the case of Mo, studied here. With nearly half-filled bands, the distortion lowers the energy of the occupied bonding states while the unoccupied anti-bonding states are raised in energy. This leads to the very low melting slopes observed ($dT/dP \sim 0$). In general, we find that early transition metals, which have narrow d -electron bands leading strong P/JT distortions, have melting slopes that are considerably lower than for the late metals Ni, and Fe, and much lower than Cu[7,9]. The melting of transition metals is intimately connected to the electronic structure of the liquid

From the perspective of the present author, much of the present controversy regarding Mo, stems from the reluctance of theoreticians, and computer simulators[5], to accept the validity of the DAC melting measurements. In section II of this paper we review the experimental evidence provided by the two different detection techniques, optical and X-rays, used in laser heated DAC melting measurements. These measurements are in agreement, and show that bcc Mo melts to a liquid phase at least up to 110 GPa and 3300 K, the highest pressure to which such measurements have been made. In section III we use the sound speed shock data, reported by Hixson et al., to calculate the Poisson Ratios at pressures along the Hugoniot. They show that the 210 GPa shock cannot be of bcc to hcp as initially suggested [1], but is instead of a bcc to a solid-like, but non-crystalline phase. This implies that there is a transition from the liquid to the solid-like phase at a pressure between 110GPa and 210 GPa. Section IV describes calculations made with a free energy model that place the transition near 150 GPa, and a new phase diagram is proposed. In section V, we examine the possibility that the melting observed in the DAC is a bcc to an hcp transition[5d]. Calculations made including the thermal electron entropy show that over the temperature range of

interest here, there is no support for a bcc to close-packed transition. The results of this study and conclusions are summarized and discussed in section VI.

II. Evidence for a solid to liquid melting curve up to 110 GPa (3300K).

The first measurements of Mo melting at very high pressure were made with the laser-heated DAC technique, and using the onset of laser speckle motion to detect the liquid phase[3]. This technique is very well suited to distinguish between solid-solid, and solid-liquid transitions. When a solid-liquid transition is crossed, by increasing the laser power, speckle motion is maintained even when the laser power is held constant. In contrast, whenever a solid-solid or solid-glass transition is crossed one observes a discontinuous, single event change in the laser speckle pattern. In all of the melting measurements, speckle motion was clearly observed. The earlier measurements have now been confirmed by a second method; by X-ray diffraction in a double-sided laser-heated DAC using synchrotron radiation and extended up to 110 GPa and 3250 K[4]. The results of both sets of measurements are plotted in figure 1, and are in excellent agreement.

In the x-ray diffraction measurements melting was detected by several criteria; the appearance of diffusive scattering characteristic of the liquid state, the disappearance of Bragg peaks, and the onset of rapid crystallization, which is not observed in a solid-solid transition. On cooling the Mo-bcc diffraction spots reappeared at the same time as the diffused scattering disappeared indicating freezing. In other words the process is reversible, bcc to liquid and back to bcc without intermediate structures. In the case of Ta, which has a melting curve similar to Mo, the melting curve determined in the DAC by observing speckle motion, has also been confirmed by using X-ray diffraction in to detect melting[6,10]. This is further evidence that the two experimental methods provide consistent evidence for a bcc-liquid transition with a low melting slope. There is no evidence from the DAC X-ray measurements in support of Mo, or Ta, undergoing a transition from bcc to another crystalline or solid-like structure, at least up to 110 GPa. The failure of computer simulations to reproduce these results does not constitute proof.

III. Evidence of a solid-like complex melt phase near 210 GPa

While there is strong experimental evidence for the 210 GPa shock transition from the sound speed measurements, there is little evidence as to the nature of the high pressure phase. Some insight can be obtained from an examination of the longitudinal(C_L) and bulk(C_B) sound speed measurements[1]. The two sound speeds are related to the Poisson Ratio(ν) by the expression,

$$C_L/C_B = [3(1-\nu)/(1+\nu)]^{1/2}.$$

The Poisson Ratio is the ratio of strain in the lateral direction to the strain in the longitudinal direction. For isotropic materials, such as ideal bcc and close-packed structures like hcp and fcc, $\nu=0.25$, and for liquids $\nu=0.5$. For most metals it is typically in the range 0.28 to 0.35. For Mo $\nu = 0.31$, and for Al, $\nu = 0.32$.

For the purpose of gaining some guidance in interpreting the Mo data, consider first the melting of Al. It is well understood as a transition directly from fcc solid to a pure liquid. The DAC melting curve and shock melting for Al are in excellent agreement[11]. Plotted in figure 2, are measurements of the sound speeds of shock compressed Al[12] and Mo[1], versus the Hugoniot pressure. The sound speeds for fcc Al, increase linearly with pressure up to 120 GPa and then show a discontinuous drop to the liquid phase. A data point has been taken in the mixed phase region. The Poisson Ratios for Al are plotted in figure 3. They show a small increase in the Ratio from 0.32 to 0.34 near 120 GPa, then a discontinuous jump to 0.5, the liquid value. The mixed phase regime in Al ranges from $\nu=0.35$ to 0.5, with an experimental point at 0.46.

In the case of Mo, an interpretation of the sound speed data is problematical. While fcc Al, and bcc Mo, have sound speeds with nearly the same pressure derivative, the intermediate range Mo sound speeds are more liquid-like, providing evidence for a loss of shear strength relative to the crystalline solid. The values of ν calculated from the sound speeds are plotted in figure 4. In analogy with Al, we assume that starting from the crystalline value of 0.31, ν remains constant to 150 GPa where it increases to $\nu=0.42$. The data near 150 GPa to 200 GPa, shows some irregularity, in that from two points at

150 GPa, v drops in a continuous fashion from 0.42 to 0.36 at 200 GPa. This may be evidence of a shock overshoot, or indicate the onset of the transition near 150 GPa. This would place it in good agreement with a linear extrapolation of the DAC melting. Unfortunately, there are no sound speed measurements below 150 GPa that might help better define this pressure range. At the 210 GPa shock discontinuity, the value of v increases linearly to 0.44 at 380 GPa, where it jumps to the liquid value of $v=0.5$ at 390 GPa. The values of v over the pressure range above 150 GPa, is evidence of a mixed phase that melts to a liquid at 390 GPa.

These results are evidence that at a pressure of the 210 GPa discontinuity and above, Mo is neither a liquid nor a crystalline metal, and in analogy with Al, it is a mixed phase. However, since the mixed phase supports longitudinal sound waves, it has shear strength and is solid-like, and possibly glass-like. Hixson et al.[1] had noted, that at 210 GPa the Poisson ratio of 0.4 was considerably higher than the normal density value. Since the DAC measurements provide evidence for a liquid melt phase up to at least 110 GPa, and evidence from shock measurements of a solid-like mixed phase at 210 GPa, then there is reason to expect the presence of a transition from the liquid melt to the solid-like phase at some intermediate pressure.

IV. Free energy model calculations of Mo melting, and a liquid to solid-like transition.

While a rigorous theoretical effort to predict the melting of Mo, and a transition to a complex-solid like phase is beyond the scope of this study, a considerable degree of clarification can be gained by the use of a free energy model, reported earlier in some detail[13], in which we first introduced the idea that local structures in liquid Mo would significantly influence the melting. Subsequently we learned that local polytetrahedral structures and ISROs have been detected in liquid transition metals at low pressure and since they are denser than the normal liquid, and are energetically favored, their stability and concentration is enhanced with increasing pressure increasing the communal entropy, further stabilizing the liquid, lowering the freezing temperature, thereby maintaining a low melting slope[7,8].

The excess Helmholtz free energy of the solid and liquid, for a system of atoms interacting by inverse-power repulsive potentials, $\phi(r)=B/r^n$, can be expressed as,

$$\begin{aligned} F_{ex}^s &= U_M + F_{th-inv}^s, \\ F_{ex}^l &= U_M + F_{th-inv}^l. \end{aligned} \quad (1)$$

In each expression, the first term is the Madelung energy(U_M) of the solid and the second is of the thermal free energy of atomic motion in the solid and liquid respectively. The thermodynamic properties of the inverse power potential has been studied extensively by computer simulations, and the thermal free energy terms in (1) have been fitted to analytic expressions[14]. A useful simplification for applications to real systems is to replace the Madelung energy, U_M , by U_{Lat} the lattice energy determined from a Birch-Murnaghan fit to the experimental room temperature isotherm by Ruoff et al. [15], corrected to $T=0$ K. The excess Helmholtz free energy can now expressed written as,

$$\begin{aligned} F_{ex}^s &= U_{Lat} + F_{th-inv}^s. \\ F_{ex}^l &= U_{Lat} + F_{th-inv}^l. \end{aligned} \quad (2)$$

The model has the attractive feature that it reproduces the room temperature solid isotherm, and provides a thermodynamically consistent set of solid and liquid free energy functions. Melting is determined by matching free energies of the two phases. As it stands, the model requires two adjustable parameters, B and n , both in the potential. In the present application we chose $n=6$, and $B= 400$ eV-cm⁶. These values had been determined in an earlier paper by fitting the model predictions to the experimental Mo Hugoniot[13].

Using the parameters B and n , two sets of melting calculations were made. In one set, using equations (1), atoms in the bcc solid melt to an atomic liquid. In the second set, terms were added to the liquid free energy in order to account for the influence local structures or clusters. In the latter case, the free energy of the liquid is modified to,

$$F_{ex}^l = U_{Lat} + F_{th-inv}^l + xU_{cl}^l + kT[x \ln x + (1-x)\ln(1-x)]. \quad (3)$$

The added terms are, U_{cl} the binding energy of a local cluster, and the communal entropy of liquid-cluster mixing. Since U_{cl} is an unknown, and to avoid additional

fitting parameters, we set $U_{cl}=0$. The variable x is a “generalized” cluster fraction, defined here as the volume fraction of local clusters the melt, $x=V_{cl}/V$. It is employed here as a parameter to fit the DAC melting measurements and the 210 GPa shock discontinuity. In effect, x implicitly includes contributions from U_{cl} and the influence of geometric frustration, and jamming that are not thermodynamic drivers, but do act to inhibit long-ranged crystalline formation. The present model is clearly not predictive. It is intended to examine the physics responsible for the low melting temperatures recorded by the experimental measurements, and to clarify the role played by local structures that are neglected in computer simulations[5]. In this regard, computer simulations are valuable because they point out that atomic liquids don’t work.

Plotted in figure 5 are the two sets of DAC melting measurements, the shock melting points, and calculations made with the free energy of the model of the melting curves calculated with, and without clusters, and the Hugoniot of a bcc solid and the liquid. Figure 6 shows that the cluster fraction needed to fit the DAC measurements and the 210 GPa point reaches a maximum value of $x=0.5$ near 150 GPa. This maximum can be interpreted, that at 150 GPa (3500K) the fraction of clusters has become sufficiently large as to create a solid-like mixed phase. This agrees with the conclusions from the analysis of the Poisson Ratio plot (figure 4), that a transition exists between the liquid melt and a solid-like phase at a pressure between 110GPa and 210GPa. Figure 7 is a proposed phase diagram with the transition starting at 150 GPa, and extended to 390 GPa where it crosses the Hugoniot. A similar suggestion had been made by Errandonea[10]. Since the local tetrahedral and ISRO structures are denser and have a lower energy than the close-packed crystalline structures, then with increasing pressure the fraction of denser structures will be favored, thereby increasing the communal mixing entropy, lowering the liquid free energy, and maintaining a low melting temperature despite the increasing pressure. However, geometric incompatibility due to local structures will frustrate any tiling of the entire space and inhibit the formation of a crystalline solid with long-range order. At some concentration of local structures the melt phase will lose its liquidity and solidify, but not into a crystalline phase. It remains uncertain

whether the transition is continuous, or first order, or if the final is possibly a glass. The failure of theoretical calculations to correctly predict the melting can be attributed to the neglect of locally preferred structures.

V. The high temperature bcc to close-packed transition

Despite the fact that the DAC melting measurements obtained by observing speckle motion, and by x-ray diffraction, both show clear evidence for a bcc to liquid phase, there remains some skepticism that the measurements are in fact of a transition of bcc to a close-packed solid, rather than melting [5]. Possibly, the most complete study of the temperature dependence of the bcc-hcp transition has been that of Moroni et al.[16], who examined the thermal stability of eight early transition metals at $P=0$, by calculating the temperature dependence of the Gibbs free energy. In their calculation, the total electronic and vibrational free energy was obtained using *ab initio* local density band theory. They examined the relative importance of each energy term in regard to its importance in determining a structural change. They found that in the change going from bcc to hcp, the vibron free energy is relatively unimportant, in comparison to the lattice energy and the electron thermal free energy. In fact the driving force for the transition is dependent on the relative magnitudes of the bcc and hcp electron density of states at the Fermi surface.

Bcc Mo is extremely stable. Room temperature DAC X-ray diffraction measurements have found that the bcc structure is stable to at least 560 GPa[17]. A recent theoretical prediction places the bcc-hcp transition at 620 GPa, and the hcp-fcc transition at about 700 GPa[18]. In the present study predictions of a possible high temperature bcc-hcp transition were made by calculating free energies using the same model used to calculate the melting curve in the previous section(III). That is, except for the addition of a third term for the electron thermal free energy[2]. The Helmholtz free energy for the two phases is expressed as,

$$A_{bcc} = E_{lattice}^{bcc} + A_{inv6-th}^{bcc} + A_{el-th}^{bcc}$$

$$A_{hcp} = E_{lattice}^{hcp} + A_{inv6-th}^{hcp} + A_{el-th}^{hcp},$$

and

$$A_{el-th} = -\frac{\pi^2}{6} \rho(E_F)(k_B T)^2,$$

$\rho(E_F)$ is the electron density of states(EDOS) at the Fermi level, valid for $kT \ll E_F$. The values of $\rho(E_F)$ used in the calculations were taken from Moriarty[19], and were made using electron band theory. The bcc-hcp transition is determined by equating the Gibbs free energy of the bcc and hcp phases. $G = A + PV$, where P and V are the pressure and volume of each phase. A simplifying feature in calculating, $G_{bcc} - G_{hcp}$, is to use $E_{hcp} - E_{bcc} = 36.5$ (mRy/atom) from Moroni et al. The total pressure is obtained using a Birch-Murnaghan fit to the DAC room temperature isotherm, and corrected to 0 K as the lattice pressure. By adding the vibrational pressure of the atomic motion, and thermal electron pressure we have: $P = P_{lattice} + P_{vib} + P_{el-th}$.

Plotted in figure 8 are the Gibbs free energies from Moroni et al. at $P=0$, and those of the present model calculations at $P=0$, and at 210 GPa. The calculations of Moroni et al. were made to only 4000 K, but by plotting and extrapolating their results to higher temperatures we find a bcc-hcp transition is predicted near 7500 K ± 1000 K. This is in reasonable agreement with our prediction near 7000 K. At 210 GPa our model predicts a transition to hcp near 11000 K. These temperatures are well above the DAC melting and the 210 GPa shock transition temperature(4100K).

An interesting feature of the calculations is how the pressure dependence of the electron density of states influences the bcc-hcp transition temperature. The values of $\rho(E_F)$ used in these calculations[2] are plotted in figure 9. We see that with increasing pressure the bcc $\rho(E_F)$ remains relatively constant while for hcp it is decreasing. Since bcc is energetically very stable compared to hcp, this means that with increasing pressure, and decreasing hcp EDOS, a transition from bcc to hcp requires a compensating increase in temperature. This is in order to provide an electronic entropy that is sufficiently large to overcome the much lower bcc energy. This leads to a rise in the transition temperature from 7000 K at $P=0$, to near 11,000 K at 210 GPa. We find, in agreement with Moroni et al., that the difference in energy, $E_{hcp} - E_{bcc} = 36.5$ (mRy/atom), is so large that the crossover in Gibbs free energy can only happen at temperatures much above the melting temperature.

V. Summary and Discussion

The DAC measurements of Mo melting that originally showed melting to be from bcc to liquid, and made by detecting the liquid speckle motion, have now been confirmed by the x-ray diffraction studies of Santamaria-Perez et al[4]. We can conclude that, to at least 110 GPa (3300K), melting is directly from bcc to liquid. These measurements cannot be conveniently ignored in favor of a bcc-hcp or fcc transition [5]. At higher pressure, near 210 GPa (4100K), an examination of the Poissons Ratio obtained from the shock sound speed measurements leads to evidence that pressure induces a non-crystalline solid-like, possibly polymorphic mixed phase. In combination the DAC measurements and shock sound speed measurements point to the presence of a transition at an intermediate pressure, predicted by model calculations to be near 150 GPa. Extrapolating from this pressure the phase line rises to cross the Hugoniot near 390 GPa. Since the DAC and shock melting measurements examine different regions of pressure and temperature, they are highly complementary. The proposed phase diagram resolves what appeared to be experimental discrepancies. The presence of local structures in the liquid provides the simplest, and most direct, physical explanation for the melting curves and phase diagram, including the failures of computer simulations to correctly predict the melting curve. The challenge facing predictive models, employing computer simulation methods, is the need to include the contribution of local structures to the free energy, since it is the essential and unavoidable feature of the physics.

From a broader perspective, it is now well established that elements with partially filled *p*-electron valence shells have directional bonding and local liquid structures[20]. Therefore, it should come as no surprise, that transition metal liquids with partially filled *d*-electron bands might also exhibit directional bonding, forming structured liquids, and undergo pressure-induced transitions to polymorphic phases. The scarcity of experimental evidence for recognizing similar features in transition metals is at least partially due to the relatively high temperatures of their liquids. However, with the advent of the laser-heated diamond-anvil-cell technique it has now become possible to

access melting curves of transition metals up to at least 110 GPa and 3500K, and to investigate the influence of the liquids electronic structure.

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Figure captions.

Fig. 1 Experimental and theoretical Melting data: DAC measurements of Errandonea et al[3](open circles) and x-ray diffraction measurements of Santamaria-Perz et al.[4](filled circles). Shock sound speed discontinuities(crosses)[1]: Calculated Hugoniot (solid curve) and melting curve (dashed curve)[2].

Fig. 2 Longitudinal and bulk sound velocities for Al[12] and Mo[1].

Fig. 3 Poisson Ratios for Al versus pressure, calculated from sound velocities.

Fig. 4 Poisson Ratios for Mo versus pressure, calculated from sound velocities.

Fig. 5 Melting curves. DAC open circles[3,4]. Calculated melting curves and Hugoniot, plotted are indicated and described in text

Fig. 6 Calculated cluster volume fractions in melt versus pressure.

Fig. 7 A proposed Mo phase diagram.

Fig. 8 Gibbs free energy difference for bcc and hcp Mo ($G_{bcc} - G_{hcp}$). Moroni et al.[16] (dashed curve). Present calculations (solid curves),

Fig. 9 The electron density of states of bcc and hcp Mo[19].

Figure 1

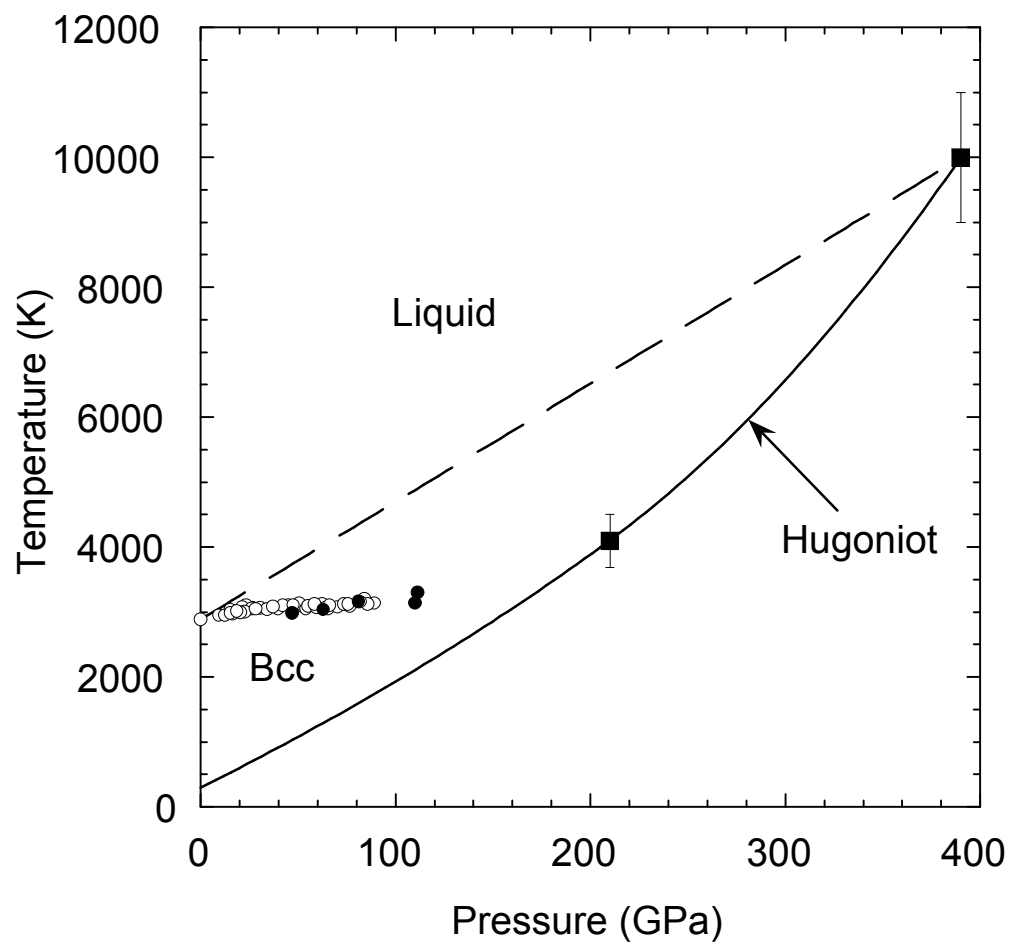


Figure 2

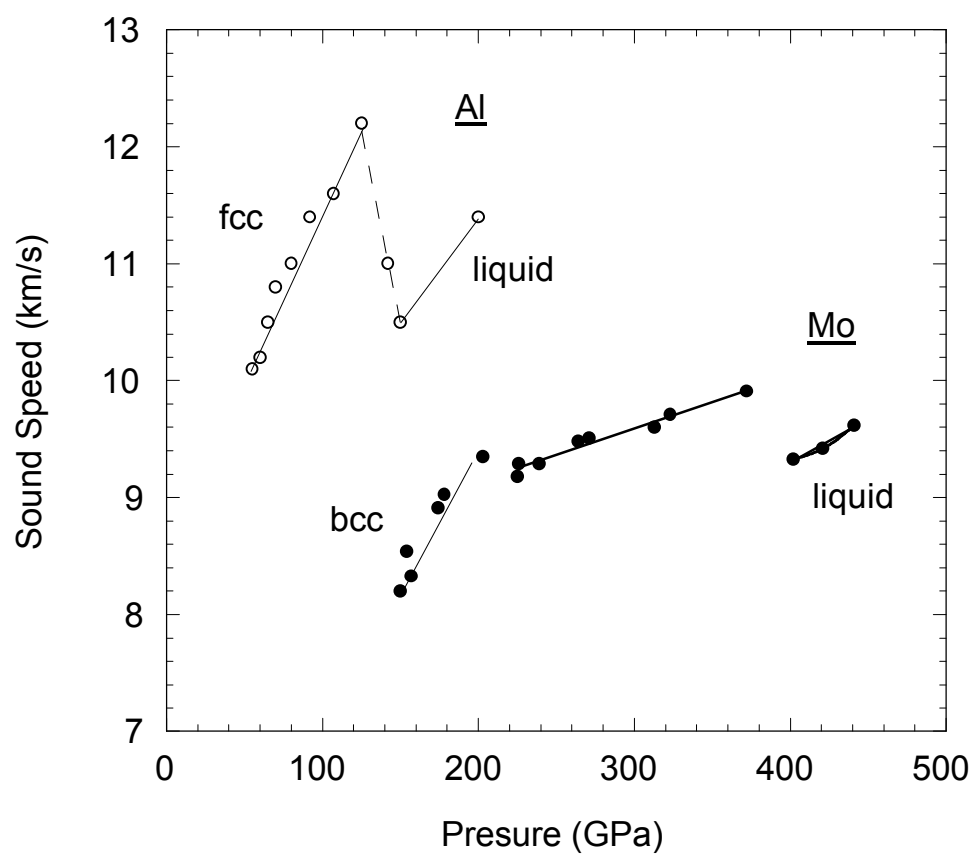


Figure 3

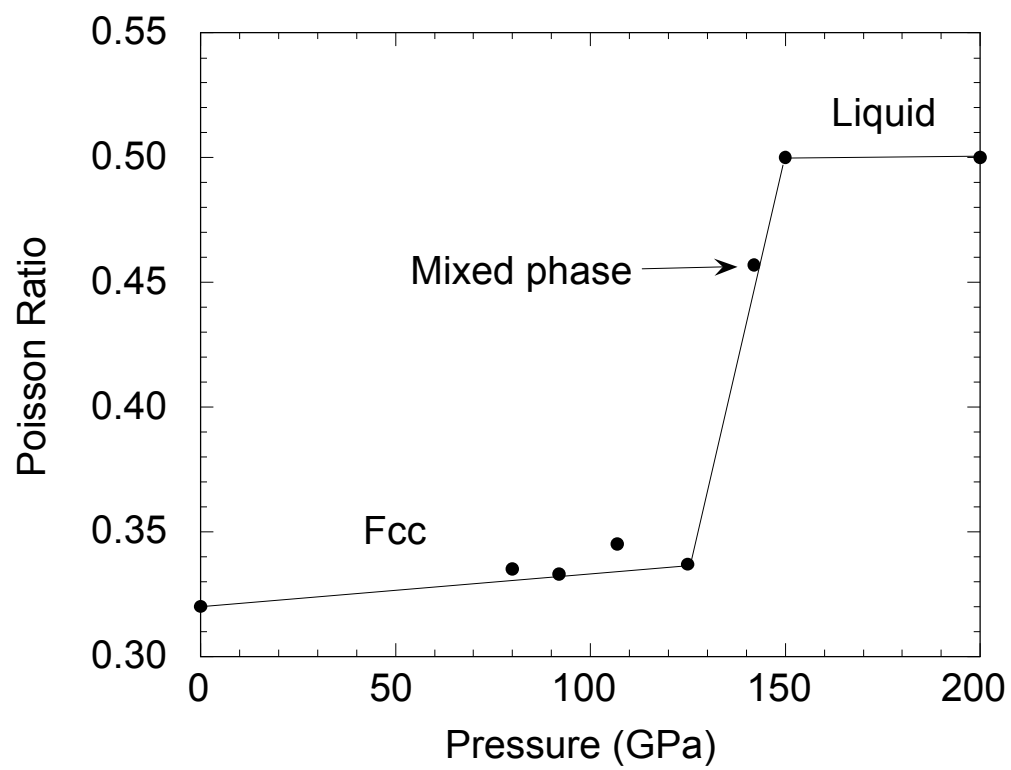


Figure 4

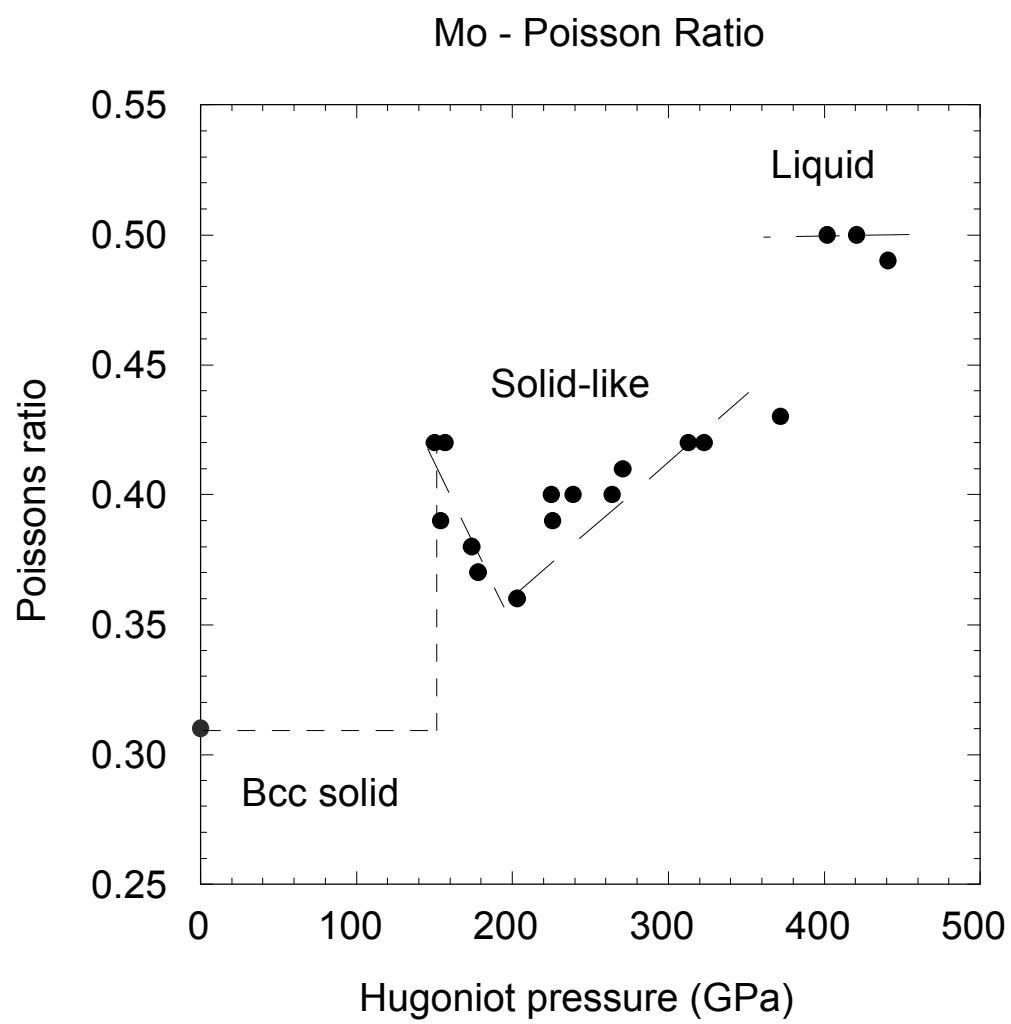


Figure 5

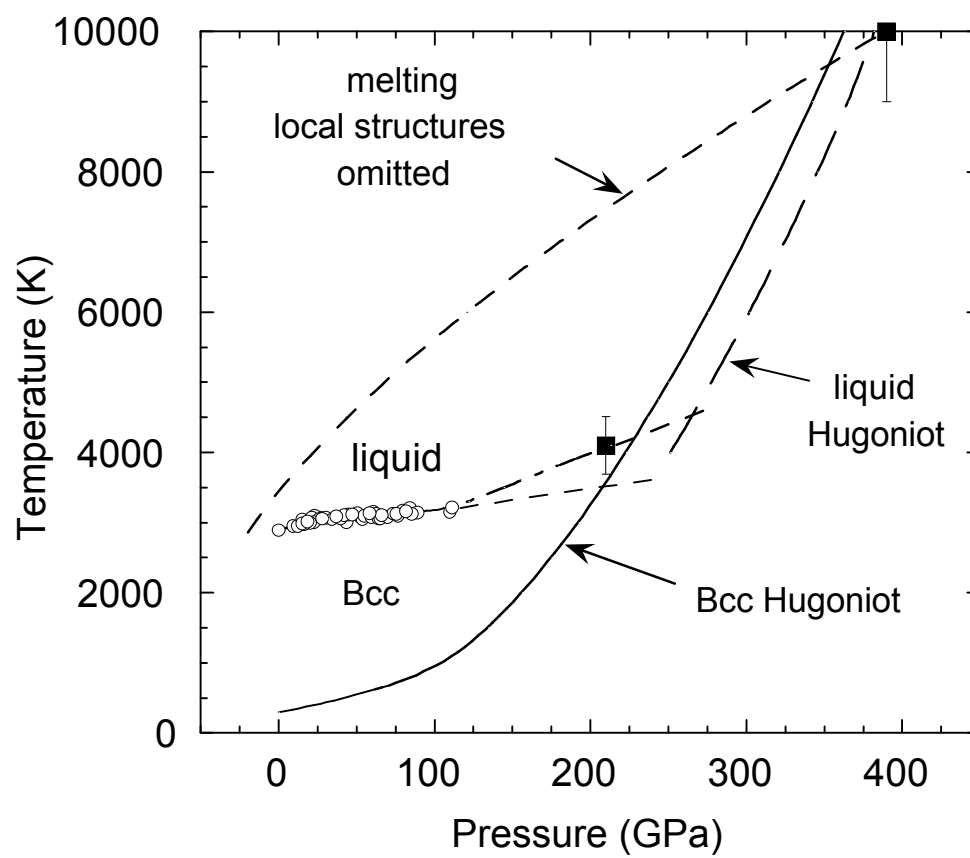


Figure 6

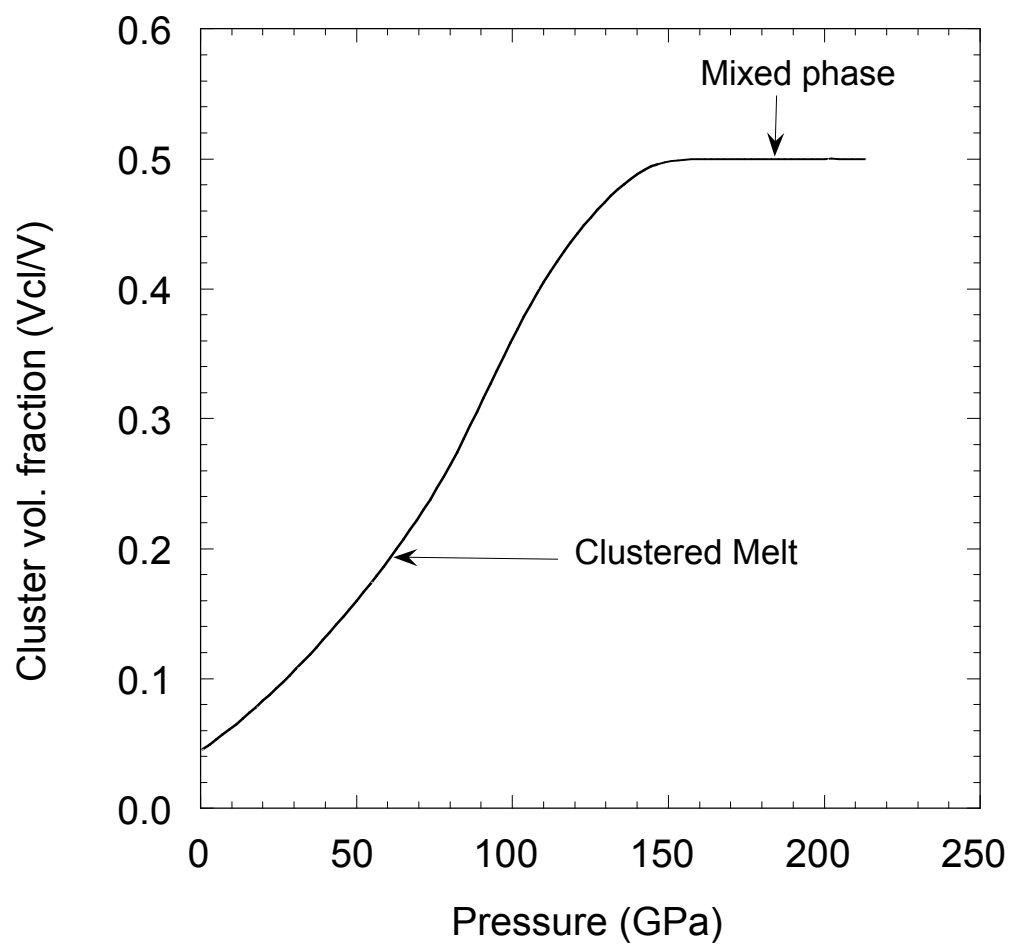


Figure 7

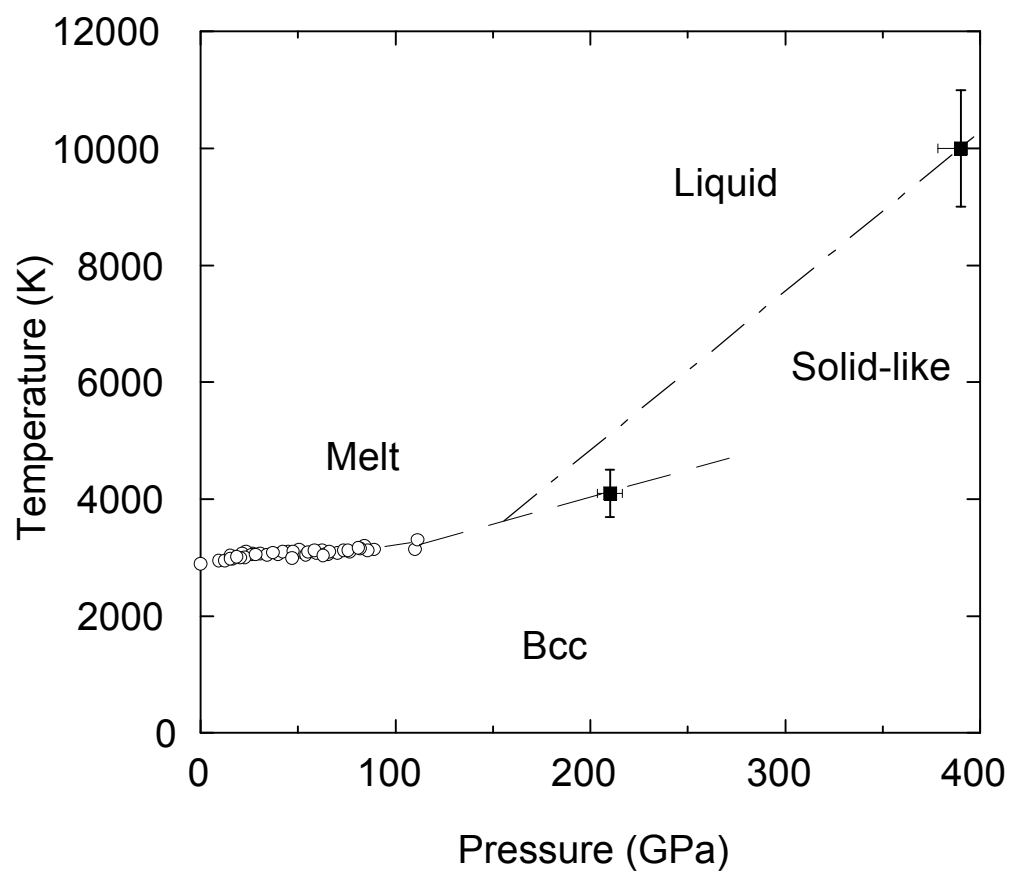


Figure 8

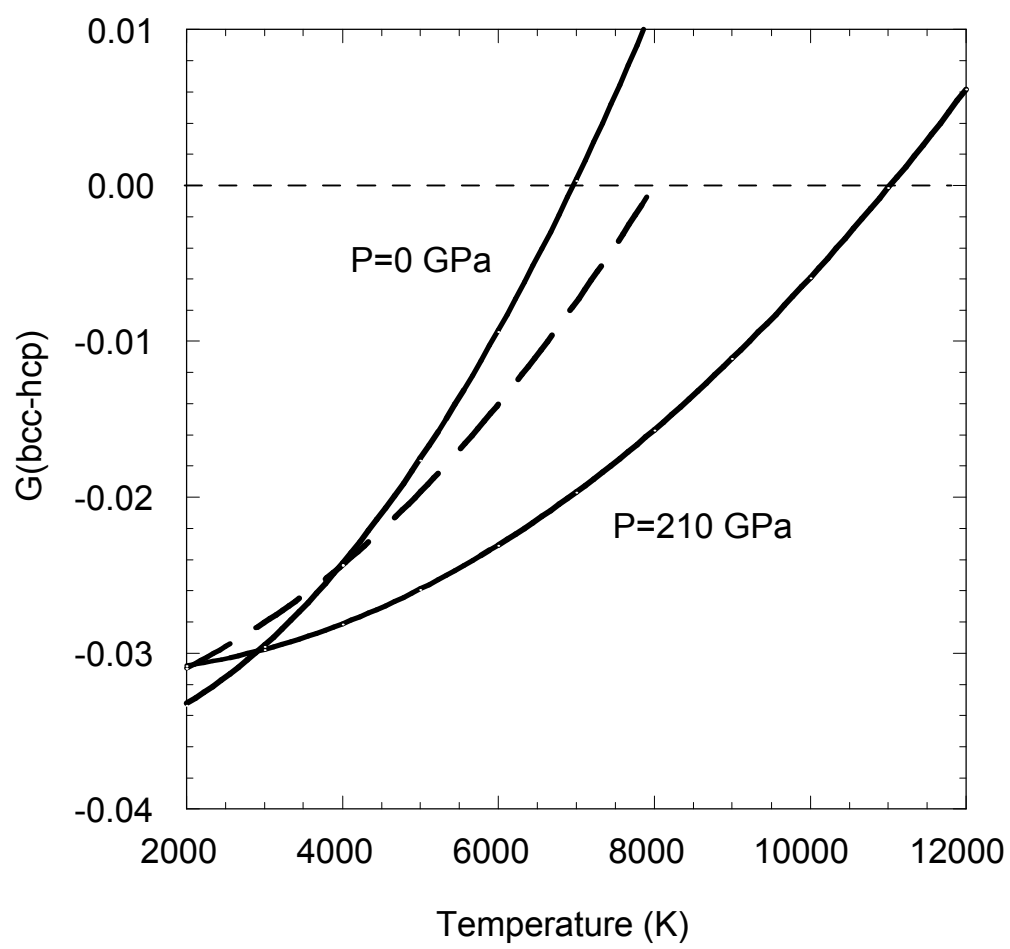


Figure 9

