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FIRST-PRINCIPLES PRESSURE-TEMPERATURE PHASE DIAGRAMS IN METALS

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Using interatomic potentials derived from first-principles generalized pseudopotential theory, finite-temperature phase transitions in both simple and transition metals can be studied through a combination of analytic statistical methods and molecular-dynamics simulation. In the prototype simple metal Mg, where volume and pair forces adequately describe the energetics, a complete and accurate phase diagram has thereby been obtained to 60 GPa. A rapidly temperature-dependent hcp-bcc phase line is predicted which ends in a triple point on the melting curve near 4 GPa. In central transition metals such as Mo or Fe, on the other hand, the energetics are complicated by *d*-state interactions which give rise to both many-body angular forces and enhanced electron-thermal contributions. We have made a detailed study of these phenomena and their impact on melting in the prototype case of Mo and a full melting curve to 2 Mbar has been obtained. In the case of Fe, we are examining the high-pressure phase diagram and the question of whether or not there exists a high-pressure, high-temperature solid bcc phase, as has been speculated. To date, we have shown that the bcc structure is both thermodynamically and mechanically *unstable* at high pressure and zero temperature, with a large and increasing bcc-hcp energy difference under compression.

INTRODUCTION

The calculation of pressure-temperature phase diagrams in elemental materials from basic quantum-mechanical principles has been of long-standing interest in condensed-matter theory. Central to this task for any given material is the need for both an accurate and flexible total-energy functional, $E_{\text{tot}}(R_1 \dots R_N)$, which expresses the configuration dependence of the energy for any arbitrary arrangement of the atoms. Modern density-functional quantum mechanics in the local-density approximation (LDA) [1] has provided a practical first-principles framework from which to proceed. Combined with self-consistent electronic-band-structure techniques, LDA quantum mechanics can explain both the observed structural trends in the periodic table at ambient conditions as well as pressure-induced solid-solid phase transitions at zero temperature [2]. In some cases it has even been possible to predict high-pressure phase transitions prior to experiment [3]. More difficult, however, is the temperature axis of the phase diagram where the high symmetry of the zero-temperature environment is lost. One effective strategy in this regard has been to develop E_{tot} systematically in terms of transferable interatomic potentials which apply equally to all phases of a material, both ordered and disordered. For simple and transition metals, this has been done successfully from LDA quantum mechanics via generalized pseudopotential theory (GPT) [3-5] by expanding the total energy in weak pseudopotential and *d*-state tight-binding and hybridization matrix elements coupling different sites. Such interatomic potentials have then been combined with appropriate statistical-mechanics tools, including both analytic methods and molecular-dynamics (MD) computer simulation, to address the full pressure-temperature phase diagram. In this paper we will discuss some recent examples which illustrate the

current capabilities of this approach.

SIMPLE-METAL PHASE DIAGRAMS

In bulk nontransition metals, the GPT total-energy functional can be expressed in terms of a pure volume term E_{vol} and a central-force two-ion pair potential v_2 :

$$E_{\text{tot}}(R_1 \dots R_N) = NE_{\text{vol}}(\Omega) + \frac{1}{2} \sum_{i,j}' v_2(R_{ij}, \Omega), \quad (1)$$

where Ω is the atomic volume, $R_{ij} \equiv |R_i - R_j|$ is the separation distance between ions *i* and *j*, and the prime on the summation excludes the *i* = *j* term. As desired, the pair potential v_2 is structure independent and applies to any phase of the metal, including the liquid. Equation (1) is valid not only for simple *sp*-bonded simple metals, but also for series-end transition metals including the heavy-alkaline-earth, noble, and group-IIB metals with empty, nearly-filled, and filled *d*-bands, respectively. In all such cases, one can calculate first-principles GPT functionals E_{vol} and v_2 with only the atomic number as input.

With regard to the calculation of the phase diagram, the total-energy functional (1) also implies many additional simplifications. Interatomic forces and force constants can be readily expressed in terms of the first and second radial derivatives of v_2 , and quasi-harmonic phonons can be calculated from standard lattice-dynamical expressions. Anharmonic contributions in the high-temperature solid are typically small or even negligible and can be addressed with various approximation techniques. In the liquid phase, variational-perturbation theory (VPT) based on the use of simple analytic reference potentials can yield accurate thermodynamic properties [6]. Computer simulation techniques such as Monte Carlo and

molecular dynamics can be used to benchmark such approximation methods, if desired, but one usually does not have to generate thermodynamic data in this manner. The only significant complication in applying Eq. (1) to metals is the long-range oscillatory tail of the potential v_2 , which arises from electron screening via the nearly-spherical Fermi surface of nontransition metals. It can be necessary to include as many as 500 neighbors in the sums over v_2 to obtain accurate results.

One case of current interest is the phase diagram of the simple metal Mg. This metal is unique in that it is the only element on the left-hand side of the periodic table which does not melt out of the bcc structure at ambient pressure. There is, however, a pressure-induced hcp $\rightarrow$ bcc transition near 50 GPa, which was first predicted theoretically on the basis of both GPT and linear-muffin-tin-orbital (LMTO) LDA total-energy calculations [3] and then later found in diamond-anvil-cell (DAC) experiments [7]. We have recently studied the temperature dependence of the hcp-bcc phase line to 1000 K in the quasi-harmonic approximation using GPT interatomic potentials [8]. The transition pressure is found to decrease rapidly with increasing temperature, so that there is indeed a temperature-induced transition to bcc at high pressure. Thermodynamically, the bcc structure is favored at high temperature due to the relatively high entropy associated with its soft T_1 [110] phonon modes. The detailed nature of the hcp $\rightarrow$ bcc phase transition has also been studied with a variable-cell MD technique [9]. The transition is martensitic and proceeds by the classic Burgers mechanism [10] in which (001) planes of the hcp structure are continuously distorted into (110) planes of the bcc structure. There is a small (100 K) energy barrier along the transition path and the pressure-induced transition displays a thermal hysteresis similar to that observed in the DAC experiments [7].

Very recently, the full phase diagram of Mg, including the melting curve, has been calculated to 60 GPa in pressure and 3500 K in temperature. This result is plotted in Fig. 1. Here the liquid has been treated with VPT and an r^{-12} reference system [6]. Anharmonic effects in the solid have been found to be negligible and are not included in Fig. 1. The qualitative features of the phase diagram are similar to those of the earlier semi-empirical result of Pelissier [11], but quantitatively, the present phase diagram appears to be considerably more accurate. The hcp-bcc phase line is here predicted to end in a triple point on the melting curve at about 4 GPa and 1200 K. Below this point in pressure, the bcc structure becomes mechanically unstable, with the long-wavelength T_1 [110] phonons calculated to be imaginary. This explains the absence of a high-temperature bcc phase in Mg at ambient pressure. Finally, the calculated melting curve below 4 GPa is in good agreement with experiment [12].

CENTRAL TRANSITION METALS

In central transition metals, where d -state interactions dominate the energetics, the GPT total-energy functional must be generalized to accommodate angular-force three- and four-ion potentials, v_3 and v_4 :

Figure 1. Temperature-pressure phase diagram of Mg as calculated from first-principles GPT interatomic potentials (solid lines) and compared with experiment (solid circle, Ref. 7; dots, Ref. 12).

$$E_{\text{tot}}(R_1 \dots R_N) = NE_{\text{vol}}(\Omega) + \frac{1}{2} \sum'_{i,j} v_2(ij) + \frac{1}{6} \sum'_{i,j,k} v_3(ijk) + \frac{1}{24} \sum'_{i,j,k,l} v_4(ijkl). \quad (2)$$

Here $v_2(ij) \equiv v_2(R_{ij}, \Omega)$, etc. Again the potentials v_2 , v_3 , and v_4 are structure independent and are transferable to all phases of the metal. These potentials can also be calculated entirely from first-principles, but due to the nonanalytic, multi-dimensional nature of v_3 and v_4 , their direct application is very limited. In the present work, we use Eq. (2) in the simplified model GPT or MGPT form [5], where v_3 and v_4 have been reduced to analytic forms based on a canonical treatment of the d bands. This allows one to do both quasi-harmonic lattice dynamics for the low-temperature solid and MD simulations of the high-temperature solid and liquid.

With regard to the calculation of phase diagrams, there are several additional complicating factors for central transition metals which are not present in simple metals. First, anharmonic effects in the solid are typically much larger and must be treated accurately. Second, analytic tools such as fluid VPT no longer apply because of the presence of multi-ion potentials, so the liquid must be treated by computer simulation. Finally, there can be very large and phase-dependent electron-thermal components to the free energy in transition metals. These arise from the large d -electron density of states (DOS) at the Fermi level, as evidenced by the high measured specific heat in the liquid [13]. Such electron-thermal components can substantially

alter the shape and position of phase boundaries and must be taken into account. Below we consider application of MGPT interatomic potentials to Mo and Fe, where all of the above complications are present.

Molybdenum Melting Curve

The phase diagram of Mo is of current experimental [14–17] and theoretical [14,18] interest. There is now evidence that the normal bcc structure is destabilized at high pressure through one or more solid–solid phase transitions. Experimentally, a transition to an unknown structure has been observed at 2.1 Mbar and 4000 K from dynamic acoustic–velocity measurements [14]. Theoretically, a transition to an hcp structure, driven by $s \rightarrow d$ electron transfer, has been predicted from first–principles LMTO calculations [18]. Here we focus on the high–temperature portion of the Mo phase diagram and the melting transition out of the bcc phase.

We first separate zero–temperature, ion–thermal, and electron–thermal components of all thermodynamic quantities. The zero–temperature components have been fixed from LMTO total–energy calculations for bcc Mo [5] and our MGPT potentials are constrained by these results. The ion–thermal components are then calculated using these potentials, while the remaining electron–thermal components are obtained via separate calculations of the electronic DOS for each phase.

Our investigation of the ion–thermal contribution to melting has been approached in two very closely–related ways. In the first approach, we have cycled up and down through the dynamically observed melting point at constant volume, $\Omega = \Omega_0$, doing parallel MD calculations with the multi–ion potentials and also with an effective–pair potential

$$v_2^{\text{eff}} = v_2 + \langle v_3 \rangle + \langle v_4 \rangle, \quad (3)$$

where the angular dependence of v_3 and of v_4 have been averaged and combined with v_2 . While v_2^{eff} gives a poor description of the structural, mechanical, and vibrational details of the bcc solid, it can reproduce average solid properties such as the bulk modulus and the Debye temperature. Our interest here has been to investigate the importance of the angular forces contained in v_3 and v_4 to melting and to liquid properties. With the multi–ion potentials, ion–thermal melting is found to occur at about 8750 K and 0.30 Mbar, whereas with the effective–pair potential it occurs at about 9750 K and 0.28 Mbar. Above the melting point, however, v_2^{eff} does give a reasonably good account of the structure and thermal energy of the liquid and this improves with increasing temperature. The multi–ion and effective–pair potentials also show very interesting and contrasting behavior upon cooling. In both cases the liquid can be super–cooled to the vicinity of 4000 K before the onset of freezing. In the effective–pair–potential case, a bcc structure is nucleated, while in the multi–ion potential case an amorphous glass–like structure is obtained. The latter appears to be related to the metastable and energetically competitive A15 structure.

Figure 2. Melting curve of Mo as obtained from free energies with (solid curve) and without (dashed curve) the electron–thermal component, from MD simulation (solid square point), and from experiment (Ref. 13).

In our second approach to melting in Mo, we have used the multi–ion potentials to calculate an accurate ion–thermal free energy A_{ion} for both the solid and liquid phases over substantial ranges in volume and temperature. In the solid, A_{ion} has been calculated as a sum of a quasi–harmonic–phonon contribution and an anharmonic contribution obtained from MD calculations of the thermal energy and pressure. In the liquid, A_{ion} has been obtained entirely from MD calculations. The resulting ion–thermal melting curve is plotted as the dashed line in Fig. 2. The dynamical ion–thermal melting point discussed above is seen to lie exactly on this curve, indicating that there has been no super–heating in the MD simulation of melting. To obtain a final melting curve, one must add the electron–thermal component of the free energy

$$A_{\text{el}}(\Omega, T) = -\frac{\pi^2}{6} N(E_F) (k_B T)^2, \quad (4)$$

where $N(E_F)$ is the DOS at the Fermi level. In the bcc solid, the required bcc DOS as a function of volume has been calculated with the LMTO method, while in the liquid a simple, but realistic Friedel model has been used. In Mo, with half–filled d bands, there is a big increase in the DOS upon melting and thus a big decrease in the free energy. The net effect of A_{el} is to lower the calculated melting curve by about a factor of two in temperature, as shown in Fig. 2. The final calculated melting properties near zero pressure are in generally good agreement with experiment [13]. A full account of our studies on Mo are given elsewhere [19].

Figure 3. Calculated LMTO structural energies in compressed Fe at zero temperature.

High-Pressure Phases of Iron

The high-pressure phase diagram of Fe has been of long-standing interest due its important geophysical implications. While there have been intensified experimental efforts on this problem in recent years, the location of the melting curve on the phase diagram and the nature of the solid phase from which it melts remain uncertain. The shock data of Brown and McQueen [20] indicate a solid-solid phase transition just prior to melting on the Hugoniot at about 2.4 Mbar. This could be the just the ϵ (hcp) $\rightarrow$ γ (fcc) transition obtained from an extrapolation of the low-pressure phase diagram, or it could indicate a new solid phase. Ross, et al. [21] have argued in favor of the latter, based on recent DAC measurements of the γ - ϵ phase boundary [22], and have further speculated that the new phase is bcc, in analogy with simple metals such as Mg.

Theoretically, we are attempting to address the high-pressure phase diagram of Fe from the same fundamental perspective we have outlined above for Mo. We have begun with a series of self-consistent LMTO calculations of the zero-temperature equation of state (EOS) and structural phase stability for the nonmagnetic metal. The hcp (ϵ) phase is predicted to be the lowest energy structure at high pressure with no indications of any phase transition, as shown in Fig. 3. This is in agreement with room-temperature DAC measurements to 3 Mbar [23] and is consistent with the absence of any $s \rightarrow d$ electron transfer in this metal. At high pressure above 1 Mbar, the calculated EOS is also in good agreement with the DAC data. The hcp-bcc energy difference is calculated to be large (about 4700 K at 1.6 Mbar) and increasing with compression.

We have further constructed preliminary MGPT multi-ion potentials for Fe which are constrained to the

LMTO results. We have then used these potentials to calculate hcp, fcc, and bcc quasi-harmonic phonons over the entire volume range shown in Fig. 3. The hcp and fcc structures are both found to be mechanically stable for $\Omega < \Omega_0$, with entirely real phonons. In contrast, the bcc structure is predicted to be everywhere mechanically *unstable*, with imaginary [111] and T_1 [110] phonons. The latter correspond to a negative C' elastic constant. We next plan to use these potentials to study high-temperature phase stability and the melting transition in the high-pressure regime.

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