Melting curve of materials: theory versus experiments

D Alfè[1,2]**, L Vočadlo**[1]**, G D Price**[1] **and M J Gillan**[2]

[1] Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK

[2] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Abstract
A number of melting curves of various materials have recently been measured
experimentally and calculated theoretically, but the agreement between
different groups is not always good. We discuss here some of the problems
which may arise in both experiments and theory. We also report the melting
curves of Fe and Al calculated recently using quantum mechanics techniques,
based on density functional theory with generalized gradient approximations.
For Al our results are in very good agreement with both low pressure diamond-
anvil-cell experiments (Boehler and Ross 1997 *Earth Planet. Sci. Lett.* **153** 223,
Hänström and Lazor 2000 *J. Alloys Compounds* **305** 209) and high pressure
shock wave experiments (Shaner *et al* 1984 *High Pressure in Science and
Technology* ed Homan *et al* (Amsterdam: North-Holland) p 137). For Fe
our results agree with the shock wave experiments of Brown and McQueen
(1986 *J. Geophys. Res.* **91** 7485) and Nguyen and Holmes (2000 *AIP Shock
Compression of Condensed Matter* **505** 81) and the recent diamond-anvil-cell
experiments of Shen *et al* (1998 *Geophys. Res. Lett.* **25** 373). Our results
are at variance with the recent calculations of Laio *et al* (2000 *Science* **287**
1027) and, to a lesser extent, with the calculations of Belonoshko *et al* (2000
Phys. Rev. Lett. **84** 3638). The reasons for these disagreements are discussed.

1. Introduction

The melting curves of materials have great scientific and technological interest. The problem
is to understand how a solid melts and to determine the temperature where this happens. A
number of theoretical models have been proposed to explain this phenomenon, among which
two in particular deserve special consideration. These are the Lindemann criterion [10] and
the Born criterion [11]. The Lindemann criterion is based on the concept that melting occurs
when the root mean square displacement of the atoms reaches a critical fraction of the nearest-
neighbour distance, so it relates melting to a vibrational instability. The Born criterion instead

is related to an elastic instability, i.e. melting occurs when the shear modulus vanishes and the crystal no longer has the rigidity to withstand melting.

Experimentally, a number of high pressure melting curves of different materials have been measured, including Cu [12], Ta [13, 14], Mo [13, 15], W, V, Ti, Cr [13], Al [1–3], Mg, Sr, Ca, Ba [17], MgO [18] and Fe [19, 20, 6, 7, 21, 4, 5, 22]. At zero pressure these measurements are mainly performed in diamond-anvil cells (DAC) and present relatively few problems. As pressure is increased beyond about 100 GPa DAC experiments become progressively more difficult, and above 200 GPa the only data available are those based on shock wave (SW) experiments. It is important to note, however, that even in the low pressure region some DAC experiments seem to show problems. An historical example is the low pressure melting curve of iron, for which discrepancies between different groups at 50–60 GPa are still of the order of 500 K [20, 6, 7]. Discrepancies between DAC melting curves extrapolated to high pressure and data extracted from SW experiments do not always agree. Unlike the case of Al, for which DAC and SW agree very well [1–3], we can find disagreements in Fe of up to 1000 K [20, 6, 7, 4, 5, 22] (depending on which DAC melting curves one considers). Disagreement between DAC and SW becomes spectacular in Ta and Mo, with differences in T_m estimated to be up to 6000 K at 300 GPa [13–15]. It is well known that in SW experiments temperatures are not measured, but rather estimated using some assumption for the Grüneisen parameter and the specific heat. Therefore it is mandatory to use some caution when considering melting temperatures based on SW. However, data based on DAC should also be considered with care, especially in light of the large discrepancies still present for iron. These large discrepancies point to unresolved problems in the DAC community. Estimates of T_m from DAC have at least three sources of uncertainties. The first is that temperature is often measured by fitting emission data to black body radiation, which therefore implies knowledge of the emissivity as a function of light wavelength λ and pressure p. This is not always known, so the assumption of the independence of the emissivity on λ and p is usually used. The second problem is with the identification of melting. For example, for determining the melting temperature of Fe, in some cases [20] melting was determined visually as the onset of convective motion on the surface. As pointed out by Shen *et al* [16] visual observation (fluid flow) is less obvious as pressure increases, with the existence of temperature gaps between occasional small movement (not fluid flow) and fluid-like motion. Therefore there is difficulty in identifying the precise onset of melting. In other cases [6] the appearance of x-ray diffraction peaks was used as a signature of the presence of the crystalline phase. In this case one can only be sure of the presence of the crystalline solid, as the disappearance of the diffraction peaks does not necessarily mean melting, so these measurements only provide a lower bound to the melting temperature. A second problem of this technique is that x-ray diffraction peaks come from the bulk, and if the sample is heated from the surface with a laser, the bulk is usually at a lower temperature than the surface. Therefore this lower bound of the melting temperature can be overestimated. A third problem in the experiments is the possibility of super-heating or under-cooling. This has sometimes been used to address the problem of the differences in the melting temperatures of Fe, V, Mo, W and Ta between DAC and SW experiments. However, recently Luo *et al* [23] analysed the systematics of super-heating and under-cooling and showed that super-heating would have to be too large to explain these differences.

An alternative approach to the experimental melting of materials is based on determining T_m by theoretical calculations which go beyond the Lindemann and/or the Born criteria. These calculations are based on explicit simulations of materials in which the interatomic interactions are accurately modelled. The first calculations of melting properties relied on the use of model potentials constructed so as to reproduce some well known experimental properties of the material. More recently, with the increased availability of large computer power, it has been

possible to refine these models with the help of quantum mechanical calculations. It is now possible to construct model potentials which accurately reproduce a wider range of physical properties of the system, as calculated using quantum mechanics. Finally, in the past few years it has even become possible to calculate melting curves directly from first principles, as shown for the first time by Sugino and Car [24] who calculated the zero-pressure melting temperature of Si using density functional theory (DFT) with the local density approximation (LDA), and later by de Wijs *et al* [25] who used DFT-LDA to calculate the zero-pressure melting point of Al.

The melting temperature T_m at a chosen pressure p is defined by the point where the Gibbs free energy of solid and liquid are equal:

$$G_{\text{solid}}(p, T_m) = G_{\text{liquid}}(p, T_m). \tag{1}$$

Two different approaches to melting have traditionally been used. The first is based to the explicit calculation of G_{solid} and G_{liquid} as a function of pressure and temperature. We call this the *free energy approach*. The second approach is based on the explicit simulation of solid and liquid in coexistence. We call this the *coexistence approach*. Melting curves based on either of these two techniques and classical model potentials are available for a number of materials, including MgO [26, 27], Al [28–31], Fe [32, 9, 8], Cu [33, 34] and Ta [35]. Some of these calculations reproduce very accurately the experiments, as for Al and Cu for example, but this is not the case for MgO, Fe and Ta. For MgO there is a large discrepancy in the slopes of the melting curve between the experiments of Zerr and Boehler [18], who report a very low value of $dT_m/dp \approx 30$ G GPa^{-1} and the calculations of Vočadlo and Price [26], with $dT_m/dp \approx 100$ G GPa^{-1}. Recently Tangey and Scandolo [27] have used a much more refined interatomic potential for MgO which reproduces extremely well a number of physical properties, including the whole phonon spectrum. They calculate the value of the melting slope at zero pressure to be between 152 and 170 K GPa^{-1}. The discrepancy with the experiment of Zerr and Boehler [18] is serious. The melting of Ta has been calculated recently by Moriarty *et al* [35], using the *model generalized pseudopotential theory*. This is a highly sophisticated approach in which the interaction potential is formally written as the sum of two-, three- and four-body terms. These terms are then parametrized and the parameters are fitted to full quantum mechanical calculations. The calculated melting curve is in very good agreement with the shock datum, but again is in very serious disagreement with the extrapolations of DAC experiments [13]. Once again, the calculated slope of the melting temperature is much larger than the experimental one. For Fe the situation is more complicated, as a relatively large number of experiments and calculations exist to date. At low pressure (<75 GPa) the results of Boehler [20] are about 500 K lower than the more recent findings of Shen *et al* [6], which are reported to be a lower bound to the melting temperature. At high pressure the extrapolations of the DAC measurements of Boehler fall well below the shock datum of Brown and McQueen [4] and the more recent experiments of Nguyen and Holmes [5]. Recently, calculations of the melting curve of Fe based on model potentials have shown significant discrepancies. The Laio *et al* [8] calculations are in agreement with the melting curve of Boehler [20], but Belonoshko *et al* [9] find appreciably larger temperatures. These calculations were based on model potentials fitted to quantum mechanical calculations so, as is usually the case, there is no guarantee that these models can reproduce the physical properties of materials away from the region where they have been constructed. In particular, to accurately predict the melting temperature the model is required to describe both solid and liquid with the same quality. Since melting is defined by the point where the Gibbs free energies of solid and liquid are equal, a small error in the description of the energy differences between solid and liquid can result in a large error in the melting temperature. We return to this issue below.

Recently, we have approached the problem of melting from a different point of view: we have calculated the melting curves of Fe [36, 37], Al [39, 40] and Cu [41] using direct quantum mechanical calculations. In this paper we summarize the main ideas which are at the root of our calculations and we report the melting curves of Fe and Al. The melting curve of Cu will be reported elsewhere [41].

We have used two approaches to the problem of melting. First, we have explicitly calculated the free energy of solid and liquid and determined the melting curve from equation (1). This has been applied both to Al [39] and Fe [36, 37]. Subsequently, we have used the coexistence approach for Fe [38] with a model, as a full quantum mechanical simulation of solid and liquid iron in coexistence is still out of reach of current computational power. We showed that, once appropriate corrections are introduced [38], the point on the melting curve calculated using the model can be corrected to extract the full *ab initio* results and the results are the same as those obtained from the full quantum mechanical free energy approach.

Despite being still prohibitive for Fe, it has become possible to perform direct coexistence simulations on Al, and we have recently used this approach to calculate the melting curve of Al close to zero pressure. We showed that the results are in very good agreement with those obtained from the free energy approach, as expected. These calculations will be reported elsewhere [40].

2. Calculation methodology

The calculations are based on density functional theory (DFT) techniques [42]. The exchange-correlation functional E_{xc} is the generalized gradient approximation known as Perdew–Wang 1991 [43, 44]. For Al we used the ultrasoft pseudopotential method [45]. For Fe, we used the projector-augmented-wave (PAW) implementation of DFT [46–48], a technique that shares the properties both of all-electron methods, such as full-potential linearized augmented plane waves (FLAPW) [49], and the ultrasoft pseudopotential method [45]. The calculations were done using the VASP code [50, 51], with the implementation of an efficient extrapolation of the electronic charge density [52]. Brillouin-zone (BZ) sampling was performed using Monkhorst–Pack (MP) special points [53]. Convergence with respect to BZ sampling was carefully checked in all cases. The plane wave cut-off was 130 eV for Al and 300 eV for Fe. The time step used in the dynamical simulations was 3 fs for Al and 1 fs for Fe.

2.1. Free energies

The techniques used to calculate free energies for solids and liquids have been reported and extensively discussed in previous papers [54, 37], so we only outline the main ideas here. The Helmholtz free energy of a system of N atoms in a volume V at temperature T is given by

$$F = -k_B T \ln \left\{ \frac{1}{N! \Lambda^{3N}} \int d\mathbf{R}_1 \cdots d\mathbf{R}_N \, \exp[-\beta U(\mathbf{R}_1, \ldots, \mathbf{R}_N; T)] \right\}, \quad (2)$$

where $\Lambda = h/(2\pi M k_B T)^{1/2}$ is the thermal wavelength, with M being the nuclear mass, $\beta = 1/k_B T$, h is the Planck constant and k_B is the Boltzmann constant. We emphasize that $U(\mathbf{R}_1, \ldots, \mathbf{R}_N; T)$ is the free energy of the electrons in the system and therefore depends on T. A direct use of equation (2) to calculate the free energy of the system is impractical, as one would need to know the value of the (free) energy U for every position of the atoms in the system. An alternative approach is to use the technique known as thermodynamic integration (see, for example, [55]), which is a completely general procedure for determining

the difference of free energies F_1-F_0 of two systems whose total-energy functions are U_1 and U_0. The basic idea is that F_1-F_0 represents the reversible work done on continuously and isothermally switching the energy function from U_0 to U_1. To do this switching, a continuously variable energy function U_λ is defined as

$$U_\lambda = (1 - \lambda)U_0 + \lambda U_1, \tag{3}$$

so that the energy goes from U_0 to U_1 as λ goes from 0 to 1. In classical statistical mechanics, the work done in an infinitesimal change $d\lambda$ is

$$dF = \langle dU_\lambda/d\lambda \rangle_\lambda \, d\lambda = \langle U_1 - U_0 \rangle_\lambda \, d\lambda, \tag{4}$$

where $\langle \cdot \rangle_\lambda$ represents the thermal average evaluated for the system governed by U_λ. It follows that

$$F_1 - F_0 = \int_0^1 d\lambda \, \langle U_1 - U_0 \rangle_\lambda. \tag{5}$$

In practice, this formula can be applied by calculating $\langle U_1 - U_0 \rangle_\lambda$ for a suitable set of λ values and performing the integration numerically. The average $\langle U_1 - U_0 \rangle_\lambda$ is evaluated by sampling over configuration space. It is obvious that the final result for F_1 does not depend on the particular choice of the reference system, but the computational effort crucially depends on this choice. The reason for this is that in order to evaluate the quantity $\langle U_1 - U_0 \rangle_\lambda$ with a chosen statistical accuracy one needs to sample the phase space at a number of points which depends on the size of the fluctuations of $U_1 - U_0$, so it is important to look for a reference system which minimizes the size of these fluctuations.

2.2. Solid–liquid coexistence

In this section we discuss the coexistence approach. With this method solid and liquid are simulated in coexistence and the p, T values extracted from the simulation give a point on the melting curve. The method can be implemented in a number of different ways. In the work of Morris *et al* [30], coexisting solid and liquid Al were simulated with the total number of atoms N, volume V and internal energy E fixed. They showed that, provided V and E are appropriately chosen, the two phases coexist stably over long periods of time and the average pressure p and temperature T in the system give a point on the melting curve. An alternative procedure would be to simulate at constant (N, V, T). Yet another approach was used in the work of Laio *et al* [8] on the high-pressure melting of Fe; this used constant-stress simulations, with enthalpy almost exactly conserved. The approach of Belonoshko *et al* [9] is different again. Here, the (N, p, T) ensemble is used. The system initially contains coexisting solid and liquid, but since p and T generally do not lie on the melting line the system ultimately becomes entirely solid or liquid. This approach does not directly yield points on the melting curve, but instead provides upper or lower bounds, so that a series of simulations is needed to locate the transition point. Whichever scheme is used, some way is needed of monitoring which phases are present. In the (N, V, E) method of Morris *et al* [30], graphical inspection of particle positions appears to have been used, supplemented by calculation of radial distribution functions to confirm the crystal structure of the solid. In the (N, p, T) method of Belonoshko *et al* [9], the primary diagnostic is the discontinuity of volume as the system transforms from solid to liquid.

As mentioned earlier in the paper, since the coexistence method is intrinsically computationally more demanding than the free energy approach, all the calculations of melting properties performed so far have been done using classical potentials, including the melting curves of Fe produced by Laio *et al* [8] and Belonoshko *et al* [9]. It follows, as noted earlier,

that the melting properties are those of the potentials used in the calculations. In particular, the melting curves will in general be different from those that would be obtained by a direct coexistence simulation using first-principles calculations. However, as we showed in our previous paper [38], it is possible to assess these errors and correct them, which is done as follows.

The difference in the melting temperature at a fixed pressure can be formulated in terms of the differences of the Gibbs free energies between the model potential and the *ab initio* system. At a chosen pressure p, the melting temperatures of the two systems T_{AI} and T_{mod} are defined by: $G_{AI}^{ls}(p, T_{AI}) = 0$ and $G_{mod}^{ls}(p, T_{mod}) = 0$, where G^{ls} is the difference between the Gibbs free energies of the liquid and solid. The *ab initio* and the model potential melting temperatures are different, in general, because $G_{AI}^{ls}(p, T_{mod}) \neq 0$. Working at the given pressure, we take the variable p as read and express the *ab initio* value of G^{ls} as

$$G_{AI}^{ls}(T) = G_{mod}^{ls} + \zeta \Delta G^{ls}(T), \tag{6}$$

where we denote differences between the *ab initio* system and the model potential with the symbol Δ and the parameter ζ is introduced so that the *ab initio* melting temperature T_{AI} can be written as a power series:

$$T_{AI} = T_{mod} + \zeta T' + \cdots. \tag{7}$$

Since the Gibbs free energies are equal in the two phases, this T_{AI} is the solution of $G_{AI}^{ls}(T) = 0$, which is

$$G_{mod}^{ls}(T_{mod} + \zeta T' + \cdots) + \zeta \Delta G^{ls}(T_{mod} + \zeta T' + \cdots) = 0. \tag{8}$$

Expanding in powers of ζ and equating powers, one obtains for T':

$$T' = \Delta G^{ls}(T_{mod})/S_{mod}^{ls} \tag{9}$$

where S_{mod}^{ls} is the entropy of fusion of the model potential. Since entropies of fusion are of the order of k_B/atom, then a difference ΔG^{ls} of 10 meV/atom implies a shift of melting temperature of about 100 K, so that substantial errors will need to be corrected for unless the reference total energy function matches the *ab initio* one very precisely. The free energy differences ΔG^{ls} can be calculated using thermodynamic integration, or if the model potentials mimic the *ab initio* system closely enough, a perturbational approach. If the calculations are performed in the (N, V, T) ensemble it is easy to show that

$$\Delta F = \langle \Delta U \rangle_{mod} - \tfrac{1}{2}\beta \langle \delta \Delta U^2 \rangle_{mod} + \cdots, \tag{10}$$

where $\delta \Delta U \equiv \Delta U - \langle \Delta U \rangle_{mod}$ and the averages are taken in the model potential ensemble. The relation between ΔG and ΔF, is readily shown to be

$$\Delta G = \Delta F - \tfrac{1}{2}V\kappa_T \Delta p^2, \tag{11}$$

where κ_T is the isothermal compressibility and Δp is the change of pressure when U_{mod} is replaced by U_{AI} at constant V and T.

3. Results and discussion

3.1. Aluminium

In figure 1 we report the melting curve of Al (full curve) compared with the DAC experiments of [1, 2] and the SW experiments of [3]. The agreement is exceptionally good and, as mentioned in the introduction Al is one special case in which DAC and SW experiments agree very well.

We want to discuss one technical point here which will become particularly important in the discussion of the results for Fe. As mentioned in our previous paper [39], the GGA
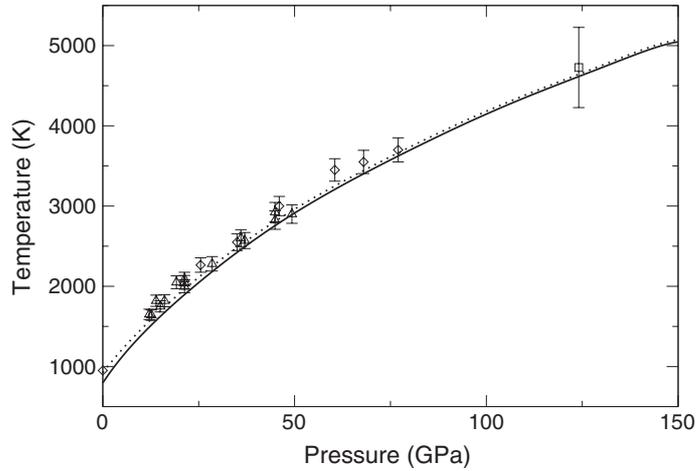
Figure 1. Comparison of our calculated melting curve of Al with experimental results. Full and dotted curves: our results from [39] without and with free-energy correction (see the text); diamonds and triangles: DAC measurements of [1] and [2], respectively; squares: shock experiments of [3].

does not describe the zero-pressure phonon spectrum of Al very accurately. The reason can be traced to the calculated GGA zero-pressure lattice parameter, which is calculated to be too large. This error directly propagates in the Gibbs free energy and therefore affects the melting curve. We noted [39] that if the phonons are calculated at the experimental lattice parameter then the agreement with experiments is excellent. Therefore, we devised a *correction* to the Helmholtz free energy such that the pressure is rectified:

$$F_{\text{corr}} = F + \delta p V. \tag{12}$$

Using F_{corr} in our calculations we found the *corrected* melting curve, represented by the dotted curve in figure 1, where we assumed δP to be the same in the whole P/T range. The zero-pressure corrected melting temperature is 912 K, which is in very good agreement with the experimental value 933 K. The correction is less important at high pressure, where dT_m/dP is smaller.

3.2. Iron

In figure 2 we report the melting curve of Fe (full curve) compared with the DAC experiments of [20, 6, 19, 7], the SW experiments of [4, 5, 22] and the calculations of [8, 9]. The early results of Williams *et al* [19] lie considerably above those of other groups and are now generally discounted. This still leaves a range of about 400 K in the experimental T_m at 100 GPa. Even allowing for this uncertainty, we acknowledge that our melting curve lies appreciably above the surviving DAC curves, with our T_m being above that of Shen *et al* [6] by about 400 K at 100 GPa. Our melting curve agrees quite well with the SW results [4, 5].

On the same figure we also report the *corrected* melting curve (broken curve) resulting from a modification of the Helmholtz free energy according to equation (12). Here we take the pressure error $\delta p \equiv -(\partial \delta F/\partial V)_T$ to be linear in the volume, so that δF can be represented as $\delta F = b_1 V + b_2 V^2$, where b_1 and b_2 are adjustable parameters determined by least-squares fitting to the experimental pressure. We find that this free-energy correction leads to a lowering of the melting curve by about 350 K in the region of 50 GPa and by about 70 K in the region of 300 GPa. This correction brings our low-temperature melting curve into quite respectable
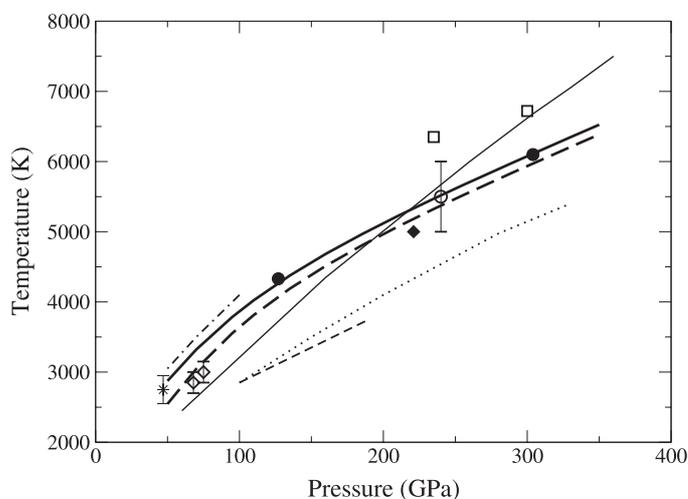
Figure 2. Comparison of our calculated melting curve of Fe with experimental and different *ab initio* results: heavy solid and long dashed curves: our results from [37, 38] work without and with free-energy correction (see text); filled circles: present corrected coexistence results (see text); dotted curve: *ab initio* results of [8]; light curve: *ab initio* results of [9]; chained curve and short dashed curve: DAC measurements of [19] and [20]; open diamonds: DAC measurements of [6]; star: DAC measurements of [7]; open squares, open circle and full diamond: shock experiments of [22, 4] and [5]. Error bars are those quoted in the original references.

agreement with the DAC measurements of Shen *et al*, while leaving the agreement with the shock points of Nguyen and Holmes essentially unaffected. There is still a considerable discrepancy with the DAC curve of Boehler [20] and the *ab initio* results of Laio *et al* [8].

We now turn the discussion to the discrepancies with the calculations of Laio *et al* [8] and Belonoshko *et al* [9]. These two sets of calculations were performed using model potentials fitted to *ab initio* simulations in different ways. As mentioned earlier, the melting curve obtained in these calculations is necessarily the melting curve of the model potential, and not the *ab initio* one. We have repeated the simulation of Belonoshko *et al* [9] at the two volumes $v = 7.12$ and 8.6 and reproduced melting temperatures close to those originally calculated [9]. In figure 2 we report the melting temperatures at the pressures corresponding to these two volumes after we applied the corrections described in section 2.2. As expected, the results are in perfect agreement with those obtained using the free energy approach. This resolves the discrepancies between the work of Belonoshko *et al* [9] and ours [36, 37]. We argue that a similar argument would also resolve the discrepancies with the results of Laio *et al* [8].

4. Conclusions

We have reported the melting curve of Al in the pressure range 0–150 GPa and the melting curve of Fe in the pressure range 50–350 GPa. Our calculations are based on quantum mechanics within the framework of density functional theory, with the use of the generalized gradient corrections. We have shown that our results are robust with respect to different approaches to melting, namely the direct calculation of free energies or the coexistence approach with the aid of a well constructed model potential. We believe that this work settles the issue regarding the difference between our melting curve of iron [36, 37] and that calculated by Belonoshko *et al* [9]. The other melting curve by Laio *et al* [8] is also based on the coexistence method

and we argue that this also would come into close agreement with ours once the corrections described here and our previous paper [38] are applied.

Our melting curve agrees quite well with the shock datum of Brown and McQueen [4] and the point obtained from the measurements of Nguyen and Holmes [5]. It also agrees with the low pressure DAC experiments of Shen *et al* [6], but there is still a considerable discrepancy with the DAC data reported by Boehler [20]. We stress that large discrepancies still exist between the DAC experiments performed in the group of Boehler and SW experiments for a number of materials, including Fe, and especially Mo and Ta. Discrepancies between different DAC experiments on Fe are also still very large. In particular, it appears that the slopes of the melting curves obtained in the DAC experiments of the Boehler group are always very low. In some cases, like W, Ta and Mo [13], the slopes even approach zero. This implies zero volume change on melting, which is possible, but seems unlikely. We believe that more experimental work is therefore needed in order to resolve these issues.

Acknowledgments

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