The role of anharmonicity in a variety of phase transitions controlled by pressure, including melting, brittle-to-ductile transition, and the liquid-vapour critical point

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Abstract. A variety of phase transitions controlled by pressure are addressed, in which anharmonicity plays a central role. After a brief discussion of the melting temperature of some transition metals as a function of pressure, the brittle-to-ductile transition is treated. Finally, quantum critical points are briefly referred to, in relation to singular behaviour of the Grüneisen ratio.

Key words: melting and brittle-to-ductile transition; liquid-vapour phase transition; Grüneisen ratio.

1. Background and outline

In earlier work [1, 2], some attention has been focussed on both point and extended defect properties, particularly of the transition metals [3]. Here we extend the above work, which concerned ambient pressure properties, to treat variation of the melting temperature, $T_m$ say, with pressure $P$. Some attention has also been devoted to a precursor phase change, namely the brittle-to-ductile transition (BDT) [4, 5, 6], again in relation to $T_m$ at ambient pressure. Proposals will be made here concerning the potential interest in studying the BDT in transition metals, and also in chemically bonded Si and in graphite, as a function of $P$.

These considerations are developed somewhat in sections 2 and 3 below, where an analysis on $T_m(P)$ for transition metals by Burakovsky and Preston [7] has already focussed on the relation of a key fingerprint of anharmonicity, namely Grüneisen’s constant, in gaining insight into the variation of $T_m(P)$ with pressure in metals like Pd and Pt. Section 3 proposes explanations of possible correlation between $T_m(P)$ and the BDT transition temperature $T_{BDT}(P)$, both in transition metals and in Si and graphite. Then section 4 considers briefly the critical point in relation to melting temperature, especially in the alkali metals. In section 5, future directions are pointed out in relation to experiments on the variation of Grüneisen’s constant with pressure.
Figure 1. Shows melting temperature of Pd (upper panel) and Pt (lower panel) as a function of density. Redrawn after Burakovsky and Preston [7].

2. Melting temperature of transition metals and variation with pressure
Matthai and Bacon [8] have made computer simulation calculations on metals for a variety of point defect properties. In the interpretation of their simulation results for various point defects, they establish an intimate relation with Grüneisen’s constant. This is highly relevant to the present theme, since an intimate connection between the monovacancy formation energy, $E_{1f}$ say, and the thermal energy $k_BT_m$, has been known to materials scientists for a long time. The approximate result

$$\frac{k_BT_m}{E_{1f}} \sim 10$$

works surprisingly well at ambient pressure, though lack of experimental data on $E_{1f}$ under hydrostatic pressure $P$ leaves open whether the correlation remains simple as a function of $P$.

Taking up the emphasis of Matthai and Bacon [8] on Grüneisen’s constant, we note next the study of Burakovsky and Preston [7] on the melting temperature of metals like Pd and Pt as a function of pressure. Their work involves, in fact, also the variation of Grüneisen’s constant itself with pressure. We have reproduced in Fig. 1 $T_m(P)$ vs $P$ for Pd(Pt): Burakovsky and Preston [7] get fairly good agreement between their phenomenological theory and the experimental results. Since some emphasis is placed on the role of Grüneisen’s constant here, we note briefly that Burakovsky and Preston [7] model the density dependence of the Grüneisen parameter $\Gamma$ as

$$\Gamma(\rho) = \frac{1}{2} + \frac{\gamma_1}{\rho^{1/3}} + \frac{\gamma_2}{\rho^q},$$

where $\gamma_1$, $\gamma_2$ and $q$ (> 1) are constants.
3. Is the brittle-to-ductile (BDT) transition temperature \( T_{BDT}(P) \) connected with melting temperature \( T_m(P) \): with reference to transition metals and to Si.

The ductile-brittle transition is exhibited in bcc metals, such as low carbon steel, which become brittle at low temperature or at very high strain rates. In metals, it is generally agreed that the mechanism for plastic deformation at room temperature is by dislocation motion. The stress required to move a dislocation depends on the atomic bonding, crystal structure, and obstacles such as solute atoms, grain boundaries, precipitate particles and other dislocations. If the stress required to move the dislocation is too high, the metal will fail instead by the propagation of cracks and the failure will be brittle. Thus, either plastic flow (ductile failure) or crack propagation (brittle failure) will occur, depending on which process requires the smaller applied stress.

In fcc metals, the flow stress, i.e. the force required to move dislocations, is not strongly temperature dependent. Therefore, dislocation movement remains high even at low temperatures and the material remains relatively ductile. In contrast to fcc metal crystals, the yield stress or critical resolved shear stress of bcc single crystals is markedly temperature dependent, in particular, at low temperatures. The temperature sensitivity of the yield stress of bcc crystals has been attributed to the presence of interstitial impurities on the one hand, and to a temperature dependent Peierls-Nabarro force on the other. However, the crack propagation stress is relatively independent of temperature. Thus the mode of failure changes from plastic flow at high temperature to brittle fracture at low temperature.

A soft brittle-to-ductile transition (BDT) is one in which there is a gradual increase in dislocation activity at the crack tip as the temperature is increased until fracture. The transition region is fairly wide and the transition temperature is consequently hard to define precisely. Most single crystals display this form of transition. In a sharp BDT, the stress intensity rises sharply as the transition temperature is reached and there is an abrupt, rapid increase in dislocation activity. This form of transition is observed in dislocation-free Si crystals. As most BDT are soft, it means that it is the mobility of dislocations that plays a central role in determining the transition temperature.

In fracture measurements, it has been found that the loading rate, \( \dot{K} \), is related to transition temperature, \( T_{BDT} \), through some activation energy for dislocation generation or dislocation mobility, \( Q_{BDT} \), by an exponential relation

\[
\dot{K} = A \exp \left( -\frac{Q_{BDT}}{k_B T_{BDT}} \right).
\]

Thus, comparing the measured activation energy with the energies associated with the various defect energies, it is possible to get an understanding about the mechanism for the transition from brittle to ductile behaviour. However, there has been some uncertainty associated with this. Thus, for example, Gumbsch et al. found the activation energy in tungsten to be about 0.2 eV [9] suggesting that plasticity in tungsten is controlled by the glide of non-screw (edge) dislocations. By contrast, the more recent studies by Giannattasio and Roberts [10] on tungsten point to a much higher activation energy \( \sim 1 \) eV which is equal to the energy of double-kink formation on screw dislocations.

On a macroscopic level, fracture is related to elastic properties of a material. Based on Griffith’s theory of micro-cracks and Cottrell’s model of fracture [11], Petch [12] developed an equation for the transition temperature

\[
T_{BDT} \sim \log C - \log \left[ \frac{4\beta G\gamma}{D} - D \right] - \log d^{-1/2},
\]

where \( d \) is the grain diameter, \( \beta \) is a constant related to the resistance of the lattice to deformation, \( C \) and \( D \) are constants; \( G \) is the shear modulus and \( \gamma \) the effective surface energy of
Table 1. BDT and melting temperatures for 8 elements at ambient pressure.

| Element | $T_{BDT}$ [K] | $T_m$ [K] |
|---------|---------------|-----------|
| Si      | 1040          | 1687      |
| Ge      | 700           | 1211      |
| Fe      | 150           | 1808      |
| V       | 150           | 2163      |
| Nb      | 75            | 2741      |
| Ta      | 120           | 3269      |
| Mo      | 225           | 2890      |
| W       | 400           | 3680      |

the crack surfaces. The important feature here is the dependence of $T_{BDT}$ on the shear modulus. Burakovsky et al. [13] constructed a model of melting as a dislocation-mediated phase transition and showed that the melting temperature can be expressed in the form

$$k_B T_m = \Omega G \times S_B,$$

(5)

where $G$ is the shear modulus, and $S_B$ denotes a structure dependent factor, while $\Omega$ is the atomic volume.

Thus, the role of dislocations and its connection with both the melting temperature $T_m$ and the BDT transition temperature $T_{BDT}$ suggest a connection between the two quantities. In this vein, Klein and March [4] have discussed the BDT transition as a precursor phase transition to melting, at ambient pressure. Indeed, it has been accepted by materials scientists that for dislocation free single crystals

$$T_{BDT} \sim \frac{2}{3} T_m.$$  

(6)

However, the bcc transition metals show much lower BDT transition temperatures (see Table 1) due to presence of dislocations and in these materials, the activation energy for dislocation glide or disclinations might be the determining factor. The brittleness of metals such as Fe at high pressures is of interest because of their use in pressurized containers as well in understanding materials in the earth’s core. So, it is of interest to gain an understanding of the pressure dependence of the BDT temperature, $T_{BDT}(P)$. Following the work of Matthai and March [14] relating the pressure dependence of the point defect energy to that of the melting temperature, it is worthwhile asking if the pressure dependence of the precursor BDT temperature $T_{BDT}(P)$ also correlates with $T_m(P)$ as a function of pressure $P$.

Khantha et al. [5] proposed a model for the BDT based on the Kosterlitz-Thouless theory of the melting transition. In their model, they found that the rapid rise in free dislocation density occurs at the transition temperature

$$T_{BDT} = \frac{1}{2k_B} \left[ \frac{q^2}{\epsilon \langle r_c \rangle} - \frac{\sigma b r_c}{2} \right],$$

(7)

where $\sigma$ is the stress, $b$ the Burger’s vector and $r_c$ the average size of the dislocation loops at the critical temperature. $\epsilon$ is the polarizability and the quantity $q$ is related to the shear ($G$) and bulk moduli ($B$), $q^2 = GB/(G+B)$. Now, in fracture theory, it is known (see Ref. [15], p. 291) that when hydrogen collects in microcracks it exerts an internal pressure, $P$, which may be added directly to the external stress $\sigma$ to produce a total stress ($P+\sigma$) for propagation. In
Figure 2. Melting temperatures $T_m$ vs critical temperatures $T_c$ of the first five alkali metals Li, Na, K, Rb, and Cs (bottom to top) at ambient pressure. Solid line is a best fit to the experimental data, $T_m = AT_c + B$ [17], with $A \approx 1/8$.

determining the effect of hydrostatic pressure on the transition temperature, we can apply this result by adding it to the external stress leading to

$$T_{	ext{BDT}}(P) = \frac{1}{2k_B} \left[ \frac{q^2(P)}{\epsilon(r_c)} - \frac{(\sigma + P)br_c}{2} \right]. \tag{8}$$

The pressure dependence of the BDT transition temperature appears to be more complicated than that of the melting temperature. However, it is clear from the above equation that a major contributory term in the slope of $T_{	ext{BDT}}(P)$ at ambient pressure is

$$\frac{\partial T_{	ext{BDT}}}{\partial P} \sim \frac{br_c}{2}. \tag{9}$$

Thus, in contrast with the slope of the melting curve, the slope of the BDT temperature is predicted to be negative, i.e., the BDT temperature decreases with increasing pressure. This is consistent with the findings of Churbaev et al. [16] for polycrystalline Mo and W. Of course, further experimental studies of $T_{	ext{BDT}}$ at high pressure will be essential in showing future directions for theory, and how the above very basic considerations are to be refined.

4. Critical point temperature $T_c$ in relation to melting temperature $T_m$, especially for the alkali metals

Leys et al. [18] and March et al. [19], for the alkali metals, have stressed the correlation which exists between the critical temperature $T_c$ and the melting temperature $T_m$. This can be written in the form $T_m = AT_c + B$ [17], with $A = 1/8$ (see Fig. 2), which is the inverse of the coordination number for the body-centred cubic lattice, as is appropriate for most solid alkali metals, including Rb and Cs. This is relevant to the present study since Rosenfeld [20] has
argued for a correlation between critical point behaviour and anharmonicity. Unfortunately, the critical points of other metals are experimentally rather inaccessible, with of course the notable exception of Hg.

5. Summary and future directions
The main results of the present study set out above concern classical phase transitions involving high pressure. We have emphasized the importance of further experimental work, especially on the BDT temperature $T_{BDT}(P)$ under pressure, and its possible relation to $T_m(P)$. Below we stress the interest for the future of quantal phase transitions, for reasons we elaborate on briefly below.

5.1. Quantum critical points and the behaviour of Grüneisen’s constant
Quite recently, there has been considerable interest in the way that the Grüneisen’s parameter behaves near quantum critical points. The Grüneisen’s ratio $\Gamma$ [21, 22, 23] involves both the molar specific heat $c_p = (T/N)(\partial S/\partial T)_P$ and the thermal expansion $\alpha$ by

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N} = -\frac{1}{V} \left( \frac{\partial S}{\partial P} \right)_{T,N},$$

(10)

where a Maxwell thermodynamic relation has been invoked to reveal that $\alpha$ relates to the pressure derivative of the entropy $S$, whereas $c_p$ measures its response to temperature. Following Zhu et al. [23], we define $\Gamma$ as simply

$$\Gamma = \frac{\alpha}{c_p} = -\frac{1}{V_m T} \frac{\partial S/\partial P}{\partial S/\partial T},$$

(11)

$V_m$ denoting the molar volume $V/N$. Older definitions of the so-called effective or thermodynamic Grüneisen parameter are equivalent to $\Gamma c_p/\kappa_T c_V$, where $\kappa_T$ denotes the isothermal compressibility. However, neither $\kappa_T$ nor the specific heat ratio is expected to diverge at a quantum critical point (QCP), whereas (at least for magnetic QCPs) $\Gamma$ in Eq. (11) is indeed singular. This is to be contrasted with classical phase transitions. Close to such transitions, $\Gamma$ will be constant.

5.1.1. Some experimental results on heavy Fermion compounds
In heavy Fermion compounds, we briefly note that there is a competition between magnetic interactions and the Kondo effect, which can be controlled by pressure. There is a considerable sensitivity to pressure $P$, due to the exponential dependence of the Kondo temperature on the parameters of the specific heavy Fermion material.

Such work on quantal phase transitions, and its relation to anharmonicity, seems to afford a promising parallel to the classical phase transitions discussed in sections 2–4 above.

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