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The fcc–bcc structural transition: II. A mean field model for finite-temperature effects.

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Abstract. We present a model for temperature induced martensitic phase transitions where the excitations leading to the phase instability are local fluctuations of the respective order parameter which describes the displacement of a single atom or an atomic plane when transforming structure A into structure B. The fluctuations of the order parameter are treated in the framework of a Landau–Ginzburg model and allow us to describe the temperature induced first-order phase transition as being driven by strain fluctuations (caused by anharmonicities) rather than by phonon softening. In some materials this phenomenological mean field treatment represents a possible model for martensitic phase transitions.

1. Introduction

The finite-temperature modelling of martensitic phase transitions (MPTs) is a topic which is still under hot debate among theoreticians. The main controversy concerns the question whether MPTs are driven by soft phonons or by a different mechanism which relies on little or no phonon softening. In addition to this open question about the microscopic nature, the MPT is governed by several physical processes on different length scales and kinetics. In contrast to diffusive phase transitions the MPT is a collective phenomenon where a crystal undergoes a first-order transition from one crystal structure into another over a finite temperature range (hysteresis).

The first idea about a possible mechanism for MPTs goes back to the work of Zener [1] who suggested that a softening of the shear mode is responsible for the instability of the parent lattice. Experimentally such a softening has hardly been observed, leading Friedel [2] to conclude that these transitions are driven by changes in the entropy. The excess entropy of the (in most cases high-temperature) bcc phase with respect to the low-temperature phase (which is often close packed) should be due to a lowering of the phonon frequencies related to the smaller coordination number in the bcc lattice. The further development of microscopic theories for the MPT was pioneered by Cochran [3] and Anderson [4] who independently formulated the soft-mode model. In this model it is assumed that at a temperature T_0 the effective frequency of one phonon branch becomes zero, triggering the phase transition. However, it has been pointed out [5] that actually only very few systems show this behaviour. Krumhansl and Gooding [6] proposed a phenomenological model which only requires anharmonicities in the order parameter of a Landau-type model to describe first-order phase transitions. Recently Vul and Harmon [7] suggested the possibility of a fluctuationless mechanism where the MPT is caused by defects in the crystal structure. Lindgård and Mouritsen [8] noticed a formal similarity between structural and

magnetic phase transitions. They discussed structural phase transitions by mapping their properties to an Ising model where they assume that the two structural modifications can formally be identified with a ferromagnetic and an antiferromagnetic solution of the Ising Hamiltonian. In a later paper [9] these authors presented a fluctuation model based on their magnetic Hamiltonian. The anharmonic model proposed by Krumhansl and Gooding [6, 10] describes the MPT in terms of a Landau expansion of the free energy by assuming local displacements which are scaled to low-lying phonon modes. Recently a mean field model has been presented by Kerr and Rave [11] who treat the thermal properties on the basis of fluctuations of mean square displacements. All these latter models have one thing in common, namely that they no longer rely on softening of a certain phonon mode but find small-scale excitations sufficient to trigger the phase transition.

From this brief overview it becomes clear that a theoretical model which covers all aspects mentioned above will be hard to develop and is indeed not yet at hand. However recent years have seen an enormous advance in the understanding of this highly complex phenomenon [12].

The present paper deals only with the microscopic part of the MPT where we try to explain how one structure can be transformed into another and how these two modifications are in a thermodynamic equilibrium. We start from quantum mechanical ($T = 0$ K) total energy calculations (see part I of the present paper [13] for a specific lattice transformation which provides the basis for a thermodynamic model where we assume that the MPT is triggered by local fluctuations of the ‘geometrical’ patterns mediating the lattice transformation. It will be shown that the excess entropy created by these fluctuations stabilizes the high-temperature phase. This model will be applied in section 3, where we illustrate for one example, namely the Bain [14] transformation in Ca, that it successfully describes the first-order phase transition from fcc to bcc. In addition, other systems and transformations are mentioned.

2. A mean field model for MPTs

2.1. The fluctuation Hamiltonian

The basic idea of our model relies on the combination of various techniques which are available nowadays. In part I of this paper [13] we have calculated the total energy $E(c/a, V)$ along the Bain transformation between the fcc and bcc lattice by a continuous change of the c/a ratio in a body centred tetragonal (bct) unit cell, where $c/a = 1$ describes the bcc and $c/a = \sqrt{2}$ corresponds to the fcc structure at a given volume V . This quantum mechanical result provides the basis for a thermodynamic Landau–Ginzburg model which contains thermally excited fluctuations of the order parameter. Our finite-temperature model should contain the $T = 0$ K results (without fluctuations) as a special case for which the total energy is given by the band structure calculations. This $T = 0$ K total energy can be written as a polynomial in powers of the order parameters, which in our case are the Bain variable c/a and the volume V (for details see appendix of part I [13]):

$$E(c/a, V) = \sum_{i=0}^n \sum_{j=0}^m A_{ij} (c/a)^i V^j. \quad (1)$$

Now we generalize the Landau expansion given by (1) by introducing local fluctuations of the order parameters, namely $\xi(r)$ (along c/a) for the Bain variable and $\nu(r)$ for the volume. Formally this means that we replace the order parameter c/a by $\langle c/a + \xi(r) \rangle$, and V by $\langle V + \nu(r) \rangle$ where $\langle \rangle$ denotes the statistical average over the phase space of the

fluctuations in the Gaussian approximation. For the first six powers of the order parameter one obtains

$$\begin{aligned}
\langle (c/a + \xi(r)) \rangle &= c/a \\
\langle (c/a + \xi(r))^2 \rangle &= (c/a)^2 + \langle \xi^2(r) \rangle \\
\langle (c/a + \xi(r))^3 \rangle &= (c/a)^3 + 3(c/a)\langle \xi^2(r) \rangle \\
\langle (c/a + \xi(r))^4 \rangle &= (c/a)^4 + 6(c/a)^2\langle \xi^2(r) \rangle + 3\langle \xi^2(r) \rangle^2 \\
\langle (c/a + \xi(r))^5 \rangle &= (c/a)^5 + 10(c/a)^3\langle \xi^2(r) \rangle + 15(c/a)\langle \xi^2(r) \rangle^2 \\
\langle (c/a + \xi(r))^6 \rangle &= (c/a)^6 + 15(c/a)^4\langle \xi^2(r) \rangle + 45(c/a)^2\langle \xi^2(r) \rangle^2 + 15\langle \xi^2(r) \rangle^3
\end{aligned} \tag{2}$$

and completely analogous equations for the volume and its fluctuations. In the Gaussian approximation the statistical average over odd powers of the fluctuations vanishes, and any average over an even power of the fluctuation can be expressed in terms of powers of $\langle \xi^2(r) \rangle$ according to

$$\langle \xi^{2k}(r) \rangle = (2k - 1)!! \langle \xi^2(r) \rangle^k. \tag{3}$$

Consequently the thermal properties of the resulting free energy including c/a fluctuations are governed by the thermal dependence of a single variable, namely $\langle \xi^2(r) \rangle$ (and analogously for $\langle v^2(r) \rangle$). At $T = 0$ K, where the fluctuation amplitude vanishes, the expressions given in (2) guarantee that the original Landau expansion of the ground state (1) is recovered.

By introducing fluctuations the energy becomes a function of four variables, $E(c/a, V, \langle \xi^2(r) \rangle, \langle v^2(r) \rangle)$, where the fluctuations are assumed to be non-centered random variables varying on a spatial scale larger than the range of interactions. In the Landau–Ginzburg expansion of the free energy, non-local effects are taken into account by the lowest-order gradient terms and the Hamiltonian reads

$$H = \frac{1}{V} \int d^3r \left\{ E(c/a + \xi(r), V + v(r)) + \frac{K}{2} (\nabla \xi(r))^2 + \frac{Q}{2} (\nabla v(r))^2 \right\}. \tag{4}$$

Using this Hamiltonian we calculate the free energy via a classical partition function integral over the phase space of the fluctuations. In general this functional integral cannot be calculated but the best possible approximation to the exact free energy is obtained by using the Peierls [15]–Feynman [16] inequality, a procedure which essentially describes a variational derivation of a mean field mode [17].

We arrive at an expression for the free energy F which reads

$$\begin{aligned}
F = E + \phi - \frac{k_B T}{2} \sum_{k \leq k_c} \ln \frac{\pi k_B T}{2((K/2)k^2 + \partial \phi / \partial \langle \xi^2(r) \rangle)} - \langle \xi^2(r) \rangle \frac{\partial \phi}{\partial \langle \xi^2(r) \rangle} \\
- \frac{k_B T}{2} \sum_{k \leq q_c} \ln \frac{\pi k_B T}{2((Q/2)k^2 + \partial \phi / \partial \langle v^2(r) \rangle)} - \langle v^2(r) \rangle \frac{\partial \phi}{\partial \langle v^2(r) \rangle}
\end{aligned} \tag{5}$$

where the energy contribution of the fluctuations is given by the function ϕ defined by

$$\phi = \frac{1}{V} \int d^3r [E(c/a + \xi(r), V + v(r)) - E(c/a, V)]. \tag{6}$$

The mean square of the fluctuation $\langle \xi^2(r) \rangle$ is given by the k -space integral over the k -dependent susceptibility (we use the term *susceptibility* in analogy to magnetic systems, but in its more general meaning of a response function), which for a system isotropic in k gives

$$\langle \xi^2(r) \rangle = \frac{V}{(2\pi)^3} \frac{k_B T}{2} \int_0^{k_c} \frac{4\pi k^2}{(K/2)k^2 + \partial \phi / \partial \langle \xi^2(r) \rangle} dk \tag{7}$$

with an analogous equation for the volume fluctuation $\langle v^2(r) \rangle$. In (7) two new parameters appear, namely the ‘stiffness’ constant K which determines the width of the momentum distribution and the cut-off wave vector k_c that defines the largest k -vector (shortest wavelength) of the fluctuations. (For the volume fluctuation the stiffness constant Q and the cut-off q_c are used.) This cut-off k -vector is needed because the correlation function (integrand in (7) is of Ornstein–Zernicke form and thus requires an upper limit in the integration to keep the integral finite.

The equations of state are derived by minimizing E and ϕ with respect to the variables c/a and V which gives

$$\begin{aligned} \partial E/\partial(c/a) + \partial\phi/\partial(c/a) &= 0 \quad (V = \text{constant}) \\ \partial E/\partial V + \partial\phi/\partial V &= -P \quad (c/a = \text{constant}) \end{aligned} \quad (8)$$

where P is the external uniform pressure. The equations of state together with the expressions for $\langle \xi^2(r) \rangle$ and $\langle v^2(r) \rangle$ (7) must be solved self-consistently for any given temperature to determine the respective equilibrium values of c/a , V , $\langle \xi^2(r) \rangle$, and $\langle v^2(r) \rangle$.

From the general properties of the function ϕ in (6) the stiffness constants K and Q are related to the corresponding $T = 0$ K correlation lengths, namely λ for the strain fluctuations and μ for the volume fluctuations, via

$$K = 2(\partial\phi/\partial\langle \xi^2(r) \rangle)\lambda^2 = VC'\lambda^2 \quad Q = 2(\partial\phi/\partial\langle v^2(r) \rangle)\mu^2 = (B/V)\mu^2 \quad (9)$$

where the derivatives are taken at $T = 0$ K. In order to derive (9) we have implicitly assumed the c/a variation along Bain’s path. In this case the constants K and Q can be expressed in terms of the tetragonal shear constant C' and the bulk modulus B . These relations reflect the physical intuition that these long-wavelength fluctuations are governed by macroscopic quantities describing the elastic behaviour of the crystal.

2.2. Solutions for the transition temperature and the entropy

Let us now explore the behaviour of our model at the transition temperature T_M where the first and the second derivative of the free energy with respect to the order parameters must vanish. This knowledge allows us to calculate the respective values for c/a and V but also the related critical fluctuations $\langle \xi^2(r) \rangle_c$ and $\langle v^2(r) \rangle_c$. It should be stressed that all these four quantities are entirely determined by the ground state properties of the system. By combining the condition $\partial\phi/\partial\langle \xi^2(r) \rangle = 0$ with the value for $\langle \xi^2(r) \rangle_c$ we obtain an expression for the transition temperature T_M by carrying out the k -space integration in (7) at $T = T_M$:

$$k_B T_M = 2\pi^2(\lambda^2/k_c)C'\langle \xi^2(r) \rangle_c. \quad (10)$$

(10) shows that T_M is proportional to the elastic constant (at $T = 0$ K) relevant for the transition path in accordance with the physical intuition that the stiffer the lattice (with respect to a particular distortion) the higher the transition temperature. The $T = 0$ K correlation length λ determines the shape of the k -distribution and thus describes the dynamical response of the lattice to long-wavelength excitations.

These classical fluctuations should be essentially linear in T , as required by the fluctuation–dissipation theorem. Therefore the temperature dependence of the fluctuation given in (7) can be rewritten in the approximated form:

$$\langle \xi^2(r) \rangle = \langle \xi^2(r) \rangle_c T/T_M. \quad (11)$$

In most cases the temperature dependence of the fluctuation is well described by this linear relation which has the advantage that the two parameters K and k_c can be replaced by the

transition temperature which, however, must be taken from experiment. If the dependence of the total energy on the order parameter is known from band structure calculations (e.g. for Bain’s path according to (1)), the finite-temperature properties of the phase transition depend only on these ground state results and a single ‘adjustable’ parameter, namely the experimental transition temperature. In addition, the application of this explicit temperature dependence has the advantage that for some of the models discussed [6] analytic solutions can be found (see the appendix).

From the free energy (5) we can also calculate the entropy contribution of the strain fluctuations:

$$S = \frac{k_B}{2} \sum_{k \leq k_c} \left(1 + \ln \left(\frac{\pi k_B T}{2((K/2)k^2 + \partial\phi/\partial\langle\xi^2(r)\rangle)} \right) \right); \quad (12)$$

the respective term for the volume fluctuations is completely analogous. It is easy to see that this expression for the entropy, which is based on a classical high-temperature expansion, diverges for $T = 0$. However, if the temperature is high enough, the system should be in a classical regime so (12) is valid.

With this expression for the entropy we can formulate the total energy from the free energy given in (5):

$$U = E + \phi - \langle\xi^2(r)\rangle \frac{\partial\phi}{\partial\langle\xi^2(r)\rangle} + \frac{k_B T}{2} \sum_{k \leq k_c} -\langle v^2(r)\rangle \frac{\partial\phi}{\partial\langle v^2(r)\rangle} + \frac{k_B T}{2} \sum_{k \leq q_c} \quad (13)$$

which is easy to evaluate. The total energy U contains contributions from both order parameters c/a and V . The two sums in (13) are typical for our classical model. They simply count the number of degrees of freedom (number of waves) and just lead to a constant energy shift. With a plot of U for a chosen temperature as a function of c/a and V we can visualize the temperature evolution of the order parameter describing the structural transition. This treatment is similar to a previous investigation on the magnetovolume anomalies in Invar alloys (see figure 4 of [18]). In the application below we will show that the entropy contribution to the total energy stabilizes the high-temperature phase and consequently our fluctuation model describes an entropy driven phase transition, similar to the model given by Kerr and Rave [11].

3. Applications of the fluctuation model

3.1. The fcc to bcc transition in calcium

Now we apply our model to calcium assuming the Bain transformation. (For a detailed discussion of the basic mechanism of Bain’s path see part I of this work [13].) Ca is a group II element and its ground state is fcc [19]. At atmospheric pressure Ca undergoes a martensitic phase transition to the bcc structure at a temperature of about 725 K. At a pressure of about 19.5 GPa (and $T = 0$ K) there is a transition into the bcc structure [20] which has also been explained by band structure calculations [13, 21]. It was suggested that the transition is of Bain type, although phonon measurements using inelastic neutron scattering [22] exhibited neither a softening of C' , as expected for a Bain mechanism, nor any pronounced phonon anomalies near the martensitic phase transition. In the bottom panel of figure 1 we show the band structure results [13] for the total energy as a function of both c/a and the volume V . The total energy has a local minimum at both ‘cubic’ values for the c/a ratio ($c/a = 1$ for bcc, $c/a = \sqrt{2}$ for fcc) but the minimum at $c/a = 1$ is very shallow and is higher in energy than that at $c/a = \sqrt{2}$ corresponding to the fcc ground state. There

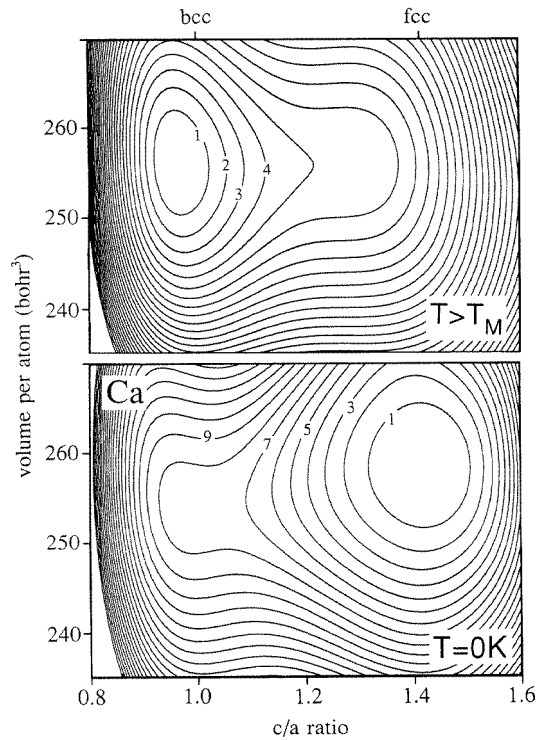


Figure 1. Total energy contours $E(c/a, V)$ for Ca for $T = 0$ K (lower panel) and for a temperature just above the phase transition (upper panel). The volume is given in $\text{bohr}^3/\text{atom}$ and the energy difference between adjacent contour lines is 0.1 mRyd.

is a small difference in the calculated equilibrium volumes, namely $V_{fcc} = 257 \text{ bohr}^3$ and $V_{bcc} = 254 \text{ bohr}^3$ which leads to a positive coupling between c/a and the volume since both c/a and V are larger in fcc than in bcc. For our finite-temperature calculations we take the $T = 0$ K energy surface and assume a transition temperature of 725 K [19]. For the cut-off wave vectors and the stiffness constants the following values are used: $K = 21.0$, $Q = 0.2$, $k_c = 9.5$, $q_c = 7.0$ (all quantities are in atomic units). K is determined according to (9) from the low-temperature correlation length $\lambda = 10 \text{ \AA}$, a value we took from Petry *et al* [23], who derived it for Ti by neutron diffraction experiments. The cut-off parameter k_c is adjusted to the experimental transition temperature T_M , while Q and q_c , (associated with the volume fluctuations) hardly influence T_M . Nevertheless these small volume fluctuations are needed, since the coupling between c/a and volume V stabilizes the high-temperature phase.

We now solve (self-consistently) our fluctuation model for a set of temperatures and thus obtain the temperature dependence of various macroscopic quantities describing the state of the system. In figure 2 we display, as a function of temperature, the c/a ratio and the logarithm of the correlation length ζ which is defined as

$$\zeta^2 = K / (2\partial\phi/\partial(\xi^2(r))). \quad (14)$$

The c/a ratio shows almost no temperature variation below T_M but jumps discontinuously from $\sqrt{2}$ (fcc) to unity (bcc) at T_M (the small deviations from these values are due to the polynomial fit according to (1) and the numerical solution). This jump is associated

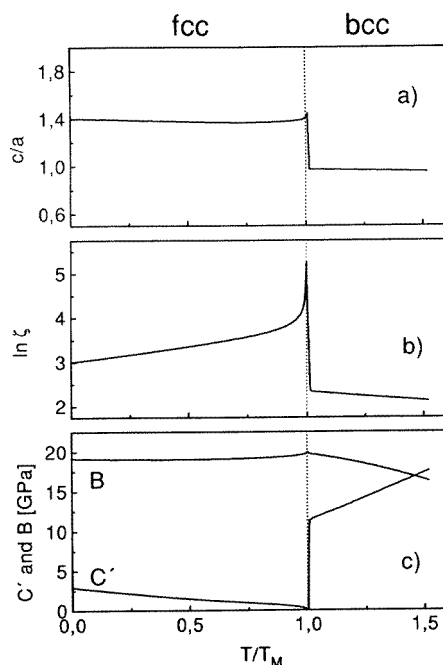


Figure 2. The temperature variation of (a) the Bain variable c/a , (b) the logarithm of the correlation length, $\ln(\xi)$, and (c) the tetragonal shear constant C' and the bulk modulus B .

with a divergence of the correlation length ξ (figure 2(b)). The two elastic properties, the bulk modulus B and the tetragonal shear constant C' (figure 2(c)) behave differently. The bulk modulus B shows only a weak temperature dependence, whereas the tetragonal shear constant C' vanishes at the transition temperature and then jumps to a large finite value for the bcc structure. At low temperatures the system is in a minimum corresponding to the fcc structure. As the temperature is raised, this minimum becomes metastable when the first and second derivatives with respect to c/a vanish ($C' = 0$), which defines T_M . Here a first-order phase transition to the new stable minimum (now at fcc) occurs. In this special case of the Bain transformation we observe a softening of $C'(T)$ which is the relevant elastic constant, in accordance with the proposal made by Zener [1]. If the crucial order parameter is not c/a , another elastic constant (or a linear combination of those elastic constants associated with the transformation path) will vanish at the transition temperature. This interpretation corresponds to the condition for the localized soft-mode model proposed by Clapp [24].

In the upper panel of figure 1 we show the total energy surface (13) for a temperature above the transition temperature of 725 K. We find a single stable minimum at $c/a = 1$ (bcc). The minimum at $c/a = \sqrt{2}$ (fcc), which described the ground state at $T = 0$ K (bottom panel of figure 1), has disappeared but its traces remain and cause an anharmonicity in the total energy surface which gradually weakens with increasing temperature. Figure 3 shows the high-temperature solutions for the entropy ΔS (12) with a positive discontinuity at the transition temperature as expected for an ‘entropy driven’ MPT. The numerical value of the discontinuity is about $0.15 \text{ J mol}^{-1} \text{ K}^{-1}$ and compares fairly well with the experimental [25, 26] result of $0.32 \text{ J mol}^{-1} \text{ K}^{-1}$.

Ignoring quantum effects one may speculate that by slow cooling from temperatures above T_M Ca can be stabilized in the bcc structure, since even at $T = 0$ K there is a

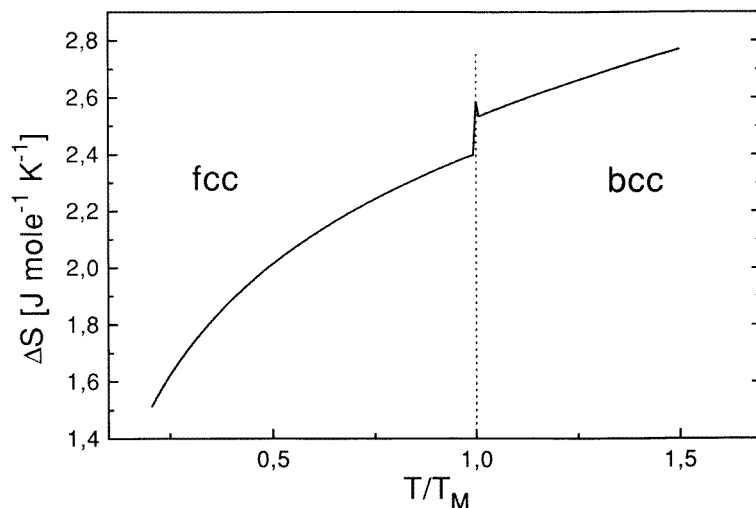


Figure 3. The excess entropy ΔS near the transition temperature.

metastable minimum for $c/a = 1$. However, it should be noted that zero-point fluctuations might be enough to destabilize this local minimum so that this metastable low-temperature bcc phase may not exist. In the case of Li, which shows a similar total energy surface [13], it has been found that very slow cooling of dispersed particles keeps them in the bcc structure [27].

By adding a $-PV$ pressure term to the free energy we can also study the influence of pressure on the transition temperature. For Ca we find that for small pressures the slope of the phase boundary dP/dT (at $T = T_M$) separating the fcc and the bcc phase is positive, in agreement with experiment [19].

3.2. Application to other systems

In part I of this paper we presented band structure calculations for the Bain transformation in the simple metals Li, K, Rb, Ca and Sr, and for the early transition metals Ti and V. The five simple metals have comparable energy surfaces and in all cases the fluctuation model can be applied and describes a first-order phase transition between fcc and bcc. (The detailed results for Sr have been published elsewhere [28].) As discussed in the first part of this paper, the energy surfaces for the transition metals differ significantly from those of the simple metals. For Ti we find a minimum at $c/a = \sqrt{2}$ (fcc) but a saddle point at $c/a = 1$ (bcc) and vice versa for V (for details see [13]). If we apply the fluctuation model to Ti we find a first-order phase transition from fcc to bcc. (One should note, however, that the ground state of Ti is hcp and not fcc, but, since these two structures are closely related to each other, the fcc structure should be a fairly good approximation to the true ground state.) For vanadium the ground state is bcc and there is a saddle point at $c/a = \sqrt{2}$ (fcc). The energy difference between these two extrema in V is about 20 mRyd compared to 3 mRyd for Ti. If we keep all parameters as in the calculation for MPT in Ti ($T_M = 1155$ K) we find for V a first-order phase transition from bcc to fcc but at a temperature of about 9000 K which is well above the melting point. Therefore this large energy difference between the bcc and fcc structure explains the high stability of the bcc V phase.

Our fluctuation model is not restricted to the Bain transformation. Ye *et al* [29]

calculated the hcp–bcc and 9R–bcc transformations in Na (9R is a close-packed hexagonal polytype of the hcp structure). This transformation is based on a conjection by Burgers [30] and relies on a different order parameter from c/a . If we use their band structure results for the total energy along these transformation paths as an input to our fluctuation model we find a first-order phase transition from hcp to bcc, and a weakly first-order transition from 9R to bcc (details will be given in a forthcoming publication).

4. Conclusion

The fluctuation model for martensitic phase transitions described in this paper represents a generalization of those models which rely on little mode softening. We find that no softening of a specific mode is necessary for the transition whereas order parameter fluctuations are sufficient to trigger a first-order phase transition. Since the order parameter for a structural phase transition usually describes the motion of single atoms or atomic planes in the crystal, the fluctuations along the transformation path can be seen as random and local distortions with long wavelength. The properties of the fluctuation model rely on the relevant elastic constants for the specific transformation path. Since the elastic constants describe the properties of the phonon system in the limit of small k -vectors (long wavelength) the amplitude of the fluctuations is directly related to the phonon dispersion in the centre of the Brillouin zone. With the fluctuation model we could show that these small- k (long-wavelength) displacements are sufficient to trigger a first-order phase transition. It should be noted that our fluctuation model is no alternative for those systems which are truly based on phonon softening (e.g. ferroelectrics). It will of course depend on the specific energy scale of a certain transition, which of the mechanisms (soft phonons or fluctuations) will govern the behaviour at the transition temperature. It may well be that at low temperatures a system starts off with random fluctuations which at higher temperature, when shorter-wavelength components of the fluctuations become excited, decay into the respective phonons so that finally a mechanism as described by Krumhansl and Gooding [6] leads to the phase transition.

Appendix

Krumhansl and Gooding [6] formulated a generic model for martensitic phase transitions with little phonon softening and expressed the free energy as a function of the relevant order parameter x :

$$F = A(T)x^2/2 - x^3/3 + x^4/4. \quad (\text{A1})$$

In their publication [6] they gave a detailed discussion of various cases where transformations can be described by only varying the coefficient A . We note that the curve with $0 < A(T = 0) < 2/9$ describes the alkaline metals, while a negative value for $A(T = 0)$ corresponds to the case found for Bain transformations of transition metals (see part I of this paper [13]). They introduced the effect of temperature by assuming that $A(T)$ has the form

$$A(T) = \omega^2 + aT \quad (\text{A2})$$

where ω^2 is the characteristic frequency of a low-lying phonon mode. They were able to show that a variation of $A(T)$ can trigger a first-order phase transition. For a detailed discussion of the properties of this model we refer to [6] and [10]. A negative value for $A(T = 0)$ leads to conceptual problems since it would represent a negative phonon

frequency (overdamping). Kerr and Rave [11] have introduced order parameter fluctuations which affect the shape of the on-site potential energy using an alternative interpretation of (A1) for displacive transitions [10].

Let us now rewrite (A1) by including fluctuations g of the order of parameter x , where g is an abbreviation for the statistical average over the square of the respective fluctuation, so that g is analogous to the quantity defined by (7):

$$F = (A/2)(x^2 + g) - \frac{1}{3}(x^3 + 3xg) + \frac{1}{4}(x^4 + 6x^2g + 3g^2). \quad (\text{A3})$$

Reordering (A3) in powers of x gives

$$F = \left(\frac{3}{4}g^2 + (A/2)g\right) - xg + (x^2/2)(A + 3g) - x^3/3 + x^4/4. \quad (\text{A4})$$

The last three terms of (A4) exactly resemble the properties described by the generic model discussed earlier [6]. The coefficient A becomes renormalized by the fluctuations which make it temperature dependent (note that g is essentially linear in T) so that we find a justification for the *ansatz* in (A2). The first term defines a temperature dependent shift of F . A new feature is found in the linear term $-xg$ which causes a pseudostrain along the direction of the transition path increasing with temperature and which acts as a restoring force. A similar feature has also been noted by Kerr and Rave [11] who discussed it together with an extensive analysis of the properties of the asymmetric order parameter model. If their model is applied to 'real' systems as for the Bain transformation in simple metals, the two minima of the free energy function according to (A1) can be identified with the corresponding minima in the total energy curve found for example in Ca (figure 6 in part I [13]) where the stable minimum (with a finite value of x) corresponds to the fcc phase (stable at $T = 0$) and the metastable minimum (at $x = 0$) corresponds to the bcc phase (stable for $T > 725$ K). If the fluctuations should describe a phase transition between the low-temperature fcc and the high-temperature bcc phase, the order parameter x must jump at the transition temperature from a finite value to $x = 0$ which would then describe the bcc phase.

In general the (fluctuation induced) restoring pseudostrain counteracts a possible phase transition so that this effect could make these strain driven transformations less favorable than transformations along a phononic order parameter as described by the Burgers transformation [30].

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