Local Stability of Nonequilibrium Phases

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(Received 29 December 1993)

The relative structural stability of the transition metals and their alloys for a tetragonal deformation is investigated. Total energy calculations demonstrate that the nonequilbrium cubic structures are *locally unstable* with respect to this deformation mode at low temperatures, i.e., the cubic elastic constants $(c_{11}-c_{12})$ are negative. Thus, these phases are not appropriate reference states for alloy phase diagram constructs and if such phases do occur at high temperature, the local stability must be due in large part to entropy contributions to the free energy.

PACS numbers: 81.30.Bx, 64.10.+h, 65.50.+m, 71.45.Nt

The properties of both nonequilibrium and low-temperature equilibrium phases affect the phase diagrams of metals and alloys. The simplest case is when there is a phase transition to a different structure at high temperature. Even when this is not the case, these phases may represent competing phases that can have important consequences such as determining which phases may occur upon alloying. Many of these phases may be related to each other by lattice distortions. A condition regarding the topology of the energy surface along certain distortions will be considered in this paper. Calculations will show that a large class of excited phases, which are generally assumed to be metastable, are locally unstable. These results have significant consequences for the thermodynamic modeling of alloy phase diagrams.

During the last decade, the accuracy of the local density approximation (LDA) for the *ab initio* computation of physical properties of the elemental metals and their compounds has been firmly established. Comparison between calculated and low-temperature equilibrium properties usually leads to satisfactory agreement which, in turn, has resulted in the almost universal acceptance of the LDA for the prediction of this class of properties. Whereas, *a priori,* there is no reason to suspect that the LDA will be less accurate in the description of nonequilibrium structures, a significant body of thermodynamic analysis points to substantial and long-standing discrepancies. In particular, in the 1960's, Kaufman and Bernstein [1] developed empirical methods that are currently widely used to fit equilibrium phase diagrams and thermochemical data of binary and multicomponent alloys. In this approach, the energy difference between equilibrium and nonequilibrium structures of the pure elements plays a key role. Shortly after their empirical estimate, the promotion energies were also obtained using electronic structure calculations [2-4]. Although for some cases there was agreement between the theoretical and empirical estimates, large discrepancies were found for metals around the middle of the transition series. Since then, several attempts have been made in order to reconcile these discrepancies which, to this date, remain essentially unchanged [5-8]. The present results indicate that the structural promotion energies used in thermodynamic constructs are not, in fact, the energy differences between structures.

Although the promotion energies of the elements of the middle of the transition metal row are not amenable to direct experimental determination, it is clear that important constraints are imposed by related thermochemical data. For example, if one assumes that the nonequilibrium structure is stable relative to the liquid at $T=0$ K, then the heat of fusion provides an upper bound to the promotion energy. (Experimental thermodynamic data are available for the Sc and Ti columns and *a priori* theory is in agreement with these values.) These constraints and their implications have been discussed extensively in the literature [7]. We note, however, that the physical meaning of the promotion energies and their utilization in the calculation of equilibrium phase diagrams is strongly dependent on the metastability of the nonequilibrium structures.

In this paper, we present a systematic study of the energy of the transition metals in hypothetical tetragonal structures as a function of a volume-conserving Bain distortion in c/a. The Bain distortion takes the system from a bcc structure at $c/a=1$ to an fcc structure at $c/a=\sqrt{2}$. A derivative will be sketched which demonstrates that the derivative of the total energy with respect to a volume-conserving Bain distortion must be zero valued at c/a values corresponding to the cubic structures; i.e., the elemental phases must have maxima, minima, or inflection points at both the fcc and bcc structures along the Bain distortion. Our calculated results show that the nonequilibrium structures (either fcc or bcc) in the middle of the 3*d*, 4*d*, and 5*d* transition metal rows are local *maxima,* implying that they are *unstable* with regard to this volume-conserving deformation mode for reasonable atomic volumes. This instability leads to a negative value of the cubic elastic constants $(c_{11}-c_{12})$. In those instances for which the nonequilibrium phase is stable at high temperatures, the mechanical instability in question might become apparent, for example, by extrapolating

0031-9007/94/72(19)/3076(4)$06.00

phonon frequencies to low temperatures [9,10]. Furthermore, these results imply that such high temperature phases must be stabilized by entropy contributions and the empirical lattice promotion energies used in phase diagram constructs need not—and do not—correspond to the actual energy differences between the lattice structures involved.

Our results are established as follows. First we determine, on the basis of general symmetry arguments, the conditions under which the energy should display extrema at the two special points ($c/a=1$ and $c/a=\sqrt{2}$) along the volume-conserving deformation path. Second, the mechanical stability (or instability) for the middle of all three transition metal series is investigated using the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA). Finally, full-potential linearized augmented Slater-type orbital (LASTO) calculations were used to check the LMTO-ASA results and also to study Ti and Li, which have high temperature bcc phases, and RuNb.

The structural energy of systems constrained to have tetragonal symmetry can be written in terms of the lengths a and c of the two independent axes. To first order in the displacements δa and δc, a general distortion that maintains the tetragonal symmetry will cause a change in energy of

$$\delta U(a,c)=2\frac{\delta U}{\delta a}\delta a+\frac{\delta U}{\delta c}\delta c\,. \tag{1}$$

For a volume-conserving deformation, δa and δc are related to first order by $a\delta c=-2c\delta a$. Combining these results gives

$$\delta U(a,c)=2\delta a\left[\frac{\delta U}{\delta a}-\frac{c}{a}\frac{\delta U}{\delta c}\right]. \tag{2}$$

For general tetragonal symmetry, there is no simple relationship between $\delta U/\delta a$ and $\delta U/\delta c$ since there are no symmetry operations connecting the a and c axes. Thus, the value of c/a for which $\delta U=0$ depends on details of the system. If, however, there is an increase in the symmetry of the system for some c/a, then additional relationships between $\delta U/\delta a$ and $\delta U/\delta c$ may exist. For the elemental systems at $c/a=1(\sqrt{2})$, the symmetry group is now O_h and $\delta U/\delta a=\delta U/\delta c$ $[\delta U/\delta c=\delta U/\delta(\sqrt{2})]$. Hence, at these values of c/a, $\delta U=0$ by symmetry. (A different derivation for the cubic elements has been given in [11].)

For alloys, there may or may not be symmetry-dictated extrema at $c/a=1$ and $\sqrt{2}$ depending on the atomic ordering of the lattice. In the case of an AB alloy with, for example, A atoms at the corners of the cell and B's at the centers, the structure for $c/a=1$ is that of CsCl, which has full cubic (O_h) symmetry; thus, the energy will again display an extremum. On the other hand, at $c/a=\sqrt{2}$ the symmetry remains intrinsically tetragonal ($L1_0$), despite the fact that the lattice of atomic positions is fcc; in this case, the energy need not (although it may) show an extremum.

A few comments concerning symmetry-dictated extrema are in order. These extrema may be local maxima, minima, or inflection points. The electronic structure results that follow show that the symmetry criterion is obeyed in all cases investigated. Other extrema along the Bain distortion besides those required by symmetry may (and do) also occur. The number of extrema is not fixed except that there must be one more minimum than maxima. (The energies at $c/a=0$, $c/a=\infty$ diverge since this corresponds to overlapping atoms.) Similar symmetry required extrema in the energy for different structures and distortion paths may occur anytime when the symmetry increases. In these cases, however, the constraint relating the independent variables may not be the volume-conserving one appropriate to the Bain distortion, but will depend on the particular symmetries involved.

Self-consistent LMTO-ASA calculations were carried out for the middle of the three transition metal series as a function of c/a and volume. The results of the calculations are shown in Fig. 1. Elements at both ends of the transition rows are not shown since the relative errors of the LMTO-ASA calculations are expected to be of the order of the small energy differences in these cases. The plots are grouped into elements sharing the same low energy structure along the deformation path, and this structure is used as the reference. The atomic volume for each of the plots in Fig. 1 is kept constant and equal to the volume at which the energy displays its absolute minimum. (Using the volumes corresponding to the high energy phase does not qualitatively change the curves and hence are not shown.) The energy differences between the bcc and fcc structures are in good agreement with previous calculations [2–4,8], underscoring, once again, the outstanding discrepancies between the theoretical and empirical estimates. Furthermore, we see that, without exception the energy of the higher lying phase is locally a maximum, i.e., $c_{11}-c_{12}$ is found to be negative for the nonequilibrium structures which, in turn, implies that these structures are mechanically unstable at low temperatures. This instability continues to hold if other reasonable choices for the atomic volume (for example, the experimental or high energy phase's volume) are used. As mentioned, this mechanical instability poses a new challenge to the interpretation and use of promotion energies in phase diagram computations.

Several further observations should be noted. First, for all the cases shown in Fig. 1, there is clearly another minimum outside the range $1\leq c/a\leq\sqrt{2}$. These minima may be locally stable or saddle points, i.e., unstable to some other distortion. The existence of these extra minima does not alter the fact that the high energy cubic phases are unstable and therefore does not affect the conclusions of our paper. The minima seen for the low energy phases are stable against a Bain distortion, but could possibly be unstable to some other distortion. Clearly

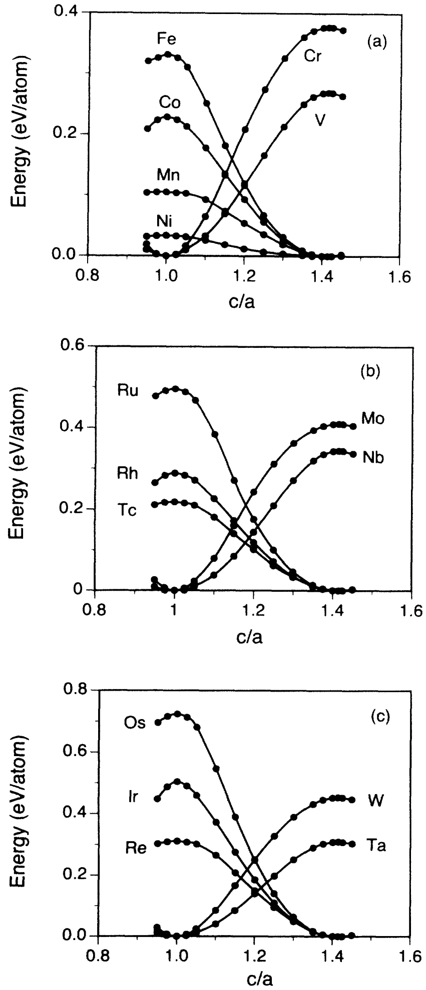

FIG. 1. Self-consistent LMTO-ASA results for the transition metals along the tetragonal deformation path. Energies are relative to the low energy structure of the elements along the path for the (a) $3d$, (b) $4d$, and (c) $5d$ rows.

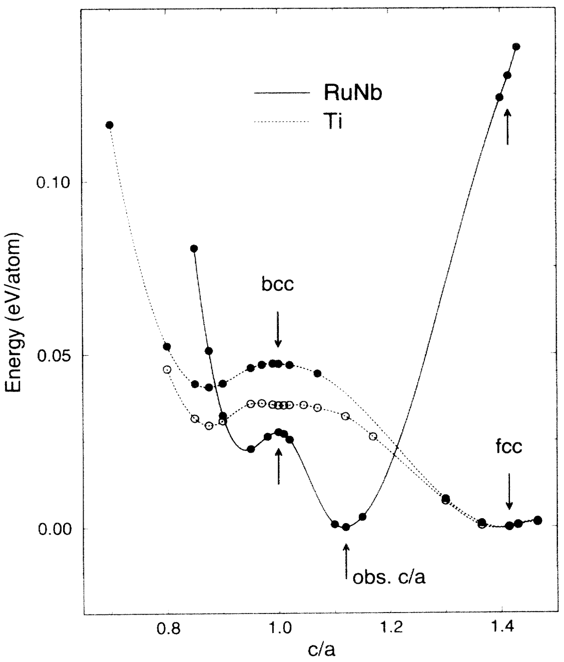

FIG. 2. Paramagnetic self-consistent full-potential LASTO results along the tetragonal Bain distortion at fixed volume. The RuNb calculations were done at the observed volume. For Ti, the results corresponding to both the observed volume (filled circles) and the calculated bcc volume (open circles) are shown. The latter shows a shallow minimum at $c/a = 1$. (The calculated bcc volume corresponds to a $\sim 3\%$ reduction in lattice constant; the calculated fcc volume lies between these two values. The minima at $c/a = 1$ and ≈ 0.87 become more pronounced at still smaller lattice volumes.) Energies are relative to the low energy structure at each volume.

some elements are unstable to other distortions since they have ground state crystal structures other than fcc or bcc.

Self-consistent full-potential (LASTO) calculations [12] were also done for several of the elements. The results were in essential agreement with the plots of Fig. 1. Similar full-potential LASTO calculations have been reported [13] previously for Cu and Pd, in which the higher energy bcc structure is also found to be at a local maximum. Furthermore, other full-potential calculations reported recently for Cu [11], magnetic Co [14], and Fe [15] also show that the higher energy structure is unstable to a tetragonal distortion at the observed volumes.

Although all the curves shown in Fig. 1 showed maxima at the high energy phase, clearly there should exist cases where minima exist at both values of c/a. Ti provides one of the most likely candidates for obtaining a stable high energy phase since the energy differences are smaller than those in Fig. 1 and the bcc structure actually occurs at high temperature ($T > 1153$ K). LASTO results for Ti are plotted in Fig. 2 for the atomic volumes corresponding to the observed low-temperature hcp phase and for the calculated bcc volume. The lower energy fcc structure lies at a minimum along the Bain distortion path while the energy difference to the higher energy bcc phase is consistent with experiment. Whether a maximum or a shallow minimum occurs for the excited bcc phase depends on the particular volume chosen; for the calculated $T = 0$ K bcc volume, the results in Fig. 2 show a shallow minimum. However, this shallow minimum is not enough to fully explain the stability of the bcc phase: The well depth is comparable to or smaller than thermal vibrational energies, but more importantly, a calculated curve taking into account the thermal expansion ($\sim 3\%$) between the low- and high-temperature phases will no longer have a shallow minimum, but rather a maximum at $c/a = 1$. Thus, the observed high temperature bcc phase must be stabilized to a large degree by entropy contributions to the free energy. Similar LASTO calculations for elemental Li display a local maximum for the high-temperature bcc phase throughout the full range of reasonable atomic volumes; in this case, however, the promotion energy (2 meV/atom) is more than an order of magnitude smaller than that of Ti.

The structure of RuNb ($L1_0$, CuAu-I or $P4/mmm$) lies on the Bain distortion line between CsCl at $c/a=1$ and "ideal" $L1_0$ at $c/a=\sqrt{2}$. Its c/a has been reported [16] as ranging between 1.116 and 1.126. Going to the Nb-rich side, at $Nb_{0.62}Ru_{0.38}$ the system takes on the CsCl structure [16]. The calculated overall energy minimum, which is not dictated by symmetry, is obtained for a c/a of 1.12, at the center of the experimentally reported values. This good agreement is typical: Local density calculations generally do very well in predicting the c/a of hexagonal or tetragonal systems. LMTO-ASA results for RuNb yield an energy minimum in agreement with the present results [17]. At a $c/a=1$, the energy has an extremum as required by symmetry, but shows no hint of one at $\sqrt{2}$. As for the case of the elemental metals, the extremum of the excited structure is a local maximum.

In conclusion, for a volume-conserving tetragonal Bain distortion, the crystal potential energy should, by symmetry, take on an extremal value whenever the distortion passes through structures of different (higher) symmetry. Calculations for a variety of elemental metals and for the compound RuNb are in agreement with this result. Symmetry-dictated extrema also will exist for other lattices and/or displacive distortions; excited phases that are local minima as well as maxima are expected to occur.

The plots of Figs. 1 and 2 show that the high energy structures (fcc or bcc) of all of the elemental metals investigated here (except for Ti at reduced volumes) are unstable with respect to a tetragonal distortion. For the elements shown in Fig. 1, any reasonable choice of volume will lead to the same conclusion. The absence of a local minimum in the electronic energy precludes the use of these structures as reference states (at $T=0$ K) for free energy computations. These structures, however, may still display local stability and thus be at least *metastable* at higher temperatures. If so, the entropy must be responsible for their local stability. A direct implication of our results is that empirical estimates of the promotion energies (lattice stabilities) do not bear a direct relation to the energy differences obtained by means of electronic structure calculations, which are generally carried out at $T=0$ K and neglect vibrational modes. This is not the common view.

We thank Peter Miodownik, Gören Grimvall, and Philip Allen for discussions. The work at Brookhaven was supported by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016 and by a grant of computer time at the National Magnetic Fusion Energy Computing Center, Livermore, California. The work at The University of Texas at Austin was supported by the National Science Foundation under Grant No. DMR-91-14646.

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[1] L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams* (Academic, New York, 1970).

[2] D. G. Pettifor, J. Phys. C. **3**, 367 (1970).

[3] H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).

[4] J. W. Davenport, R. W. Watson, and M. Weinert, Phys. Rev. B **32**, 4883 (1985).

[5] A. P. Miodownik, *Computer Modeling of Phase Diagrams*, edited by L. H. Bennet (The Metallurgical Society, Warrendale, PA, 1986).

[6] N. J. Saunders, A. P. Miodownik, and A. T. Dinsdale, Calphad **12**, 351 (1988).

[7] A. F. Guillermet and M. Hillert, Calphad **12**, 337 (1988).

[8] G. W. Fernando, R. E. Watson, M. Weinert, Y. J. Wang, and J. W. Davenport, Phys. Rev. B **41**, 11813 (1990).

[9] P. J. Craievich and J. M. Sanchez, in Proceedings of Calphad XXII, Salou, Catalonia, Spain, 16–21 May 1993 (unpublished).

[10] Following Ref. [9], Grimvall and co-workers have studied phonon instabilities in W-Pt [G. Grimvall (private communication)].

[11] T. Kraft, P. M. Marcus, M. Methfessel, and M. Scheffler, Phys. Rev. B **48**, 5886 (1993).

[12] G. W. Fernando, J. W. Davenport, R. E. Watson, and M. Weinert, Phys. Rev. B **40**, 2757 (1989).

[13] G. W. Fernando, J. Mei, R. E. Watson, M. Weinert, and J. W. Davenport, Phys. Rev. B **47**, 13636 (1993).

[14] A. Y. Liu and D. J. Singh, Phys. Rev. B **47**, 2757 (1993).

[15] S. Peng and H. J. F. Jansen, J. Appl. Phys. **67**, 4567 (1990). Their energy contour plot is consistent with the extremal conditions at the fcc and bcc structures. Depending on the volume chosen, these may be local maxima or minima.

[16] P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (ASM, Materials Park, OH, 1991).

[17] J. D. Becker and J. M. Sanchez, Mater. Sci. Eng. A **170**, 161 (1993).