Calculation of Thermodynamic Properties and Phase Diagrams of Binary Transition-Metal Alloys

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A model tight-binding Hamiltonian including off-diagonal disorder and Hartree-Fock electronic self-consistency is used to calculate the enthalpies of formation of the Mo-Cr, Mo-Nb, and Mo-Ta alloys. The approach combines the coherent-potential approximation, the generalized perturbation method, and the cluster-variation method. The model is also used to calculate the phase diagram and the equilibrium activities for the Mo-Cr system.

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The calculation of thermodynamic potentials and phase diagrams of binary alloys requires the precise knowledge of the enthalpy of alloy formation ΔH and, in particular, of the underlying interatomic interactions (pair and many body). First-principles and microscopic theories are available which can account for the general trends observed in the enthalpy of formation of binary alloys of transition metals.[1-5] It is generally agreed, however, that most implementations of these microscopic theories fall short of the required accuracy for a phase-diagram computation. Thus, for the calculation of thermodynamic potentials and phase diagrams, a strictly phenomenological approach has been preferred in the past.[6,7] The approach is based on a physically reasonable model for the enthalpy of alloy formation ΔH plus an accurate treatment of the configurational entropy by means of the cluster-variation method (CVM). For the reasons mentioned above, the several parameters characterizing ΔH are not calculated by use of microscopic theories, but instead are determined from selected thermodynamic data. This phenomenological approach has been successfully applied to the description of the equilibrium phase diagram for several binary alloys[6,7] and it has encountered a good measure of success in predicting, for example, metastable states in Al-Li alloys.[7,8] In addition to its practical value as a semipredictive theory of alloy phase diagrams, the phenomenological calculations have also served to point out the crucial role played by short-range order (SRO) in the details of the equilibrium and metastable phase diagram.

Several of the first-principles electronic theories of binary alloys include SRO, either explicitly or implicitly, in the calculation of the enthalpy of formation. For example, Connolly and Williams[1] used *ab initio* results for the cohesive energy of ordered compounds to estimate pair and many-body interactions. These interactions could then be used to describe the enthalpy of formation of disordered alloys. This approach, which relies strictly on localized interactions for the description of ΔH, has not been put to a quantitative test against experimental thermodynamic data or phase-diagram calculations.

An alternative approach, proposed by Bieber *et al.*[2] consists of calculating ΔH for the alloy with SRO by extrapolation from the random system (rather than extrapolating from the ordered compounds as done by Connolly and Williams). The method of Bieber *et al.* is based on the calculation of ΔH for a random alloy using the coherent-potential approximation (CPA) followed by a perturbation expansion of ΔH in terms of short-range-order parameters. This technique, known as the generalized perturbation method (GPM), is used to calculate localized interactions (pair and many body), which contribute to ΔH in addition to the nonlocal CPA energy of the random alloy. The GPM has been studied extensively in the tight-binding (TB) approximation and has been very valuable in elucidating general trends in the alloying behavior of the transition metals. However, some of the additional approximations usually made in actual implementations of the GPM, such as neglect of the effects of charge transfer and the off-diagonal disorder in the TB Hamiltonian, generally preclude a quantative comparison between the calculated and the experimentally determined ΔH. Thus, no phase-diagram calculations for real systems have been attempted using the GPM.

Recently, the cluster–Bethe-lattice method (CBLM) (Refs. 3–5) was used together with the CVM in order to calculate the enthalpy of formation and the associated phase diagrams for Cr-Mo, Cr-W, and Mo-W binary alloys.[4,5] These calculations were carried out by use of a self-consistent Hartree-Fock Hamiltonian in the TB approximation with a six-orbital basis per atom (one *s* and five *d* orbitals). Despite the fact that the CBLM relies on a rather severe topological approximation that replaces the real crystal lattice with a Cayley tree, the results of the calculations were in general agreement with experiment.[4,5] The CBLM results also showed that in order to achieve the accuracy in ΔH needed for phase-diagram calculations, one must include off-diagonal disorder in the TB Hamiltonian and, in addition, carry out a self-consistent treatment of charge transfer.

In this Letter, we present a microscopic theory based on the TB approximation for the calculation of the

TABLE I. Bandwidths (Ref. 10) and on-site energies (Ref. 17) in electronvolts.

Element	d on-site energy	d band width
Molybdenum	−3.95	9.98
Chromium	−3.14	6.56
Niobium	−3.22	9.72
Tantalum	−2.86	11.12

enthalpy of formation of transition-metal alloys. The following features, which result in significant improvements over previous calculations, are implemented: (i) the topological approximation of the CBLM is lifted by use of the CPA together with the GPM, (ii) off-diagonal disorder is included in the TB Hamiltonian, and (iii) the effects of charge transfer in the random alloy are treated self-consistently within the Hartree-Fock approximation.

The TB Hamiltonian is described with a basis of five d orbitals per atom. Accordingly, the effects of s and p electrons on the enthalpy of formation are neglected. This approximation is expected to work relatively well for the nearly half-filled d-band alloys for which the d-electron contribution to ΔH dominates. The hopping integrals for the pure elements are determined with canonical Slater-Koster parameters[9] according to the prescription of Harrison.[10] The Slater-Koster parameters between unlike atoms in the alloy are estimated, following Shiba,[11] as the geometric mean of those for the pure metals. The onsite energy ϵ_i^0 for pure metal i is taken to be equal to the d-energy level in the excited-free-atom configuration $s^1 d^{(z_i-1)}$, where z_i is the total number of valence electrons. This configuration is close to the $s^{1.3} d^{(z_i-1.3)}$ configuration predicted by band-structure calculations for the pure metals.[12] In all our calculations, we have taken the number of d electrons per i atom to be equal to $z_i - 1.3$. The on-site energy ϵ_i, at a site occupied by element i in the alloy, is determined self-consistently from[13]

$$\epsilon_i = \epsilon_i^0 + U(n_i - n_i^0), \tag{1}$$

where U is an effective direct-exchange Coulomb integral, $n_i^0 = z_i - 1.3$ is the number of d electrons in the pure metal, and n_i is the actual d-electron count for species i in the alloy. In this study, we have taken

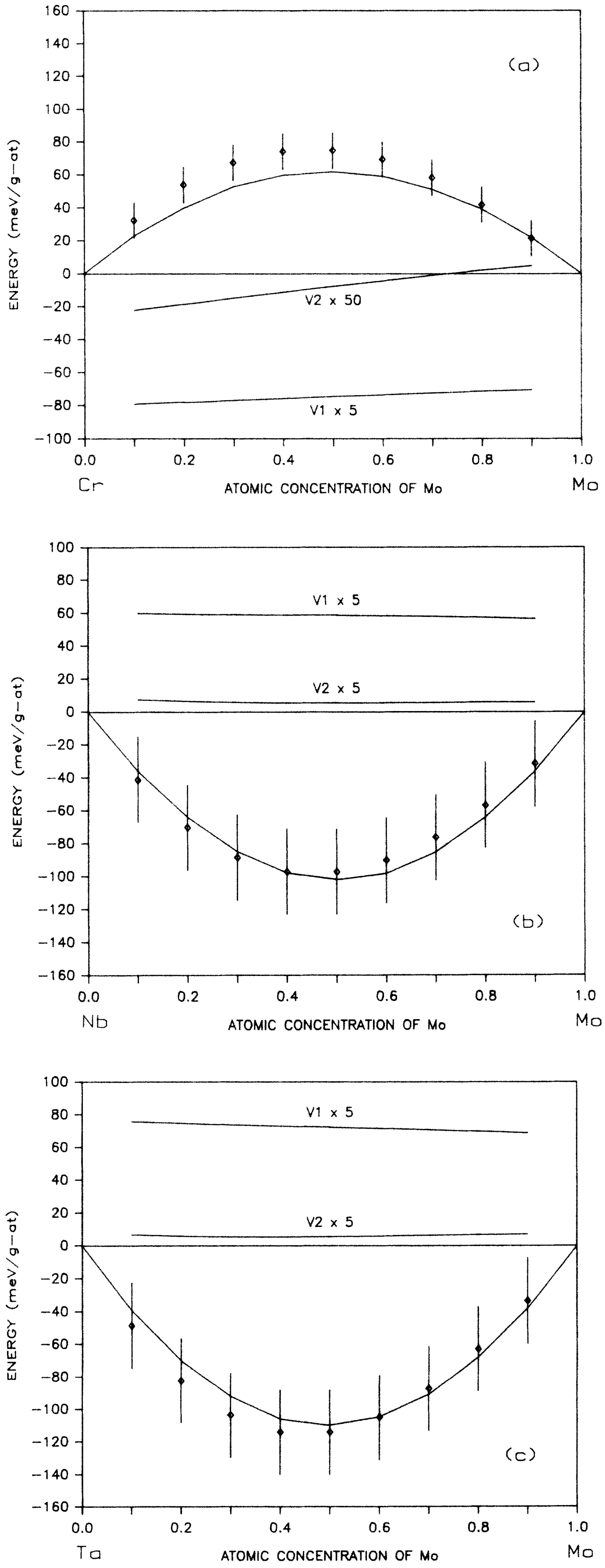

FIG. 1. Calculated effective-pair interactions for first (V_1) and second (V_2) neighbors, and comparison of the predicted random-alloy enthalpy of formation (solid line) with the experimental measurements (lozenges with error bars) for the (a) Mo-Cr, (b) Mo-Nb, and (c) Mo-Ta systems. The temperatures at which the measurements were made are 1471 K for Mo-Cr (Ref. 19) and 1200 K for Mo-Nb (Ref. 20) and Mo-Ta (Ref. 21).

$U = 3$ eV for all elements. In Eq. (1) we consider only the intra-atomic effects of charge transfer on the on-site energies. This is consistent with the fact that, in our calculations, electronic self-consistency is only implemented for the random alloy for which interatomic corrections to the on-site energy vanish.[3-5]

The local densities of states for the pure metals are obtained by use of five levels of the recursion method, which guarantee that the first eleven moments of the density of states are reproduced exactly.[14,15] For a random alloy, the local densities of states are obtained with the CPA. In general, the total energy of the alloy is given by three terms: (i) the one-electron energy, obtained from the calculated density of states; (ii) intra-atomic and interatomic electron-electron energies, which are subtracted from the energy of the alloy since they are counted twice in the one-electron term; and (iii) the ion-ion electrostatic energy.[3] For a random alloy, however, the ion-ion energy and the interatomic electron-electron correction cancel each other, and, thus, these terms do not appear explicitly in ΔH.[3] The enthalpy of formation ΔH is obtained, as usual, by subtracting from the total energy of the alloy the energies of the pure elements weighted by their concentrations.

The effect of SRO on the enthalpy of alloy formation is described in terms of first- and second-neighbor effective-pair interactions (EPI) calculated with the GPM.[2] In the alloy with SRO, we also include a small contribution to the EPI arising from the electrostatic interaction between the different atomic species as a result of the net charge transfer.[16]

We report in this Letter the results obtained for the nearly half-filled d-band systems Mo-Cr, Mo-Nb, and Mo-Ta, for which detailed experimental data are available. The calculations are done in a bcc lattice. The TB Hamiltonian parameters which are used, namely, the on-site energies and d-band widths, are given in Table I. A comparison of the calculated enthalpy of formation of the random alloys with high-temperature experimental measurements[18-21] is given in Figs. 1(a)-1(c) for Mo-Cr, Mo-Nb, and Mo-Ta, respectively. Also shown in Fig. 1 are the predicted EPI for first (V_1) and second (V_2) neighbors. It should be noted that, at these high temperatures, the SRO contribution to the enthalpy of formation (arising from the EPI) is approximately $\frac{1}{10}$ of the ΔH for the random alloy. For the three alloys investigated, the EPI are almost concentration independent because the difference in the number of d electrons of the components in the alloys is small. The slight asymmetry found in the experimental enthalpy of formation is explained well by the small decrease in the magnitude of the EPI as the content of Mo increases. The EPI of Mo-Cr are negative which indicates, as found experimentally, a segregation tendency, whereas the EPI of Mo-Nb and Mo-Ta are positive, indicating an ordering tendency. In fact, our results predict the existence of a stable B_2 ordered phase below 1040 and 830 K for Mo-Ta and Mo-Nb, respectively. To the best of our knowledge, however, no experimental evidence is currently available concerning the existence of the B_2 phase.

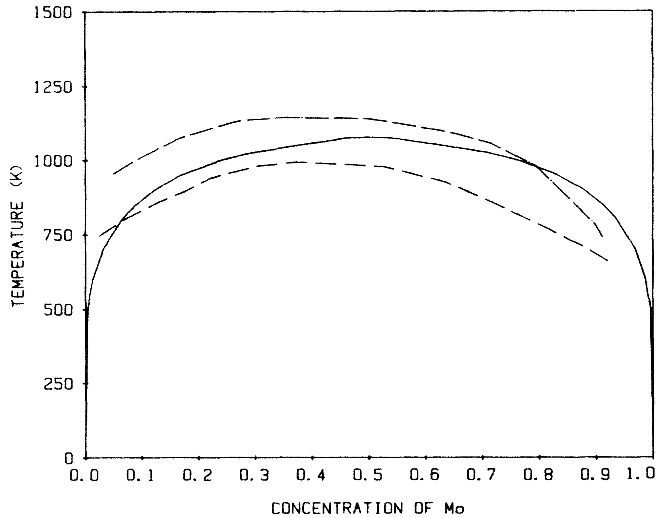

FIG. 2. Comparison of the predicted (solid lines) and previously assessed (dashed lines, Ref. 18; dot-dashed lines, Ref. 19) solid-state phase diagram for the Cr-Mo system.

We have also calculated the solid-state equilibrium phase diagram for the Mo-Cr system using the predicted enthalpy of formation of the random alloy and the pair interactions given in Fig. 1(a). The configurational entropy for this system was calculated with the tetrahedron approximation of the CVM. The vibrational entropy of formation, ΔS_{vib}, was determined by comparison of the calculated configurational free energy with the total free energy of formation measured at 1471 K for an alloy of atomic composition 50% Mo, 50% Cr.[18] The adopted form for ΔS_{vib}, which is consistent with the experimental results and also accounts for the effect of SRO in the vibrational entropy, is

$$\Delta S_{\mathrm{vib}} = C(\xi_2 - 1), \qquad (2)$$

where $C = 1.06 \times 10^{-2}$ meV/[K (g atom)] and ξ_2 is the pair-correlation function defined in Refs. 6 and 7.

In Fig. 2, we compare the calculated phase diagram with previous experimental assessments by Kubaschewski and co-workers.[18,19] In Fig. 3, we also compare the predicted Cr and Mo activities with experimental data obtained at 1471 K.[18] As can be seen, good agreement with experiment is obtained for both the calculated equilibrium phase diagram and the calculated activities in the solid phases.

In conclusion, we have shown that the enthalpy of formation of the isomorphic bcc alloys can be accurately calculated from a simple model based on (i) a

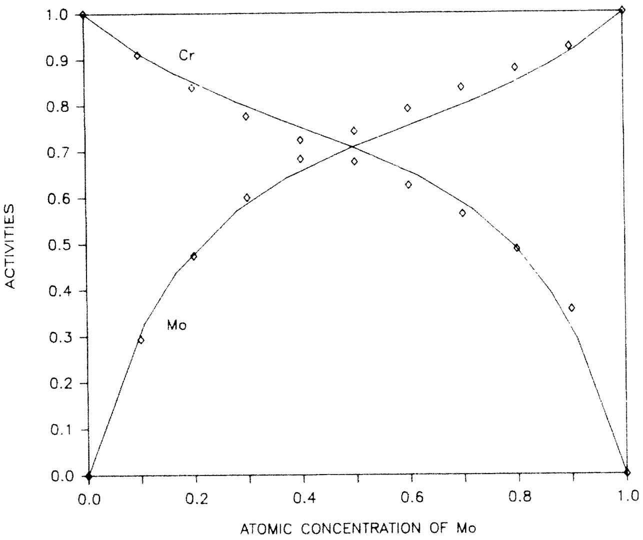

FIG. 3. Comparison of the predicted (solid lines) and experimental (lozenges, Ref. 18) activities for the Cr-Mo system at 1471 K.

tight-binding approximation for the Hamiltonian of the alloy; (ii) the coherent-potential approximation; and (iii) the generalized perturbation method. The success of these calculations depends critically on the accurate choice of on-site energies and d-band widths for the pure elements. In addition, our calculations showed that off-diagonal disorder and the self-consistent treatment of charge transfer are significant. In the case of the Mo-Cr system, for which an estimate of the vibrational entropy could be made from experimental measurements, the results of the electronic calculation combined with the CVM give an accurate description of the phase diagram and thermodynamic potentials.

Finally, we note that we have neglected s and p electrons in the calculation of ΔH. This approximation is expected to work relatively well for the half-filled d-band systems studied here. The contribution of ΔH of s and p electrons should be more significant for alloys involving elements near the end of the transition series. Nevertheless, we have also applied the model to alloys of Ti, Zr, and Hf, with Ni, Pt, and Pd, which have large negative enthalpies of formation, and found good agreement with experiment. The results of these calculations will be reported in a forthcoming publication.

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