

INVERTIBLE AND NON-INVERTIBLE ALLOY ISING PROBLEMS

C. Wolverton,^a Alex Zunger^a and B. Schönfeld^b

^aNIST, 1B, 440, U.S. Dept. of Commerce, Boulder, CO 80545, U.S.A.

^bInstitut für Angewandte Physik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland

(Received 18 September 1996; accepted 7 October 1996 by S. G. Louie)

Physical properties of alloys are compared as computed from ‘direct’ and ‘inverse’ procedures. The direct procedure involves Monte Carlo simulations of a set of local density approximation (LDA)-derived pair and multibody interactions $\{\nu_f\}$, generating short-range order (SRO), ground states, order–disorder transition temperatures, and structural energy differences. The inverse procedure involves ‘inverting’ the SRO generated from $\{\nu_f\}$ via inverse-Monte Carlo to obtain a set of pair only interactions $\{\tilde{\nu}_f\}$. The physical properties generated from $\{\tilde{\nu}_f\}$ are then compared with those from $\{\nu_f\}$. We find the following: (i) Inversion of the SRO is possible (even when $\{\nu_f\}$ contains multibody interactions but $\{\tilde{\nu}_f\}$ does not). (ii) Nevertheless, the resulting problem interactions $\{\tilde{\nu}_f\}$ agree with the input

can be produced by drastically different sets $\{\nu_f\}$. Thus, the effective interactions deduced from inverting SRO are not unique. (iv) Inverting SRO always misses configuration-independent (but composition-dependent) energies such as the volume deformation energy $G(x)$; consequently, the ensuing $\{\tilde{\nu}_f\}$ cannot be used to describe formation enthalpies or two-phase regions of the phase diagram, which depend on $G(x)$. ©1997 Elsevier Science Ltd

Keywords: A. disordered systems, D. order–disorder effects, D. thermodynamic properties

The physical properties of $A_{1-x}B_x$ alloys are usually analyzed and interpreted via ‘cluster expansion’ models [1–3]: Each of the N sites of an alloy, $i = 1, \dots, N$, is labeled by a spin variable $\hat{S}_i = -1$ or $+1$ if site i is occupied by an A or B atom, respectively. The set of spin variables $\{\hat{S}_i\}$ defines a configuration. The energy of any of the 2^N possible configurations is then written [4]

$$E(\sigma, V) = J_0(V) + \sum_i J_i(V) \hat{S}_i + \sum_{j < i} J_{ij}(V) \hat{S}_i \hat{S}_j + \sum_{k < j < i} J_{ijk}(V) \hat{S}_i \hat{S}_j \hat{S}_k + \dots, \quad (1)$$

third over all triplets, etc. We refer to these elementary clusters as ‘figures’ f .

If the set of interactions $\{J_f(V)\}$ is known for a given alloy system, one may apply standard methods of lattice statistical mechanics (e.g. mean field, cluster variation or Monte Carlo methods) to the expression and compute ground state structures or finite-temperatures thermody-

tion of temperature-composition phase diagrams and ground state structures of transition metal [1–3] and semiconductor [2] alloys, mixing enthalpies of disordered, partially ordered, and off-stoichiometric alloys [2, 3] and short-range order (SRO) of solid solutions [5, 6]. We refer to this approach as the ‘direct approach’.

Table 1. The values of the input interaction energies ν_f and the interaction energies $\tilde{\nu}_f$ reconstructed via IMC simulations of the SRO computed from ν_f (meV/atom). Designation of the 'figures' f follows the notation of Table IV

atom) $L = 96$, $J = 44.5$, $I = 64.5$, $M = 41.1$, $O = 81.2$ and $K = 120.1$. Structural energy differences and random alloy mixing energy at $x = 1/4$ are shown (meV/atom), as are transition temperatures (K). 'NA' means not

Clusters	Designation	Set 1		Set 2		
		Direct	Inverse	Direct	Inverse	
Empty	J_0	$D_f \nu_f$ -233.2	$D_f \tilde{\nu}_f$ NA	$D_f \nu_f$ -233.2	$D_f \tilde{\nu}_f$ NA	
Point	J_1	252.9	NA	252.9	NA	
Pairs	J_2	152.0	157.2	152.0	690.0	
	K_2	-20.0	-21.0	-20.0	17.6	
	L_2	58.9	60.0	58.9	-19.2	
	M_2	33.5	33.3	33.5	103.2	
	N_2			0.0	-3.6	
	O_2			0.0	-0.4	
	P_2			0.0	13.2	
		$\delta E(L1_2, D0_{22})$	-4.0	-4.8	+103.3	+76.2
		$\delta E_{\text{ord}}(L1_2)$	-42.6	-45.1	-41.9	-79.8
	$G(x = 1/4)$	112.1	NA	112.1	NA	
	$\Delta H_{\text{mix}}(1/4)$	-56.2	-172.1	-227.7	-600.6	

atom-atom pair correlation for the n th atomic shell) is used in an inverse statistical approach (e.g. the inverse Monte Carlo (IMC) method [7] to deduce a set of effective interactions [8]. These interactions are sub-

necessary to deform the constituents from their equilibrium volume to the volume $V(x)$ of σ . The second term of equation (3) describes the spin flip excess energy of forming σ from $A + B$ already prepared at the volume V .

In this paper we explore the extent to which the inverse approach can be applied to a well-characterized $\alpha(n)$ obtained through a direct procedure.

In the following it is convenient to introduce the excess energy $\Delta E(\sigma, V)$ of configuration σ , defined as the energy of this configuration at volume V , relative to the energies $E_A(V)$ and $E_B(V)$ of equivalent amounts of solid A and B .

$$\Delta E(\sigma, V) = E(\sigma, V) - [(1-x)E_A(V_A) + xE_B(V_B)]. \quad (2)$$

If the equilibrium volume $V(\sigma)$ depends primarily on the composition x and only weakly on the configuration σ , then the variables σ and x can be rigorously separated in equation (2) giving [9]

$$\Delta E(\sigma, V) = G(x) + \sum_f D_f \nu_f \bar{\Pi}_f(\sigma). \quad (3)$$

Here, the first term $G(x)$ describes the elastic energy

denoting an average over the D_f symmetry equivalent sites. Equation (1), but here the effective interaction energies $\{\nu_f\}$ are volume-independent pure spin flip energies.

We will examine the invertibility of the inverse approach by performing a 'controlled experiment'. As input, we use two 'exact' sets of interactions $\{\nu_f\}$. Equation (1) is then used along with these 'exact' quantities such as SRO parameters $\alpha(n)$, structural energy differences $\delta E(\sigma, \sigma')$ between configurations σ and σ' , transition temperatures T_c , and the mixing energy of the random alloy ΔH_{mix} . We then contrast the results of this 'direct procedure' with those of the 'inverse procedure', in which the set $\{\alpha(n)\}$ (obtained in the direct procedure from the known, exact $\{\nu_f\}$) is used as input to deduce the interactions $\{\tilde{\nu}_f\}$ by IMC simulations from which we then obtain $\tilde{\alpha}(n)$, $\delta \tilde{E}(\sigma, \sigma')$, \tilde{T}_c and $\Delta \tilde{H}_{\text{mix}}$.

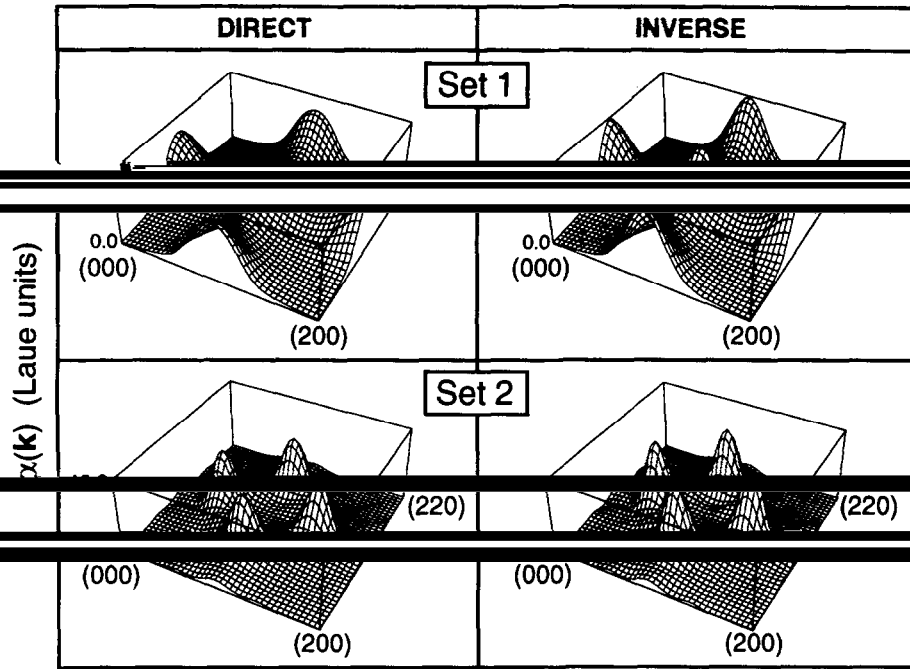


Fig. 1. Comparison of the (001) planes of $\alpha(\mathbf{k})$ and $\tilde{\alpha}(\mathbf{k})$ for A_3B alloys.

We use as input two sets of interaction energies $\{v_f\}$ upon inclusion of multibody interactions. Also, note (Table 1) that all interactions of length M are included in Table 1 that $\alpha(\mathbf{k})$ is a significant fraction of

lations of formation energies of ordered FCC-based both multibody interactions and the elastic energy $\sigma(\mathbf{x})$

many of the measured physical properties. This involves using the directly calculated $\alpha(\mathbf{k})$ and the

tions. Set 1 is identical to Set 2, except that we have set equal to zero all multibody interactions.

pair interactions were retained in the energy expression of IMC. First, configurations were produced which reproduced the input values of 25 shells of $\alpha(\mathbf{n})$

We first contrast the directly calculated alloy proper

MC calculations, a system size of 4096 atoms was used with periodic boundary conditions, 1200 Monte Carlo steps (MCS) were used for equilibration, and averages

for Sets 1 and 2. IMC simulations were performed on three crystals compatible with the sets of $\alpha(\mathbf{n})$, and averages were taken over these three crystals. Tests

$T = 630$ K and 2500 K were used for the SRO calculations of Set 1 and 2. Figure 1 shows the SRO $\alpha(\mathbf{k})$

cedure with respect to the number of pairs included. Most differences of formation energies

difference is dramatic: $\alpha(\mathbf{k})$ of Set 1 shows peaks at the X-points (100) whereas $\alpha(\mathbf{k})$ of Set 2 shows peaks at the W-points $(1\frac{1}{2}0)$ as seen experimentally in Ni_3V [10].

Short-Range Order

Figure 1 compares the recalculated $\tilde{\alpha}(\mathbf{k})$ (computed from $\tilde{\alpha}$) and $\alpha(\mathbf{k})$ (computed from α). Both sets of SRO

these two structures, $\alpha(\mathbf{k})$ changes from -7 to $+103$ meV/atom and T_c changes from 630 to 1850 K

shown previously by many authors (see e.g. [13, 14]). However, in these previous studies, measured SRO was

used as input to the IMC, and thus the interactions which produced the input SRO were not known. We have shown that even when multibody interactions are used to produce $\alpha(x)$ (as in Set 2), the IMC procedure (using pair interactions)

We compare the values of ν_f vs $\bar{\nu}_f$ in Table 1. For Set 1, the IMC algorithm closely reproduces the input set of pair interactions; the standard deviation between $\{\nu_f\}$

and inverse sets of interactions differ dramatically in several respects:

IMC calculation of $\{\nu_f\}$.

(ii) There are huge differences in pair interactions (the standard deviation of the first four pairs is 275 meV/atom).

(iii) Seven pair interactions were required in the IMC to reproduce $\alpha(n)$, whereas only four pair interactions

was reported in [12].)

However, even though there are enormous differences between ν_f and $\bar{\nu}_f$ of Set 2, they both produce nearly identical SRO patterns (see Fig. 1). This surprising

uniqueness was also found by Schweika and Carlsson [12], (Fig. 3a), who in contrast to the present work, used a high-temperature expansion (whereas we use IMC) to invert SRO generated by pair and multibody interactions.] We assert that due to the non-uniqueness of pair

compared with other sets of pair interactions, when multibody interactions are physically important, the non-uniqueness of these sets make such comparisons meaningless. For example, Schweika and Carlsson [12]

which were temperature-dependent even though the

dependence is not due to physical effects (e.g. vibrational or

that a pair-only inverse scheme does not recover information on the multibody interactions $\{\nu_f\}$.

Structural energies, ground states, and transition

those computed from $\{\nu_f\}$ in Table 1.

Mixing Energies

Table 1 also shows values of the mixing enthalpy of the random alloy $\Delta H_{\text{mix}}(x = 1/4)$. For Set 1, where $\{\bar{\nu}_f\} = \{\nu_f\}$, the direct and inverse values of ΔH_{mix}

differ because of the absence of $G(x)$ in the inverse procedure. This absence leads to an error of more than 100 meV/atom, even in cases (such as Set 1) dominated by pair interactions. In Set 2, the comparison of ΔH_{mix} is

Deducing values of ΔH_{mix} is clearly not reliable in the inverse procedure.

quantities (e.g. SRO) other than $E(\sigma, V)$ may lead to a loss of information. We now use equation (3) to distinguish different classes of alloy generation and diagram

(a) Physical properties that depend on both $G(x)$ and on the spin-flip energies $\{\nu_f\}$ include any quantity which involves the energetics of two or more concentrations and, hence, two or more volumes. [Note that $G(x)$ depends on x , but not on the particular atomic arrangement ('configuration').] Examples include the formation energy of a structure [which involves ν_f , ν_A and ν_B , see equation (2)], the mixing energy ΔH_{mix} of the random

perature phase diagram. Since 'type-(a)' properties such as the set $\{\Delta E(\sigma, V)\}$ contain complete information on both $G(x)$ and on all $\{\nu_f\}$, given the measured $\alpha(x)$ in the

equation (3) and in principle extract the 'exact' $G(x)$ and $\{\nu_f\}$, as demonstrated in [9]. Thus, the inversion of 'type-(a)' properties involves no loss of information.

(b) Physical properties that do not depend on $G(x)$ include energy differences of isocompositional configurations σ and σ' , $\Delta E(\sigma, \sigma')$. The order-disorder transition

temperature T_c at stoichiometric composition also falls into this class since it involves the energy difference

partially ordered low-temperature phase, both at the

depend on $G(x)$ is the atomic SRO. $\alpha(n)$ involves a competition between energies of a random and a short

range ordered structure, both at the same volume $V(x)$; therefore, $\alpha(x)$ (even if determined for several compositions)

contains no information about $G(x)$. Therefore, inversion of a 'type-(b)' property, such as SRO, cannot provide any information on $G(x)$, even if the SRO covers

calculation of 'type-(a)' properties, such as formation energies [equation (2)], mixing energies, or the phase-coexistence regions of the phase diagram. This point is highlighted by recent studies [5] on $\text{Ni}_{1-x}\text{Au}_x$. This is a phase-separating system; however, the SRO is of

ordering type. Inverting the SRO will thus inevitably produce ordering-type $\{\bar{\nu}_f\}$, which are useless for predicting the miscibility gap phase diagram of the correct AM_2 ($\nu_f > 0$). These conflicts are resolved [5] by using $G(x)$

We conclude that:

(i) The IMC algorithm provides a set of pair interactions which accurately reproduces the input SRO whether or not multibody interactions are used to generate the SRO.

of structural energy differences, ordering energies, and

(ii) However, when multibody interactions are physically important, even the pair interactions are incorrectly determined by the inversion of SRO. The structural

can thus contain substantial errors.

(iii) Finding a set of interactions which reproduces a given set of SRO is found to be a non-unique process: dramatically different sets of interactions (one set with pairs only, one set with pairs and multibodies) may still

interactions may be unwarranted. However, comparing a theoretical SRO pattern to a measured one is a sound procedure.

(iv) Inverting the SRO always removes information on energy terms that are SRO-independent, e.g. $G(x)$.

Office of Energy Research (OER) [Division of Materials Science of the Office of Basic Energy Sciences (BES)], U.S. Department of Energy, Washington, D.C. 20545-0001, AC36-83CH10093.

REFERENCES

1. Ducastelle, F. *Order and Phase Stability in Alloys*, Elsevier, New York, 1991.
2. Zunger, A., in *Statics and Dynamics of Alloy Phase Transformations* (Edited by T. E. A. Pechen and A. Zunger), Springer-Verlag, New York, 1987, p. 1.
3. de Fontaine, D., *Solid State Phys.*, **47**, 1994, 33. *Physica*, **112b**, 1984, 557.
5. Lu, Z.-W. and Zunger, A., *Phys. Rev.*, **B50**, 1994, 6626.
6. Wulfer, G., *Acta Metall.*, **37**, 1989, 250.
7. Golov, V. and Kern, J., *Acta Metall.*, **35**, 1987, 393.
8. Schweika, W. and Haubold, H.-G. *Phys. Rev.*, **B37**, 1988, 9240; Reinhard, L., Schönfeld, B., Kostorz, G. and Bühner, W., *Phys. Rev.*, **B44**, 1990, 1727; Reinhard, L., Robertson, I. I., Moss
9. Ferreira, L.G., Mbaye, A.A. and Zunger, A., *Phys. Rev.*, **B37**, 1988, 10547.
10. Caudron, R., Sarfati, M., Barrachin, M., Finel, A., Ducastelle, F. and Solal, F., *J. Phys. I. France*, **2**, 1992, 1145.
11. Smith, J.E. in *Phase Diagrams of Binary Alloys*, ASM International, 1992, 1145.

Acknowledgements—This work was supported by the