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INVERTIBLE AND NON-INVERTIBLE ALLOY ISING PROBLEMS

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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 $\{\nu_j\}$ 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 [redacted] 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 $G(x)$.

Keywords: A. disordered systems, D. order–disorder effects, D. thermo- [redacted]

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, $i = 1,\ldots,N$, 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 [redacted] any of the 2^N possible configurations is then written [4] [redacted]

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

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 [redacted] ground state structures or finite-temperatures thermody- [redacted] 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'.

[redacted]

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 [redacted]

		Set 1		Set 2	
		Direct	Inverse	Direct	Inverse
Clusters	Designation	$D_f\nu_f$	$D_f\tilde{\nu}_f$	$D_f\nu_f$	$D_f\tilde{\nu}_f$
Empty	J_0	−233.2	NA	−233.2	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
	$\delta E_{\rm ord}(L1_2)$	−42.6	−45.1	−41.9	−79.8
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
	$G(x = 1/4)$	112.1	NA	112.1	NA
	$\Delta H_{\rm mix}(1/4)$	−56.2	−172.1	−227.7	−600.6

atom–atom pair correlation for the nth atomic shell) is used in an inverse statistical approach (e.g. the inverse Monte Carlo (IMC) method [7] to deduce a set of [redacted]

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 [redacted]

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

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 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 [redacted]

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 $\{\nu_f\}$. [redacted]

'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 $\Delta H_{\rm mix}$. 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 simula- [redacted] $\Delta\tilde{H}_{\rm mix}$.

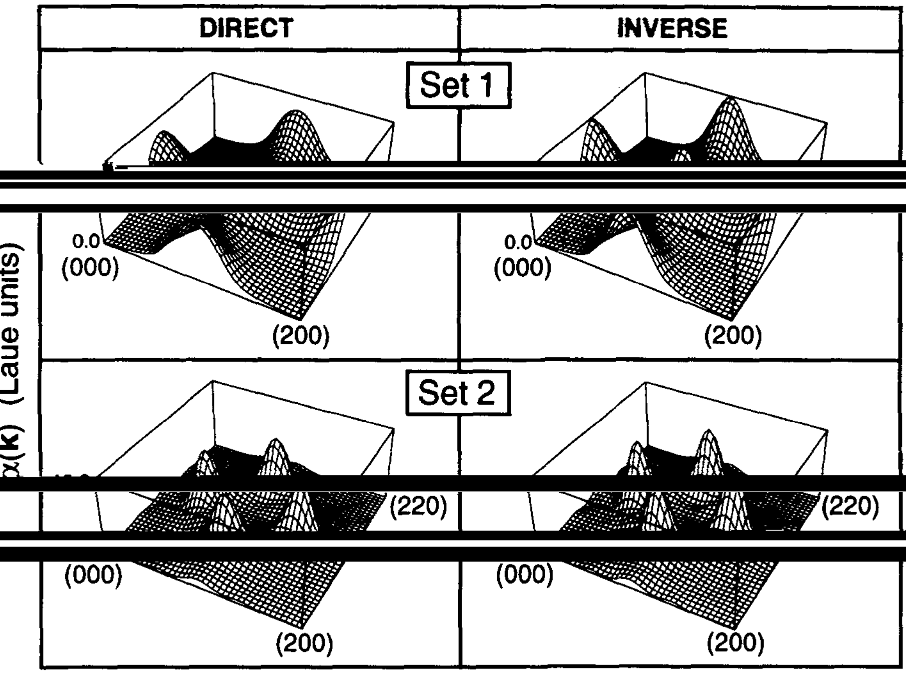

Fig. 1. Comparison of the (0 0 1) planes of $\alpha(\mathbf{k})$ and $\tilde{\alpha}(\mathbf{k})$ for A_3B alloys.

We use as input two sets of interaction energies $\{v_f\}$ [illegible] lations of formation energies of ordered f.c.c.-based [illegible] many of the measured physical properties. This realistic [illegible] tions. Set 1 is identical to Set 2, except that we have set equal to zero all multibody interactions.

We first contrast the directly calculated alloy proper- [illegible] 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 [illegible] $T = 850$ K and 2500 K were used for the SRO calcula- [illegible] difference is dramatic: $\alpha(\mathbf{k})$ of Set 1 shows peaks at the X-points $\langle 1\,0\,0 \rangle$ whereas $\alpha(\mathbf{k})$ of Set 2 shows peaks at the W-points $\langle 1\tfrac{1}{2}0 \rangle$ as seen experimentally in Ni_3V [10]. [illegible] these two structures, $\delta E(L1_2, D0_{22})$, changes from −4 to +103 meV/atom and T_c changes from 630 to 1850 K

upon inclusion of multibody interactions. Also, note [illegible] both multibody interactions and the elastic energy $G(x)$ [illegible] pair interactions were retained in the energy expression of IMC. First, configurations were produced which reproduced the input values of 35 shells of $\alpha(n)$ [illegible] for Sets 1 and 2. IMC simulations were performed on three crystals compatible with the sets of $\alpha(n)$, and averages were taken over these three crystals. Tests [illegible] cedure with respect to the number of pairs included. [illegible]

Short-Range Order

Figure 1 compares the recalculated $\tilde{\alpha}(\mathbf{k})$ (computed [illegible] However, in these previous studies, measured SRO was

[redacted]

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 [redacted]

We compare the values of ν_f vs $\tilde{\nu}_f$ in Table 1. For Set 1, the IMC algorithm closely reproduces the input set of [redacted] and inverse sets of interactions differ dramatically in several respects:

[redacted] 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 [redacted] was reported in [12].)

[redacted] ences between ν_f and $\tilde{\nu}_f$ of Set 2, they both produce nearly identical SRO patterns (see Fig. 1). This surprising [redacted] 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 [redacted] meaningless. For example, Schweika and Carlsson [12] [redacted] which were temperature-dependent even though the [redacted] dence is not due to physical effects (e.g. vibrational or [redacted] that a pair-only inverse scheme does not recover information on the multibody interactions $\{\nu_f\}$.

Structural energies, ground states, and transition [redacted]

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 [redacted]

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

[redacted] quantities (e.g. SRO) other than $E(\sigma, V)$ may lead to a loss of information. We now use equation (3) to distin- [redacted]

(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 arrange- [redacted] perature phase diagram. Since 'type-(a)' properties such as the set $\{\Delta E(\sigma, V)\}$ contain complete information on [redacted] 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 config- [redacted] into this class since it involves the energy difference [redacted] partially ordered low-temperature phase, both at the [redacted] depend on $G(x)$ is the atomic SRO. $\alpha(n)$ involves a [redacted] range ordered structure, both at the same volume $V(x)$; [redacted] tions) 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 [redacted] 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 [redacted] ordering type. Inverting the SRO will thus inevitably produce ordering-type $\{\tilde{\nu}_f\}$, which are useless for pre- [redacted]

We conclude that:

(i) The IMC algorithm provides a set of pair interactions which accurately reproduces the input SRO [redacted]

(ii) However, when multibody interactions are physically important, even the pair interactions are incor- [redacted]

(iii) Finding a set of interactions which reproduces a [redacted] dramatically different sets of interactions (one set with pairs only, one set with pairs and multibodies) may still [redacted] 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 [redacted]

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