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A NOVEL VIEWPOINT ON THE Cu-Au PHASE DIAGRAM:

THE INTERPLAY BETWEEN FIXED ISING ENERGIES

AND ELASTIC EFFECTS

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Abstract--Theoretical models of temperature-composition phase diagrams of binary A-B systems
have traditionally been based on various approximate solutions to the same broad class generalized Ising model. Common t

interaction energies between sites, pairs or multi-atom clusters of A and B by some fixed (volume-
independent) parameters. Despite extensive attempts to improve on the method of solution to the statistical
problem (quasi chemical approach, cluster variation method i.e. CVM, high-temperature expansions,
Monte Carlo), or to increase the range of the interaction to further neighbors, numerous qualitative
discrepancies with real phase diagrams (briefly reviewed here) remain. We show that the source of the
difficulty is not in the satistical method or range of interaction, but rather in the physical content of the interaction energies used. Recognizing that all successful classical packing models of solids require a description of the competition between fixed-volume "chemical" energies (representable as fixed Ising interaction parameters) and size-mismatch "elastic" energies (not representable by fixed energies), we include both on the same footings in a generalized lsing-like approach. Calculating both terms from first-principles self-consistent band theory we show through CVM calculations on the prototype Cu-Au phase diagram how many of the deficienciesof the "chemical-only" Ising models can be cured. This reveals
the dominant role of lattice relaxation in determining many of the thermodynamic properties and the
phase diagram.

R~nm~---Les modules th~oriques des diagrammes de phases temp6rature-composition pour les syst~mes
binalres A-B ont ~t~ bas~s traditionnellement sur diverses solutions approch~es appartenant ~i la m~me
et vaste classe d'hamiltoniens physiques, ie module d'Ising g6n~ralis~. Le point commun /t toutes ces
approches est il demeure de nombreux d~saccords qualitatifs deux types d'~nergie darts uric approche g~n~ralis6~ qui r

calculant les deux termes ~. partir d'une th~orie des bandes auto-coh~rente bas~e sur les premiers principes,
nous montrons~i l'aide de calculs r6alis~s par la m6thode de la variation des amas, dans le cas du
diagramme de phases module Cu-Atr---comment l'on peut rem~dier aux d~fauts des modules d'Ising qui
ne sont bas~s que sur raspect chimique. Ceci r6v~le le r61e dominant de la relaxation du r~seau pour
d~terminer de nombreuses propri~t~s thermodynamiques ainsi que le diagramme de phases.

Zusammenfassung~Theoretische Modelle yon Phasendiagrammen (Zusammensetzung/Temperatur) bin/irer A-B-Systeme werden traditionell aufgebaut auf verschiedenen N/iherungsl6sungen derselben breiten Klasse yon Hamilton-Gleichungen----dem verallgemeinerten lsingmodell. Alle diese N~iherungen haben die Beschreibung der Wechseiwirkungsenergien zwischen Gitterpl~itzen, Paaren oder Multiatom-clustern yon A- und B-Atomen durch einige feste (volumunabhfingige) Parameter gemeinsam. Trotz ausfiihrlicher Versuche, die L6sungsmethode des statistischen Problems (quasichemische N~iherung, Clustervariationsmethode, Hochtemperaturen~iherungen, Monte-Carlo) zu verbessern oder den Bereich der Wechselwirkung zu weiteren Nachbarn zu vergr6Bern, bleiben doch viele qualitative Diskrepanzen zu den (hier kurz dargesteliten) realen Phasendiagrammen. Wir zeigen, dab die Ursache der Schwierigkeit nicht in der statistiscben Methode oder im Bereich der Wechselwirkung liegt, sondern vielmehr in der physikalischen Bedeutung der benutzten Wechselwirkungsenergien. Aus der

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I. INTRODUCTION: THE ISING APPRO90m<3 BT 3 Tr 1 0 0 1 57.60 367.92 Tm 1 1 1 rg /F0 8.64 Tf 0.28 Tc 0 Tw 100 Tz (where)

tetrah=¼E,,[A,24 _.] _n1 1 r216.56 0 TD 1 1 1 rgm 1 1 1 rg~he

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configurations of the crystal that can be constructed from packing a given "cluster" of sites. The size of the cluster and hence the number of possible modes of occupancy of its sites define a "topological count-ing range", not to be confused with the "interaction range" within which h atoms are physically coupled through a potential Jh. (Often, but not always, the "topological counting range" is set to be equal to the "interaction range".) Different approximations to the evaluation of the entropy are distinguished by using different topological counting ranges and by the various ways in which one attempts to correct for conflicting occupancies of two or more adjoining clusters (e.g. a configuration in which some sites occur simultaneously in a A-A and a B-B pair is conflicting). Since inclusion of conflicting con-figurations spuriously stabilizes ordered phases over disordered phases, it overestimates the critical order-disorder temperature To.
Various applications of the generalized lsing model to calculate the phase diagram of the classical test case--the all-f.c.c. Cu-Au system--are hence dis-tinguished by the choice of (i) the physical interaction range (i.e. the numer of Js) retained (First nearest neighbors, second nearest neighbors, retention in the first nearest neighbor model of single sites; pairs, etc.), (ii) the topological counting range (pair, tetra-hedron, tetrahedron-octahedron, etc.) and (iii) the algorithm used to calculate the entropy (or cor-relation functions) within a prescribed topological counting range (MC, CVM, etc.).
Early application by Shockley [6] of the Bragg-Wiiliams technique [7] (points only for both topological and interaction ranges) to the Cu-Au system revealed a phase diagram which fails to separate the distinct Cu3Au ~ Cuo.TsAuo.25 and the CuAu 3 ~ Cu0.zsAu0.75 order-disorder transitions from that of CuAu ~ Cu05Au0.5, described the latter erroneously as a second order transition, and in the case of ferromagnetic interactions the phase separation critical temperature was kTJIZI 2 = 1.0. This approach produced a symmetry of the phase diagram about x = 0.5, unlike the data. Bethe's [8] use of a site-only interaction range but including pairs in the topological counting range and an improved counting algorithm (equivalent to the

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by considering the special state of order a where
all of the N a tetrahedra have the same occupation
number n, hence ~,,,(n) of equation (7) is just 6.,..
This corresponds to an ordered crystal (e.g. Ll0.
or L12) whose repeat unit is a given (fixed)
tetrahedron A~_,,B,,. The volume-dependent energy E.[A,,B~ .... V] is then simply the (T = 0) equation of state of this solid, and the value of AE(n, V) of equation (11) at the equilibrium volume V. [which minimizes E,,(V)] is the formation enthalpy of this ordered phase from its constituent elemental solids, i.e.

AH (") - AE(n, V.) (12a)

or,

AH ''~ = E'"'[A,B,_,] - nE[A] - (4 - n)E[B]. (12b)

Clearly, from equations (11) and (12)

AE(n. V) = AH ¢"J + F(V - V.) (13)

where F is a general (harmonic or anharmonic) positive function.
The physical content of equation (13) can be further appreciated by considering the formation of an ordered structure AM_,nB m with N A A atoms and N B B atoms (N = N A+ N a in total) from the con-stituent solids in two formal steps. First, compress or dilate the pure crystals A M_,.A,. from its equilibrium volume ~ to the volume V akin to the final structure
(A~ .... B,,,): do the same for pure BM_,,B,,, changing
its volume from I"~ to V. Clearly, since in both cases deformation of equilibrium structures is involved, this
step requires the investment of some elastic energy

NA

AF[N A, 93 Tz (AF[f 421.44 Tm 1 some) Tj 24_32 0 9.84 0 TD 1 1 1

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sizes in solids [23-28]--was largely neglected in phase diagram calculations. In what follows, we describe the shortcomings of such traditional nearest-neighbor Ising

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introducing an ad hoc composition dependence into
the Es. our fundamental objection remains that such
approaches have but a limited informational con-
tent in terms of the ph.vsical insights being gained. In
particular, such approaches do not provide a link
between the electronic structure of the constituents on one hand and the phase stability and phase interconventions which these constituents exhibit when mixed, on the other hand.
We next describe how treating "'chemical" (~) and "'elastic Tc 0 Ttoi o. Ttoi ot

3. TREATING CHEMICAL AND ELASTIC ENERGIES ON THE SAME FOOTINGS

We represent the Cu-Au system at all states of order a as a mixture of five basic tetrahedral clusters Cu4_,,Au,, with energy functions AE(n, V). To treat "chemical" and "'elastic" interactions on the same footing, and, at the same time establish a link be-tween the phase diagram and the electronic structure we identify these AE(n, V) with the excess energy of ordered periodic structures Cu4_,Au, (the f.c.c. ground state phases [1-4]). While these basic inter-action energies could be modelled by various semi-classical approaches [23-27] of the size-mismatch factor, the electrochemical, or the "electronic" factor, we propose at the first stage to compute AE(n, V) self-consistently from first-principles band theory for the corresponding crystals. We use the f.c.c, struc-tures for Cu and Au, the L10 structure for CuAul, and the LI., structure for both Cu3Au and CuAu3. For each phase we hence calculate, using the local density formalism [34] as implemented in the general-potential linear augmented plane wave method [35] (LAPW) the five functions AE(n, V) for a full range of volumes V. Such self-consistent solutions to the band structure and total energy naturally incorporate both "'chemical" and "'elastic" effects (on the same footing) in a first-principles manner. The resulting excess energy curves for the ordered structures are depicted in Fig, t: the values at the minima give the

0.5

- °oi I~ 0.3

~ 0.1

uJ <w -0.1 n ¢
(Cu) n- 1 n:2 n=3
-0.2
-0.3
3.5 316 317 318 319 410 411 4.2

Lattice Parameter (~,)
Fig. 1. Calculated excess energies AE(n, V) [equation (11)] for periodic Cu 4_"AuÈ solids (f.c.c. for n = 0 and 4; LI 0 for n = 2: Lh for n = 1, and 3). Arrows point to the equilibrium lattice parameters.

equilibrium volumes V, and formation enthalpies AH q"'. Note that AH 4"~ are negative (-0.83, -1.45 and -0.61 kcal/g-atom for n = 1. 2 and 3. respect-ively), differ considerably from the ~'") values which fit the phase diagram in an ~-only approach [21.32] (- 3.99. - 5.27 and - 3.64 kcal, g-atom, respectively). and that AE(n, I') show pronounced volume de-pendences. Nevertheless. the calculated equilibrium properties deviate somewhat from the measured results (e,g. the measured AH ~n' values arc [17.36]
- 1.71, -2.10 and ~-l.4kcalg-atom. and the calculated equilibrium volumes deviate by ~ I% from experiment [36]). We return to this point in Section 3.2. The calculated AE(n. V) were fitted for convenience of use to a Murnaghan equation of state [37]. We use these {AE(n, V) I as input to solve the

Phase Diagrams of the
CUl..xAu x System
1800 (a)

1600 ~ Using first-principles
calculations on
1500 ~ ordered structures

1400

1300 ~-~,,,Au

120(]"

1100 ~ 0 \CuAu lOOOoo
800 ~ + D
700

A 600
:g 500 • •

-= (b) Cu3Au Models 1
1000 I'l /~-,,~ CuAu Using asptl. L.T,

I data on ordered

900 structures

I- 800 • ~C~Au3

700
600

500
4O0

1000 (C) Modal C:
I Using L.T, axptl, data
900 I and sublettlCl
/3 = y : [relaxation

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can be reduced if the equilibrium molar volumes I,,
of each cluster will relax (differently for each com-
position x) to better accommodate the volume
mismatch. Hence, the variation of the equilibrium
volumes of the Cu4_,,Au° clusters in the alloy

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3.76 (a) Phase Transition
Disordered

3.76

3.74 i I J i J I h I 850 860 670 680 690 700 710 720 730

3.88 (b)
Disordered

~: 3.87
Cu Au

3,86 I i h t t I I I

690 700 710 720 730 740 780 760 770 I,c, 3"99 m D
cuAu3
3.98 i i ~ I i
470

730

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19. K. Binder. Phys. Rer. Lett. 45, 811 (19801: U. Gahn.
J. Phys. Chem. Solids 47, 1153 (1986): A. Finel and
F. Ducastelle, Europhys.