NASA Technical Memorandum 105304

Lattice Parameters of fcc Binary Alloys Using a New Semiempirical Method

Guillermo Bozzolo
Analex Corporation
Brook Park, Ohio

and

John Ferrante
Lewis Research Center
Cleveland, Ohio

January 1992

NASA

LATTICE PARAMETERS OF fcc BINARY ALLOYS USING A NEW SEMIEMPIRICAL METHOD

Guillermo Bozzolo[1,2] and John Ferrante[2]
(1) Analex Corporation, 3001 Aerospace Parkway, Brook Park, OH 44142-1003
(2) National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135

There has been substantial success in predicting the heats of formation of binary alloys both with ab-initio and semiempirical methods (1-8). There is still a good deal of progress to be made, however, in that experimental trends in the cohesive energies, heats of formation and lattice parameters as a function of composition are often not accurately reproduced.

Recently, a new method for the computation of alloy formation and defect energies was introduced by Bozzolo, Ferrante and Smith (BFS) (7). We tested the method ability to predict the heat of formation as a function of alloy composition for disordered binary alloys. In this paper we present a further property of interest, the variation of the lattice parameter with composition. At present, Vegard's law (9), which is a simple compositional linear average, is the primary method of choice. However, it is well known that the lattice parameter variation often deviates from linearity (10). In this paper we present the predictions of the BFS method for the lattice parameter. A second goal of this paper is to provide a simple formulation of the algorithm for performing defect calculations. We will see that accurate prediction of the composition dependence of lattice parameters can be made with our simple method.

BFS (7) requires information only about pure metal properties and certain experimentally determined alloys properties. We build on the formulation of equivalent crystal theory (ECT) (11-12), by dividing the total binding energy of the alloy into a chemical energy and a strain or structural energy (see, e.g., Refs. 2-4). We now outline the procedure for calculation of the heat of formation and lattice parameter versus concentration for fcc binary alloys. We first apply the method to ordered alloy structures and then use the Connolly-Williams (CWM) (13) procedure for relating the ordered compounds to the disordered ones.

Consider a unit cell containing N_X atoms of atomic species X, (X = A,B,...), so that the total number of atoms in this cell is given by $N = \Sigma_X N_X$. The heat of formation of this cell is

$$\Delta E_{cell} = E_{cell} - \sum_X N_X E_X \tag{1}$$

where E_{cell} is the total energy of the cell and E_X is the energy of an atom of species X in a pure crystal of its own species. IF $E'(i,X)$ denotes the energy of the i^{th} atom in the cell ($i = 1,...,N_X$) of species X then

$$\Delta E_{cell} = \sum_X \sum_{i=1}^{N_X} E'(i,X) - E_X = \sum_X \sum_{i=1}^{N_X} e_{i,X}. \tag{2}$$

In our simulation of the process of alloy formation, each individual atom undergoes two separate transformations with respect to its initial state given by a perfect, pure crystal of its own species. Each transformation contributes to the heat of formation of the alloy.

The first process (strain energy) deals with the structural change arising from neighbor locations in the alloy being different from in the elemental single-crystal environment. In order to compute the strain energy of the i-th atom of species X, $e^S_{i,X}$, we just 'flip' every atom in the actual alloy structure, surrounding atom (i,X), into an atom of the same species X, and perform a regular ECT calculation (see Ref. 12 for details). Then,

$$e^S_{i,X} = E^X_C\left[1-\left(1 + a^{S*}_{i,X}\right)e^{-a^{S*}_{i,X}}\right], \quad a^{S*}_{i,X} = \left(a^S_{i,X} - a^X_e\right)/l_X. \tag{3}$$

where a_e^X denotes the equilibrium lattice constant of a pure X crystal, E_C^X is the cohesive energy and l_X is a scaling length (12). The equivalent lattice parameter $a_{i,X}^S$ is determined by solving the appropriate ECT equation applied to atom (i,X), in the defect (but pure) crystal (12). For the simple case considered in this work, $a_{i,X}^S$ is just the actual alloy lattice parameter. The second process deals with the change in chemical composition. The chemical energy contribution to the heat of formation from atom (i,X), $e_{i,X}^C$, is the energy change due to some neighbors of atom (i,X) being of a different atomic species. Here, we 'freeze' the neighbor locations to be those corresponding to a pure X crystal allowing only for a change of identity of the neighboring atoms. Rigourously, this change in chemical composition cannot be considered a 'defect' in the context of ECT. However, to a good approximation, the underlying concepts of ECT should remain valid in the case of alloys, and we will adopt a similar formulation to describe the perturbation due to the dissimilar atomic species. We assume that the global property parameterized by the ECT parameter α (12) (i.e., the tails of the overlapping electron densities) can be separated into pairs of interacting atoms. In this approximation, the electron density in the region between two atoms of the *same* species would be unaffected by the presence of neighboring atoms of a different species so that the perturbation would be localized in the region between two *dissimilar* atoms. This assumption enables us to define the parameter α_{XY} as $\alpha_{XY} = \alpha_X + \Delta_{YX}$, where α_X is the α value for the pure metal X and Δ_{YX} is a correction introduced by the presence of a neighbor of species Y. The parameters Δ_{YX} and Δ_{XY} are the only new parameters introduced in our method, and they will be determined by fitting to appropriate experimental data.

With the introduction of the parameters Δ_{YX} and Δ_{XY} we can compute the chemical energy of atom (i,X) using ECT. The chemical energy $e_{i,X}^C$ is obtained by performing two similar ECT calculations:

$$e_{i,X}^C = e_{i,X}^C(\Delta_{Y,X}) - e_{i,X}^C(0). \tag{4}$$

For the first term, as explained above, the chemical composition is included in the appropriate value of $\Delta_{Y,X}$

$$e_{i,X}^C(\Delta_{Y,X}) = \gamma_{i,X} E_C^X \left[1 - \left(1 + a_{i,X}^{C*}\right) e^{-a_{i,X}^{C*}}\right], \quad a_{i,X}^{C*} = \left(a_{i,X}^C - a_e^X\right)/l_X \tag{5}$$

with $\gamma_{i,X} = 1$ if $a_{i,X}^{C*} > 0$ and $\gamma_{i,X} = -1$ otherwise. The equivalent lattice parameter $a_{i,X}^C$ is obtained by solving the following ECT equation (12)

$$\begin{aligned} &N R_1^{p_x} e^{-\alpha_X R_1} + M R_2^{p_x} e^{-\left(\alpha_X + \frac{1}{\lambda_X}\right) R_2} \\ &= \sum_Y N_{YX} r_1^{p_x} e^{-\alpha_{YX} r_1} + M_{YX} r_2^{p_x} e^{-\left(\alpha_{YX} + \frac{1}{\lambda_X}\right) r2} \end{aligned} \tag{6}$$

where N (M) is the number of nearest-(next-nearest)-neighbors in a perfect crystal of species X,$R_1(R_2)$ is the nearest-(next-nearest)-neighbor distance in the equivalent crystal of lattice parameter $a_{i,X}^C$. The sum on the r.h.s. of Eq. (6) is over the atomic species Y of the N_{YX} (M_{YX}) nearest-(next-nearest)-neighbors of atom (i,X) located at a distance $r_1(r_2)$. The second term in Eq. (4), $e_{i,X}^C(0)$ involves a calculation similar to Eqs. (5-6) but with $\Delta_{YX} = 0$. This is done in order to free the chemical energy from any structural defect (e.g., a surface) thus retaining only the contribution of the chemical composition of the surroundings of atom (i,X).

Finally, the contribution $e_{i,X}$ of atom (i,X) to the heat of formation (Eq. (2)) is

$$e_{i,X} = e^{S}_{i,X} + g_{i,X} e^{C}_{i,X} \tag{7}$$

where the coupling factor between the strain and chemical energy contributions, $g_{i,X} = e^{-a^{s*}_{i,X}}$ ensures that the chemical energy vanishes at large interatomic distances.

In this work, we are concerned with the fcc-based disordered binary alloys A_xB_{1-x}, which, in keeping with CWM, we will compute from the corresponding ordered structures A_mB_{4-m}(m = 0(B,fcc); 1(AB_3,$L1_2$); 2(AB,$L1_0$); 3(A_3B,$L1_2$); 4(A,fcc)). If no relaxation of the individual atomic sites is allowed, then the strain energy, e^s_x, is given by Eq. 3 with $a^s_x = r$, where r is the actual interatomic distance. Within this approximation, the second term in the chemical energy (Eq. (4)) vanishes, since there are no structural defects. For a given ordered structure m, the ECT equation for the equivalent lattice parameter $a^C_{i,X}$ (Eq. (5)) is obtained from Eq.(6) with M=12, M=6, $R_1 = \frac{\sqrt{2}}{2} R_2$; $R_2 = a^C_X$; $r_1 = \frac{\sqrt{2}}{2} r_2$ and $r_2 = a^X_e$. The parameters p_X, α_X, and λ_X are listed in Ref. 12 and the coefficients N_{XX}, N_{XY}, M_{XX}, and M_{XY} are obtained from the number of nearest and next-nearest neighbors of each species for all the possible structures A_mB_{4-m}. The excess energy, $\Delta E_m(r)$, as a function of the lattice parameter r is easily computed with Eq. (2) and, following Connolly-Williams approach (13), the heat of formation is obtained from

$$\Delta E_D(r,x) = \sum_m \binom{4}{m} x^m (1-x)^{4-m} \Delta E_m(r) \tag{8}$$

by finding, for each concentration x, the value of r that minimizes $\Delta E_D(r,x)$. For different alloys A - B, the parameters Δ_{AB} and Δ_{BA} were determined by reproducing the experimental heats of solution E_{BA} and E_{AB}. In Table I, we list the parameters Δ_{ij} for some binary alloys of Ag, Ni, Cu, Au, Pd, Pt, and Al,

Table I. Experimental values of the heats of solution E_{AB} and E_{BA} used to determine the parameters Δ_{AB} and Δ_{BA} for some binary alloys of Al, Cu, Ni, Ag, Au, Pd, and Pt.

A	B	E_{AB}	E_{BA}	Δ_{AB}	Δ_{BA}	A	B	E_{AB}	E_{BA}	Δ_{AB}	Δ_{BA}
Ni	Pd	-0.088	0.057	-0.0401	-0.04665	Ag	Pd	-0.108	-0.289	-0.0431	-0.02033
Cu	Ni	0.09	0.03	-0.0131	0.02395	Cu	Pt	-0.299	-0.532	-0.0568	-0.0444
Cu	Pd	-0.392	-0.436	-0.04205	-0.04795	Ag	Au	-0.16	-0.19	-0.0313	-0.0219
Au	Pd	-0.195	-0.355	-0.0439	-0.0348	Cu	Ag	0.25	0.39	-0.0321	-0.0394
Ni	Pt	-0.330	-0.282	-0.0603	-0.0529	Cu	Au	-0.126	-0.19	-0.0588	-0.05095
Cu	Al	-0.20	-0.35	-0.0626	-0.0526	Ni	Au	0.22	0.28	-0.0614	-0.0512

as well as the experimental heats of solution used in this work. The experimental heats of solution are estimated from the experimental heats of formation curves in Ref. 14. A complete list of the parameters needed to calculate defect energies once the geometry and composition are known, and can be found in Ref. 12. In order to apply the method for a specific defect, e.g., a surface, one needs only know the position of each atom and the nature of their neighbors (i.e., A or B).

In Fig. 1 we show results for Ni-Cu, Cu-Pd, Ni-Pd chosen because of the different behavior exhibited by each one of these compounds. We display the heat of formation, compared to experiment (14), and the lattice parameter obtained with our approach. Figure 2 shows our predictions for the lattice parameter of other binary systems. We also compare these results with experiment (10) and Vegard's law (9). Note that our method is able to reproduce the particular features of the Ag-Au system, where, for a certain range of concentrations, the lattice parameter shows a contraction from the equilibrium lattice parameter of the pure components (10). We reproduce this exceptional behavior rather accurately, which is surprising since we are dealing with differences of hundredths of angstroms. In all cases, the agreement with experiment is excellent. In Figs. 1(a) and 1(b) we also present a comparison with an appropriate version of the embedded atom method (EAM) (4,16), Miedema's empirical approach (15) and experiment (14), for Ni-Pd. There is another EAM calculation of Ni-Pd (5). However, the parameterization used there is different from the original EAM formulation for alloys (8).

In conclusion, we have developed a new semiempirical procedure for the concentration dependence of the heats of formation and lattice parameters of binary alloys consistent with ECT. This method accurately predicts the experimental behavior qualitatively and quantitatively.

Acknowledgments

Helpful discussions with Dr. Herbert Schlosser and Dr. John R. Smith are gratefully acknowledged. This work was partially supported by the Engineering Directorate, NASA Lewis Research Center.

References

1. S.-H. Wei, A.A. Mbaye, L.G. Ferreira, and A. Zunger, Phys. Rev. B36, 4163 (1987).
2. K. Terakura, T. Oguchi, T. Mohri, and K. Watanabe, Phys. Rev. B35. 2169 (1987).
3. S. Takizawa, K. Terakura, and T. Mohri, Phys. Rev. B39, 5792 (1989).
4. R.A. Johnson, Phys. Rev. B39, 2554 (1989).
5. P.R. Maarleveld, P.B. Kaars, A.W. Weeber, and H. Bakker, Physica B 142, 328 (1986) and references therein.
6. G.J. Ackland and V. Vitek, Phys. Rev. B41, 324 (1990).
7. G. Bozzolo, J. Ferrante, and J.R. Smith, Phys. Rev. B45 (1992) (in press).
8. S.M. Foiles, M.I. Baskes, and M.S. Daw, Phys. Rev. B33, 7983 (1986).
9. L. Vegard, Z. Physik 5, 17 (1921).
10. W.B. Pearson, Handbook of Lattice Spacings and Structures of Metals, Pergamon Press, New York (1967).
11. J.R. Smith, G. Bozzolo, A. Banerjea, and J. Ferrante, Phys. Rev. Lett. 63, 1269 (1989).
12. J.R. Smith, T. Perry, A. Banerjea, J. Ferrante, and G. Bozzolo, Phys. Rev. B44, 6444 (1991).
13. J.W.D. Connolly and A.R. Williams, Phys. Rev. 27, 5169 (1983).
14. R. Hultgren, R.L. Orr, P.D. Anderson, and K.K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, OH (1973).
15. A.R. Miedema and P.F. de Chatel, in Theory of Alloy Phase Formation, L.H. Bennett, ed., AIME, New York, pp. 344-389 (1980).
16. R.A. Johnson (private communication).

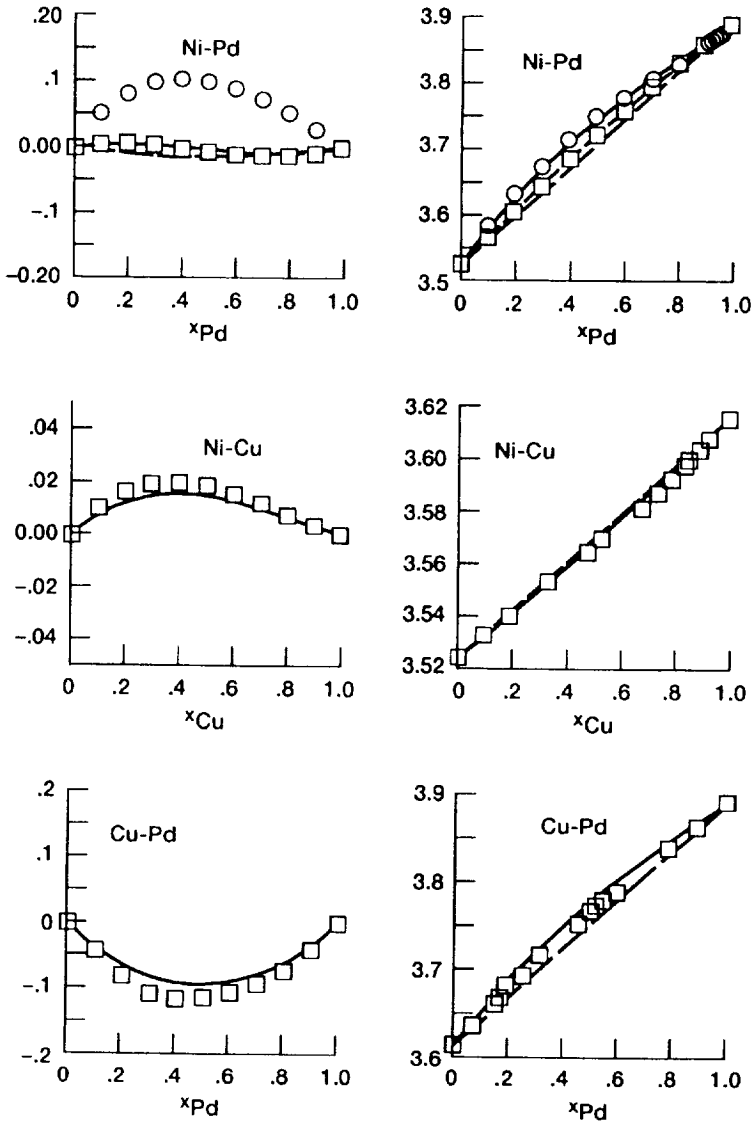

Figure 1.—(Left column) Comparison between the heat of formation as a function of concentration for Ni-Pd, Cu-Ni and Cu-Pd alloys: the solid curve indicates the results obtained in this work and the solid squares indicate the experimental values. The Ni-Pd figure also displays the results obtained with Miedema's approach (dashed curve) and Johnson's EAM (4,16) results (dash-dot curve). (Right column) comparison of lattice parameters of Ni-Pd, Cu-Ni and Cu-Pd alloys as obtained in this work (solid line) and the corresponding experimental values (solid squares). The Ni-Pd figure also displays the results obtained with Miedema's approach (dashed curve) and Johnson's EAM (4,16) results (dash-dot curve).

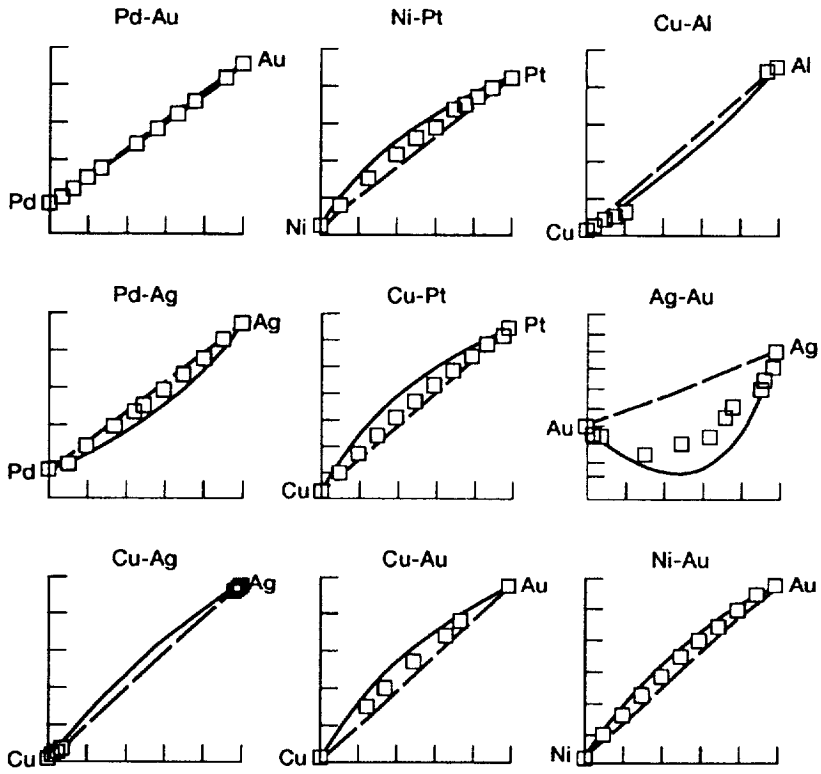

Figure 2.—Comparison between experimental values (solid squares) and the results obtained with this approach (solid lines) for the lattice parameter of several binary alloys of Ag, Ni Al, Au, Pd, Cu, and Pt. The results predicted by Vegard's law (dashed line) are also shown.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	January 1992	Technical Memorandum

4. TITLE AND SUBTITLE

Lattice Parameters of fcc Binary Alloys
Using a New Semiempirical Method

5. FUNDING NUMBERS

WU-505-90-54

6. AUTHOR(S)

Guillermo Bozzolo and John Ferrante

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E-6653

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM-105304

11. SUPPLEMENTARY NOTES

Guillermo Bozzolo, Analex Corporation, 3001 Aerospace Parkway, Brook Park, Ohio 44142; John Ferrante, NASA Lewis Research Center, (216) 433-6069.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 26

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

We present a new method for the calculation of heats of formation, lattice parameters and cohesive energies of binary alloys. We apply the method to some fcc alloys and compare with experimental data, as well as other semiempirical results.

14. SUBJECT TERMS

Alloys; Lattice constants

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

PRECEDING PAGE BLANK NOT FILMED