Departamento de Física Teórica, Universidad de Valladolid[1])

The Atomic Size-Mismatch Contribution to the Enthalpy of Formation of Concentrated Substitutional Metallic Solid Solutions

By

J. M. López and J. A. Alonso

One of the contributions to the enthalpy of formation ΔH of substitutional metallic solid solutions is the elastic energy due to atomic size mismatch between solute and solvent. Starting with a formula due to Eshelby and valid in the dilute regime, a multi-step process is derived which permits to generalize Eshelby's formula to the concentrated alloy regime. Miedema's chemical (liquid-like) contribution to ΔH is then added, and the final expression for ΔH is used to compute the free energy of formation of binary substitutional solid solutions of transition metals.

L'énergie élastique, due à la différence de grandeurs atomiques entre le solute et le solvant, est une des contributions à l'enthalpie de formation des solutions substitutionelles solides des metaux. A partir d'une formule de Eshelby, valable pour le régime dilué, nous présentons un processus en plusieurs étapes, lequel nous permet de géneraliser la formule de Eshelby pour les alliages en régime concentré. Nous ajoutons alors à ΔH la contribution chimique (de type liquide) de Miedema; ainsi l'expression finale de ΔH est utilisée pour la computation des énergies de formation des solutions solides substitutionelles binaires pour des métaux de transition.

1. Introduction

The enthalpy of solution of a solid metal A in a solid metal B is composed of three contributions [1]

$$\Delta h(\text{A in B}) = \Delta h^c + \Delta h^e + \Delta h^s . \tag{1}$$

Δh^c is the chemical contribution due to electron redistribution, and has been extensively studied by Miedema and coworkers [2 to 6]. In the case of alloys of two transition metals Δh^c is equal to the enthalpy of solution in the liquid state (where the other two terms are absent). Δh^e is an elastic contribution due to the difference in atomic volume between solute and solvent [1, 7]. It has been computed by Eshelby [8] and Friedel [9] using the classical elasticity theory. The chemical and size-mismatch contributions are also important controlling factors for the occurrence of metastable alloys [10 to 18]. Finally Δh^s is a structure dependent energy which has been worked out by Miedema and Niessen [1] for the case of dilute alloys of two 4d and 5d transition metals, and is related to the preference of these metals for one of the main three crystallographic structures, h.c.p., f.c.c., and b.c.c.

Niessen and Miedema [1] have studied the consequences of (1) in relation to alloy phase diagrams. But a complete treatment needs the calculation of the enthalpy of formation $\Delta H(c^A, c^B)$ of concentrated substitutional solid solutions. There is no problem with the chemical contribution ΔH^c in this respect [4]. On the other hand, the calculation of the elastic size-mismatch contribution ΔH^e in concentrated alloys

_____

1) Valladolid, Spain.

is a difficult task, not even attempted, to the best of our knowledge. In a previous paper [7] the authors have used an expression derived by Eshelby [8] and valid at low solute concentration c^A

$$\Delta H^e(c^A, c^B) = c^A \left[1 - c^A \frac{(\gamma - 1)\,\gamma}{(\beta - 1)\,\beta} \right] \Delta h^e \ (A \text{ in } B)\,, \tag{2}$$

where Δh^e (A in B) is given by

$$\Delta h^e \ (A \text{ in } B) = \frac{2\mu_B}{3\beta} \frac{(V_A - V_B)^2}{V_B} \tag{3}$$

and

$$\gamma = 1 + \tfrac{4}{3}\,\mu_B X_B\,, \tag{4}$$

$$\beta = 1 + \tfrac{4}{3}\,\mu_B X_A\,. \tag{5}$$

μ_B is the shear modulus of the host, and X_A and X_B are the compressibilities of solute and host, respectively. Calculations of the free energy of formation of substitutional solid alloys of two transition metals gave reasonable results at low solute concentration [7]. Nevertheless, the calculations indicate unambiguously that (2) is inadequate for concentrated solid solutions. To remedy the situation we present in this paper a method to calculate the elastic energy in a concentrated substitutional alloy, which can be considered as a generalization of Eshelby's result. The procedure has been applied in particular to those alloys for which complete solubility was predicted in [7]. Finally, we propose a simple interpolation formula for the heat of formation which gives results very similar to those computed using the general method.

2. Elastic Energy in a Concentrated Substitutional Solid Solution

The formation of a concentrated substitutional alloy can be considered as a process in which solute atoms are first extracted from bulk metal A and then placed substitutionally in the host lattice. It is clear that, as the solute concentration increases, the average atomic volume and the elastic constants of the alloy change smoothly. To illustrate the calculation of the elastic energy in an alloy with a solute concentration c^A we first consider a simple two-step process. In a strict sense this two-step process is valid only if c^A is small, but it can be readily generalized to a many-step process to cover the concentrated regime.

Let us start with N^B moles of the host metal. In a first step, N_1^A solute moles are added, until the solute concentration c_1^A is equal to $c^A/2$. Since c_1^A is small, (2) can be used for the elastic energy in this step. This energy is (per mole of alloy with solute concentration c_1^A)

$$\Delta H^e(c_1^A, 1 - c_1^A) = c_1^A \left[1 - c_1^A \frac{(\gamma - 1)\,\gamma}{(\beta - 1)\,\beta} \right] \Delta h^e \ (A \text{ in } B)\,. \tag{6}$$

At this point let us consider the alloy as an effective monatomic host metal with atoms (labelled B*) having the following characteristics: an atomic volume given by Vegard's Law

$$V_{B*} = c_1^A V_A + (1 - c_1^A)\,V_B \tag{7}$$

and elastic constants

$$X_{B^*} = \alpha_1^A X_A + (1 - \alpha_1^A) X_B, \tag{8}$$

$$\mu_{B^*} = \frac{\mu_A \mu_B}{\alpha_1^A \mu_B + (1 - \alpha_1^A) \mu_A}, \tag{9}$$

where α_1^A is the volume concentration of element A

$$\alpha_1^A = \frac{c_1^A V_A}{c_1^A V_A + (1 - c_1^A) V_B}. \tag{10}$$

Equation (8) is a consequence of the ideal mixture approximation [19]. Equation (9) can be justified if we recall the approximate relation between compressibility, shear modulus, and Poisson's ratio σ of a metal [20]

$$X = \frac{3(1 - 2\sigma)}{2(1 + \sigma) \mu}. \tag{11}$$

Assuming that the value of σ is the same for both metals (in fact, σ is approximately constant for most materials [20]), and using (8), then (9) follows immediately.

In the second step N_2^A solute moles of A are added until the final concentration of solute atoms is c^A. The elastic energy of this second step is calculated using again (2), where the host is now characterized by the parameters V_{B^*}, X_{B^*}, μ_{B^*}. This elastic energy is (per mole of the final alloy)

$$\Delta H^e(c_2^A, 1 - c_2^A) = c_2^A \left[1 - c_2^A \frac{(\gamma_1 - 1)\gamma_1}{(\beta_1 - 1)\beta_1} \right] \Delta h^e \text{ (A in B*)}, \tag{12}$$

where

$$\Delta h^e \text{ (A in B*)} = \frac{2\mu_{B^*}}{3\beta_1} \frac{(V_A - V_{B^*})^2}{V_{B^*}}. \tag{13}$$

γ_1 and β_1 are obtained from (4) and (5) by just substituting B by B*. c_2^A in (12) is the concentration of A atoms in the alloy formed by N_2^A moles of A atoms and $(N_1^A + N^B)$ moles of B* atoms. The total elastic energy of formation of the alloy is obtained from (6) and (12)

$$\Delta H^e(c^A, 1 - c^A) = (1 - c_2^A) \Delta H^e(c_1^A, 1 - c_1^A) + \Delta H^e(c_2^A, 1 - c_2^A), \tag{14}$$

where $\Delta H^e(c_1^A, 1 - c_1^A)$ has been multiplied by the factor $(1 - c_2^A)$ in order to express the elastic energy of the first step per mole of the final alloy. This two-step process is immediately generalized to an arbitrairy number of steps. The results presented in Section 3 have been obtained using a many-step process. Finally, the free energy of formation of a concentrated substitutional alloy

$$\Delta G = \Delta H - T \Delta S = \Delta H^c + \Delta H^e - T \Delta S \tag{15}$$

is computed easily, using the same form for ΔH^c and for the entropy of formation ΔS as in [7]. In order to compare with the results of [7], the structural term ΔH^s has been neglected. We show in Section 3 that this many-step process leads to a substantial improvement with respect to the one-step calculation of [7].

We have also found a useful interpolation formula for $\Delta H(c^A, c^B)$ which reproduces accurately the results of the many-step calculation. To find that formula we first notice that Miedema's theory [4, 6] for the chemical part of the heat of formation of

a random alloy can be easily manipulated to obtain

$$\Delta H^{c}(c^{A}, c^{B}) = \frac{c^{A}c^{B} \, \Delta h^{c} \, (\text{B in A}) \, \Delta h^{c} \, (\text{A in B})}{c^{A} \, \Delta h \, (\text{A in B}) + c^{B} \, \Delta h^{c} \, (\text{B in A})}. \tag{16}$$

The same formula is also obtained for the heat of formation in the conformal solution model (or the regular solution model in the zeroth approximation [21]), or in Flory's theory [22]. This expression suggests the following generalization:

$$\Delta H(c^{A}, c^{B}) = \frac{c^{A}c^{B} \, \Delta h \, (\text{B in A}) \, \Delta h(\text{A in B})}{c^{A} \, \Delta h \, (\text{A in B}) + c^{B} \, \Delta h \, (\text{B in A})}, \tag{17}$$

where $\Delta h = \Delta h^{c} + \Delta h^{e}$ and $\Delta H = \Delta H^{c} + \Delta H^{e}$. Evidently, (17) has the correct limiting behaviour for $c^{A} \to 0$ or $c^{A} \to 1$.

3. Results

The calculated free energy of formation ΔG of substitutional solid solutions at $T = 1000$ K is plotted in Fig. 1 for several transition metal alloys (ScY, ZrSc, ScHf, TiHf, VCr, VNb, VMo, and VW). The results obtained in [7] using one single step in the calculation of ΔH^{e} have also been plotted in the figures. ΔG has now a reasonable behavior as a function of solute concentration. In other words, the unphysical behavior in the concentrated regime shown by ΔG in [7] has now been corrected (see especially Fig. 1 a). A small discontinuity still persists at the equiatomic concentration and it occurs because the procedure used to calculated ΔH^{e} is not completely symmetric in the solute. The figures show that the eight alloys studied here have a negative near-zero value of ΔG over the whole concentration range at 1000 K. This fact is consistent with the experimental phase diagrams of those alloys [5], which show continous solid solubility at that temperature. Quantitative information also exists on the heat of formation of VCr [23]. The experimental $\Delta H(\text{V}_{0.5}\text{Cr}_{0.5})$ at $T = 1376$ to 1748 K is (-456 ± 200) cal/mol, whereas our (average) calculated value, -192 cal/mol, is less negative (see nevertheless the discussion below). The results for ΔG obtained using (17) have also been included in the figures. It can be concluded that (17) provides a useful interpolation formula. But we stress than its validity is only guaranteed a posteriori. In other words, starting from (16) it is not evident a priori that a similar formula should apply to $(\Delta H^{c} + \Delta H^{e})$. Only after showing that (17) gives results very similar to those of the complete calculation of $\Delta H^{c} + \Delta H^{e}$, we trust (17).

To close this paper, a few comments are in order. Several improvements can be introduced in the calculation of ΔH which have not been considered in this paper in order to compare the new results with those of [7] in the most faithful way, that is, using the same approximations, except for the change from a single step to a multi-step calculation of ΔH^{e}. First the atomic volumes V_{A} and V_{B} must be corrected, since they are in fact a little bit different from the pure metal volumes, as a consequence of charge transfer [1]. This charging effect tends to reduce $(V_{A} - V_{B})^{2}$, since the more electronegative component is usually the one with smaller atomic volume. This effect will make the elastic energy a little bit less positive. Second, since we compare the results with high temperature solubility data, the temperature dependence of the elastic constants should be considered [1]. This would reduce a little bit more the elastic energies (especially in the alloys ScY, ScZr, ScHf, and TiHf). Consideration of those two effects will evidently improve the agreement with the experimental heat of formation of VCr. Finally, structural effects do not play a significant role in the
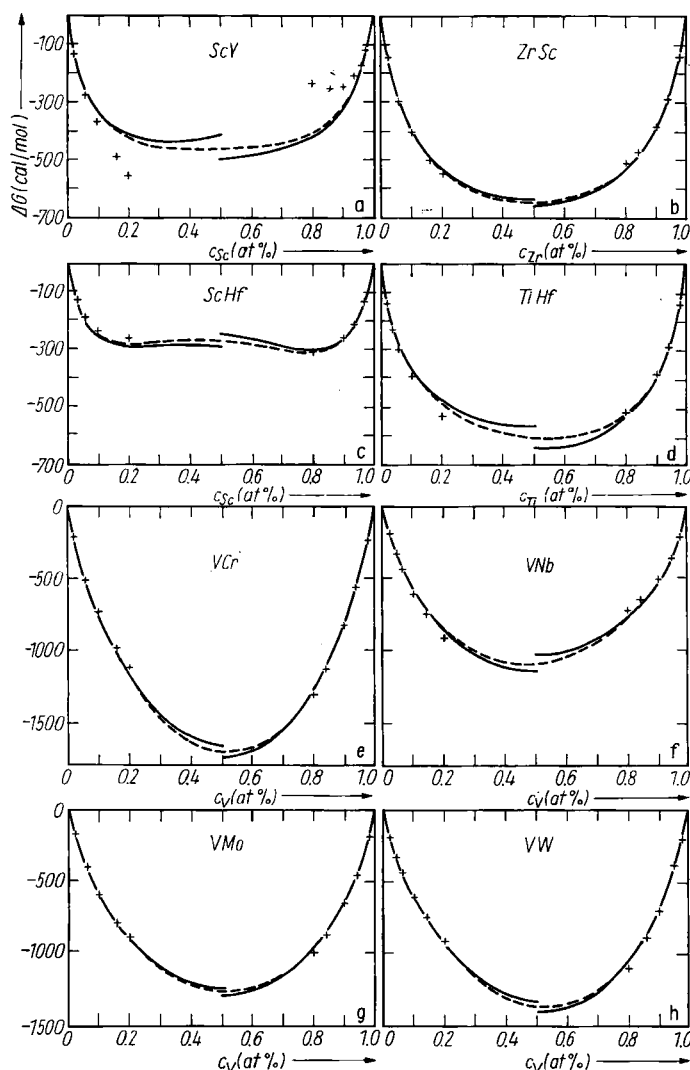
Fig. 1. Free energy of formation of substitutional metallic alloys versus concentration, at $T =$ $= 1000$ K. a) ScY, b) ZrSc, c) ScHf, d) TiHf, e) VCr, f) VNb, g) VMo, b) VW. ——— Many-step calculation (this work), ++++ one-step calculation [7], ————— interpolation formula ((17) of this work)

alloys treated in this paper. In ScY, TiHf, and VNb, the two elements have the same number of valence (s + d) electrons and the same crystal structure. On the other hand, in ScZr, ScHf, VCr, VMo, and VW, the two elements have the same crystal structure (h.c.p. in the first two alloys and b.c.c. in the other three) and the difference in the number of valence (s + d) electrons is one. These two features imply that the structural contribution is absent or very small (see Table II of [1]).

Acknowledgements

References

[1] A. K. Niessen and A. R. Miedema, Ber. Bunsenges. phys. Chem. **87**, 717 (1983).
[2] A. R. Miedema, F. R. de Boer, and P. F. de Châtel, J. Phys. F, **3**, 1558 (1973).
[3] A. R. Miedema, Philips tech. Rev. **36**, 217 (1976).
[4] A. R. Miedema, P. F. de Châtel, and F. R. de Boer, Physica (Utrecht) **100B**, 1 (1980).
[5] F. R. de Boer, R. Boom, and A. R. Miedema, Physica (Utrecht) **101B**, 294 (1980).
[6] A. R. Miedema and P. F. de Châtel, in Theory of Alloy Phase Formation, Ed. L. H. Bennett, The Metall. Soc. of AIME, Warrendale 1980 (p. 344).
[7] J. M. López and J. A. Alonso, phys. stat. sol. (a) **76**, 675 (1983).
[8] J. D. Eshelby, Solid State Phys. **3**, 79 (1956).
[9] J. Friedel, Adv. Phys. **3**, 446 (1954).
[10] J. A. Alonso and J. M. López, Phil. Mag. A **45**, 713 (1982).
[11] J. M. López and J. A. Alonso, phys. stat. sol. (a) **72**, 777 (1983).
[12] J. A. Alonso and S. Simozar, Solid State Commun. **48**, 765 (1983).
[13] S. Simozar and J. A. Alonso, phys. stat. sol. (a) **81**, 55 (1984).
[14] B. C. Giessen and S. Whang, J. Physique **41**, C8–95 (1980).
[15] B. C. Giessen, Proc. 4th Internat. Conf. Rapidly Quenched Metals, Vol. 1, Ed. T. Masumoto and K. Suzuki, Japan Inst. of Metals, Sendai 1982 (p. 213).
[16] B. Rauschenbach and K. Hohmuth, phys. stat. sol. (a) **72**, 667 (1982).
[17] K. Hohmuth, B. Rauschenbach, A. Kolitsch, and E. Richter, Nuclear Instrum. and Methods **209/210**, 249 (1983).
[18] B. C. Giessen, in: Alloy Phase Diagrams, Ed. L. H. Bennett, T. Massalski, and B. C. Giessen, Mater. Res. Soc. Symp. Proc., Vol 19, North-Holland Publ. Co., 1983 (p. 263).
[19] J. R. Christman and H. B. Huntington, Phys. Rev. **139**, A83 (1965).
[20] K. A. Gschneidner, Solid State Phys. **16**, 275 (1964).
[21] A. E. Guggenheim, Mixtures, Oxford University Press, Oxford 1952.
[22] P. J. Flory, J. chem. Phys. **10**, 51 (1942).
[23] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, Selected Values of Thermodynamic Properties of Binary Alloys, American Soc. for Metals, Ohio 1973.