

ON THE ELASTIC MISMATCH IN THE ORDER-DISORDER TRANSFORMATION AND SOLID STATE AMORPHIZATION OF INTERMETALLIC COMPOUNDS—I. ESTIMATION OF THE ELASTIC MISMATCH ENERGY DURING ORDER-DISORDER TRANSITION

D. L. BEKE†, P. I. LOEFF and H. BAKKER

Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65,
NL-1018 XE Amsterdam, The Netherlands

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Abstract—Using a method similar to the thermodynamic theory of almost completely ordered alloys an expression for the elastic mismatch energy of an ordered alloy as a function of the long-range order parameter, η , is derived from the continuum elastic theory. It is shown that, similarly to the chemical ordering energy in Bragg–Williams approximation, this has a simple $(1 - \eta^2)$ -type dependence. It is illustrated by detailed calculations that the relation obtained can also be derived requiring that the slope of the elastic mismatch energy at $\eta = 0$ should be equal to zero. It is also shown that the expression proposed for the elastic mismatch energy of a (disordered) solid solution in the Miedema-model contains the interactions between the image elastic fields as well and can be considered to be on the same level of approximation as our result. The maximum elastic energy which can be stored during a disordering process is compared to the elastic mismatch energy of the solid solution (at the same atomic fraction). It is concluded that the differences between the above values are comparable to the differences obtained by using uncorrected volumes for the atoms and holes or using corrected values of them according to the Miedema-model.

Résumé—En utilisant une méthode semblable à la théorie thermodynamique des alliages presque parfaitement ordonnés, on trouve, à partir de la théorie du continuum élastique, une expression de l'énergie de désaccord élastique d'un alliage ordonné en fonction du paramètre d'ordre à longue distance η . On montre que, comme l'énergie de mise en ordre chimique de l'approximation de Bragg et Williams, cette énergie varie simplement en $(1 - \eta^2)$. Par des calculs détaillés, on montre que la relation obtenue peut aussi être démontrée en écrivant que la pente de l'énergie de désaccord élastique à $\eta = 0$ doit être nulle. On montre aussi que l'expression proposée pour l'énergie de désaccord élastique d'une solution solide (désordonnée) dans le modèle de Miedema tient compte aussi des interactions entre les champs élastiques images et qu'elle peut être considérée comme étant du même niveau d'approximation que nos résultats. L'énergie élastique maximale qui peut être stockée pendant le processus de désordre est comparée à l'énergie élastique de désaccord de la solution solide (pour la même fraction atomique). On conclut que les différences entre les valeurs ci-dessus sont comparables aux différences obtenues en utilisant des volumes non corrigés pour les atomes et les trous ou en utilisant leurs valeurs corrigées d'après le modèle de Miedema.

Zusammenfassung—Mit einer Methode, die der thermodynamischen Theorie nahezu vollständig geordneter Legierungen ähnelt, wird ein Ausdruck für die elastische Fehlpassungsenergie einer geordneten Legierung in Abhängigkeit vom Fernordnungsparameter η aus der Kontinuumselastizitätstheorie abgeleitet. Es wird gezeigt, daß dieser Ausdruck ähnlich der chemischen Ordnungsenergie in der Bragg–Williams-Näherung eine einfache Abhängigkeit vom Typ $(1 - \eta^2)$ aufweist. Mit ausführlichen Berechnungen wird dargelegt, daß der erhaltene Zusammenhang auch aus der Forderung abgeleitet werden kann, daß die Steigung der elastischen Fehlpassungsenergie bei $\eta = 0$ gleich Null sein muß. Außerdem wird gezeigt, daß der im Miedema-Modell für die elastische Fehlpassungsenergie eines (ungeordneten) Mischkristalles vorgeschlagene Ausdruck die Wechselwirkung zwischen den elastischen Bildfeldern ebenso enthält und als auf demselben Niveau wie unsere Näherung angesehen werden kann. Die größte elastische Energie, die während eines Entordnungsprozesses gespeichert werden kann, wird mit der elastischen Fehlpassungsenergie des Mischkristalles (bei demselben Atomanteil) verglichen. Es wird gefolgert, daß die Unterschiede zwischen den vorgenannten Werten vergleichbar den Unterschieden sind, die sich bei Verwendung unkorrigierter Volumina für Atome und Löcher oder korrigierter Werte hierfür entsprechend dem Miedema-Modell ergeben.

†Permanent address: Department for Solid State Physics, Institute of Physics, L. Kossuth University, H-4010 Debrecen, P.O. Box 2, Hungary.

1. INTRODUCTION

The role of the elastic mismatch energy or the atomic size disparity in ordered compounds is important at least for two reasons. First, because this could be an important factor in lowering the energy of the ordered lattice relative to that of a random arrangement [1–4] (by packing atoms of different sizes in a minimum volume [5]). Secondly, because the increase of the elastic energy of an initially ordered compound can be important in the solid state amorphization processes observed during irradiation or ball-milling (see e.g. [6, 7] and also papers in [8]).

The problem of estimation of the elastic mismatch energy during an order–disorder transformation in the solid state has not been investigated satisfactorily until now in the literature and there are no results published for this energy as a function of the order parameter in substitutional alloys. For example Khachaturyan [3] treated a somewhat different problem: the stress-induced ordering phenomena in interstitial solid solutions. With the help of the concentration wave technique, which is a rather elegant but complicated method, the treatment was possible outside the framework of the model of the nearest and next nearest neighbor interactions as well. Like another similar atomistic theory of the stress interactions of interstitials [9, 10] this is successful in describing the stress-induced ordering in these alloys. On the other hand, Egami and Waseda [7] investigated the correlation between the atomic size ratio and the glass forming ability by rapid quenching. They considered a binary solid solution and obtained that this solution can become topologically unstable when the concentration of the atoms of one species reaches a critical limit. No similar treatment of the stability of ordered compounds are published till now in the literature.

In the present paper, following a similar method as was used in [11] and which is called “the thermodynamic theory of almost completely ordered alloys”, we will derive an expression for the elastic mismatch energy as a function of the order parameter, η , from the continuum elastic theory. Our results—as it is expected—will give a good description for the elastic energy close to $\eta = 1$. The extension of the relations obtained to a higher degree of disorder will be done in two ways. First, the η -dependence of the input parameters in the expressions (elastic moduli and volumes) are taken into account and fixed in such a way that, for example, in the $\eta = 0$ limit the volumes of the holes on the α and β sublattices (into which B or A atoms are placed, respectively) are both equal to the average atomic volume in the fully disordered solid solution. The second way is rather phenomenological: it is supposed that the first derivative of the elastic energy with respect to η at $\eta = 0$ is equal to zero (i.e. the exchange of A one and B atom in a fully disordered solid solution results in a negligible additional elastic mismatch energy). It will be shown by detailed calculations that the result obtained from the

first way of refinement are in a very good agreement with the above macroscopic condition and the dependence of the elastic mismatch energy on η can be given as a simple $(1 - \eta^2)$ -type dependence.

Our results will be compared to the elastic mismatch energies in solid solutions calculated at the same atomic fractions from the Miedema-model [12, 13]. It is shown that the expression proposed for the elastic mismatch energies in this model contains the interactions between the image elastic fields of the atoms as well and can be considered to be on a similar level of approximation as our results derived from the condition on the slope of the elastic energy at $\eta = 0$.

2. ESTIMATION OF THE ELASTIC MISMATCH ENERGY

2.1. Concentration independent parameters

In order to give the elastic energy, stored during disordering, as a function of η we can use considerations similar to those used by Eshelby [14] in deriving the elastic energy of (disordered) solid solutions. It follows from this sphere-in-hole model calculations that the elastic mismatch energy of an A atom on a β -lattice site in an otherwise completely ordered compound is given by

$$E_{A\beta} = 2\mu_{AB}[W_{\beta 0} - W_A]^2/3W_{\beta 0}\gamma_A \quad (1)$$

where μ_{AB} is the shear modulus of the compound. $W_{\beta 0}$ is the volume of a hole on the β -sublattice and W_A is the volume of the A atom in the compound. γ_A expressed as

$$\gamma_A = 1 + 4\mu_{AB}W_A/3K_AW_{\beta 0}, \quad (2)$$

with K_A the bulk modulus of pure A. Analogously, when as the only defect in the crystal a B atom is placed on a wrong lattice site, the energy that is added to the system is

$$E_{B\alpha} = 2\mu_{AB}[W_{\alpha 0} - W_B]^2/3W_{\alpha 0}\gamma_A \quad (3)$$

with γ_B defined analogously to γ_A .

If we create a new antisite A atom in a crystal, having already $N_{A\beta} = c_{A\beta}N = cN$ antisite atoms present (N is the number of atoms in the system and for stoichiometric compounds $c_{A\beta} = c_{B\alpha} = c$), there is an additional energy term due to the interaction energy with the image field of all its predecessors [14]. The image hydrostatic pressure is $-K_{AB}\Delta V_{A\beta}^1$ times the number of defect per unit volume. Since the image pressure builds up linearly with composition the mean interaction energy is [14, 15]

$$-cK_{AB}\Delta V_{A\beta}^1\Delta V_{A\beta}/\bar{W}. \quad (4)$$

The extra term due to the interaction of an A antisite atom with B atoms on the α -sublattice is

$$-cK_{AB}\Delta V_{B\alpha}^1\Delta V_{A\beta}/\bar{W} \quad (5)$$

where K_{AB} and \bar{W} are the bulk modulus of the compound and the average value of $W_{\alpha 0}$ and $W_{\beta 0}$

($\bar{W} = [W_{\alpha 0} + W_{\beta 0}]/2$), respectively. The various volume changes appearing in equations (4) and (5) are expressed in terms of the atomic volumes and the elastic moduli as

$$\begin{aligned}\Delta V_{A\beta}^I &= [W_{\beta 0} - W_A][\gamma - 1]/\gamma_A, \\ \Delta V_{B\alpha}^I &= [W_{\alpha 0} - W_B][\gamma - 1]/\gamma_B, \\ \Delta V_{A\beta} &= [W_{\beta 0} - W_A]\gamma/\gamma_A, \\ \Delta V_{B\alpha} &= [W_{\alpha 0} - W_B]\gamma/\gamma_B,\end{aligned}\quad (6)$$

and γ is defined as

$$\gamma = 1 + 4\mu_{AB}/3K_{AB}. \quad (7)$$

In the case of site-antisite disordering the positions of the A and B atoms are exchanged, and so the production of A and B antisite atoms occurs simultaneously. Thus the total change in the elastic energy producing a "pair" of defects is

$$\begin{aligned}dE &= E_{A\beta}(c) + E_{B\alpha}(c) \\ &- cK_{AB}[\Delta V_{A\beta} + \Delta V_{B\alpha}][\Delta V_{A\beta}^I + \Delta V_{B\alpha}^I]/\bar{W}.\end{aligned}\quad (8)$$

Using expressions (6) this can be rewritten into the form

$$dE = E_0(c) - 2cQ(c) \quad (9)$$

with

$$E_0(c) = E_{A\beta}(c) + E_{B\alpha}(c) \quad (10)$$

$$Q(c) = Q_A(c) + Q_B(c) \quad (11)$$

where

$$\begin{aligned}Q_A(c) &= \gamma W_{\beta 0}[1 + P(c)]E_{A\beta}(c)/\gamma_A \bar{W} \\ Q_B(c) &= \gamma W_{\alpha 0}[1 + 1/P(c)]E_{B\alpha}(c)/\gamma_B \bar{W}.\end{aligned}\quad (12)$$

Here $P(c)$ has the form

$$P(c) = \gamma_A[W_{\alpha 0} - W_B]/\gamma_B[W_{\beta 0} - W_A]. \quad (13)$$

In the above expressions, in principle, the volumes of the atoms and holes and the elastic moduli are also concentration dependent (and only for the sake of clarity were not indicated before).

Since equation (9) gives the increase in the Gibbs free energy of the system (because of the temperature dependence of the elastic moduli we obtain the Gibbs free energy instead of the internal energy), the total change when in an originally completely ordered compound cN pairs of defects are produced is

$$\Delta G_{el} = \int_0^c E_0(c) \{1 - 2cQ(c)/E_0(c)\} dc. \quad (14)$$

If the concentration dependence of the elastic moduli and the volumes would be neglected, we would have

$$\Delta G_{el} = E_0 c \{1 - cQ/E_0\} \quad (15)$$

with $Q = Q_A(0) + Q_B(0)$ [see also (11) and (12)]. Even in this case to evaluate ΔG_{el} we need the values of the following atomic volumes and elastic moduli: W_A , W_B , $W_{\alpha 0}$, $W_{\beta 0}$, μ_{AB} , K_{AB} , K_A , K_B .

Since there are only few experimental data for μ_{AB} , in our calculations the following expression will be used

$$\mu_{AB}(c=0) = 1.25[F_A\mu_A + F_B\mu_B] \quad (16)$$

where F_A and F_B are the atomic fractions of A and B atoms, respectively ($F_A + F_B = 1$). The experimentally observed change in μ_{AB} during disordering lies between 5 and 50% [16, 17], and there is a similar scatter in the differences between μ_{AB} and the corresponding concentration weighted average of the shear moduli of the pure metals (i.e. the estimated value for a solid solution) [18]. However, since in both cases μ_{AB} is usually larger than $F_A\mu_A + F_B\mu_B$ and since the difference in average is about 25% we introduced the factor 1.25 in (16). Furthermore, according to the experimental data for the bulk moduli of metals [19], there is an empirical relation for the μ/K ratio: $\mu/K = 0.45$. It will be supposed that the above relation holds for the intermetallic compounds as well, i.e.

$$\mu_{AB} = 0.45K_{AB} \quad (17)$$

and so $\gamma = 1.6$ and $\gamma - 1 = 0.6$ will be used in the calculations. The elastic moduli of pure elements will be taken from [19].

As input data we need also the values of $W_{\alpha 0}$, $W_{\beta 0}$, W_A and W_B . First we can suppose, as the simplest case, that all volumes are independent of their environments and make also the reasonable assumption that $W_A = W_{\alpha 0} = \Omega_{A \text{ in } A}$ and $W_B = W_{\beta 0} = \Omega_{B \text{ in } B}$. (Here e.g. $\Omega_{A \text{ in } A}$ means the atomic volume of A in pure A metal.)

On the other hand, following Miedema (see e.g. [12]) we can also make volume corrections originating from the different charge transfer between the atom and its different neighbors. Accordingly, the corrected volumes of A and B atoms in a wrong lattice place can be easily calculated from expressions given in Chaps 2.1, 3.2 and 5.1 of [12]. The corrected volumes of the holes can be obtained as follows. Since the elastic mismatch energy is negligible in the ordered state the volume of the hole, produced by taking off e.g. one B atom, should be equal to the volume of the B atom in this (right) place. Now, putting one A atom into this hole (i.e. producing one antisite defect) we can calculate the corresponding volume correction of the hole again with the help of similar expressions given by Miedema *et al.* The same procedure can be applied for $W_{\alpha 0}$.

We have to note that in principle the use of the Miedema corrections would be important because if we want to separate the elastic and chemical contributions in disordering, then a certain correction before calculating the *pure* elastic energy term inevitably would be necessary. The difficulty is that the microscopic elastic and electrostatic fields in crystals are not independent [20] and there is a danger to take things into account twice. For example if we start from a model where the impurity in a solvent

is described by two parameters (say by a bonding strength and bonding length perturbation [21]) then these parameters—because of the above reason—will not be independent. Now, imagine that we would like—even if rather arbitrarily—to separate the perturbation, caused by a solute, into two parts in such a way that one of them gives the “pure” size effect. Then we would first have to calculate the size change caused by the bonding strength perturbation alone in the system. Now, modifying the (original) size perturbation by this change we could estimate something which could be considered to be more or less a “pure” size effect. Since, in our opinion, the Miedema corrections intuitively are the best corrections in this respect, and because this can be easily given for all systems, we will also use these in the estimation of $W_{\alpha 0}$, $W_{\beta 0}$, W_A and W_B .

Finally, it is worth to mention that since the connection between c and the order parameter, η , can be given as [15]

$$c = [1 - \eta]F_A F_B = [1 - \eta]/m \quad (18)$$

(14) and (15) can be easily expressed as a function of the order parameter as well.

2.2. Concentration dependent parameters

Let us see now the case when we do not neglect the concentration dependence in Q and E_0 [see equation (9)] and suppose that the volumes and μ_{AB} are weakly dependent on c

$$\begin{aligned} W_{\alpha 0}(c) &= W_{\alpha 0}(0) + \Delta W_{\alpha 0}mc \\ &= W_{\alpha 0}(0)[1 + \epsilon_{\alpha}mc] \end{aligned} \quad (19)$$

$$\begin{aligned} W_{\beta 0}(c) &= W_{\beta 0}(0) + \Delta W_{\beta 0}mc \\ &= W_{\beta 0}(0)[1 + \epsilon_{\beta}mc] \end{aligned} \quad (20)$$

$$\begin{aligned} W_A(c) &= W_A(0) + \Delta W_A mc \\ &= W_A(0)[1 + \epsilon_A mc] \end{aligned} \quad (21)$$

$$\begin{aligned} W_B(c) &= W_B(0) + \Delta W_B mc \\ &= W_B(0)[1 + \epsilon_B mc] \end{aligned} \quad (22)$$

and

$$\mu_{AB}(c) = \mu_{AB}(0) \{1 - [2 - mc]mc/4\}. \quad (23)$$

Here the values of $\Delta W_{\alpha 0}$ and $\Delta W_{\beta 0}$ are fixed in such a way that if $c = 1/m$ [$1/m$ is the maximum value of c ; see e.g. equation (18)]

$$W_{\alpha 0}(1/m) = W_{\beta 0}(1/m) = \underline{W}_{ss} = F_A \underline{W}_A + F_B \underline{W}_B \quad (24)$$

with

$$\underline{W}_A = F_A \Omega_{A \text{ in } A} + F_B \Omega_{B \text{ in } A} \quad (25)$$

$$\underline{W}_B = F_A \Omega_{A \text{ in } B} + F_B \Omega_{B \text{ in } B}. \quad (26)$$

(Here e.g. $\Omega_{A \text{ in } B}$ is the volume of A in pure B can also be given with or without Miedema corrections [12].) Accordingly, for example

$$\Delta W_{\alpha 0} = \underline{W}_{ss} - W_{\alpha 0}(0). \quad (27)$$

Similarly, ΔW_A and ΔW_B are determined by the condition that \underline{W}_A or \underline{W}_B at $c = 1/m$ be equal to their values in the solid solution at F_A

$$\Delta W_A = \underline{W}_A - W_A(0) \quad (28)$$

$$\Delta W_B = \underline{W}_B - W_B(0). \quad (29)$$

Relation (24) expresses that the volumes of the holes in the α and β sublattices are equal to the average atomic volume in the solid solution in the limit $\eta = 0$. In (23) the factor $-1/4$ reflects the experimentally observed fact that the elastic moduli in average can decrease by about 25% during disordering [see equation (17)] and that μ_{AB} depends on η as $\{1 - \eta^2\}$ [17]. The ϵ_i ($i = A, B, \alpha, \beta$) values in (19), ... (22) are usually considerably less than unity since the concentration dependence of the volumes is weak.

In the following treatment it will be assumed that the concentration dependence of the ratios of two atomic volumes or two elastic moduli cancels. Consequently the concentration dependence of the γ_A and γ_B quantities will be similar and determined by the concentration dependence of μ_{AB} alone. At the same time in $E_{A\beta}$ (or $E_{B\alpha}$) the concentration dependence of the differences of the corresponding volumes will be taken into account. However, P will be considered to be constant (without Miedema corrections the ratio of the differences of the corresponding volumes is equal to -1). Thus making a Taylor series expansion of (9) and performing the integration in a simple way in (14) we arrive at

$$\Delta G_{el} = E_0(0)c[1 - cQ^*(c)/E_0(0)] \quad (30)$$

with

$$\begin{aligned} Q^*(c) &= Q(0) \{1 - E'_0/2Q(0) \\ &\quad + 2c[Q'/Q(0) - E''_0/4Q(0)]/3 \\ &\quad + 2c^2[Q''/2Q(0) \\ &\quad - E'''_0/12Q(0)]/4 + \dots\} \end{aligned} \quad (31)$$

where the primes above E_0 and Q denote the first, second and third derivatives of them at $c = 0$. The numerical values of terms in the brackets on the right hand side of (31) can be easily obtained from (10), (11), (12) and (13) with the help of (19), ..., (23). For example

$$\begin{aligned} E'_0 &= m[E_{A\beta}(0)\{-1/2 + 2\delta_A - \epsilon_{\beta} \\ &\quad + (1 - 1/\gamma_A)/2\} + E_{B\alpha}(0)\{-1/2 \\ &\quad + 2\delta_B - \epsilon_{\alpha} + (1 - 1/\gamma_B)/2\}] \end{aligned} \quad (32)$$

where

$$\begin{aligned} \delta_A &= [\underline{W}_{ss} - \underline{W}_A]/[W_{\beta 0}(0) - W_A(0)] - 1, \\ \delta_B &= [\underline{W}_{ss} - \underline{W}_B]/[W_{\alpha 0}(0) - W_B(0)] - 1. \end{aligned} \quad (33)$$

Determination of ΔG_{el} is now easy because the numerical values of Q^* and E_0 in (31) are known.

According to the weak concentration dependence of μ_{AB} and the input volumes, in our calculations terms higher in order than c^4 will be neglected.

It can be seen from the comparison of (15) and (30) that the values of Q and Q^* could be significantly different. For example they will be different even at $c=0$ because of the linear terms in c of $E_0(c)$. Although the value of Q at $c=0$ as well as its concentration dependence can be calculated, because the continuum elastic theory itself has its limits (it is questionable whether it is applicable on an atomic scale) we can also try to determine the value of Q and Q^* in (15) or (30) using more phenomenological condition. Accordingly, let us suppose that the dependence of Q^* on c is not significant (or can be decreased by an appropriate choice of Q^*). Since it is expected that the change in the elastic energy during the exchange of one A and one B atom in the disordered state will be very small (in this limit the distinction between the α and β sublattices has no meaning) we can suppose that the slope of $\Delta G_{el}(\eta)$ at $\eta=0$ is zero. Accordingly, we have from (15) or (30) with the help of (18) that

$$Q^* = Q = E_0 m/2. \quad (34)$$

Consequently

$$\Delta G_{el}(\eta) = E_0[1 - \eta^2]/2m. \quad (35)$$

Obviously, the reality of the above suppositions [i.e. that the dependence on the concentration in Q^* is weak and (34) is valid] should be checked by detailed calculations. This will be done in Section 3 where it will be illustrated that the agreement between the $Q_{av}^* = [Q^*(c=0) + Q^*(c=1/m)]/2$ values and the $E_0 m/2$ is quite good.

As it is expected (35) gives zero elastic mismatch in the fully ordered state and the maximum elastic mismatch energy is

$$\Delta G_{el}^m = E_0/2m = [E_{B\alpha} + E_{A\beta}]/2m. \quad (36)$$

2.3. Elastic mismatch energy in solid solutions

For the elastic mismatch energy of a dilute solid solution Eshelby [14] derived an expression which is very similar to (15) and can be given as

$$E_{el}^{B \text{ in } A} = E_A^B F_B (1 - F_B q_B) \quad (37)$$

if we have a dilute solution of B in A and a similar expression holds for $E_{el}^{A \text{ in } B}$. Here E_A^B has the form

$$E_A^B = 2\mu_A [\Omega_{AWB} - \Omega_{BWA}]^2 / 3\gamma_A \Omega_{AWB} \quad (38)$$

where

$$\gamma_B = 1 + 4\mu_B \Omega_{A \text{ in } B} / 3K_A \Omega_{BWA}. \quad (39)$$

Here Ω_{AWB} is the volume of the atom A in contact with the solute B (i.e. the volume of the hole in pure A): its value can be calculated again with or without Miedema corrections. Without this correction $\Omega_{AWB} = \Omega_{A \text{ in } A}$.

Furthermore, in (37) q_A can be written as [14]

$$q_A = \gamma_{B0}(\gamma_{B0} - 1)/\gamma_B(\gamma_B - 1) \quad (40)$$

where

$$\gamma_{B0} = 1 + 4\mu_B/3K_B. \quad (41)$$

Similar expressions are valid for E_B^A , γ_B and q_B .

It is expected that (37) gives the elastic energy as a function of the concentration in dilute alloys only. Indeed these expressions are equivalent to the approximation involved in case 2.1 (i.e. when the parameters are independent of the concentration). Owing to this fact there are different attempts in the literature to find a reasonable expression for the case of concentrated solid solutions (see e.g. [15, 22, 23]). More recently [24, 13] the following expression was proposed

$$\Delta G_{el}^{ss} = [F_B E_B^A + F_A E_A^B]/m. \quad (42)$$

In the derivation of (42) the argument was similar to that used in the Miedema-model: the degree to which atoms are surrounded by dissimilar neighbors was taken into account with the help of the factors f_A^B and f_B^A (for their meaning see [12]). Now, taking the concentration weighted average of $F_A f_B^A E_B^A$ and $F_B f_A^B E_A^B$ we obtain (42) if we take into account that for a random alloy $f_B^A \cong F_B$ and $f_A^B \cong F_A$. However, because the forces are long range forces in the elastic theory, the above arguments (with the contacts between neighbors) seems to be questionable. Furthermore it is also not clear, at least at first sight, whether the long range image fields are somehow involved in (42) or not.

We can try to get an expression for the concentrated solid solutions in a similar way as it was done in the case of the ordered alloys. Let us require now that the slopes of the elastic energy, which is composed as

$$\Delta G_{el}^{ss} = E_{el}^{A \text{ in } B} F_B + E_{el}^{B \text{ in } A} F_A \quad (43)$$

be equal to E_B^A and E_A^B , respectively at the two ends of the phase diagram. It is easy to see that this leads to

$$q_A = q_B = 1 \quad (44)$$

and so we obtain for ΔG_{el}^{ss} the same expression as (42). Consequently, relation (42) contains the interactions between the image fields of the defects as well, and is equivalent to (35) in that sense that both expressions were obtained with the introduction of plausible conditions for the slopes of the elastic energy.

2.4. Effect of the temperature dependence of the elastic moduli

In many cases we need ΔH_{el}^m and ΔH_{el}^{ss} instead of ΔG_{el}^m and ΔG_{el}^{ss} . These quantities can be estimated by taking into account the temperature dependence of the shear moduli only in E_0 , E_A^B and E_B^A and neglect the temperature dependence of the volumes and

ratios of elastic constants. (This can be done because they depend similarly on the temperature.) Thus we can write for example

$$\begin{aligned} E_0(T) &= E_0(0) \{1 + (\partial E_0 / \partial T)_{T=0} T / E_0(0)\} \\ &= E_0(0) \{1 + (\partial [\mu_{AB} / \mu_{AB}(0)] / \partial [T / T_m])_{T=0} T / T_m\}. \end{aligned} \quad (45)$$

Now, according to Zener [25] in pure metals

$$\partial [\mu / \mu_0] / \partial [T / T_m] = -\lambda_z \quad (46)$$

where λ_z is a constant and equals to 0.35 [26]. Supposing that the same relation holds for inter-metallic compounds as well, we have at $\eta = 0$

$$\Delta G_{cl}^m(T) = \Delta G_{cl}^m(0) \{1 - \lambda_z T / T_m\} \quad (47)$$

and according to general thermodynamic definitions ($\Delta H = \partial [\Delta G / T] / \partial [1 / T]$ and $\Delta S = -\partial \Delta G / \partial T$)

$$\begin{aligned} \Delta G_{cl}^m(0) &= \Delta H_{cl}^m = E_0(0) / 2m \\ &= E_0(T) / \{1 - \lambda_z T / T_m\} 2m \end{aligned} \quad (48)$$

and the entropy term can be given as

$$\Delta S_{cl}^m = E_0(0) \lambda_z / 2m T_m. \quad (49)$$

Similarly we can write from (42)

$$\begin{aligned} \Delta H_{cl}^{ss} &= \Delta G_{cl}^{ss}(T) / [1 - \lambda_z T / T_m] \\ &= [F_A E_A^B + F_B E_B^A] / m [1 - \lambda_z T / T_m]. \end{aligned} \quad (50)$$

Since we used the elastic moduli measured at room temperature $T \cong 300$ K was taken in our calculations.

3. RESULTS AND DISCUSSION

The columns of Table 1 contain the calculated Q , $Q^*(\eta = 0)$, Q_{av}^* , $E_0(0)m/2$, $E_0(0)$, ΔH_{cl}^m [equation (48)] and ΔH_{cl}^{ss} [equation (50)] values, respectively for a set of intermetallic compounds using corrected values for the input volumes according to Miedema. The last column shows the ΔH_{cl}^m values obtained without Miedema's correction.

It can be seen that, as expected, the values of Q are much less than the values of Q^* . This supports the idea that the corrections connected with the concentration dependence of the parameters in equation (14) are very important. It is also seen that the $Q^*(c = 0)$ and the Q_{av}^* values are not so much different and so the concentration dependence of Q^* is relatively weak. Furthermore from the comparison of $E_0m/2$ and Q_{av}^* values we can conclude that they are in quite good agreement and thus the condition (34) is supported by these microscopic calculations.

The elastic mismatch energies in the solid solutions are, as expected, in the same order of magnitude as the ΔH_{cl}^m values. As we have seen in the preceding section this difference could not arise from the different levels of approximations for ΔH_{cl}^{ss} and ΔH_{cl}^m . Moreover, it is not expected that a quite precise

agreement can be achieved between ΔH_{cl}^m and ΔH_{cl}^{ss} if we take into account the limits of the elastic theory itself and the fact that the reference states are different in the above cases [i.e. we started from the ordered compound for (35) and in deriving (42) the reference state is composed from pure metals and their structural differences were neglected].

It seems rather plausible to attribute the above difference to the problem of the determination of the volumes in different states as well. For example the volumes of the atoms and holes are determined in both cases, according to the Miedema corrections, by expressions derived for metals. If the actual sizes of atoms (and holes) are different from those values proposed for metallic systems the estimations for intermetallic compounds should be corrected. Unfortunately we do not know too much about the actual sizes of atoms in compounds: the estimation of this would be possible only in a few simple cases from the geometrical data of the lattice structure. In order to illustrate the effect of the corrections in the volumes we carried out calculations for ΔH_{cl}^m and ΔH_{cl}^{ss} without Miedema's corrections as well, i.e. supposing that $W_A = W_{\infty} = \Omega_{A \text{ in } A}$ and $W_B = W_{\beta 0} = \Omega_{B \text{ in } B}$ (see the last column in Table 2). We have checked that the role of the volume corrections is not significant and that all conclusions drawn above for the values of Q , Q^* and $E_0m/2$ remain valid in this case too. This confirms again that the condition (34) is supported by microscopic calculations. Furthermore, the differences between ΔH_{cl}^{ss} and ΔH_{cl}^m are comparable to the differences between ΔH_{cl}^m values obtained with and without Miedema's corrections for the atomic volumes: ΔH_{cl}^{ss} usually lies between them.

From the above comparison, we can conclude that our model gives quite reasonable results; the accuracy of the data is within the accuracy of our knowledge on the volumes of atoms and holes in the system.

Finally, the problem of the determination of the shear moduli of the compounds have to be mentioned. Since in the equation (17) the factor 1.25 was introduced as an average value deduced from the deviations of the shear moduli from the concentration weighted average of the moduli of the constituents, it is possible that the choice of this factor involves a systematic deviation. For example with a higher value of this factor the agreement would be better between ΔH_{cl}^m and ΔH_{cl}^{ss} . In the future, having more experimental data for the shear moduli of the intermetallic compounds, the above choice can be re-examined and corrected if it will be necessary.

The results of our calculations can be summarized as follows:

(i) Using a method similar to the thermodynamic theory of almost completely ordered alloys we derived an expression for the elastic mismatch energy of an ordered alloy as a function of the order parameter, η .

Table 1. Calculated Q , $Q^*(0)$, Q_{av}^* , $E_0(0)m/2$, $E_0(0)$, ΔH_{el}^m [equation (48)] and ΔH_{el}^{ss} [equation (50)] values with Miedema's correction for the volumes of atoms and holes. The last column shows the ΔH_{el}^{ss} (uncorr.) values without the above correction (all quantities are given in units kJ/mol)

Compound	Q	$Q^*(0)$	Q_{av}^*	$E_0m/2$	E_0	ΔH_{el}^m	ΔH_{el}^{ss}	ΔH_{el}^{ss} (uncorr.)
LaAu	47.24	350.36	303.25	195.82	97.91	13.10	15.37	23.08
La ₂ Co ₃	372.94	1438.62	1194.31	734.80	352.70	46.26	29.64	60.10
LaCu ₂	221.08	1065.49	890.17	594.60	262.93	32.12	25.66	46.96
LaNi	445.47	1562.33	1300.13	769.03	384.51	53.98	31.03	70.60
GdCo ₃	110.48	1004.27	828.67	599.14	224.68	22.58	23.77	53.98
Gd ₂ Co ₇	98.92	1029.93	845.25	619.11	212.48	18.34	21.80	49.88
PdZr	1.73	104.88	84.51	61.48	30.74	4.08	12.05	12.96
PtZr	1.69	97.88	77.53	53.33	26.67	3.48	11.51	13.06
PtZr ₂	23.14	222.32	171.12	115.78	51.20	5.96	8.19	10.86
Zr ₇ Cu ₁₀	15.14	364.20	312.59	247.60	119.79	16.08	20.43	23.48
ZrCu	19.50	360.79	311.17	239.60	119.80	16.40	21.72	23.98
NiZr ₂	70.81	682.92	528.27	405.72	179.41	21.46	27.02	28.48
NiZr	41.29	517.48	405.77	322.66	161.33	21.64	30.33	34.68
CoZr	42.68	518.28	406.44	324.28	162.14	21.62	29.21	33.92
Zr ₂ Al	1.35	76.74	62.88	52.42	23.18	2.74	4.69	5.02
Zr ₃ Al	1.97	96.74	78.91	65.49	24.56	2.48	4.11	4.34
RuZr	30.27	342.59	267.53	205.20	102.60	13.42	18.18	29.92
Cr ₂ Zr	33.94	535.40	453.93	367.32	162.43	18.98	22.19	32.68
CuTi ₂	3.76	125.70	102.30	85.90	38.16	4.80	7.32	7.32
CuTi	1.97	107.94	88.66	75.57	37.79	5.16	7.39	8.08
Ti ₃ Cu ₄	1.29	111.37	95.38	78.55	38.51	5.14	6.99	7.94
Ti ₂ Cu ₃	1.05	115.02	98.25	81.30	39.03	5.08	6.71	7.76
TiCu ₄	0.20	201.35	168.97	143.10	45.79	4.02	4.07	5.30
NiTi	4.64	155.55	125.77	101.88	50.94	6.82	12.32	13.46
NiTi ₂	13.68	214.78	170.81	134.75	59.59	7.18	11.00	11.32
Ni ₃ Ti	0.03	185.88	152.78	123.75	46.41	4.64	9.31	10.96
Co ₂ Ti	0.61	153.74	128.77	104.59	46.25	5.50	10.46	12.24
CoTi	4.90	154.54	132.96	101.88	50.94	6.82	11.64	12.98
Fe ₂ Ti	0.23	120.53	100.77	83.83	37.07	4.36	8.33	9.68
FeTi	2.84	121.45	104.07	81.73	40.86	5.46	9.23	10.32
Mn ₂ Ti	0.31	104.92	86.77	80.93	35.79	4.24	6.86	6.44
RuTi	0.45	31.60	24.92	16.81	8.41	1.10	4.57	6.74
CuZn	1.34	35.76	29.11	25.08	12.54	1.74	2.29	2.70
AuZn	0.91	56.43	47.08	44.24	22.12	3.10	0.70	0.54
Cu ₃ Au	4.60	207.86	179.99	183.67	68.88	7.04	3.69	5.32
AuCu	1.14	209.81	178.56	149.06	74.53	10.24	5.15	6.58
CuAu ₂	0.04	316.63	258.25	185.76	69.66	7.12	3.99	4.48
Ni ₃ Mn	0.43	3.80	2.57	1.42	0.53	0.06	0.73	0.48
Ni ₆ Nb	4.03	231.06	188.95	154.77	76.89	10.22	16.71	16.32
NiMo	0.27	185.92	155.54	134.88	67.44	8.94	11.93	12.20
Ni ₃ Al	0.62	104.99	87.67	72.89	27.33	2.74	4.40	7.26
NiAl	5.12	106.80	92.31	69.60	34.80	4.60	5.39	8.46
FeCo	0.00	2.59	2.19	1.82	0.91	0.12	0.27	0.24
FeAl	3.51	82.02	66.19	55.50	27.75	3.72	4.04	6.32
PdIn	9.46	163.63	129.06	95.19	47.60	6.40	3.07	13.50
CuPd	0.19	132.14	111.06	101.02	50.51	6.80	2.57	2.80
CoGa	29.38	270.88	212.23	171.73	85.87	11.66	12.41	17.66
CoAl	5.46	106.61	85.59	70.08	35.04	4.64	5.18	8.12
Fe ₂ Al	0.84	85.78	72.22	61.82	23.18	2.32	3.21	5.32
Cu ₃ Sn	87.34	825.72	704.15	570.06	213.77	22.48	15.15	25.26
Pd ₃ Sn	3.43	244.36	204.54	164.75	61.78	6.20	9.80	16.54

(ii) We have shown, by detailed calculations based on the continuum elastic theory, that the dependence of the elastic mismatch energy on η can be given by equation (35). It is also illustrated that this relation can be considered as a result of the following condition for the slope of the elastic energy at $\eta = 0$; the change in the elastic energy is negligible when one A and B atom are exchanged in a fully disordered solid solution.

(iii) The elastic mismatch energy depends on η as $(1 - \eta^2)$. This dependence is similar to the dependence of the chemical interaction energy of an ordered alloy in quasichemical approximation. This similarity leads to simple expressions for the general condition of amorphization (see [27], Part II).

(iv) It was shown that the expression proposed for the elastic mismatch energy of a (disordered) solid

solution in the Miedema-model contains the interactions between the image elastic fields as well and can be considered to be on the same level of approximation as equation (35).

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APPENDIX

$$E_{A\beta}(c) = E_{A\beta}(0) \{1 - mc/2 + m^2 c^2/4\} \\ \times \{1 + \delta_A mc\} / \{1 + \epsilon_B mc\} \\ \times \{1 + \Gamma_A (m^2 c^2/4 - mc/2)\} \\ = E_{A\beta}(0) F_A(c)$$

where

$$\gamma_i(c) = \gamma_i(0) \{1 + \Gamma_i (m^2 c^2/4 - mc/2)\}, \\ (\Gamma_i = 1 - 1/\gamma_i(0)) \quad i = A, B$$

and

$$[W_{\beta 0}(c) - W_A(c)]/[W_{\beta 0}(0) - W_A(0)] = 1 + \delta_A mc$$

$$E'_0 = E'_{A\beta} + E'_{B\alpha} = E_{A\beta}(0)F'_A + E_{B\alpha}(0)F'_B$$

similar expressions hold for the higher order derivatives.

$$F'_A = m \{2\delta_A - \epsilon_\beta + \Gamma_A/2 - 1/2\}; \\ F'_B = m \{2\delta_B - \epsilon_\alpha + \Gamma_B/2 - 1/2\} \\ F''_A = m^2 \{2\delta_A^2 - 4\delta_A \epsilon_\beta + 2\delta_A \Gamma_A - 2\delta_A \\ + 2\epsilon_\beta^2 - \epsilon_\beta \Gamma_A + \epsilon_\beta + \Gamma_A^2/2 + 1/2\} \\ F'''_A = m^3 \{-6\delta_A^2 \epsilon_\beta + 3\delta_A^2 \Gamma_A - 3\delta_A^2 \\ + 12\delta_A \epsilon_\beta^2 - 6\delta_A \epsilon_\beta \Gamma_A + 6\delta_A \epsilon_\beta \\ + 3\delta_A \Gamma_A^2 - 6\delta_A \Gamma_A + 3\Gamma_A - 6\epsilon_\beta^3 \\ + 3\epsilon_\beta^2 \Gamma_A - 3\epsilon_\beta^2 - 3\epsilon_\beta \Gamma_A^2/2 \\ + 3\epsilon_\beta \Gamma_A - 3\epsilon_\beta/2 + 3\Gamma_A^3/4 \\ - 9\Gamma_A^2/4 + 3\Gamma_A/2\}$$

$$Q(c) = Q_A(c) + Q_B(c)$$

$$Q_A(c) = Q_A(0)F_A(c)G_A(c);$$

$$Q_B(c) = Q_B(0)F_B(c)G_B(c)$$

$$G_i(c) = 1/\{1 + \Gamma_i (m^2 c^2/4 - mc/2)\},$$

$$i = A, B$$

$$Q' = Q'_A + Q'_B$$

$$Q'_i(0) = Q_i(0) \{F'_i(0) + G'_i(0)\}$$

$$Q''_i = Q_i(0) \{F''_i(0) + G''_i(0) \\ + 2F'_i(0)G'_i(0)\}$$

$$G'_i(0) = \Gamma_i m/2;$$

$$G''_i(0) = \Gamma_i m^2 \{\Gamma_i - 1\}/2.$$