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Methodological aspects of calculations of the thermodynamic factor in interdiffusion

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Abstract. Self-diffusion can be studied in binary systems for which appropriate radioisotopes for both constituents of the alloy are available. With respect to the Fe-Al system suitable radioisotopes are available for the Fe component (*e.g.* ^{59}Fe) but not for Al. In the framework of the Boltzmann-Matano method further insight into the diffusion behaviour of Fe-Al intermetallics can be gained from interdiffusion experiments. The *interdiffusion coefficient* is related *via* the modified Darken equation to the tracer diffusivities of the constituents. The thermodynamic factor Φ entering the Darken equation is proportional to the second derivative of the Gibbs free energy, G, of the alloy on the molar fraction of one of the components. These relations can be used to deduce the tracer diffusivity of Al provided that the tracer diffusivity of Fe, the interdiffusion coefficient and the thermodynamic factor are known. The mixing energy, which enters G, could be calculated on the basis of the thermodynamical data or by means of non-empirical calculations. We suggest for the latter *ab initio* calculations the use of modern non-empirical methods.

PACS. 64.70.-p Specific phase transitions – 65.50.+m Thermodynamic properties and entropy – 66.30.-h Diffusion in solids

Intermetallic compounds or ordered alloys have recently attracted much attention as structural materials for high-temperature applications. Diffusion is ubiquitus at elevated temperatures and it is promoted by atomic defects. A knowledge of diffusion and of defect properties is therefore of great interest for the production of these materials and for their use in technological applications. The increasing interest in aluminides due to their technological importance has recently triggered studies on Fe-Al intermetallics using Mössbauer spectroscopy (MBS) [1] and positron annihilation spectroscopy (PAS) [2–4]. PAS studies provide information about the formation of thermal vacancies. Apart from well known geometric factors, the self-diffusivity is the product of the thermal vacancy concentration times the mobility of the vacancies. A combination of both sets of experiments can be used to deduce the mobility of vacancies.

Some diffusion data on iron-aluminium alloys are available from the work of Larikov [5] (see also the data collection [6]). These data are limited to fairly high temperatures above 1173 K. This implies that for Fe-rich alloys diffusion has been studied in the disordered A2-structure only. Any influence of the state of order and of order-disorder transitions on the diffusion behaviour is unknown. Such information requires diffusion studies over much wider temperature ranges. Recently, data on the diffusion of Fe and In-isotopes in a wide temperature range have been published [7].

It has been demonstrated that MBS can provide some insight into the atomic mechanism of Fe-atom diffusion in iron-aluminides [1]. However, MBS is not a routine method for diffusion studies. It is limited to a fairly narrow temperature window within which the jump time of Fe-atoms is comparable to the life time of the Mössbauer level of the Fe-isotope. MBS is neither able to provide information about Fe-diffusion over a wide temperature range nor can it provide any information about Al-diffusion. This is why the experimental work on diffusion in FeAl has to be complemented by theoretical research.

The progress in electronic theory allows quantitative predictions of the simple crystal structures of elements, and some binary and ternary compounds, by calculating the ground state energy of these systems (see for example [8,9]). The ability to make accurate predictions has been accompanied by the development of simple, yet reliable nearly free electron or tight-binding models which have provided physical insight into the origin of bonding and structure at the atomistic level (see, for example Refs. [10,11]). The properties of some 3d-transition metal aluminides with equiatomic compositions have been studied in the framework of the local-density-functional (LDF) theory with the full-potential linearized augmented

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plane-wave method to solve the LDF equations[12]. The energies of vacancy formation at the Fe and Al sublattices were calculated (see also Refs. [13,14]).

Diffusivities in a homogeneous alloy can be determined with high accuracy using the radiotracer method. In binary systems for which appropriate radioisotopes for both constituents of the alloy are available, comprehensive information about the diffusion behaviour can be obtained, if both tracer diffusivities are measured in homogeneous alloys of various compositions as functions of temperature. With respect to the Fe-Al system, appropriate and inexpensive radioisotopes are available for the Fe component (*e.g.* ^{59}Fe) but not for Al. Further insight into the diffusion behaviour of Fe-Al intermetallics can also be gained from interdiffusion experiments. In an interdiffusion experiment diffusion couples are formed which initially consist of two homogeneous alloys of different compositions. The composition depth distribution which develops during a diffusion anneal is determined by electron microprobe analysis and evaluated using, *e.g.*, the Boltzmann-Matano method. In this way interdiffusion coefficients $\tilde{D}$ are determined. The interdiffusion coefficient is related *via* the so-called modified Darken equation [15]

$$\tilde{D} = (D_A^* c_B + D_B^* c_A)\Phi S \tag{1}$$

to the tracer diffusivities of the constituents. Here c_i denote molar fractions, Φ the thermodynamic factor and S the vacancy wind factor introduced by Manning [16]. S is usually close to unity. The thermodynamic factor is related *via*

$$\Phi = \frac{c_A c_B}{RT}\frac{\partial^2 G}{\partial c_i^2} \tag{2}$$

to the Gibbs free energy of the alloy. G is equal to $U - TS + p\Omega$ at pressure p and a cell volume Ω. U is the mixing energy, and S is the entropy.

The free energy G may be written in the form

$$G = c_A G_A + c_B G_B + \Delta G(c_A, c_B), \tag{3}$$

where ΔG is the free energy of mixing. This value depends nonlinearly on the molar fractions of components and may be presented by means of different models for solid solutions: regular solid solutions, subregular solid solutions, *etc.* ΔG contains the internal energy of mixing ΔU and the entropy of mixing. Thus Φ is temperature- and concentration-dependent and may also be a function of the state of order of the phases studied. In any case using the representation (3) it is easy to understand that only ΔG contributes the thermodynamic factor Φ. Thus Φ is temperature- and concentration-dependent and may also be a function of the state of order of the phases studied.

The free energy of mixing may be calculated on the basis of the thermodynamical data (see for example Ref. [17]) or by means of non-empirical calculations. In reference [17] the free energy of mixing is given in the form

$$\Delta G = G_e + G_s. \tag{4}$$

In (4)

$$\begin{aligned} G_e &= L c_{Fe} c_{Al}, \\ L &= A(T) + B(T)(c_{Al} - c_{Fe}) + C(T)(c_{Al} - c_{Fe})^2, \\ G_s &= RT[c_{Fe}\ln c_{Fe} + c_{Al}\ln c_{Al}]. \end{aligned} \tag{5}$$

Here $A(T) = -139114.628 + 24.95T$, $B(T) = -58464.74 + 42.67T$, and $C(T) = -14493.54 + 6.938T$. All values are given in J/mole. Making use of equation (5) and of $c_{Fe} + c_{Al} = 1$ we obtain the following expression for Φ

$$\Phi = \frac{c_A c_B}{RT}\left[\frac{\partial^2 G_e}{\partial c_{Fe}^2} + \frac{\partial^2 G_s}{\partial c_{Fe}^2}\right], \tag{6}$$

where

$$\begin{aligned} \frac{\partial^2 G_e}{\partial c_{Fe}^2} &= -[2A(T) + 6B(T) + 10C(T)] \\ &\quad + c_{Fe}[12B(T) + 48C(T)] - c_{Fe}^2 48C(T), \\ \frac{\partial^2 G_s}{\partial c_{Fe}^2} &= RT\left[\frac{1}{c_{Fe}} + \frac{1}{1 - c_{Fe}}\right]. \end{aligned} \tag{7}$$

We use the data available from [17] to calculate Φ for disordered Fe-Al solid solutions. Equation (7) presents $\Phi(c_{Fe}, T)$ in analytical form and, for example, for $T = 1475$ K and $c_{Fe} = 0.735$ the thermodynamic factor is equal to 1.0035. We may check the consistency of this result with the well-known data of behaviour of Φ for different systems. As it was discussed in [15,18] Φ is larger than unity for phases with negative deviations from ideality and smaller than unity in the opposite case. Negative deviations and condition $\Phi > 1$ are expected for systems with the tendency to order or with order. Thus, our result based on the CALPHAD data reflects the atractive interaction between constituents in Fe-Al. The condition $\Phi > 1$ is preserved in the range $0.5 \le c_{Fe} \le 0.75$ for temperatures 700 K $\le T \le$ 1450 K. This fact is illustrated by Figure 1, where we show the surface $\Phi(c_{Fe}, T)$ in these temperature and concentration intervals.

To calculate $\Phi(c_{Fe}, T)$ for intermetallics FeAl and Fe$_3$Al we have to account for concentration and temperature dependences of the long-range order parameters which describe the state of order for these phases. Unfortunately corresponding thermodynamic CALPHAD data for this case are not available. Description of the temperature dependences of the long-range order parameter (LRO) and of the free energy of ordering may be done according to the static concentration wave (SCW) theory [19]. The SCW method allows one to take into account interatomic interactions at arbitrary distances. It establishes the relation between the statistical theory and the Landau-Lifshitz thermodynamical theory of second order transformations in the ordering of alloys.

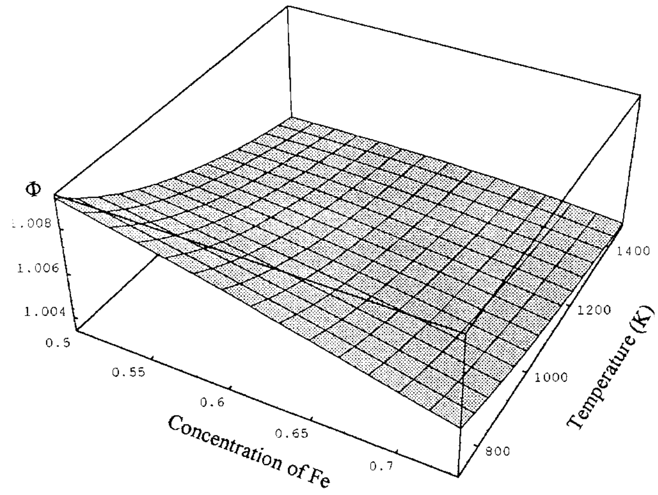

Fig. 1. The thermodynamic factor Φ dependence on the temperature (T, K) and on the concentration of iron for the disordered A2 alloy.

This method provides the possibility of predicting the structure of the ordered phase if the pairwise interatomic interactions are estimated. Thus SCW theory overcomes several principal difficulties of the traditional theories of ordering [20,21]. We combine the SCW theory with the first-principles calculations of the interatomic interaction and evaluate the above mentioned temperature dependences as well as the temperature of the order-disorder phase transformation.

Making use of the SCW theory the internal energy of mixing of completely ordered phase U may be written in terms of pairwise interactions

$$U = \frac{1}{2}V(0)c^2 + \frac{1}{2}\sum_s \gamma_s^2\eta_s^2 V(\mathbf{k}_s). \tag{8}$$

Here c is the mole fraction of the component A in the ordered phase, $V(\mathbf{k}_s)$ is the Fourier transform of the mixing potential $V(R) = V_{AA}(R) + V_{BB}(R) - 2V_{AB}(R)$ that is calculated in the superstructure reciprocal lattice vectors $\mathbf{k}_s$

$$V(\mathbf{k}_s) = \sum_{\mathbf{R}} V(\mathbf{R})e^{i\mathbf{k}_s\mathbf{R}}, \tag{9}$$

η_s - are the long-range order parameters, that are describing the ordering in the superstructure, $V(0)$ is just the same as (9) but for $\mathbf{k}_s = 0$; γ_s are the structural constants depending on the symmetry of the ordering phase. Vectors $\mathbf{k}_s$ pertain to the stars of vectors describing the superstructure. Summation in equation (9) is produced over the stars of vectors satisfying the Lifshitz criterion [22].

As an illustration of this technique we discuss the case of CsCl-type (B2) superstructure. In this case the vector $\mathbf{k}_s$ that is responsible for the formation of this phase from the disordered *bcc* solid solution is $\mathbf{k}_s = 2\pi/a(111)$. As shown in reference [19] $\gamma_s = \frac{1}{2}$ for this structure. The vector $\mathbf{k}_s$ defines the site occupation probabilities for the ordered phase that is stable with respect to the formation of antiphase domains in an alloy. The site occupation probability, $n(R)$, for B2 FeAl superstructure is

$$n(R) = c + \frac{1}{2}\eta e^{2\pi i(x+y+z)}, \tag{10}$$

where x, y, and z are the coordinates of the bcc lattice sites. At $c = \frac{1}{2}$ and $\eta = 1$ this equation describes the completely ordered phase. With equation (9) for this $\mathbf{k}_s$ it is easy to obtain

$$\begin{aligned} V(\mathbf{k}_s) = {} & -8V(R_1) + 6V(R_2) + 12V(R_3) \\ & - 24V(R_4) + 8V(R_5), \end{aligned} \tag{11}$$

and

$$V(0) = 8V(R_1) + 6V(R_2) + 12V(R_3) + 24V(R_4) + 8V(R_5). \tag{12}$$

Here we restricted ourselves to five coordination shells of the Ising lattice. Now we can get the expression for the stoichiometric composition of B2 phase energy in the form

$$U = \frac{3}{2}V(R_2) + 3V(R_3) + 2V(R_5). \tag{13}$$

It is obvious that this mixing energy in the ground state depends only on the interaction potential between atoms in such a binary phase. If this potential is known it is possible to calculate the temperature dependence of the long-range order-parameter using the equation of the Bragg-Williams (BW) type

$$\ln\left[\frac{(1-c-1/2\eta)(c-1/2\eta)}{(1-c+1/2\eta)(c+1/2\eta)}\right] = \frac{V(\mathbf{k}_s)}{kT}\eta, \tag{14}$$

and the temperature of the order-disorder phase transition

$$T_c = -\frac{c(1-c)V(\mathbf{k}_s)}{k}\cdot \tag{15}$$

Here k is the Boltzman constant. Substituting $\eta(T)$ dependence into equation (8) one can immediately obtain the temperature dependence of the internal energy of mixing.

Expression for the free energy of mixing $\varDelta G$ (neglecting of $P\varOmega$ term) is

$$\begin{aligned} \varDelta G = {} & \frac{1}{2}V(0)c^2 + \frac{1}{8}V(k_s)\eta^2 + \frac{1}{2}kT[(c+\frac{1}{2}\eta)\ln(c+\frac{1}{2}\eta) \\ & + (1-c-\frac{1}{2}\eta)\ln(1-c-\frac{1}{2}\eta) + (c-\frac{1}{2}\eta) \\ & \times \ln(c-\frac{1}{2}\eta) + (1-c+\frac{1}{2}\eta)\ln(1-c+\frac{1}{2}\eta)] \end{aligned} \tag{16}$$

Differentiating $\varDelta G$ twice with respect to concentration we obtain $\varPhi$ as a function of concentration and temperature.

This dependence is included not only directly but also from the dependence of LRO parameter, which is obviously included in Φ and has to be calculated for each temperature and concentration from (14). The value of $V(\mathbf{k}_s)$ may be obtained from diffuse X-Ray scattering data as discussed in reference [19] or may be calculated by means of first-principles calculations.

These results allow us to make predictions of the temperature dependences of the LRO parameter and of the free energy of this phase. With the assumed Morse-type potential form of the effective pair interaction (see, for example [23])

$$V(R) = A - 2Be^{-\lambda(R-r_0)} + Be^{-2\lambda(R-r_0)}, \tag{17}$$

we obtain the potential of mixing. We may estimate parameters A, B, r_0 and λ to write down U with these parameters (see Eq. (13)) and to fit to the U *vs.* volume dependence calculated *ab initio*. Taking into account equation (11) the value of $V(\mathbf{k}_s)$ may be determined, that gives us the temperature of phase transformation T_c. Direct evaluation of $V(\mathbf{k}_s)$ values from the $U(\Omega)$ dependence is not obvious because $V(0)$ and $V(\mathbf{k}_s)$ enter equation (8) in a symmetric form for the absolutely ordered B2-phase in stoichiometric composition. Equation (8) for this case has the form

$$U = \frac{1}{8}V(0) + \frac{1}{8}V(\mathbf{k}_s), \tag{18}$$

that leads to the arbitrary evaluation of $V(\mathbf{k}_s)$, and the estimation of the transition temperature becomes non-unique.

Using the obtained mixing potentials $V(R)$ we may calculate $V(0)$ and $V(\mathbf{k}_s)$, and we use these values for calculations of the free energy of mixing (see Eq. (17) for an example). This gives a direct opportunity for *ab initio* calculations of the thermodynamic factor Φ.

We have suggested in this paper the possibility for phenomenological and *ab initio* calculations of the thermodynamic factor in interdiffusion. We discussed also the applicability of the effective potential approach based on non-empirical calculations applied to the problem of evaluating the energetic parameters of the ordering process. The scheme for calculation of the volume dependence of the internal mixing energy was suggested and for simplicity was illustrated by the example of B2-phase (FeAl). The parameters of the effective potential may be estimated by fitting to the mixing energy. The latter allows one to perform calculations of the temperature dependence of the LRO parameter in the framework of static concentration waves theory of Khachaturyan. In contradiction to the traditional approaches for the description of the ordering process, we do not evaluate the partial pair potentials in our scheme. Using this formalism we have demonstrated the principal possibility of the prediction of the temperature of the order-disorder phase transition. The quality of this prediction in the case of FeAl can be checked from X-ray measurements of the diffuse scattering.

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