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Abstract. Be is a small atom ($V = 4.89$ cm^3 mol^{-1}) compared with Fe and Sn ($V = 7.09$ and 16.30 cm^3 mol^{-1} respectively). As a result, size mismatch theories predict an attractive component of the potential between Be and Sn when dissolved in iron. We present spectra of ^{119}Sn in a FeBe alloy, from which we deduce repulsive interactions at first- and second-neighbour distances. The first-neighbour interaction is in fair agreement with the semi-empirical theory of Miedema and Krolas. The repulsive interaction at the second-neighbour distance contradicts the expectation developed in earlier papers. We also make some comments on the influence of solute–solute interactions on the deduction of probe–solute interaction potentials.

1. Introduction

1.1. Earlier results and their interpretation

In the last few years, substantial advances have been made in the theory of the physical properties of metals, many of which can now be calculated with high accuracy from quantum mechanical principles (Moruzzi *et al* 1978). Less progress has been made with the more complicated problem of the structure of alloys, and for this reason there has been much interest in semi-empirical theories, of which the most successful is due to Miedema and his co-workers (Miedema *et al* 1977). Working from two parameters for each metal and a small number of correction terms depending on where the metals A and B lie in the Periodic Table, accurate predictions of the heats of solution of A in B can be made.

Miedema treats the metal atoms as small pieces of the metals in contact, and the two parameters are regarded as (i) a measure of the work function, and (ii) a measure of the charge density at the surface of the Wigner–Seitz sphere. In solution, the difference between the work functions leads to a flow of charge from one atom to another, giving rise to a negative contribution to the heat of formation of the alloy. The smoothing of the difference between charge densities at the interface between the atoms makes a positive contribution to the heat of formation.

The physical basis of the Miedema model has been criticised in several publications (Williams *et al* 1980, Chelikowsky and Phillips 1977, Pettifor 1987). We hold the view that the model is inconsistent with the quantum mechanical theory of metals. The adoption of the model, therefore, depends on (i) the simplicity with which a prediction is obtained, (ii) its accuracy, and (iii) the stimulation it may give to new lines of investigation.

In a development of the theory, Krolas (1981) proposed to regard the interaction between two solute atoms B and C, when they become near neighbours in a metal A, as arising from the break up of an AB and an AC bond and the creation of a BC bond. Thus we may write for the binding energy E_b betwen B and C

$$E_b = \Delta E_{BC} - \Delta E_{AB} - \Delta E_{AC} \tag{1.1}$$

where ΔE_{XY} represents the energy of the nearest-neighbour interaction between X and Y. He then compared this expression with

$$\delta H = \Delta H_{BC} - \Delta H_{AB} - \Delta H_{AC} \tag{1.2}$$

where ΔH_{XY} is the heat of solution of X in Y, and plotted E_b against $\delta H/Z$, where Z is the coordination number in the lattice. When the heats of solution were known experimentally, he used the experimental values. When they were not known, he used the value predicted by the Miedema expression.

Krolas observed a good correlation between E_b and $\delta H/Z$. As the heats of formation were known experimentally in only a third of the cases, it is a simple step to calculate $\delta H/Z$ for two atoms B and C dissolved in A entirely from the Miedema parameters. We then call the value of E_b in (1.1) the Miedema–Krolas prediction, E^{MK}.

The discrepancies between E^{MK} and the measured values for 27 pair interactions in hosts Au, Ag, Cu and Fe were considered by Alonso *et al* (1985), and shown to correlate with $(V_A - V_B)(V_A - V_C)$ where V_X is the atomic volume of element X, taken from Gschneidner (1964). The form of this expression was justified by reference to the work of Eshelby (1956), which indicates that the elastic contribution to the heat of solution is quadratic in the size mismatch, i.e.

$$\Delta H_{AB}^{size} \propto (V_A - V_B)^2. \tag{1.3}$$

Assuming that the constant of proportionality is the same in all cases, the given expression follows. The magnitude of the size mismatch term was found to be given by

$$E_{b_1}^{size} = \alpha(V_A - V_B)(V_A - V_C) \tag{1.4}$$

with $\alpha = 1.7\,\text{meV (atomic volume)}^{-2}$.

In a study of the interaction potentials between ^{119}Sn and s–p elements of the fourth period dissolved in iron, Cranshaw (1987a) showed that the best prediction of the potential at the first neighbour distance was

$$E_{b_1}^{pred} = E_{b_1}^{MK} + \alpha(V_A - V_B)(V_A - V_C) \tag{1.5}$$

where $E_{b_1}^{MK}$ is the Miedema–Krolas prediction, and α was again 1.7 meV (atomic volume)$^{-2}$.

At second-neighbour distances, there was no significant correlation between the measured potential and the Miedema–Krolas prediction. On the other hand, there was a strong correlation with atomic volume, giving as an expression for the second-neighbour interaction

$$E_{b_2}^{size} = -36(V_A - V_B)\,\text{meV}. \tag{1.6}$$

Note that for iron and tin, $V_A - V_C$ is -9.2, so that the size mismatch term at first neighbours is $-15.6(V_A - V_B)$, whereas at second neighbours it is $-36(V_A - V_B)$. No explanation can be given for the fact that the size mismatch energy is 2.3 times greater at the second-neighbour distance than at the first-neighbour distance, but one may

speculate that it is a property of the BCC lattice, which is not close packed.

In a later publication (Cranshaw 1987b) it was shown that for the interaction between Sn and transition element impurities, an expression like 1.5 was still a useful predictor of the interaction energy, but with $\alpha = 3.4$. At the second-neighbour distance, almost no correlation could be found between the measured interaction potential and $(V_A - V_B)$, but a least-squares straight line through the data gave almost exactly the same expression as 1.6, though the residuals are very large.

Fitting the data for s–p elements and transition elements at second-neighbour distances with a linear combination of a δV term and a Miedema–Krolas term reduced the RMS error in the prediction by less than 1%, indicating again that the Miedema–Krolas interaction acts only at first neighbours.

In Cranshaw (1987a), a short discussion was given of the uncertainty arising from the lack of definition of the atomic volume to be attributed to the BC atoms when they are near neighbours. This is an important quantity, because it determines the area of the atoms which is supposed to be in contact. The uncertainty was shown in an appendix to be equivalent to an uncertainty in coordination number, Z. It is therefore of interest to find experimentally the value of Z which gives the best predictions. Over all the data on interactions between ${}^{119}Sn$ and solute atoms in iron, the best value is found to be $Z = 8.0$ if the size effects are ignored, and 7.8 if they are included. As $Z = 8$ is the coordination number for BCC iron, we consider that these values confirm that the Miedema–Krolas theory, so far as it can be applied at all, applies to first-neighbour interactions.

A weakness in the above evidence lies in the fact that all the measured second-neighbour interactions are repulsive, and all the values of δV are either small or positive. The test of the hypothesis would clearly be more stringent if an element were found for which δV is negative, leading to the prediction of an attractive force at the second-neighbour distance, and an attractive component at the first-neighbour distance. The only atom smaller than iron which can be expected to dissolve in iron substitutionally is Be, and in this work, we present observations on an alloy of iron containing approximately 4% Be and 0.2% ${}^{119}Sn$.

1.2. The basis of the deduction of interaction potentials

We suppose that when one atom of element B and one atom of element C are dissolved in a third element A, the energy of the system depends on the distance between B and C. In order to design a practical experiment, we are forced to use finite concentrations of B and C in A. It is fortunate that good Mössbauer spectra of ${}^{119}Sn$ in iron can be obtained with an Sn concentration of 0.2%. Interactions between Sn atoms can then be neglected. A concentration of alloying element of about 3% gives reasonable numbers of B–C pairs. We then envisage neighbour shells around the Sn atom at which the potentials are E_{b_i}, $i = 1, 2 \ldots$ The concentration, C_i, of B atoms in these shells is given by (Hrynkiewicz and Krolas 1983)

$$C_i(1 - C_i)^{-1} = C_\infty(1 - C_\infty)^{-1} \exp(-E_{b_i}/kT) \tag{1.7}$$

where C_∞ is the concentration far from Sn atoms, or, in dilute systems, the sample concentration.

1.3. Solute–solute interactions

In the work on transition element solutes, it was noted that the components due to Sn atoms with a Cr first neighbour or second neighbour (called x and z in the histogram of the probability distribution of H) were sharp, but that a broad component was present

which was attributed to Sn atoms with third-neighbour Cr atoms. This implies that when a Sn atom has either a first- or second-neighbour Cr atom, it does not have third-neighbour Cr atoms. It has been a central assumption in this work that the spatial distribution of atoms is the result of central pair-wise interactions, and therefore this result must be attributed to interactions between pairs of Cr atoms. It was pointed out that DO_3 ordering, in which the Cr atoms would be confined to one FCC sublattice of the BCC iron lattice would bring about the required distribution of Cr atoms, though DO_3 ordering does not occur in iron–chromium alloys near 25% Cr, and is unlikely to occur at concentrations near 5% Cr. Nevertheless, because the spectra of ^{119}Sn in alloys of iron with Be and Cr bear some resemblances to each other, we feel it necessary to reconsider the problem of the effects of interactions between the atoms of the minor constituent of the alloy on the measurement of the interactions between these atoms and the tin probe.

Accordingly, we envisage an extreme model, called model III to distinguish it from the models used earlier, in which the solute atoms, for example, Be atoms, even at low concentrations are confined to one FCC sublattice of the BCC lattice, in accord with DO_3 order, and disregard the question of what Be–Be atom interactions might bring this about. The concentration of solute atoms on the FCC sublattice is then $4C$ where C is the alloy concentration, and even in the absence of interactions between Sn atoms and Be atoms, the probabilities of occurrence, $p(i, j, k)$, of Sn atoms with i, j, k Be atoms in the first-, second- and third-neighbour shells are strongly affected. In fact, $p(i, j, k) = 0$ if any two of i, j, k are not equal to 0. This clearly has implications for the deduction of interaction potentials from equation (1.7), and in the present work we have therefore used not only the fitting routines described in the earlier papers, but an additional routine based on the extreme model just described.

2. Experimental details

An ingot of iron with 0.5 wt% Be was made at the Royal Ordnance Factory, Cardiff. Pieces of foil rolled from this ingot to 125 μm thickness and approximately 20 mm square were cleaned by ion bombardment in an evaporating chamber, and the correct quantity of ^{119}Sn evaporated onto both sides to achieve an atomic concentration of 0.2%. The foil was then sealed in a silica capsule under $\frac{1}{3}$ atm of argon, and heated at 1273 K for 48 h to permit diffusion of the Sn throughout the foil.

The capsule was removed from the furnace and allowed to cool. Under these conditions, diffusion effectively ceases at about 700 K, and in the analysis, the state of the foil is assumed to correspond to thermodynamic equilibrium at this temperature. The spectra were taken in a conventional constant velocity spectrometer at 77 K.

The concentration was checked by taking a ^{57}Fe spectrum of a foil rolled to 25 μm. The intensities of the two satellite lines corresponding to iron with one or two Be neighbours were 24.5 and 2.2% respectively, leading to an estimate of the Be concentration of 3.6% atomic.

3. Results

3.1. Model I

The ^{119}Sn spectrum can be seen in figure 1. Below the spectrum is shown the probability distribution of H, called $p(H)$, computed using the methods of Le Caer and Dubois (1979). The value of $p(H)$ has significant intensity in three regions marked x, y, and z. The regions marked x and z are attributed to Sn atoms with Be atoms in the first- and

	1st shell	2nd shell	3rd shell
(a)			
ΔH (kOe)	65	−33	14
c (%)	0.41	0.87	(3.6)
E_b (meV)	131	85	(0)
E_b^{MK} (meV)	163	0	
E_b^{size} (meV)	−34	−79	
(b)			
ΔH (kOe)	65	−33	10
E_b (meV)	122	69	0

Table 1. *(a)* The values of the parameters found by fitting the spectrum shown in figure 1, using model I described in the text. ΔH is the change in hyperfine field, and c the Be concentration in each shell. The concentration in the third shell is not well determined, and is assumed to be the specimen concentration. In the third row, E_b is the measured value of the interaction potential. In the fourth row, E_b^{MK} is the potential predicted by the Miedema–Krolas model and in the fifth row, E_b^{size} is the interaction predicted for size mismatch effects. *(b)* The values of the parameters found by using model III described in the text.

second-neighbour shells respectively and the region marked y is attributed to Sn atoms with Be atoms in the third neighbour shell. Although the spectrum is not as striking as the spectra for Cr alloys, it is clear that the region y is appreciably broader than the regions x and z, implying that when the Sn atom has a first- or second-neighbour Be atom, it does not have Be atoms in its third-neighbour shell. We have used a model (called model I) which excludes such configurations for fitting the spectra of ^{119}Sn in transition-metal alloys (Cranshaw 1987b). The same program can be used to fit the present spectrum, and gives the result shown in table 1 *(a)*. The first row gives the value of ΔH_i, the change of field produced by the presence of a Be atom in the ith neighbour shell, $i = 1, 2, 3$. For $i = 1$ and 2, the values of ΔH are quite well determined, but the value found for the third shell depends crucially on the value of c_3, the concentration of Be in the third shell. The data are not sufficiently accurate to determine both ΔH_3 and c_3 together. We have assumed $c_3 = 3.6\%$, which is equivalent to assuming E_{b_3}, the potential at the third-neighbour distance, is zero. Because of this uncertainty, c_3 and E_{b_3} are written in brackets.

The second row gives the concentration of Be found in the first and second shell derived from the intensity of the corresponding component. We regard these values of the concentration as the equilibrium values at about 700 K. It is then straightforward to deduce the strengths of the potential at the first and second shells using equation (1.7), and these are given in the third row. The fourth and fifth rows give the predicted potentials, using the expressions given in the introduction.

3.2. Model III

In model III, Sn atoms may lie on any of the four FCC sublattices of the BCC lattice. Two of these, I and II, are equivalent, and can have four Be atoms in their first-neighbour shell. Sn atoms on sub-lattice III can have six Be atoms in their second-neighbour shell, and Sn atoms sharing sublattice IV with Be atoms can have 12 Be atoms in their third-neighbour shell. The interaction between Be atoms and Sn is now expressed by the differential occupation of these four sublattices by Sn atoms.

Let us suppose that for any sublattice, i, the probability of j Be atoms in the appropriate neighbour shell is given by $p(0), p(1), \ldots, p(j), \ldots$. The energy of a Sn atom on this sublattice will be $0, E_{b_i}, 2E_{b_i}, \ldots, jE_{b_i}$ according to the number, j, of its neighbours. Therefore the relative occupation of these sites at temperature T will be

$$1, r_i, r_i^2, \ldots, r_i^j \tag{3.1}$$

where $r_i = \exp(-E_{b_i}/kT)$. If, for simplicity, we assume that the p are given by a Poisson distribution, with mean m_i, i.e.

$$p(j) = \exp(-m_i)(1, m_i, m_i^2/2!, \ldots, m_i^j/j!, \ldots \qquad (3.2)$$

the relative occupation of the Sn sites will be

$$q(i) = A(1, m_i r_i, (m_i r_i)^2/2!, \ldots, (m_i r_i)^j/j!) \qquad (3.3)$$

i.e. a Poisson distribution with mean $m_i r_i$. In thermal equilibrium, the occupation of all zero energy sites must be equal, since atoms can be exchanged among them with no change of energy. It follows that A is given by $\exp(-m_i)$.

We have therefore to compute three components of the spectrum corresponding to the three crystallographically distinct sublattices with the relative numbers of possible Sn sites 0.5, 0.25 and $0.25 - 4C$. The magnitudes of the fields are $H_{000} + j\Delta H_i$, where H_{000} is the field at Sn in the absence of neighbours in the first three neighbour shells. In our case we have two values of r, r_1 and r_2, for the first- and second-neighbour shells. In the third-neighbour shell, we assume $r_3 = 1$.

This model was checked by a Monte Carlo calculation using a BCC lattice of dimensions $20 \times 20 \times 20$ containing 576 Be atoms and 32 Sn atoms, corresponding to concentrations of 3.6 and 0.2% respectively. The values of E_{b_1} and E_{b_2} were set at 100 meV, and the temperature at 700 K. Two initial conditions could be chosen corresponding to (i) a high temperature giving a random distribution of Sn atoms, (ii) a low temperature with all Sn atoms on the Be sublattice. The method of Metropolis *et al* (1953) was used, and after 150 exchanges of Sn atoms with Fe atoms, no difference could be detected between the final distributions of Sn atoms, indicating that thermal equilibrium had been reached. After applying equations (3.1)–(3.3) an average of 3000 repetitions gave values of E_{b_1} and E_{b_2} of 89 and 92 meV, in satisfactory agreement with the initial conditions.

The results of the fitting by model III are given in table 1(*b*), and the components due to Sn atoms on the three inequivalent sublattices are drawn on figure 1. As expected, the strengths of the interaction potentials given by model III are lower than those given by model I, an effect which is greater at second neighbours than at first.

4. Discussion

4.1. Errors in determination of potentials

4.1.1. Errors of statistical origin. We have determined the errors which arise from the statistical nature of the data for model III in the following way. From the original spectrum, sixteen new spectra were generated by adding to the count y_i in the ith channel a random number from a Gaussian distribution with mean zero and variance y_i, $i = 1$, 512. We have thus a set of spectra differing from each other by the same amount that the original spectrum may be supposed to differ from the ideal spectrum with infinitely many counts in each channel. These spectra were then fitted by the program for model III and the values of the relevant variables noted. The variance of these values is taken to be the variance of the values found for the original spectrum.

The RMS error on the potential values E_{b_1} and E_{b_2} found in this way for model III are 7 and 5 meV respectively, quite comparable with the value 13 meV found for Cr alloys obtained by observing the results for several different spectra. The RMS error on the values of ΔH of statistical origin is 3.5 kOe.

4.1.2. Uncertainties due to model dependency. We have discussed briefly the effect that
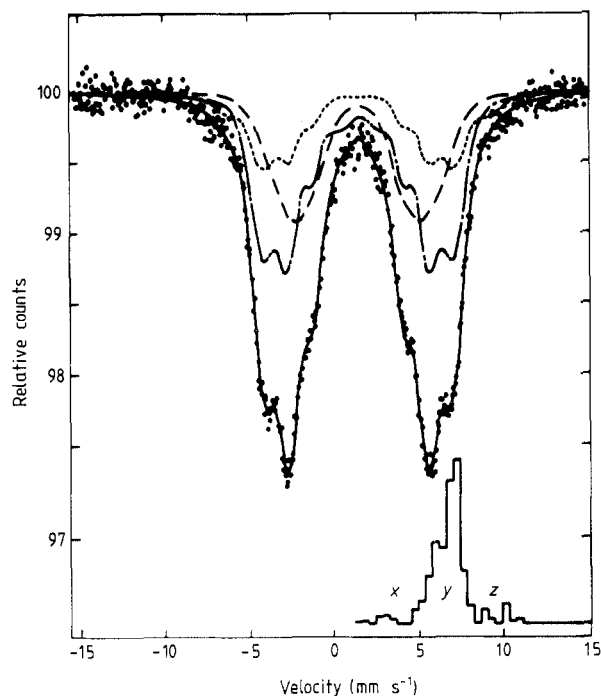
Figure 1. The spectrum of 0.2% ^{119}Sn in an alloy of iron with 3.6% Be. The full curve is the fit obtained using model III described in the text, and the broken lines show the components contributed by the three inequivalent sublattices: —·—·—, component x (first-neighbour Be atoms); — — — component y (third-neighbour Be atoms); ·····, component z (second-neighbour Be atoms).

Be–Be interactions may have on the deduction of the strength of Be–Sn interactions in the introduction, and have now shown that a rather extreme model of Be ordering produces changes of the order of 20% in the estimated value of the Be–Sn interaction. Using the same model for an iron–chromium alloy described in Cranshaw (1987b) changed the estimate of the Cr–Sn interaction at the first-neighbour distance from 59 meV to 48 meV.

A further complication arises when ordered or partially ordered models are contemplated, relating to the line widths of the components. We regard line widths greater than the natural width as due to the effects of many small changes of hyperfine field produced by distant neighbours. If the alloys are random, the extra width is the same for all sites; if the model is strongly ordered, this cannot be relied upon. We have found by experience that some models, and particularly model III become unstable and give unphysical results, such as negative intensities, if all line widths are treated as variables. As a matter of practical necessity, they have therefore been treated as the same.

4.2. Interaction potentials

Bearing in mind the comments in 4.1, table 1 (a) and (b) show that the predicted value of E_{b_1} is consistent with the range of values deduced from the spectra. At the second-neighbour distance, the predicted value of E_{b_2} is in sharp disagreement with the observations.

In an earlier paper (Cranshaw 1987b), we mentioned that the lattice expansion caused by the solution of the alloying element might *a priori* be thought to be a more reasonable parameter to account for size mismatch effects than atomic volume, but noticed that in the case of s–p elements, the parameter $d \ln a/dc$, where a is the lattice parameter and c the concentration correlated less closely with E_{b_2} than δV, the difference

in atomic volume. In the present case, Be causes a strong reduction of the lattice parameter, i.e. d ln a/dc is negative in contrast to the s–p elements under consideration, but E_{b_2} has the same sign as is found for the s–p elements. We cannot escape the conclusion that size mismatch effects whether described by δV or d ln a/dc do not adequately describe the interaction found at second-neighbour distances.

4.3. Earlier work

In earlier work, we found closer agreement between the predictions of the Miedema–Krolas theory and the measured values for s–p elements than for transition elements and the values of E_{b_2} for s–p elements behaved in a more regular fashion than the values for transition elements. It now seems possible that this may be due to a more irregular behaviour of solute–solute interactions between transition element atoms than between s–p element atoms.

5. Conclusion

(i) We have measured the interaction potential between [119]Sn atoms and atoms of Be dissolved in iron at the first- and second-neighbour distances. The interaction at the first-neighbour distance is in good agreement with the Miedema–Krolas theory, but at second-neighbour distances there is sharp disagreement with predictions based on size mismatch effects.

(ii) We have investigated possible effects of the interaction between solute atoms on the deduction of interaction potentials between the probe atom, Sn, and the alloying solute atoms. We find that at the concentrations used in this work, different assumptions about the spatial distribution of solute atoms can result in values for the interaction potentials differing by about 20% from each other.

Acknowledgment

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