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THEORY OF POINT DEFECTS AND THEIR INTERACTIONS
(Part II)

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5. Theory of point defect interactions

This is the point at which we must turn to discuss the interaction between point defects. We will first treat, in some detail, the so-called electrostatic model of such interactions in a Fermi gas. Later in the section, we shall then pay some attention to the contribution of size effects to vacancy-solute interactions in dilute metallic alloys.

5.1 Electrostatic model

Below, for simplicity of presentation, a semi-classical argument will be employed, following Alfred and March (1957). The essential result is, in fact, valid in a fully wave-mechanical treatment, as established by Corless and March (1961).

Let us suppose that point defects, 1 and 2, carrying excess charges Z_1e and Z_2e, are embedded in the bath of conduction electrons, such that the screened potential energy due to ion 1 alone is V_1 and that due to 2 is V_2. Then in the linear (Born) approximation of section2, it is evident that the total potential V due to the two defects has the superposition value

$$V = V_1 + V_2 \tag{5.1}$$

Hence each point defect is surrounded by its own displaced charge which, in such a linear theory is unaffected by bringing up further defects.

The interaction energy between the point defects, separated by a distance R say, may now be obtained directly by calculating the difference between the total energy of the metal when the point defects are separated by an infinite distance, and when they are brought up to the mutual separation R. Clearly this process is to be carried out in the Fermi sea of constant overall density and the result for the interaction energy between the point defects will depend on the conduction electron density, or equivalently on the Fermi energy.

5.1.1 Changes in Kinetic and Potential Energy

Let us consider separately the changes in the kinetic and the potential energy. The act of introducing a point defect carrying a charge, Ze say, into the Fermi gas changes the kinetic energy, since, in the semi-classical Thomas-Fermi method, the forerunner of modern density functional theory, the kinetic energy T is given in terms of the electron density $\rho(\underset{\sim}{r})$ by

$$T = c_k \int \{\rho(\underset{\sim}{r})\}^{\frac{5}{3}} d\underset{\sim}{r} \quad : \quad c_k = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}} \tag{5.2}$$

amd hence, if the point defect perturbs the initially uniform density ρo by $\Delta\rho = \rho - \rho o$, then the kinetic energy change from the unperturbed Fermi gas state is clearly, for small $\Delta\rho$, given by

$$T - T_o = E_f \int \Delta\rho d\underset{\sim}{r} + \frac{E_f}{3\rho_o} \int d\underset{\sim}{r}\, (\Delta\rho)^2 + 0(\Delta\rho^3) \tag{5.3}$$

One notes that the first term on the right-handside involves simply the normalization condition for the displaced charge, or in other words, the condition that the defect charge Ze is screened completely by the redistribution of electrons. Clearly such a term can make no contribution to the energy difference between infinitely separated point defects and the pair of defects at finite separation R.

One is now in a position to calculate the changes in both kinetic and potential energies when the defects are brought together from infinite separation. One can, in fact, readily write down the following contributions:

(i) The interaction energy between the charge Z_1e of one defect and the perturbing potential V_2 due to the other.

(ii) The interaction energy between the displaced charge $\frac{q^2}{4\pi e^2}V_1$ round the first defect and the potential V_2 due to the other.

(ii i) The change in kinetic energy.

These three terms are evidently given by:

$$\text{(i)} \quad Z_1Z_2e^2\exp(-qR)/R \tag{5.4}$$

$$\text{(ii)} \quad \frac{-q^2}{4\pi e^2} \int d\underset{\sim}{r}\ V_1V_2 \tag{5.5}$$

$$\text{(iii)} \quad \left(\frac{-q^2}{4\pi e^2}\right)^2 \frac{E_f}{3\rho_o} \left[\int d\underset{\sim}{r} \left\{ (V_1 + V_2)^2 - V_1{}^2 - V_2{}^2 \right\}\right]$$

$$= -\frac{q^2}{4\pi e^2} \int d\underset{\sim}{r}\ V_1V_2 \tag{5.6}$$

where (iii) follows essentially from eqn (5.3). Thus the contribution (ii) is precisely cancelled by the change in kinetic energy and one is left with the final result for the interaction energy $\Delta E(R)$:

$$\Delta E(R) = Z_1Z_2e^2 \exp(-qR)/R \tag{5.7}$$

But this is simply the electrostatic energy of a defect of charge Z_1e sitting in the electrostatic potential $(Z_2e/r)\exp(-qr)$ of the second defect. Before the argument presented above was given by Alfred and March (1957), Lazarus (1954) had anticipated that such a result should hold on physical grounds, in the context of a discussion on impurity diffusion in metals. It must be stressed that this electrostatic model is only precise if one restricts the discussion to the framework of the linear theory treated above.

In reality, the work of Corless and March (1961), and the independent study of Blandin (1961), shows that in a full wave theory, the interaction $\Delta E(R)$ is oscillatory at large R, the exponential decay in eqn (5.7) being an artifact of the use of the semi-classical theory (analogous to using 'geometrical optics') instead of the fully wave-mechanical theory of Corless and March

(1961; see also Ziman, 1964).

However, while the above treatment leads to relatively small vacancy-solute finding energies, in particular, in agreement with experiment, in a fully realistic theory size effects (i.e. relaxation round the solute) have to be incorporated, and this will be the focus of the remainder of this section.

5.2 Size versus bonding effects on vacancy-solute interaction

Benedek (1987) has considered very recently relations between vacancy-solute binding energies and bulk properties in metals. Below, an outline of his arguments, and a summary of his conclusions, will be presented.

His work is based on the analysis by Rockosch (1983) of diffusion data by means of the so-called five frequency model plus an ansatz due to Arnhold (1981) to find vacancy-solute binding free energies G_{vs} for 7 Cu-based and 5 Ag-based alloys.

In the light of this set of data, Benedek considers the relation between vacancy-solute binding energies E_{vs} and three 'bulk' properties:

(i) The valence difference $\Delta Z = Z_s - Z_h$

(ii) The slope of the solidus curve and

(iii) The lattice constant change per unit solute concentration.

The third of these was found by Rockosch to display a strong correlation with G_{vs}. In the work of Benedek, simple models are developed which predict linear relations between vacancy-solute binding energies and either dT_m/dc_s or da/dc_s, the subscript s denoting solute, and h denoting host.

The second of these relations is in excellent overall agreement with the values derived by Rockosch.

5.2.1. Slope of melting curve

The possible correlation between the melting curves of alloys and E_{vs} has been noted previously by Gorecki (1974) amongst others. The treatment by Gorecki is based on the assumption that the concentration of vacancies at the melting temperature is constant along the solidus curve. Benedek reports, without detail, a different model which predicts that E_{vs} is proportional to the slope of the solidus curve in the dilute limit,

$$E_{vs} = A \frac{d\ln T_m}{dc_s} \qquad (5.8)$$

where the proportionality constant is related to the vacancy formation energy of the pure host E_{1v} and the coordination number z by

z)

z)

$$A = - E_{1v}/z \qquad (5.9)$$

However, the quantitative agreement between eqn (5.8) and experiment is found to be poor, and this relation will not be pursued further here.

5.2.2 Lattice constant change

As already mentioned, Rockosch exposed a strong correlation between E_{vs} and the lattice constant change da/dc_s. In an Appendix, Benedek's use of the 'quasiatom' (or 'embedded' atom) concept (Stott and Zaremba, 1980; Daw and Baskes 1984) to obtain a proportionality between E_{vs} and $d\ln a/dc_s$ is summarized. Specifically, he finds

a/

$$E_{vs} = A \frac{d\ln a}{dc_s} \qquad (5.10)$$

where

$$A = - \frac{9B\Omega}{z} \left[\frac{d\ln n_{at}(R_1)}{d\ln R_1} \right]^{-1} \qquad (5.11)$$

Here B is the bulk modulus, Ω is the atomic volume and n_{at} is the atomic charge density of host atoms determined, say, from a Hartree-Fock calculation (Benedek has employed the wave functions given by Mann (1968) to find some values of A for particular hosts: these being in eV: Cu;1.23; Ag; 1.29. Ni, 1.50, Al, 0.83 and Nb, 2.31).

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The above equations predict that 'oversized' solutes, i.e. those for which $da/dc_s > 0$, have positive binding to vacancies. In Benedek's model described in the Appendix, the 'driving force' for this binding is the preference of such solutes to reside in regions of low electronic charge density. This preference according to Benedek is manifested both in the positive dilatation of the lattice surrounding a solute atom and in an attraction between a solute atom and a vacancy. In this picture, oversized atoms are also expected to segregate to voids and free surfaces, where the background electronic charge density is lower than at bulk substitutional sites.

Figs. 5 and 5. show E_{vs} as a function of $d\ln a/dc_s$ for Cu- and Ag-based alloys respectively. In the case of Cu, most of the points fall on a linear curve, although the slope is about 25% lower than that predicted by eqn (5.11). No explanation is offered by Benedek as to why Ge does not fit the general pattern.

In the case of Ag, shown in Fig.5, 4 of the solutes closely follow the prediction of eqn (5.10). For the Ag(Zn) system, however, the observed binding energy is positive, whereas eqn (5.10) predicts a negative value, since the solute is undersized. Benedek proposes a possible explanation of this discrepancy, to be briefly referred to below. Nevertheless, all the other values of E_{vs} given by Rockosch are predicted to within about 25% by eqn (5.10).

5.2 3 Discussion

Benedek proposes that Ag(Zn) is anomalous in that the tendencies of 'size' and 'bonding' are in conflict, i.e. $d\ln a/dc_s$ and $-d\ln T_m/dc_s$ are of opposite sign. In all of the other systems analyzed by Rockosch, both of these parameters are positive.

In the present context, Benedek also inquires about binding energies for systems for which (dlna/dc$_s$, -dlnT$_m$/dc$_s$) are (+,-) and (-,-). The evidence for such systems is scant. Alloys in the (-,-) category are expected to have a repulsive interaction (i.e. negative E_{vs}) between solute atoms, and vacanices from the standpoint of both 'size' and 'bonding'. One example is Cu(Ni). For this system, Benedek quotes an analysis of diffusion data by Herzig using the method of Rockosch which yields $E_{vs} \cong -0.03$eV; eqn (5.10) also gives a value of $\cong -0.03$eV. However, the close agreement here seems somewhat fortuitous: a similar analysis of diffusion data for C_u(Co), which is also of (-,-) type, gives $E_{vs} \cong +0.02$eV, whereas eqn (5.10) predicts $E_{vs} \cong -0.01$eV. Examples of (+,-) systems are Cu(Pd) and Cu(Pt), but no experimental values of E_{vs} seem to be available. Benedek makes the tentative suggestion that eqn (5.10) should work reasonably well for (+,+) and (-,-) systems, but cannot be regarded as reliable for the (-,+) and (+,-) cases.

Appendix

In this Appendix, following Benedek (1987) a relationship between E_{vs} and dlna/dc$_s$ is derived using the 'quasi atom' (or 'embedded atom') model (cf Stott and Zaremba, 1980). The primary quantity on which these workers focus is the energy E(n) required to embed an atom with a particular atomic number into a homogeneous electron gas with density n. When an atom is embedded in a 'real' solid, the background electron density is, of course, non-uniform and must be approximated either by the superposed charge densities of the surrounding atoms at the embedding point or by a suitable average in the region of the embedding point. If one denotes the energy function of the solute (host) as $E_s(n)$ ($E_h(n)$) then the simplest approximation to the vacancy-solute interaction is given by

$$-E_{vs} = [E_s(n_v)-E_s(n_h)] + [E_h(n_h)-E_h(n_v)] \qquad (A1)$$

where n_h is the background charge density at a substitutional site in the host and n_v is the background charge density at a neighbouring site to a vacancy, lattice relaxation being neglected.

argues

Benedek then agrees that the first term in the square brackets on the right-hand side of eqn (A1) should be dominant. Since the perfect lattice is in equilibrium, one has

$$\frac{dE_h(n_h)}{da} = \frac{dE_h(n_h)}{dn_h} \frac{dn_h}{da} = 0 \quad , \qquad (A2)$$

and therefore $E_h(n_a)-E_h(n_v)\sim(n_h-n_v)^2$ is second-order and presumably small relative to $E_s(n_v)-E_s(n_h)$, which is first order in (n_h-n_v). Benedek then further approximates eqn (A1) by expanding to first order to obtain

$$-E_{vs} = E_s'(n_h)(n_v-n_h) \qquad (A3)$$

Since n_v-n_h is negative, this relation requires that $E_s'(n_h)>0$ for positive vacancy-solute binding energies E_{vs}. Benedek points out that truncation of the power series for E_s at first order makes the present treatment formally equivalent to pair potential models.

The next step (Benedek 1987) is to relate the derivative $E_s'(n_h)$ to the lattice constant change induced by alloying. For a cubic metal, the volume change associated with a single solute atom is given by Hardy (1968) as

$$\Delta V = G/3B \qquad (A4)$$

where B is the bulk modulus. G here is the trace of the 'strength' tensor:

$$G = \sum_l \underset{\sim}{F}_l \cdot \underset{\sim}{R}_l, \qquad (A5)$$

where the sum in eqn (A5) is over lattice sites $\underset{\sim}{R}_l$. Also $\underset{\sim}{F}_l$ is the Kanzaki force on atom l due to a substitutional impurity at l = 0. In the case of a dilute alloy with solute concentration c_s one can write

$$c_s\Delta V/\Omega = 3\delta a/a \qquad (A6)$$

where Ω is the volume of the unit cell while δa is the change in the average lattice constant. Continuing eqn (A6) with eqn (A4) yields

$$\frac{d\ln a}{dc_s} = \frac{1}{9}\,\frac{G}{K\Omega}\,. \qquad (A7)$$

For simplicity, Benedek now terminates the summation in eqn (A5) at the nearest neighbours. In that case

$$G = zF_1R_1 \qquad (A8)$$

where z is the coordination number, F_1 is the Kanzaki force on the first-neighbour shell while R_1 is the near-neighbour distance. Within the embedded atom model, the Kanzaki force can be approximated by

$$F_1 = \frac{1}{\cancel{2}}\;\frac{dE_s(n_h)}{dn}\;\frac{dn_h}{dR_1}\,. \qquad (A9)$$

As a result of eqn (A2), E_h does not appear in eqn (A9). Combining eqns (A7) - (A9) yields

$$-E_s' = \frac{d\ln a}{dc_s}\;\frac{9B\Omega}{dn_h/d\ln R_1}\,. \qquad (A10)$$

Substitution of eqn (A10) in eqn (A3) yields

$$-E_{vs} = \frac{9\,B\,\Omega(n_h - n_v)}{dn_h/d\ln R_1}\;\frac{d\ln a}{dc_s}\;. \qquad \text{(A11)}$$

Further simplification is possible if the charge densities are related to the host atomic charge density n_{at} by superposition. Then using

$$n_h - n_v = n_{at}(R_1) \qquad \text{(A12)}$$

and

$$\frac{dn_h}{d\ln R_1} = \frac{z\,dn_{at}}{d\ln R_1} \qquad \text{(A13)}$$

one can rewrite eqn (A11) as

$$E_{vs} = \frac{-9B\Omega}{z}\left(\frac{d\ln\, n_{at}(R_1)}{d\ln R_1}\right)^{-1}\frac{dha}{dc_s} \qquad \text{(A14)}$$

which is the desired result (Benedek, 1987).

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