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THEORY OF POINT DEFECTS AND THEIR INTERACTIONS

(Part I)

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1. Introduction

The primary point defects in metals are defects in the lattice structure, namely vacant lattice sites and interstitial atoms of the host metal (self-interstitials). These vacancies and self-interstitials can naturally interact with both substitutional and interstitial impurity atoms. Especial attention will be focussed in these introductory lectures on:

(i) The energy E_v required to create a vacancy, by removing an atom from the bulk metal and placing it on the surface.

(ii) Possible relations, in a simple free-electron metal such as open body-centred cubic Na, between the vacancy formation energy and the energy required to form an interstitial in the pure host lattice.

(iii) Vacancy-solute atom interactions.

Since even small concentrations of point defects can have a significant influence on many physical properties and processes in metals, it is, of course, of obvious importance to determine their energy and detailed structure.

As to the structure, this is easily visualized as the defect itself, say a vacancy with some relaxation of neighbouring atoms to the vacant site. The formation energy of a configuration is defined as the difference in energy of a sample with and without the defect.

In addition to formation energy, the migration energy of a given defect is of considerable importance. Using rate theory, applied first to such defect problems by Vineyard (1957), the migration energy of a defect is

usefully approached as a difference in formation energy between a specimen with the defect at the lowest energy "saddlepoint" configuration separating two stable configurations and a specimen with the defect at one of the stable configurations.

Though these lectures are primarily on the theory of point defects and their interaction, we shall conclude this Introduction by noting first that the experimental investigation of point defects in or near thermal equilibrium may be divided up as follows (cf. Seeger, 1973).

(i) Detection, determination of the nature and quantitative measurement of the concentration of point defects in thermal equilibrium.

For metals, important techniques here are:

(a) the comparison of the relative change of specimen length $\Delta l/l_o$ and of the relative change of the X-ray lattice parameter.

(b) the measurement of the γ rays resulting from the annihilation of positions trapped at vacancies, to be discussed in detail in the lectures of Professor Lung.

(ii) Measurement of tracer diffusion.

Here, one is concerned in particular with self diffusion, and generally with the transport of matter, for example, thermo or electrotransport. When taken in conjunction with measurements of type (i) above, such experiments give information on the diffusion coefficients and on the diffusion mechanism in metal crystals.

(iii) Resonance and relaxation experiments.

In this type of experiment, information can be gleaned on the jump frequencies of nuclei and on self diffusion mechanisms. Important in this category are nuclear magnetic resonance measurements (NMR), but Mössbauer studies or ultrasonic relaxation measurements belong also to this classification

But to motivate the electron theory to follow, we want to note finally that empirical relations between vacancy formation energy E_v, melting

temperature T_m and Debye temperature θ have been known for a long time. Although a fully satisfactory theory of these intimate connections has yet to be furnished, some very definite pointers to the origin of such correlations can be obtained from very simple physical models: both electronic in nature and also, essentially, thermodynamic. This affords therefore a natural starting point for developing the theory of point defects in metals.

2. Electron theory model relating E_v and θ for close-packed simple metals

To motivate further the theory outlined below, Table 2.1 records the way in which E_v for a variety of close-packed metals correlates with the Debye temperature θ, following Mukherjee (1965).

Table 2.1

Empirical relation between vacancy formation energy E_v and

Debye temperature θ

(Ω denotes atomic volume and M is the ionic mass)

Metal	$\theta(K)$	$E_v(eV)$	$\theta/(E_v/M\Omega^{2/3})^{\frac{1}{2}}$
Cu	245	1.17	32
Ag	225	1.09	32
Au	165	0.94	34
Mg	406	0.89	34
Al	428	0.75	33
Pb	94.5	0.5	33
Pt	229	1.4	37
Ni	441	1.5	33

2.1 Jellium model of metal of valence Z

To gain insight into the origin of the remarkable correlation displayed in the final column of Table 2.1, consider an elementary free-electron model of a metal of valence Z. Remove an ion at the origin by the device of placing there a point charge -Ze.

Electrons will clearly be repelled from this 'vacancy', and one will consequently find a screened potential energy $V(r)$ describing this point defect:

$$V(r) = \frac{Ze^2}{r} \exp(-qr) \qquad (2.1)$$

where q^{-1} is the Thomas-Fermi screening radius. This length can be thought of as the product of a characteristic velocity, which in an electron gas is clearly the Fermi velocity v_f and a characteristic time, which can be shown to be the period of the Langmuir plasma oscillations of the electron gas, namely $2\pi/\omega_p)$, where ω_p is the Langmuir plasma frequency

(Greek omega)

$$\omega_p = (4\pi\rho_0 e^2/m)^{\frac{1}{2}} \qquad (2.2)$$

where ρ_0 is the conduction electron density and m the electronic mass.

Use of first-order perturbation theory, with the unperturbed wave functions as plane waves $\exp(i\underline{k}\cdot\underline{r})$, enables one to calculate the change in the sum of the one-electron energies, ΔE_s say, as

$$\Delta E_s = \Omega^{-1} \int V(r)d\underline{r} = \frac{2}{3} ZE_f \qquad (2.3)$$

where F_f is the Fermi energy. Plainly, being perturbative, this result (2.3) is strictly valid only for low valency Z.

As already mentioned above, the energy needed to form a vacancy is that required to remove an atom from the bulk metal

and place it on the surface. If atomic relaxation is neglected; a reasonable assumption in the close-packed metals under discussion, then one increases thereby the volume occupied by the conduction electrons by the atomic volume Ω. This reduces the kinetic energy of the conduction electron gas, and one finds, following Fumi (1955), a decrease of $(2/5)ZE_f$. Thus, one may write as a first approximation to the vacancy formation energy E_v:

$$E_v = \left[\frac{2}{3} - \frac{2}{5}\right]ZE_f = \alpha ZE_f \qquad (2.4)$$

where in this model α is simply 4/15.

Now lets us return to the Mukherjee correlation in Table 2.1, and consider next, by a closely related argument, the calculation of the Debye temperature θ. For an isotropic solid, this is related to the velocity of sound v_s by (see, for example, Mott and Jones, 1935)

$$\theta = \frac{v_s}{\Omega^{1/3}} \left[\frac{3}{4\pi}\right]^{\frac{1}{3}} \frac{h}{k_B} \qquad . \qquad (2.5)$$

One then follows Bohm and Staver (1952; see also Bardeen and Pines, 1955) in deriving an expression for the velocity of sound v_s by starting from the ionic plasma frequency $(4\pi\rho_i\{Ze\}^2/M)^{1/2}$, replacing the ion density ρ_i by ρ_0/Z, and in the resulting expression, screening Z by Fourier transforming eqn (2.1) to obtain

$$\frac{4\pi Ze^2}{k^2} \rightarrow \frac{4\pi Ze^2}{k^2+q^2} \qquad , \qquad (2.6)$$

the electrons this time piling up round the positive ion carrying charge Ze to screen out its Coulomb field over a distance $\sim q^{-1}$. In the long wavelength limit $k \to 0$, needed obviously to calculate the velocity of sound, eqn (2.6) means that Z is to be replaced in the ionic plasma frequency, after replacing ρ_i by ρ_0/Z, by Zk^2/q^2, which converts an 'optic' plasma mode into the accoustic mode

$$\omega = v_s k, \tag{2.7}$$

the above argument leading to the desired result

$$v_s = \left(\frac{Zm}{3M}\right)^{\frac{1}{2}} v_f. \tag{2.8}$$

Eqn (2.8) demonstrates that in a metal the velocity of sound is reduced from the Fermi velocity v_f by a factor of order $(m/M)^{\frac{1}{2}}$.

The final step is relating E_v and θ is to use eqns (2.4) and (2.8) to eliminate ZE_f, when one finds (March, 1966)

$$E_v = \frac{3}{2} M v_s^2. \tag{2.9}$$

This eqn (2.9) is important in the sense that it exhibits the fact that E_v is basically related to a 'phonon energy' Mv_s^2. Combining eqns (2.5) and (2.9) leads immediately to the relation exhibited in Table 2.1.

$$\theta = \frac{\text{constant}}{\Omega^{1/3}} \left[\frac{E_v}{M}\right]^{\frac{1}{2}}. \tag{2.10}$$

To recover the constant correctly in Table 2.1, one could choose α, say, in eqn (2.4), to be 1/6 rather than 4/15 given by the above model.

It is worth emphasizing at this point that the relation between θ and E_v has resulted directly from a study of the response of the free electron gas to (i) the repulsive potential (2.1) created by the vacancy and (ii) the attractive potential of a (vibrating) ion. Eliminating the response function between θ and E_v, and thereby some of the free-electron nature of the model, demonstrates the deeper connection of E_v with a phonon energy in eqns (2.9) and (2.10).

To press this latter point, Table 2.2 records results from non-linear electron theory, for essentially the same model as above, due to Stott et al (1970) for valencies from 1 to 5.

Table 2.2

Non-linear electron theory results for vacancy formation energy E_v in units of ZE_f

	Cu	Mg	Al	Pb	Sb
Change in eigenvalue sum plus kinetic energy change	0.194	0.166	0.156	0.138	0.134
Exchange energy correction	0.153	0.130	0.098	0.096	0.087
Self-energy correction	-0.24	-0.21	-0.22	-0.19	-0.19
E_v/ZE_f	0.11	0.09	0.03	0.04	0.03

N.B. Stott et al (1970) estimate errors in last row to range from ±0.04 for Cu to about 0.02 for Sb.

The main point to be emphasized here is that the first row

of Table 2.2 shows the non-linear analogue of eqn (2.4).

However, Stott et al correct these results for (i) the self-energy of the charge displaced round the vacancy and (ii) the exchange energy (they find correlation to be of minor importance in this application), these contributions being seen from Table 2.2 to be large and opposite in sign. Huge cancellation is then seen to occur for polyvalent metals, so that the linear model result (2.4), namely E_v/ZE_f = constant is transcended by the non-linear finding that E_v/ZE_f decreases strongly with increasing valency Z, as is quite apparent from the final row of Table 2.2.

To load into the following section, if one uses measured melting temperatures T_m to form $k_B T_m/ZE_f$, this quantity is found to parallel closely, as a function of valence Z, the variation of E_v/ZE_f in Table 2.2. Another way of expressing this is to note that Lindemann's law of melting is regained when E_v in eqn (2.10) is replaced by $k_B T_m$. Therefore, in section 3 below, a quite different approach will be introduced, designed to expose such a relation between E_v and T_m.

3. **Pair potential theory of E_v : relation to thermodynamics and to T_m**

In this section, a quite different point of view will be adopted to the electron theory treatment of section 2. Since a main objective will be to link E_v with the melting temperature T_m, it is natural now to think of E_v in the hot crystal. Since it is known experimentally that E_v is only weakly temperature dependent in metals, there is no need, with present accuracy of available theory, to distinguish E_v in the hot crystal from the T = 0 value discussed theoretically in section 2.

Bhatia and March (1984), showed that in condensed phases of rare gases, E_v in the hot crystal could be approximately linked, via pair potential theory, to the liquid structure factor $S(k)$ at the melting temperature T_m. More specifically, these workers used the direct correlation function $c(r)$, with Fourier transform $\tilde{c}(k)$ defined by

$$\tilde{c}(k) = \frac{S(k) - 1}{S(k)} \qquad (3.1)$$

to show that

$$[E_v + \tfrac{1}{4} B\Omega] = -\left[\frac{k_B T \ [c(r=0) + 2]}{2} \right]_{T_m}, \qquad (3.2)$$

B^{-1} being the isothermal compressibility K_T and Ω the atomic volume as before.

However, it is known empirically, as referred to above, that $E_v/k_B T_m$ is relatively constant and the present section is concerned with understanding this particular correlation, which is evidently more specific than that embodied in eqn (3.2), which in any case was derived for condensed rare gases.

What will be demonstrated below is that the vacancy formation energy E_v can be usefully discussed in relation to liquid properties, already invoked through $c(r=0)|_{T_m}$ in eqn. (3.2) of Bhatia and March. Specifically, the discussion below relates E_v approximately to departures from the so-called Joule's Law in the dense liquid metal phase at T_m, which law is stated as the independence of the internal energy U on volume.

3.1 Departures from Joule's Law in dense liquids

The usual thermodynamic formula relating the specific heat difference c_p-c_v to the coefficient of volume expansion and to K_T is readily shown to yield the following result for the ratio of the specific heats $\gamma = c_p/c_v$:

$$\gamma = 1 + \frac{S(o)}{c_v} \left\{ \frac{p}{\rho k_B T} + \frac{1}{\rho k_B T} \left[\frac{\partial U}{\partial V} \right]_T \right\}^2 k_B . \qquad (3.3)$$

Here the formula is written for a liquid state (p,ρ,T) with $S(o)$, the long wavelength limit of the structure factor $S(k)$ in eqn. (3.1), related to K_T by a well-established result of fluctuation theory:

$$S(o) = \rho k_B T K_T \qquad (3.4)$$

The introduction of $(\partial U/\partial V)_T$ into eqn. (3.3) was accomplished by utilizing the thermodynamic relation (see, for example, Zemansky, 1951).

$$\left[\frac{\partial U}{\partial V} \right]_v = T \left[\frac{\partial p}{\partial T} \right]_v -p . \qquad (3.5)$$

Below, eqn. (3.3), together with experimental results for γ, c_v and $S(o)$, will be used to estimate the departures for Joule's Law in some dense liquids.

3.1.1 Estimates of $(\partial U/\partial V)_T$ in dense liquids

For a dense liquid like, first of all, argon, near its triple point, it is well known that $p/\rho k_B T \ll 1$ and one can therefore neglect it in eqn. (3.3) to obtain

$$\left| \frac{1}{\rho k_B T} \left[\frac{\partial U}{\partial V} \right]_T \right| \doteq \left\{ \frac{(\gamma-1)(c_v/k_B)}{S(o)} \right\}^{\frac{1}{2}} \qquad (3.6)$$

For this case of argon near its triple point, $\gamma \approx 2.2$, $c_v \approx 2.3 k_B$, $S(o) \approx 0.06$, and one finds from eqn (3.6) that

$$\left| \frac{1}{\rho k_B T} \left[\frac{\partial U}{\partial V} \right]_T \right| \doteq 7, \qquad (3.7)$$

confirming that this is indeed the dominant term in the bracket of eqn. (3.3).

For a liquid metal, say rubidium, near freezing, $\gamma \approx 1.23$, $c_v \approx 3.4 k_B$ while $S(o) \approx 0.023$ and hence from eqn(3.6) one finds the quantity in eqn (3.6) ~ 6.

Below, pair potential theory will be employed to relate such estimates of departures from Joule's Law in dense liquids to vacancy properties in hot close-packed crystals.

3.2 Relation to vacancy formation energy

To relate $(\partial U/\partial V)$ to vacancy properties, Faber's (1972) pair potential formula for the vacancy formation energy E_v, in the $\underline{r}$-space formulation of Minchin et al (1974) will be invoked. This formula, restricted to close-packed solids because of its neglect of atomic relaxation round the vacant site (cf. section 2), can be written in terms of the pair function $g(r)$ and the pair potential $\phi(r)$ as

$$E_v = -\frac{\rho}{2} \int g(r) \, \phi(r) \, d\underline{r} \qquad (3.8)$$

and following Bhatia and March (1984) it can be usefully evaluated from the liquid pair function $g(r)$ near freezing, to yield then, as discussed already, the vacancy energy in the hot close-packed crystal.

What will be accomplished below is to relate E_v to $(\partial U/\partial V)_T$, utilizing microscopic liquid state theory. First, we deal with the simplest case, exemplified by liquid argon in which the pair potential $\phi(r)$ is independent of the density ρ. Then, invoking the usual liquid state theory for the internal energy U, one finds

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{\rho^2}{2} \int \frac{\partial}{\partial \rho} [\rho g(r)] \phi(r) \, dr \tag{3.9}$$

Utilizing the result (3.8) in eqn(3.9) and dividing both sides by $\rho k_B T$ yields (March, 1987).

$$\left[\frac{1}{\rho k_B T} \left(\frac{\partial U}{\partial V}\right)_T\right] = \frac{E_v}{k_B T} - \frac{\rho^2}{2 k_B T} \int \frac{\partial g(r)}{\partial \rho} \phi(r) \, dr \tag{3.10}$$

Using empirical data, it is clear that the dominant term in the vacancy formation energy of hot close-packed crystals like argon is that arising from departures from Joule's Law, the 'correction term' in eqn (3.10) involving the density dependence of the pair function.

Thus one is led to the approximate result

$$\frac{E_v}{k_B T_m} \doteq \left[\frac{1}{\rho k_B T} \left(\frac{\partial U}{\partial V}\right)_T\right]_{T_m} \tag{3.11}$$

Rashid and March (1987, to be published) have shown that eqn (3.11) also works for many close-packed metals, though not for the open body-centred-cubic metals (e.g. Na). This, as we discuss in the following section, is due to the neglect of atomic relaxation round the vacancy : a dominant term in the vacancy formation energy in open structures.

We summarize by saying that E_v is related to $k_B T_m$ by departures from Joule's Law in the liquid near freezing. As discussed for argon and rubidium above, the right-hand side of

eqn (3.11) is a large, rather constant, number ~ 7 - 10, explaining thereby the observed empirical correlation between E_v and $k_B T_m$ in close-packed solids.

We turn below to the case of open body-centred-cubic structures, exemplified by the nearly free electron metal Na, on which we shall focus in the following section. Here, it will be argued that relaxation round the vacancy is of great importance in calculating E_v.

4. Role of relaxation round vacancies and self-interstitials in open body-centred-cubic metals: especially alkali metals

The focus of this discussion is on (i) relaxation round vacancies in the alkali metals and (ii) self-interstitials in such open body-centred-cubic (bcc) structures.

On quite general grounds, it is to be expected that in such open structures, relaxation will play a significant role in calculating the formation energy of point defects. Flores and March (1981) have therefore studied two aspects of ionic relaxation in bcc metals.

(i)   the long-range ionic displacements

and

(ii)   the relevance of local relaxation in calculating vacancy formation energies.

Point (i) will be treated with some generality in section 4.1 below, where attention is focussed on the separate contributions from the elastic, long wavelength, region of the phonon dispersion relations and from the Fermi surface effects on the phonons. Point (ii) is then treated more specifically by referring to the alkalis, for which, with weak electron-ion interactions and consequently almost spherical Fermi surfaces, it is reasonable to adopt a Debye model for the phonons, with implied neglect of the Kohn anomaly. This is shown below to lead again, by quite different arguments, to a Mukherjee-type of relation, much as that discussed for close-packed metals in section 2.

The third aspect treated in this section is the vacancy formation volume. Although this is not immediately related to the local ionic relaxation round the vacancy, it turns out that one can estimate it from the Mukherjee-type of relation referred to above. The ratio of formation volume to atomic volume is then found to consist of two terms: a negative one from a harmonic treatment and a larger positive contribution from the variation of elastic constants with pressure, i.e. an anharmonic term.

4.1   Long-range ionic displacements round a vacancy in metals

The assumption will be made here that a linear theory is valid to discuss ionic displacements far from the vacant site. Then one has the response function T in terms of the phonon frequencies ω_{kp} as (cf Flores and March, 1981)

$$T(\underline{r}) = \frac{1}{MN} \sum_{\underline{k}p} \frac{\exp(i\underline{k} \cdot \underline{r}) \underline{e}_{kp} \underline{e}^{*}_{\underline{k}p}}{\omega^{2}_{kp}} \tag{4.1}$$

where $\underline{e}_{kp}$ denote the polarization vectors. From this linear response function (4.1) one can construct the ionic displacement $\underline{u}(\underline{R})$ at position $\underline{R}$ from the forces $\underline{F}$ as

$$\underline{u}(\underline{R}) = \sum_{\underline{R}'} T(\underline{R}-\underline{R}')\underline{F}(\underline{R}') \ . \tag{4.2}$$

It is now clear from eqns (4.1) and (4.2) that the long-range displacements reflect the singularities in the phonon

dispersion relations ω_{kp}. These singularities, in metals, are known to be of two kinds:

(i) the long wavelength elastic region where $\omega(q) \approx q$

and

(ii) the Fermi surface region as it is reflected in the Kohn anomaly which exists in the phonon spectrum.

The form of the long-range displacements is then given by

$$u(r) \sim u^{elastic}(R) + u^{Fermi\ surface}(R) . \qquad (4.3)$$

Of course, in eqn (4.3) is implied the use of exact (e.g. measured) phonon properties in regions (i) and (ii); naturally in a cubic metal crystal the elastic constants c_{11}, c_{12} and c_{44} are not independent of the presence of the Fermi surface in any first principles theory.

It is known from elasticity theory that $u^{elastic}(R)$ is given asymptotically at large R from the defect centre by

$$u^{elastic}(R) \sim \frac{\Omega}{8\pi M}\left\{ \frac{-1}{v_L^2}\frac{RR}{R^3} + \frac{I}{v_L^2 R} + \frac{1}{v_T^2}\left[\frac{RR}{R^3} + \frac{I}{v_T^2 R}\right] \right\} \quad (4.4)$$

where it proves convenient in eqn (4.4) to subsume the elastic properties into (suitably averaged) longitudinal and transverse velocities of sound u_L and u_T (for derivation, see Flores and March, 1981).

The second contribution from region (ii) above, can be obtained for a given Fermi surface topology, from the arguments of Flores et al. (1979) on the screening of a defect in a metal.

For the case of a spherical Fermi surface of diameter $2k_f$ one finds

$$u^{Fermi\ surface}(R) \sim \frac{\cos 2k_f R}{R^3}\hat{r} , \qquad (4.5)$$

which is evidently a shorter range term than the displacement in eqn (4.4).

Equally important here is that, because of the weak electron-ion interaction in the alkali metals, one expects $u^{Fermi\ surface}$ to have a relatively small amplitude. Though clearly involving approximation except in the limit R tends to infinity, the above arguments strongly point to the conclusion that, in the specific case of the alkali metals, the long wavelength contribution to the ionic displacements will be numerically dominant over the contribution from the Kohn anomaly. This assumption then allows analytical progress to be made, by permitting the adoption of a Debye model for the phonons.

4.2 Forces and local displacements in alkali metals

We turn then from the long-range ionic displacements to the local relaxation round a vacancy in the alkali metals. Though it is clearly an inessential approximation, which could be lifted, should it eventually prove necessary by using numerical summation techniques, we shall assume below that all terms in the sum over force vectors can be omitted other than for those acting on the nearest neighbours. Then one can write for the displacements, from eqn (4.2)

$$\underline{\mu}(\underline{R}) = \sum_{\substack{\text{nearest} \\ \text{neighbours}}} \underline{\underline{T}}(\underline{R}-\underline{R}')\underline{F}(\underline{R}'). \tag{4.5}$$

For the bcc structure shown in Fig. 4.1, let F_i be the force acting on each nearest neighbour due to the vacancy, while $\underline{R}_i$ is the vector from the vacant site to atom i.

4.2.1 Assumption of complete relaxation

Following Flores and March (1981), we shall proceed to estimate the force F_i in the model in which, in any open structure, it is assumed that 'complete relaxation' occurs. Furthermore, for the limit R tends to infinity, the response function $\underline{\underline{T}}$ can be replaced by its asymptotic elastic form, when one obtains (see the Appendix of Flores and March 1981):

$$\underline{\mu} \doteq \frac{\Omega}{M} \frac{2}{3\pi \textsf{v}^2_L} \, hF \, \frac{\underline{R}}{R^3} , \tag{4.7}$$

h being the nearest-neighbour distance for the bcc structure.

Whereas the conventional approach would find the relaxation from a model of the force F due to the vacancy on the nearest neighbours, the model of 'complete relaxation' of the open structure is specified by writing

$$4\pi R^2 u = -\Omega \tag{4.8}$$

or

$$\underline{\mu} \begin{smallmatrix}\text{complete}\\\text{relaxation}\end{smallmatrix} \doteq \frac{-\Omega}{4\pi} \frac{\underline{R}}{R^3} \tag{4.9}$$

Thus by utilizing eqn (4.7) in this model of complete relaxation one finds

$$F_{\substack{\text{complete}\\\text{relaxation}}} = \frac{-3M}{8h} \textsf{v}^2_L . \tag{4.10}$$

Once the force F has been determined from the above model, one can now calculate the displacement near the vacant site, where the full expression for T is to be utilized. However, Flores and March then insert the Debye model for the phonon frequencies at this stage, their result then being

$$u_{\text{nearest-neighbour}} = 0.078h. \tag{4.11}$$

In their calculation, the ratio of transverse to longitudinal velocity of sound has been assumed such that $\textsf{v}^2_L/\textsf{v}^2_T = 4$, though the result (4.11) is not sensitive to reasonable variations around this value.

It is worth noting that had one invoked a purely elastic continuum model, eqn (4.11) would have been replaced by -0.061h, instead of -0.078h in the more realistic approach outlined above.

One can compare the result (4.11) with that obtained by other workers, usually from direct pair potential calculations. Thus, the work of Ho (1971) led to the inward relaxation in the alkali metals of about 8% of the nearest-neighbour distance, in excellent agreement with eqn (4.11).

The conclusion from this comparison seems to be that the assumption of 'complete relaxation' expressed in eqns (4.8) and (4.9) is an excellent one to use for bcc alkali metals. We turn then below to use it to calculate first the vacancy formation energy and then secondly the formation volume.