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1994 J. Phys.: Condens. Matter 6 8487

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# The effect of lattice relaxation and charge transfer on mixing energies and configurational interactions in alloys: cluster calculations for the dilute BCC $\text{Ti}_{1-x}\text{V}_x$ and FCC $\text{Ni}_{1-x}\text{Al}_x$ systems

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Received 2 March 1994

**Abstract.** We present self-consistent LMTO-ASA cluster calculations of the solution energy  $Q$  and the nearest- and next-nearest-neighbour configurational interactions,  $V_1$  and  $V_2$ , for the dilute BCC  $\text{Ti}_{1-x}\text{V}_x$  and FCC  $\text{Ni}_{1-x}\text{Al}_x$  alloys. The lattice relaxation effects (LRE) are described with a proper choice of atomic volumes for the impurity and its neighbours, which are found employing the conventional phenomenological estimates for atomic displacements near an impurity. For the Ti-V system LRE are found to be important, while the charge transfer effects (CTE) are small. The results of our calculations for this system seem to indicate that the phenomenological estimates overestimate LRE contributions to  $Q$  and  $V_i$  by a factor of about two. We also present phenomenological estimates of LRE contributions to  $Q$  for impurities in 24 cubic host metals. For the Ni-Al system LRE are found to be small while CTE are significant, and taking them into account in the cluster calculations of  $Q$  and  $V_i$  seems to noticeably improve their accuracy as compared with single-site approaches.

## 1. Introduction

First-principles approaches to calculations of alloy phase diagrams and thermodynamics have recently received much attention [1–11]. These approaches are usually formulated in terms of an Ising-like Hamiltonian, which for the binary alloy A–B has the form

$$H = V_0 + \sum_i V_1 n_i + \frac{1}{2!} \sum_{ij} V_2^{ij} n_i n_j + \frac{1}{3!} \sum_{ijk} V_3^{ijk} n_i n_j n_k \dots \quad (1)$$

Here the operator  $n_i$  is unity when the site  $i$  is occupied by the atom A and  $n_i = 0$  otherwise, while the coefficients  $V_n$  with  $n \geq 2$  are called the configurational interactions. The quantity  $V_1$  for dilute alloys ( $x = \langle n_i \rangle \rightarrow 0$ ) is equal to the mixing (solution) energy per atom,  $Q$ .

The methods used for the first-principles calculations of  $V$  usually employ either various versions of the coherent-potential approximation (CPA) for the electronic structure of disordered alloys [1–3], or approaches of the Connolly–Williams (CW) type [5–7]. The reference system for the CPA-based calculations is a disordered alloy, while in CW-type approaches the configurational interactions are determined from their fit to the calculated energy values for several ordered intermetallic compounds. Therefore, from general considerations one may expect that for disordered alloys the CPA-based calculations of  $V$  can be more accurate than those using CW-type approaches.

However, a number of important effects are usually neglected in the currently used single-site (SS) versions of CPA-based calculations of  $V$ . Among them, of particular importance seem to be the local lattice distortion, or 'lattice relaxation' effects (LRE), and the charge transfer effects (CTE) between alloy constituents. The importance of both of these effects for the configurational interactions and phase stability of alloys was stressed and illustrated, in particular, in a recent review [7]. However, in the usual SS CPA these effects are disregarded. Other approximations, such as the 'tight-binding' approximation (TBA), are also often used in the currently used calculations of  $V$  (for example, in [2, 4, 8]), while the relevant errors are usually not examined.

In the most recent versions of the CW approach [5–7] the electronic structure and energies  $E_i$  for the ordered intermetallic compounds are calculated with a full allowance for both CTE and LRE (compatible with the crystal symmetry). However, the main assumption of this approach, that the alloy energy for all the concentrations and ordering types, including the disordered phase, can be interpolated by Hamiltonian (1) with the same values of interactions  $V$  (being, therefore, independent of both the concentration and the state of alloy order) raises questions about the convergence of such an interpolation with respect to the number  $N$  of non-zero interactions  $V$  retained. These interactions are determined in [5–7] from their fit to the calculated  $E_i$  for  $N \sim 10$  intermetallic compounds, and the agreement of the obtained interpolation (1) with the  $E_i$  values calculated for several 'extra'  $N' - N$  compounds (or the RMS error in the  $E_i$  fit for some  $N' > N$  intermetallics) is taken as a criterion for the convergence. However, the disordered state differs from the ordered ones in a number of qualitative aspects, in particular, in the character of its electronic structure. Therefore, the above criterion may be not quite informative for it, and the actual convergence of the CW interpolation (1) for the disordered phase can be worse than that for the ordered ones. Let us note in this connection that the phase diagrams calculated in [5, 6] for the  $\text{Ni}_{1-x}\text{Al}_x$  and  $\text{Al}_{1-x}\text{Ti}_x$  alloys, respectively, seem to disagree noticeably with the observed ones just at small  $x$ , i.e. in the description of phase equilibria with the disordered phase. Therefore, the development of direct methods for consistent calculations of configurational interactions in the disordered phase seems to remain a problem in alloy theory.

Adequate methods to treat CTE in the particular case of dilute alloys were developed by Dederichs and co-workers [9–11]. They showed that a self-consistent treatment of clusters including impurities with all their nearest neighbours enables us to properly allow for CTE in the calculations of  $V$ . In the cases when the concentration interval for stability of the disordered phase is not broad (which is characteristic for many intermetallic systems), this relatively simple 'several-impurity-cluster in host metal' approach can provide main interactions  $V$  in the whole range of practical interest. Dederichs and co-workers also found that the conventional single-site approximation (SSA) (corresponding, in particular, to the usual CPA) can be rather misleading in estimates of  $V_d$  when CTE are large. However, these authors did not consider the LRE, although the possible importance of these effects for alloys with a significant mismatch of atomic sizes was repeatedly mentioned in [9–11].

A simple estimate for the LRE (or 'deformational') contributions  $V_d$  to  $V$  in dilute alloys was suggested by Khachatryan and by Cook and de Fontaine [12–14]. They used a phenomenological expression for Kanzaki forces  $F(\mathbf{R})$  determining the lattice distortion energy at a distance  $\mathbf{R}$  from the impurity. Supposing these forces to be of short range, i.e. neglecting  $F(\mathbf{R})$  values for  $\mathbf{R}$  exceeding the nearest-neighbour distance  $R_{nn}$ , they expressed the single remaining parameter  $F(R_{nn})$  in terms of experimentally measurable quantities: the concentrational dilation coefficient and the phonon spectrum of the host metal. Two of the authors [15] recently applied these formulae to estimate resulting deformational interactions  $V_d(\mathbf{R})$  for actual substitutional alloys. We found that in many alloys these

terms are rather significant and can even exceed the other 'electronic' contributions to  $V$ . However, microscopic estimates of the quantities  $F(R)$  are still not available, thus the accuracy of these phenomenological estimates neglecting not-nearest-neighbour Kanzaki forces is, generally, unclear. Therefore, the direct microscopic estimates of deformational contributions  $V_d$  seem to be desirable.

In this paper we consider the lattice relaxation and charge transfer effects on  $Q$  and  $V_n$  values in the dilute BCC  $Ti_{1-x}V_x$  and FCC  $Ni_{1-x}Al_x$  alloys. These systems were chosen for three reasons. Firstly, the quantities  $Q$  and  $V_n$  for them are discussed in a number of theoretical and experimental works [2–5, 16–21], which results can be compared with ours. Secondly, the above-mentioned estimate [15] has shown that LRE in the BCC  $Ti_{1-x}V_x$  alloys are rather large; thus the microscopic treatment of  $V_d$  for this system enables us to appreciate the accuracy of the phenomenological estimates of  $V_d$ . Thirdly, a comparison of present self-consistent cluster calculations of  $V$  with approximate versions employed in the literature (SSA, TBA, the embedded cluster method (ECM) using the 'frozen' SSA electronic potentials within clusters [1]) may illustrate a scale of errors brought about by these approximations in resulting  $V$  for the typical alloy systems considered.

To treat impurity problems we use the linear muffin-tin orbital and atomic sphere approximations (LMTO–ASA) in the Green function method, as suggested by Gunnarsson, Jepsen and Andersen (GJA) [22], being combined with the cluster methods developed by Dederichs and co-workers [9–11]. Employing ASA implies disregarding the non-sphericity of both the electronic potential and charge distribution, which can lead to some errors, particularly in calculations of the solution energy  $Q$  [10]. On the other hand, the transparency and flexibility of the ASA also enables us to approximately treat LRE (which seems to be difficult for other methods), as well as to simply analyse the importance of different contributions to  $V$  and errors brought about by various approximations.

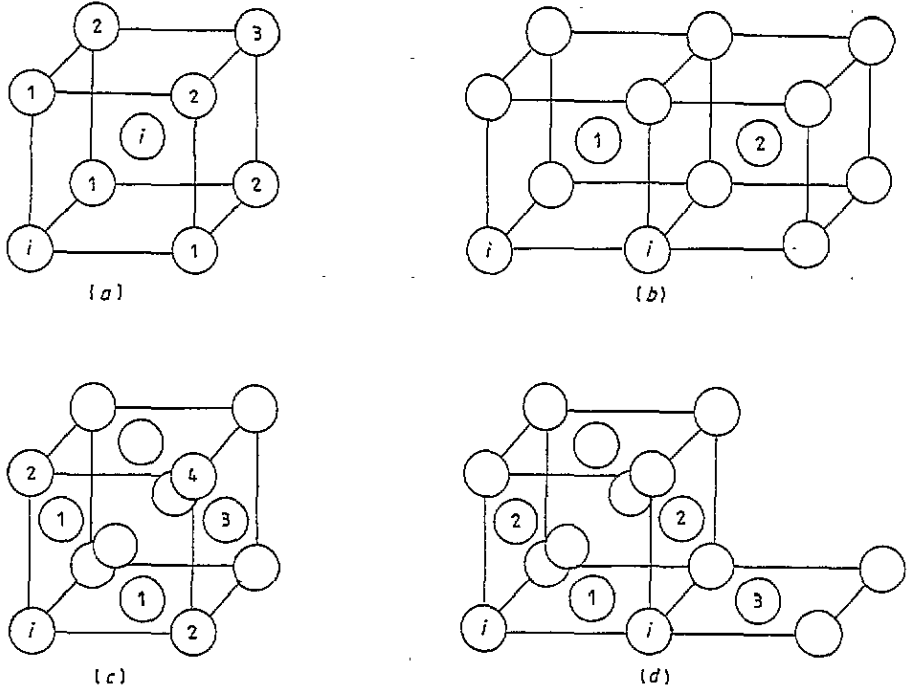
In section 2 we describe self-consistent cluster methods used in our treatment of single- and two-impurity problems within the LMTO–ASA framework. The results of their application to the dilute BCC Ti–V alloys are discussed in section 3, and those for the FCC Ni–Al alloys in section 4. The main conclusions are summarized in section 5. Some results of this work were reported earlier in [23, 24].

## 2. Method and approximations of calculations

As mentioned, we use the LMTO–ASA method as described by GJA [22] and the cluster approach similar to that of Dederichs and co-workers [9–11]. In accordance with [9–11], in our calculations of electronic structure and energies for both one- and two-impurity problems we self-consistently treat atomic clusters including impurities together with all their nearest-neighbours. For the single-impurity problem (in particular, in calculations of the solution energy  $Q$ ) it implies a treatment of clusters including 9 and 13 atoms for the BCC and FCC lattice, respectively. The two-impurity clusters needed for calculations of pair configurational interactions  $V_1$  or  $V_2$  between nearest- or next-nearest neighbours are shown in figure 1. They include 16 or 14 atoms for the BCC lattice, and 20 or 22 atoms for the FCC one. For comparison, we also calculated  $Q$  and  $V_i$  using the SSA and ECM [1], respectively, which corresponds to the conventional SS CPA for the dilute alloys under consideration.

We proceed from the conventional local-density (LD) and AS approximations. Then the energy  $E$  of valence electrons is given by formula (2.59) of GJA:

$$E = E_{\text{kin}} + E_{\text{int}} + E_{\text{Coul}} = T_{\text{vc}} + \sum_R \int_R d^3r n_{\text{vc},R}(r) \left( \frac{1}{2} \int_R d^3r' \frac{n_{\text{vc},R}(r')}{|r - r'|} \right)$$



**Figure 1.** Schematic representation of atomic clusters used in the calculations of first- and second-pair configurational interactions,  $V_1$  and  $V_2$ . (a) BCC lattice,  $V_1$ . (b) BCC lattice,  $V_2$ . (c) FCC lattice,  $V_1$ . (d) FCC lattice,  $V_2$ . The clusters in (a), (b), (c) and (d) include 16, 14, 20, and 22 atoms, respectively. The symbol  $i$  marks the impurity atom; the numbers 1, 2, 3 and 4 mark the non-equivalent host atoms in the cluster.

$$-\frac{Z_R}{r} + \epsilon_{xc}(n_{vc,R}(r)) + \frac{1}{2} \sum_{R \neq R'} \frac{q_R q_{R'}}{|\mathbf{R} - \mathbf{R}'|} \quad (2)$$

which also can be written as

$$E = E_b + E_{dc} - E_C = \int^\mu d\epsilon \in N(\epsilon) + \sum_R \int_R d^3r \left( n_{vc,R}(r) \epsilon_{xc}(n_{vc,R}(r)) - n_{c,R}(r) \epsilon_{xc}(n_{c,R}(r)) \right. \\ \left. - n_{v,R}(r) \mu_{xc}(n_{vc,R}(r)) - \frac{1}{2} \int_R d^3r' \frac{n_{v,R}(r) n_{v,R'}(r')}{|r - r'|} \right) - \frac{1}{2} \sum_{R \neq R'} \frac{q_R q_{R'}}{|\mathbf{R} - \mathbf{R}'|}. \quad (3)$$

Here we use the notation of GJA:  $R \equiv \mathbf{R}$  indicates the position of the atomic cell (being approximated by a sphere in ASA), and the lower index  $R$  on the integral sign means that the integral is in the AS at  $R$ ;  $q_R$  is the total charge of the cell  $R$  (while its nuclei charge is  $Z_R$ );  $n_{vc,R}$  is  $n_{v,R} + n_{c,R}$  where  $n_v$  and  $n_c$  is the density of the valence and core electrons;  $\epsilon_{xc}$  and  $\mu_{xc}$  are the exchange-correlation energy and potential in the LDA;  $\mu = \epsilon_F$  is the Fermi energy, and  $N(\epsilon)$  is the density of states for the valence electrons. The terms  $E_{kin}$ ,  $E_{int}$  and the 'Coulomb' term,  $E_C$ , correspond to the first, second and third term in (2), respectively, while the 'band' or 'double-counted' contributions,  $E_b$  or  $E_{dc}$ , correspond to the first or second term in the RHS of (3). Following GJA, we employ the frozen-core approximation and omit the core-electron contributions to the energy.

The solution energy  $Q$  for a single impurity is determined as the relevant change in energy

$$Q = E(N_h + 1_i) - E_h(N_h) - E_i(1_i). \quad (4)$$

Here the subscripts h or i correspond to host or impurity atoms,  $E(N_h + 1_i)$  is the alloy energy for the macroscopically large number  $N_h$  of host atoms and single impurity, while  $E_h(N_h)$  and  $E_i(1_i)$  are energies of the same number of atoms in pure components. Similarly, the pair configurational interaction  $V(R)$  in the dilute alloy considered is the difference between the energy  $E_R$  of two impurities with a relative distance  $R$  and two isolated impurities in the host metal:

$$V(R) = E_R(N_h + 2_i) - E_h(N_h) - E_i(2_i) - 2Q = E_R(N_h + 2_i) - 2E(N_h + 1_i) + E_h(N_h). \quad (5)$$

Equations (3)–(5) show that both  $Q$  and  $V(R)$  can be written as the sum of differences  $\Delta E_\alpha$  for various contributions to  $E$ :

$$\{Q, V(R)\} = \Delta E_b + \Delta E_{dc} + \Delta E_C \quad (6)$$

where  $\Delta E_\alpha$  are determined by (4) or (5).

Equations (4) and (5) show, in particular, that  $V(R)$  corresponds to the 'configurational' changes in  $E$  due to the relative displacements of impurities in the host matrix, while  $Q$  corresponds to the more complicated solution process. Thus one may expect that  $V(R)$  values are less sensitive to various approximations of calculations than  $Q$  values. The results below (as well as those of [2]) seem to support these expectations.

In the LMTO–ASA method of GJA the Hamiltonian matrix  $H = H_{RL,R'L'}$  (where  $L = l, m$  are angular momentum variables) has the two-centre form

$$H = C + \Delta^{1/2} S (1 - \gamma S)^{-1} \Delta^{1/2}. \quad (7)$$

Here  $S$  is the matrix of canonical structure constants, while  $C$ ,  $\Delta$  and  $\gamma$  are the potential parameter matrices, being diagonal in  $R$  and  $L$ :  $(C, \Delta, \gamma) = (C_{RI}, \Delta_{RI}, \gamma_{RI}) \delta_{RR'} \delta_{LL'}$ . The potential function  $P(\epsilon) = P_{RI}(\epsilon)$  (which characterizes electron scattering at the MT potential) is a fractional linear function of energy  $\epsilon$  and the potential parameters:

$$P(\epsilon) = \frac{\epsilon - C}{\gamma(\epsilon - C) - 4\Delta/s_R^2} \quad (8)$$

where  $s_R$  is the MT (atomic) sphere radius. If one neglects differences in  $\Delta_{RI}$  and  $\gamma_{RI}$  values for different atoms and sites  $R$ , the Hamiltonian (7) takes a tight-binding form with the 'diagonal' disorder matrix  $\Delta C = (C_{RI} - C_{h,I}) \delta_{RR'} \delta_{ll'}$  where  $C_{h,I}$  correspond to the pure host metal. This approximation will be referred to as the 'diagonal-disorder LMTO' (DD-LMTO) approximation; it is a self-consistent version of TBA. Below we show that this tight-binding type of approach may yield significant errors, particularly for the solution energy  $Q$ .

The self-consistent procedure used for the determination of wavefunctions  $\phi_{RI}(r, \epsilon)$  and the potential parameters  $C$ ,  $\Delta$ ,  $\gamma$  (which are expressed via  $\phi_{RI}(s_R, \epsilon)$  and

$\partial\phi_{RI}(s_R, \epsilon)/\partial\epsilon$  [22]) is similar to that described in [9–11, 22]. The Green function matrix  $g(\epsilon)$  is determined by the Dyson equation

$$g(\epsilon) = (1 + g^0\Delta P)^{-1}g^0 = g^0 + g^0Tg^0. \quad (9)$$

Here  $g^0(\epsilon) = [P^0(\epsilon) - S]^{-1}$ ,  $\Delta P = P(\epsilon) - P^0(\epsilon)$ , and  $P^0(\epsilon)$  correspond to the pure host metal. The path operator  $T$  can be expressed in terms of the single-site scattering matrix  $t_R = \Delta P_R(1 - g_{RR}^0\Delta P_R)^{-1}$  as

$$T = \sum_R t_R + \sum_{R \neq R'} t_R g_{RR'}^0 t_{R'} + \sum_{R \neq R', R' \neq R''} t_R g_{RR'}^0 t_{R'} g_{R'R''}^0 t_{R''} + \dots \quad (10)$$

where for brevity we omit the angular momentum indices. In practice, the expansion (10) in powers of  $g^0 t$  converges rapidly (which was noted, in particular, in [1]). Thus in our calculations we retained in  $T$  only the first three terms written explicitly in (10). Testing DD-LMTO calculations with the exact solution of matrix equation (9) for one- and two-impurity clusters of Al in Ni (including 13 and 20 atoms, respectively) showed that errors in  $Q$  and  $V$  values due to this truncation of series (10) do not exceed a few per cent.

As mentioned in [10], to find the band energy term  $\Delta E_b$  in (4)–(6) it is convenient to use the Lloyd relation between  $\Delta E_b$  and  $\Delta P$ . To apply it to our problem, we note the general relation between the band energy  $E_b$  and the Green function  $g$  (see, for example, [1, 22]):

$$E_b = \mu N_c + \frac{2}{\pi} \int^\mu d\epsilon \operatorname{Im} \operatorname{Tr} \ln g(\epsilon). \quad (11)$$

Therefore, the change  $\Delta E_b$  due to the substitution of  $n$  host atoms by the impurity atoms can be written as

$$\Delta E_b = E_b(N_h + n_i) - E_b(N_h + n_h) = \mu n(z_i^v - z_h^v) - \frac{2}{\pi} \int^\mu d\epsilon \operatorname{Im} \operatorname{Tr} \ln(1 - g^0\Delta P). \quad (12)$$

Here  $z_i^v$  and  $z_h^v$  is the number of valence electrons for the impurity and host atoms, respectively, and we also used (9) for  $g$ . Equation (11) enables us to directly find  $\Delta E_b$  for both the one- and two-impurity clusters.

The contributions  $\Delta E_{dc}$  in (6) and (3) are determined by the electron densities  $n_{v,R}$  and  $n_{c,R}$ , while  $\Delta E_C$  in the ASA depend only on cell charges  $q_R = \int_R n_{v,R}(r) d^3r - z_\alpha^v$  where  $\alpha = i$  or  $h$ .

For the core electron density  $n_{c,R}$  we used the frozen-core approximation and our LDA calculations for the isolated atoms. The valence electron density  $n_{v,R}$  is related to the Green function  $g$  as

$$n_{v,R}(r) = -\frac{2}{\pi} \operatorname{Im} \int^\mu d\epsilon \sum_l g_{RI,Rl}(\epsilon) \phi_{RI}^2(r) \quad (13)$$

where  $\phi_{RI}(r)$  is the radial Schrödinger equation solution for the cell  $R$  in the self-consistent potential  $V_R(r) = \delta E_{\text{int}}/\delta n_{v,R}$  with  $E_{\text{int}}$  from (2). These equations were solved with the LMTO–ASA method of GJA using the iterative procedure similar to that employed in [9–11]. The iterations were made either for  $\phi_{RI}(r) = \phi_R$  or  $n_{v,R}(r) = n_R$  with following expressions for  $\phi_R$  or  $n_R$  at the  $m$ th iteration step:

$$\phi_R^{(m)} = (1 - \alpha)\phi_R^{(m-1)} + \alpha\phi_R^{(m-2)} \quad n_R^{(m)} = (1 - \alpha)n_R^{(m-1)} + \alpha n_R^{(m-2)} \quad (14)$$

where  $\alpha$  is the damping factor. Similarly to [9–11], the optimal values of  $\alpha$  were found to be  $\alpha \simeq 0.99$ , and the convergence was achieved after 80–100 iteration steps. Integrals over  $\epsilon$  in (11)–(13) were taken in the complex plane  $\epsilon$ , shifting the integration contour to the upper half-plane by  $\Delta\epsilon = iH$ , as described in [9–11]. We used  $H \simeq 0.06$  au and  $N_H \simeq 400$  integration points at the contour.

The important parameters in the LMTO–ASA applications to impurity problems are the AS radii, that for the impurity,  $s_i$ , and those for its host neighbours,  $s_n$ . Neglecting LRE corresponds to employing for both the  $s_i$  and  $s_n$  the pure host value  $s_h = (3\Omega_h/4\pi)^{1/3}$ , where  $\Omega_h$  is the volume per host atom. However, due to the LRE, actual impurity neighbour positions differ from those for the pure host by the local distortions  $u_R$ . Values of  $u_R$  can be estimated with the use of the mentioned phenomenological approach [14], which enables us to express  $u_R$  via the observable concentrational dilation coefficient and the host phonon spectrum. Using these  $u_R$  we can find volumes  $\Omega_R$  of ‘distorted’ Wigner–Seitz (WS) cells, the impurity one,  $\Omega_i$ , and those of its neighbours,  $\Omega_n$ , as well as the radii of these distorted WS cells:  $s_R = (3\Omega_R/4\pi)^{1/3}$ . In the spirit of the LMTO–ASA approach, it seems natural for impurity problems to put  $s_R$  equal to the WS radius for this distorted WS cell:  $s_R = (3\Omega_R/4\pi)^{1/3}$ . Below we adopt this definition of  $s_R$  to approximately treat LRE in our LMTO–ASA cluster approach. This treatment neglects LRE on the structural constants  $S$  in the Hamiltonian (1). However, it seems plausible to suppose that these dimensionless geometrical constants (which are not changed under homogeneous dilations of the crystal lattice) are less sensitive to the local dilations near the impurity than the potential parameters, which are determined, in particular, by the electron wavefunction normalization within  $\Omega_R$ .

Generally, in calculations of  $Q$  and  $V(\mathbf{R})$  we can take into account the LRE in two ways, making calculations either for the relaxed lattice with  $\Omega_R = \Omega_R^{\text{rel}}$ , or for the undistorted (and thus locally stressed) lattice with  $\Omega_R = \Omega_h$ . In the first method the actual quantities  $Q$  and  $V$  are immediately given by (6). In the second approach we should add to expressions (6) the lattice relaxation contributions,  $Q_d$  and  $V_d$ :

$$\{Q, V(\mathbf{R})\} = \Delta E_b + \Delta E_{dc} + \Delta E_C + \{Q_d, V_d(\mathbf{R})\}. \quad (15)$$

If all terms entering (6) and (15) (i.e. the deformational contributions  $Q_d$ ,  $V_d$  and the others, the ‘electronic’ contributions  $Q_e$  and  $V_e$ , at both  $\Omega_R = \Omega_R^{\text{rel}}$  and  $\Omega_R = \Omega_h$ ) are calculated exactly, the resulting total  $Q$  and  $V(\mathbf{R})$  values for these two approaches must coincide. Therefore, a comparison of resulting  $Q$  and  $V(\mathbf{R})$  values for these two sets of calculations can provide an opportunity to appreciate the accuracy of the adopted treatment of LRE, in particular, of the above-mentioned phenomenological estimates of  $Q_d$  and  $V_d$  neglecting not-nearest-neighbour Kanzaki forces.

### 3. Results of calculations for BCC $\text{Ti}_{1-x}\text{V}_x$ alloys

The results of our calculations of  $Q$  and  $V_i = V(\mathbf{R}_i)$  for the dilute BCC  $\text{Ti}_{1-x}\text{V}_x$  system are presented in tables 1 and 2. The symbols CC, SSA and ECM in these tables mean, respectively, the cluster calculation with the self-consistent treatment of electronic structure for all cluster atoms; the above-mentioned single-site approximation for a single impurity when only this impurity atom (but not its neighbours) is treated self-consistently, and the embedded cluster method for calculations of interactions  $V(\mathbf{R})$  when in the sum (6) we retain only the band term  $\Delta E_b$  calculated using the ‘frozen’ SSA electronic potentials. As mentioned, for the dilute alloys under consideration the SSA or ECM correspond to the usual



Table 1. Characteristics of a single V impurity in BCC Ti.

Method	$\Omega_R$	Charges $q$ (au)			Contributions to $Q$ (eV)				Total $Q$ (eV)		
		V	Ti	Cluster	$\Delta E_b$	$\Delta E_{dc}^V$	$8\Delta E_{dc}^{Ti}$	$\Delta E_C$	Calc.	Exp.	
LMTO	CC	$\Omega_R^{rel}$	0.073	-0.011	-0.014	-2.82	3.21	-0.27	-0.012	0.12	0.12 [16]
		$\Omega_V^{rel}$	0.071	-0.009	-0.002	-2.46	3.21	-0.61	-0.012	0.13	0.19 [17]
		$\Omega_h$	0.181	-0.025	-0.016	-1.83	3.17	-1.02	—	-0.118	0.20
SSA		$\Omega_V^{rel}$	0.04	—	0.04	-2.86	2.99	—	—	0.13	
		$\Omega_h$	0.10	—	0.10	-2.24	2.60	—	—	0.36	
DD-LMTO	CC	$\Omega_R^{rel}$	0.06	-0.009	-0.008	-3.02	2.81	-0.43	-0.026	-0.67	
		$\Omega_h$	0.22	-0.029	-0.011	-2.55	2.40	-2.02	-0.167	-2.34	
	SSA	$\Omega_V^{rel}$	0.05	—	0.05	-3.27	2.43	—	—	-0.85	
		$\Omega_h$	0.13	—	0.13	-3.63	1.63	—	—	-2.00	

Table 2. Atomic charges and interactions  $V_i = V(R_i)$  for clusters including two V atoms in BCC Ti.

Method	$R_i = R_i^{VV}$	$\Omega_R$	Charges $q$ (au)					Contrib. to $V_i$ (meV)				Total	
			V	Ti <sub>1</sub>	Ti <sub>2</sub>	Ti <sub>3</sub>	Cluster	$V_b$	$V_{dc}$	$V_C$	CC	ECM	
LMTO, CC	(1,1,1)	$\Omega_R^{rel}$	0.05	-0.01	0.00	-0.01	-0.01	-493	490	9.5	6.6	9.9	
		$\Omega_h$	0.16	-0.03	-0.02	-0.02	-0.01	-716	655	74	13.4	10.3	
	(2,0,0)	$\Omega_R^{rel}$	0.04	-0.01	-0.01	—	0.00	-99	106	-24	-16.9	13.3	
		$\Omega_h$	0.17	-0.05	-0.02	—	-0.02	-53	272	-214	5.0	8.7	
DD-LMTO, CC	(1,1,1)	$\Omega_R^{rel}$	0.05	-0.01	0.00	-0.01	-0.01	-743	725	12	5.3	7.8	
		$\Omega_h$	0.05	-0.01	-0.01	—	-0.01	-200	252	-43	-8.2	20.9	

CPA approach for calculations of the quantities  $Q$  or  $V$ . The symbols Ti<sub>1</sub>, Ti<sub>2</sub> or Ti<sub>3</sub> in table 2 correspond to different types of Ti atoms in clusters, indicated in figure 1 by the symbols 1, 2 or 3.

In accordance with the two above-mentioned ways of treating LRE, we performed several sets of calculations, those for the relaxed lattice with  $\Omega_R = \Omega_R^{rel}$ , and those for the undistorted lattice with  $\Omega_R = \Omega_h$ . To appreciate the significance of LRE for the impurity and its neighbours separately, we also made calculations allowing for relaxation of cell volume only for the impurity but not for its neighbours, i.e. putting  $\Omega_V = \Omega_V^{rel}$ ,  $\Omega_n = \Omega_h$ . The results of the latter calculation (marked with  $\Omega_R = \Omega_V^{rel}$ ) are presented in the second line of table 1. In the SSA or ECM, perturbations of neighbours by the impurity are disregarded, thus LRE in these approaches are allowed only for the impurity atom:  $\Omega_R^{rel} = \Omega_V^{rel}$ . In the case of BCC Ti,  $\Omega_h = \Omega_{Ti} = 122.9$  (in a.u., here and below), while for the pure BCC vanadium metal  $\Omega_V^0 = 93.7$  [15]. Local distortions  $u_R$  needed to find values of  $\Omega_V^{rel}$  were estimated by the Khachatryan method [14, 15], using the Vegard law (which holds well for these alloys [2]). It yields  $\Omega_V^{rel} = 114.6$  for the V impurity and  $\Omega_n^{rel} = \Omega_T^{rel} = 121.7$  for its nearest Ti atoms. We see that the local dilation (compression)  $\Delta_i = (\Omega_i^{rel} - \Omega_h)/\Omega_h \simeq -0.1$  is large here, thus LRE should be significant. In calculations for the unrelaxed lattice (with  $\Omega_R = \Omega_h$ ) the 'total'  $Q$  or  $V_i$  values presented in tables 1 and 2 do not include deformational terms  $Q_d$  or  $V_i^d$  corresponding to the last term of (15). Estimating these terms with the Khachatryan method [14, 15], we obtain (in meV):  $Q_{d,K} = -160$ ,  $V_1^{d,K} = -16$ , and  $V_2^{d,K} = -40$ .

To appreciate the accuracy of tight-binding-type approaches for the problems under consideration, in tables 1 and 2 we also present results of the above mentioned DD-LMTO approach. It corresponds to the self-consistent treatment only of terms  $C_{Ri}$

(determining 'centre-of-band' positions [22]) in Hamiltonian (7), while parameters  $\Delta_{Rl}$  and  $\gamma_{Rl}$  (determining the band's width and shape) for impurity and host atoms are supposed to be the same. The actual fully self-consistent values of parameters  $C_l$ ,  $\Delta_l$  and  $\gamma_l$  are presented in table 3. Differences of  $\Delta_l$  and  $\gamma_l$  between host and impurity atoms in this table may seem to be small enough to justify neglecting them, i.e. employing the DD-LMTO approach. However, in calculations of the solution energy  $Q$  this approximation leads to large errors (see table 1 and the discussion below).

Table 3. LMTO parameters for host and impurity atoms in alloy systems considered.

$l$	$C_l$ (eV)			$\Delta_l$ (eV)			$\gamma_l$		
	0	1	2	0	1	2	0	1	2
BCC Ti	-2.58	8.36	0.63	2.01	1.86	0.27	0.43	0.12	0.012
V in Ti, $\Omega_R = \Omega_R^{\text{rel}}$	-2.99	8.22	-0.17	2.04	1.89	0.22	0.43	0.12	0.007
V in Ti, $\Omega_R = \Omega_h$	-3.85	6.81	-1.45	1.90	1.77	0.19	0.43	0.12	0.007
FCC Ni	-4.30	9.77	-2.44	2.52	2.20	0.16	0.43	0.11	0.002
Al in Ni, $\Omega_R = \Omega_R^{\text{rel}}$	-8.14	4.19	20.9	2.26	1.94	1.91	0.41	0.10	0.053

Let us first discuss the charge transfer  $q$  values for the relaxed and unrelaxed lattice. Tables 1 and 2 show that the relaxed Wigner-Seitz cells are almost neutral (which may be taken as a qualitative support for the estimates used of local distortions  $u_R$ ). However, for the unrelaxed impurity cell the charge  $q_i$  is noticeable,  $q_V \sim 0.2$ , which reflects the presence of significant local compression  $\Delta_i = \Delta_V$  under relaxation. Let us also note that in all our cluster calculations the total cluster charge  $q_{\text{cl}}$  turns out to be quite small, being lower by an order of magnitude than  $q_i$ . It illustrates a high degree of screening of impurity charges by their nearest neighbours, which was first noted by Dederichs and co-workers [10, 11]. On the other hand, in the SSA or ECM we have  $q_{\text{cl}} \equiv q_i$ , thus the screening and CTE are disregarded. Tables 1 and 2 show that this neglect can have a significant effect on the resulting  $Q$  and  $V_i$  values.

Let us now discuss possible contributions to  $Q$  or  $V_i$  of LRE for more distant host atoms, with  $R > R_1$  being disregarded in our calculations. Local dilations  $\Delta(R) = (\Omega_R^{\text{rel}} - \Omega_h) / \Omega_h$  for them decrease rather slowly with  $R$ . For example, in the employed estimate of  $u_R$ , values of  $\Delta_s = \Delta(R_s)$  for sequential impurity shells  $s = 0, 1, 2, 3, 4, 5$  and 6, are (in per cent)  $-7, -1, -1, -0.4, 0.4, 0.4$  and  $-0.1$ , respectively. However, LRE for these distant atoms probably have little effect on total energies. First, our cluster calculations with and without LRE for eight nearest host atoms (illustrated by lines 1 and 2 in table 1) have shown that these LRE make a small (about 16%) contribution to the total relaxation energy  $Q_d = Q(\Omega_R^{\text{rel}}) - Q(\Omega_h)$ , which reflects, in particular, a quadratic dependence of  $Q_d$  on  $\Delta_R$  at the small  $\Delta_R$  considered. Second, the elaborate treatment of an analogous shell convergence problem made by Dritler and co-workers [10] for the V impurity in Cu has shown that the effects of self-consistency of electronic potentials (in the Lloyd formula (12)) on  $Q$  are noticeable only for the first shell  $s = 1$  and are negligible for higher  $s$ , even though the perturbations of electronic states are of quite long range. Similarly, one may expect that local dilations of distant atoms will result only in minor variations of electronic states without significant changes in  $Q$ , which is also illustrated by a comparison of lines 1 and 2 in table 1.

As mentioned in section 2, for the relaxed lattice, values of  $Q$  and  $V_i$  presented in tables 1 and 2 (and called for brevity 'electronic' terms,  $Q_e$  and  $V_{i,e}$ ) can be considered

as final ones which can be directly compared with experimental estimates:  $Q = Q_e^{\text{rel}}$ ,  $V_i = V_{i,e}^{\text{rel}}$ . At the same time, for the unrelaxed lattice, the total calculated  $Q$  and  $V_i$  should also include deformational terms describing contributions of LRE:  $Q = Q_e^{\text{unr}} + Q_d$ ,  $V_i = V_{i,e}^{\text{unr}} + V_i^d$ . From physical considerations, the relaxation should lower energy, i.e. the deformational term  $Q_d$  should be negative. Therefore, if the approximations used are reasonable, the electronic terms  $Q_e$  should obey the inequality  $Q_e^{\text{rel}} < Q_e^{\text{unr}}$ . For the interaction constants  $V_1$  and  $V_2$  we can anticipate a similar inequality,  $V_{i,e}^{\text{rel}} < V_{i,e}^{\text{unr}}$ , since in the non-additive deformational contributions to (5) for the unrelaxed lattice (corresponding to the 'overlapping' of surroundings of neighbouring impurities) a predominance of repulsion can be expected (see, for example, the estimates of  $V_i$  in [15]). Table 1 shows that the inequality  $Q_e^{\text{rel}} < Q_e^{\text{unr}}$  holds for the fully self-consistent LMTO approach, but that it is drastically violated in the DD-LMTO approach, which ignores variations of width and form of electronic bands under solution. This violation may illustrate a possible unreliability of approaches of the tight-binding type in calculations of mixing energies  $Q$ . At the same time, for interaction constants  $V_i$  analogous inequalities  $V_{i,e}^{\text{rel}} < V_{i,e}^{\text{unr}}$  are fulfilled in both LMTO and DD-LMTO calculations (in particular, at  $\Omega_R = \Omega_h$  the latter yield  $V_1^{\text{unr}} \simeq 25$ , and  $V_2^{\text{unr}} \simeq 32$  meV), and differences in  $V_i$  calculated with both methods are usually not large, particularly for the relaxed lattice. It may illustrate that the interaction constants  $V_i$  are much less sensitive than  $Q$  to the approximations of calculations, in particular to using DD-LMTO instead of LMTO. It agrees with similar conclusions of Sluiter and Turchi [2] as well as with the considerations in section 2.

As mentioned above, if calculations of both electronic and deformational terms,  $Q_e$ ,  $V_{i,e}$  and  $Q_d$ ,  $V_i^d$ , were exact, the resulting  $Q$  or  $V_i$  values calculated using a relaxed or an unrelaxed lattice,  $Q^{\text{rel}} = Q_e^{\text{rel}}$  and  $Q^{\text{unr}} = Q_e^{\text{unr}} + Q_d$ , or  $V_i^{\text{rel}} = V_{i,e}^{\text{rel}}$  and  $V_i^{\text{unr}} = V_{i,e}^{\text{unr}} + V_i^d$ , should coincide with each other. If we employ for  $Q_e$  and  $V_{i,e}$  the LMTO values in tables 1 and 2, and for  $Q_d$  and  $V_i^d$ , the mentioned above estimates  $Q_{d,K}$  and  $V_i^{d,K}$ , we see that both the equations  $Q^{\text{rel}} = Q^{\text{unr}}$  and  $V_i^{\text{rel}} = V_i^{\text{unr}}$  are poorly satisfied: deformational contributions appear to be too large. However, if we suppose that the phenomenological estimates [12–15] neglecting not-nearest-neighbour Kanzaki forces do actually overestimate deformational terms by about a common factor  $1/\alpha > 1$ ,  $Q_d \simeq \alpha Q_{d,K}$ ,  $V_i^d \simeq \alpha V_i^{d,K}$ , then at  $\alpha \simeq 0.5$  we obtain for  $Q^{\text{unr}}$ ,  $V_1^{\text{unr}}$  and  $V_2^{\text{unr}}$  values (in meV) 120, 5, and  $-15$ , respectively, which are close to the 'relaxed' values 120, 7 and  $-17$  in tables 1 and 2.

To discuss possible grounds for the overestimation of  $Q_d$  and  $V_i^d$  in the approximation neglecting not-nearest-neighbour Kanzaki forces  $F(\mathbf{R})$ , let us write the conventional expressions relating  $F(\mathbf{R})$  to the crystal energy  $H$ , the concentrational dilation coefficient  $u_0 = d \ln a / dx$  ( $a$  being the lattice constant) and deformational contributions  $Q_d$  and  $V_i^d$  [14, 15]:

$$H = H_e + \sum_{\mathbf{R}} F(\mathbf{R}) u_{\mathbf{R}} + \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} A_{\alpha\beta}(\mathbf{R} - \mathbf{R}') u_{\mathbf{R}}^{\alpha} u_{\mathbf{R}'}^{\beta} \quad (16a)$$

$$u_0 = \frac{1}{3B\Omega} \sum_{\mathbf{R}} \mathbf{R} F(\mathbf{R}) = \frac{1}{3B\Omega} \sum_s \sum_{\mathbf{R}_s} \mathbf{R}_s F(\mathbf{R}_s) \quad (16b)$$

$$V^d(\mathbf{R}) = \frac{1}{N} \sum_{\lambda\mathbf{k}} \frac{|e_{\lambda\mathbf{k}} \cdot \mathbf{F}(\mathbf{k})|^2}{M\omega_{\lambda\mathbf{k}}^2} \exp(i\mathbf{k}\mathbf{R}). \quad (16c)$$

Here  $H_e$  describes the energy of an alloy with impurities in the undistorted host crystal lattice,  $u_{\mathbf{R}}^{\alpha}$  is the  $\alpha$  component of the host atom displacement  $u_{\mathbf{R}}$  at distance  $\mathbf{R}$  from the

impurity, and  $A_{\alpha\beta}(\mathbf{R})$  is the dynamic matrix;  $B$  is the bulk modulus,  $s$  is the number of the impurity shell that includes lattice vectors  $\mathbf{R}_s$ ,  $N$  is the total atom number,  $\omega_{\lambda k}$  and  $e_{\lambda k}$  are the frequency and the polarization vector for the phonon of branch  $\lambda$  with quasimomentum  $\mathbf{k}$  in the host metal,  $M$  is the host atom mass, the integration goes over the Brillouin zone, and  $F(\mathbf{k}) = \sum_{\mathbf{R}} F(\mathbf{R}) \exp(i\mathbf{k}\mathbf{R})$  is the Fourier component of  $F(\mathbf{R})$ . The quantities  $V^d(\mathbf{R})$  in (16c) are related to  $Q_d$  and  $V_i^d$  by  $Q_d = \frac{1}{2}V^d(0)$ ,  $V_i^d = V^d(\mathbf{R}_i)$  [14, 15].

It seems natural to suppose that Kanzaki forces  $F(\mathbf{R})$  in cubic metals are approximately central, i.e.  $F(\mathbf{R}_s) \simeq f_s \mathbf{R}_s / R_s^2$ , and the quantities  $f_s$  making the main contributions to (16) have the same sign. Then one may expect that neglecting not-nearest contributions with  $s \geq 2$  in (16) (at a given experimental  $u_0$ ) should overestimate  $V^d$  values: due to strong oscillations of terms  $\sim f_s f_{s'} \exp[i\mathbf{k}(\mathbf{R}_s - \mathbf{R}_{s'})]$  with  $s \neq s'$  in sums over  $s$ ,  $\mathbf{R}_s$  and  $s'$ ,  $\mathbf{R}'_s$  in (16c), their contribution in the quantities  $V^d$  is actually suppressed, while for the quantity  $u_0 \sim \sum f_s$  such suppression is absent. Therefore, approximating the true equation (16b) with 'truncated' relations,  $u_0 \sim f_1$  and  $f_s = 0$  for  $s \geq 2$ , we evidently overestimate  $V^d(\mathbf{R})$ . If we suppose that for  $R$  equal to 0,  $R_1$  and  $R_2$  in (16c) this overestimation has a similar scale  $\simeq 1/\alpha$ , we obtain estimates  $Q^d \simeq \alpha Q^{d,K}$ ,  $V_i \simeq \alpha V_i^{d,K}$  employed above.

We note that in our calculations of  $Q_e^{\text{rel}}$  and  $V_e^{\text{rel}}$  we used values of local distortions  $u_R$  found phenomenologically, neglecting not-nearest Kanzaki forces, while for estimates of  $Q_d$  and  $V^d$  we suppose the latter approximation to be quantitatively unreliable. However, one may expect that for the quantities  $u_R$  linear in  $f_s$  the fit employed of  $u_0$  to its experimental value should absorb a significant part of the errors connected with neglect of not-nearest  $f_s$ . Employing more consistent estimates of  $u_R$  may then not significantly change our results for  $Q_e^{\text{rel}}$  and  $V_e^{\text{rel}}$ , though this point, of course, needs further examination.

In the comparison of our calculated value of the solution energy  $Q \simeq 0.12$  eV with the experimental values given in final column of table 1, we should consider that this value is lower by a factor of about 5–10 than typical  $Q$  values for the transition metal alloys [10]. Thus various approximations of the calculations may significantly affect the result. In particular, we neglect charge and potential non-sphericity, as well as the higher angular momenta  $l \geq 3$  contributions to the Green function, while for the vanadium solution energy in FCC copper, for example, these effects were found to be important [10]. Keeping this in mind, we can consider the agreement of our calculated  $Q$  with experiments to be quite reasonable. As for the configurational interactions  $V_i$ , we are not aware of their experimental estimates for Ti–V alloys. However, we can compare our estimates of  $V_i$  with the TBA-CPA calculations of Sluiter and Turchi [2], who found the following for the dilute  $\text{Ti}_{1-x}\text{V}_x$  alloys (in meV):  $V_1 \simeq -6$ ,  $V_2 \simeq -8$  (and  $Q \simeq 180$ ). Therefore, the results of the two calculations of  $V_i$  agree only in the order of magnitude (being rather small, though), but disagree in meaningful figures. A more detailed comparison of our results with those of [2] is hampered by the number of semi-phenomenological approximations used in [2]: the TBA with a volume-dependent Slater–Koster parametrization, neglect of self-consistency of electronic potentials, non-diagonal disorder, LRE, etc. Thus the disagreement mentioned may characterize a scale of errors brought about by these approximations (and possibly also by the atomic sphere approximations of the present work) in calculations of  $V$ .

To conclude this section, we comment upon the LRE contributions to  $Q$  for impurities in other dilute alloys. These points were discussed, in particular, by Drittler and co-workers [10] who suggested that disagreements with experiments in their calculated  $Q$  for some systems (for example, for Cr and Mn impurities in Cu) may be due to neglecting LRE. Our results for the  $\text{Ti}_{1-x}\text{V}_x$  alloys seem to show that the phenomenological approach of [12–15], generally, can be used for semi-quantitative estimates of  $Q_d$  and  $V_i^d$ , even though it somewhat overestimates their values. For the interaction constants  $V_i^d$  such estimates have

been presented for 24 cubic host metals in [15]. In table 4 we present analogous estimates for the deformational contribution  $Q_d$  to the solution energy. It is related to the concentrational dilation coefficient  $u_0 = d \ln a / dx$  as [14, 15]

$$Q_d = -w_0 u_0^2. \quad (17)$$

The values of  $w_0$  in table 4 were calculated using the same methods and data as those in [15].

**Table 4.** Values of the parameter  $w_0$  in (17) for the deformational contribution  $Q_d$  to the solution energy  $Q$  in dilute alloys.

BCC host	Li	Na	K	Rb	Cs	Ba	Ti	Zr	V
$a$ (Å)	3.50	4.28	5.31	5.69	6.12	5.02	3.31	3.61	3.03
$w_0$ (eV)	1.87	1.97	2.40	2.90	2.00	4.27	26.1	29.3	18.8
BCC host	Nb	Ta	Cr	Mo	W	Fe			
$a$ (Å)	3.29	3.30	2.88	3.14	3.16	2.86			
$w_0$ (eV)	26.6	32.9	12.3	28.9	34.1	12.9			
FCC host	Ca	Sr	Al	Ni	Pd	Pt	Cu	Ag	Au
$a$ (Å)	5.58	6.09	4.04	3.52	3.88	3.92	3.61	4.08	4.07
$w_0$ (eV)	1.86	1.94	3.70	8.63	12.0	21.4	6.44	7.31	14.6

The dilation coefficient  $u_0$  in (17) can be estimated using the Vegard law (which for many alloys is even obeyed quantitatively). It implies  $u_0 \approx (a_i - a_h)/a_h \approx (\Omega_i - \Omega_h)/3\Omega_h$  where the index h or i corresponds to the pure host or solute metal. Table 4 and equation (17) show that values of  $Q_d$  do not usually exceed 0.1–0.2 eV (also keeping in mind a probable overestimate of  $Q_d$  with this estimate). Thus LRE can significantly affect values of  $Q$  only for alloys with a large mismatch of atomic sizes and at small valency difference  $\Delta Z = Z_i - Z_h$ , when the ‘electronic’ contribution  $Q_e$  is small, as it is for the Ti–V system. For the case of Cr and Mn impurities in Cu discussed in [10] the valency difference  $\Delta Z$  is significant, while the atomic volume difference is quite small,  $|\Omega_i - \Omega_h|/\Omega_h \sim 2\text{--}3\%$ , and the estimate (17) gives  $|Q_d| < 1$  meV. Therefore, LRE can hardly be important for  $Q$  in these systems.

#### 4. Results of calculations for FCC $\text{Ni}_{1-x}\text{Al}_x$ alloys

Discussing the Ni–Al system, we first note that LRE for this system are much less important than for the Ti–V system, even though the values of concentrational dilation coefficients  $u_0 = d \ln a / dx$  are similar:  $u_0 \approx 0.051$  for the FCC  $\text{Ni}_{1-x}\text{Al}_x$  alloys [20], and  $u_0 \approx -0.078$  for the  $\text{Ti}_{1-x}\text{V}_x$  alloys. The relative insignificance of LRE for Ni–Al alloys is due to two reasons.

First, local atomic displacements  $u_R$  near the impurity in the close-packed FCC lattice are much lower than those in the BCC lattice. In particular, phenomenological estimates [14, 15] yield, for displacements  $u_R = u_s$  of Ni atoms near the Al impurity,  $u_1^x = u_1^y = 0.026$  and  $u_2^x = -0.01$ , while the FCC lattice constant is  $a \approx a_{\text{Ni}} = 6.66$ , and the local dilation  $\Delta_s = (\Omega_s - \Omega_h)/\Omega_h$  is 2.3, 0.6 and 0.2% for shell  $s = 0, 1$  and 2, respectively. At the same time, for the BCC  $\text{Ti}_{1-x}\text{V}_x$  alloys with  $a \approx a_{\text{Ti}} = 6.25$  we have, with similar estimates,  $u_1^x = u_1^y = u_2^z = -0.11$ ,  $u_2^x = 0.07$  and  $u_3^x \approx u_3^y = -0.04$ , and values of  $\Delta_s$  mentioned in section 3 exceed those for the Ni–Al system by several times.

Second, tables 5 and 6 show that the 'electronic' contributions to  $Q$  and  $V_i$  in Ni-Al alloys are much higher than those in Ti-V alloys (which reflects a stronger bonding in the Ni-Al system), and they considerably exceed deformational terms  $Q_d$  and  $V_i^d$ . For example, using estimates from table 4 and [15] for  $Q_d$  and  $V_i^d$  in  $Ni_{1-x}Al_x$ , we obtain (in meV),  $Q_d \simeq 22$ ,  $V_1^d \simeq -12$  and  $V_2^d \simeq -3.3$ , which is much smaller than the electronic terms in tables 5 and 6. Therefore, below we do not discuss LRE for the Ni-Al system, and present only results for the 'relaxed' lattice with the phenomenologically estimated atomic volumes  $\Omega_{Al}^{rel} = 75.6$  and  $\Omega_1(Ni) = 74.3$ , being close to the host volume  $\Omega_h = \Omega_{Ni} = 73.9$ .

Table 5. Characteristics of a single Al impurity in fcc Ni.

Method	Charges $q$ (au)			Contributions to $Q$ (eV)				Total $Q$ (eV)		
	Al	Ni	Cluster	$\Delta E_b$	$\Delta E_{dc}^{Al}$	$12\Delta E_{dc}^{Ni}$	$\Delta E_C$	Calc.	Exp.	
LMTO	CC	-0.42	0.04	0.05	-7.12	0.92	5.11	-0.70	-1.79	-1.6 [18]
	SSA	-0.26	-	-0.26	-4.85	2.88	-	-	-1.97	
DD-LMTO	CC	-0.64	0.06	0.07	-11.81	3.43	8.87	-1.60	-1.11	
	SSA	-0.40	-	-0.40	-7.58	6.04	-	-	-1.54	

Table 6. Atomic charges and interactions  $V_i = V(R_i)$  for clusters including two Al atoms in fcc Ni. Contributions to  $V_i$  and total  $V_i$  are measured in meV.

Method	$R_i = R_i^{AlAl}$	Charges $q$ (au)						Contrib. to $V_i$			Total $V_i$	
		Al	Ni <sub>1</sub>	Ni <sub>2</sub>	Ni <sub>3</sub>	Ni <sub>4</sub>	Cluster	$V_b$	$V_{dc}$	$V_C$	CC	ECM
DD-LMTO	(1,1,0)	-0.56	0.12	0.06	0.05	0.05	0.09	1006	-1672	852	187	235
CC	(2,0,0)	-0.64	0.13	0.05	0.06	-	0.09	325	-125	-250	-49	33

Considering the characteristics of a single Al impurity presented in table 5, we note that its charge transfer  $q$  to host atoms is significant, and close to that for the ordered  $Ni_3Al$  compound where  $q \simeq 0.5$  [25]. Tables 1 and 5 also show that single-site approximations underestimate values of  $q$ . The electronic structure of both Al and Ni atoms found in the self-consistent cluster calculation noticeably differs from that calculated in SSA, and partial contributions  $\Delta E_b$ ,  $\Delta E_{dc}$  and  $\Delta E_C$  to the solution energy  $Q$  found in the CC and SSA differ greatly from each other. In particular, significant terms  $\Delta E_{dc}^{Ni}$  and  $\Delta E_C$  are absent in SSA. However, the difference in total  $Q$  values calculated in CC and SSA turns out to be small, thus errors of SSA due to the neglect of intersite interactions seem to cancel each other to a considerable extent. Such a cancellation (which has been discussed by a number of authors, see for example [8] and references therein) probably reflects variational properties of energy in the density functional approach. Note, however, that employing the more consistent LMTO-CC instead of the LMTO-SSA method results in lowering the disagreement between calculated and observed values of  $Q$  by a factor of about two, though this improvement may be partly accidental.

We now discuss an application to the same impurity problems of the above-mentioned DD-LMTO approach. Table 5 shows that it results in an overestimation of  $q$  and an underestimation of  $Q$  in the cluster calculation by about 30%. However, a comparison of tables 1 and 5 shows that errors brought about by the DD-LMTO approach in  $Q$  values for Al in Ni are much lower than those for V in BCC Ti. The latter can be understood if one

compares LMTO parameters for the Al impurity and Ni host atoms in table 3. We see that for s and p states (which include about 90% of the total number of occupied states for Al in Ni [23]) values of  $\Delta_i$  and  $\gamma_i$  for host and impurity atoms are similar. Therefore, employing the DD-LMTO approximation,  $\Delta_i^{\text{Al}} \simeq \Delta_i^{\text{Ni}}$ ,  $\gamma_i^{\text{Al}} \simeq \gamma_i^{\text{Ni}}$ , brings in significant errors only for a small part of the impurity electrons, unlike the V in Ti case where impurity electrons mainly fill just d states.

As mentioned in section 3, the interaction constants  $V_i$  seem to be less sensitive to approximations of calculations than the mixing energy  $Q$ . For example, tables 1 and 2 show that employing DD-LMTO instead of full LMTO for V impurities in Ti changes the calculated  $Q$  value by a factor of  $-5$  (which implies inapplicability of the DD-LMTO approach to this problem), while  $V_i$  values change only by 20–50%. Thus for the case of an Al impurity in Ni, where analogous changes in  $Q$  are only about 30%, one may expect that the difference in DD-LMTO and full LMTO results for  $V_i$  should be significantly lower than that for V in Ti, and may not exceed 5–10%. In addition to that, in the course of this work we made DD-LMTO calculations, while cluster computations of  $V_i$  are time consuming. Therefore, in table 6 we present only  $V_i$  values calculated with the DD-LMTO. We hope that they are sufficiently close to the full LMTO results, and plan to examine them elsewhere.

A comparison of  $V_i$  values found using the cluster calculations (CC) and the SSA-type ‘embedded cluster method’ (ECM) enables us to appreciate the importance of CTE for the interaction constants  $V_i$ . A comparison of tables 5 and 6 (as well as tables 1 and 2) shows that CTE in  $V_i$  are more pronounced than in the solution energy  $Q$ . This may be connected with a greater importance of the intersite Coulomb contribution  $V_C$  for total  $V_i$  as compared with that of the analogous term  $\Delta E_C$  for  $Q$ . The ECM seems to overestimate the  $V_1$  value by about 30%, while for  $V_2$  the ECM and CC results even differ in sign.

Table 7. Estimates of interactions  $V_i = V(R_i)$  (in meV) for dilute Ni–Al alloys.

	Calculations				Experiments			
	[3]	[4]	[5]	This work, DD-LMTO		[19]	[20]	[21]
				ECM	CC			
$V_1 = V(1, 1, 0)$	204	290	$\simeq 250$	235	187	252	145	65
$V_2 = V(2, 0, 0)$	10	—	$\simeq 70$	33	–49	14	–18	–21

In table 7 we compare the results of various theoretical and experimental estimates of  $V_i$  for dilute  $\text{Ni}_{1-x}\text{Al}_x$  alloys (the values in the third column are taken from figure 7 of [5]). For the first constant  $V_1$  various theoretical estimates are, generally, close to each other, though in our cluster calculation  $V_1$  is somewhat lower than in others. For the second constant  $V_2$  our CC value is negative, unlike in other calculations. We mention in this connection that for higher concentrations  $x$  the negative  $V_2$  values promote  $L1_2$ -type ordering, which is actually observed in the  $\text{Ni}_{1-x}\text{Al}_x$  alloys at  $x \simeq 0.25$ .

The experimental estimates of  $V_i$  in table 7 reveal a large scatter, which prevents their detailed comparison with calculations. One may only note that the latest measurements [19, 20] seem to show a tendency to lower values of  $V_1$  and negative values of  $V_2$ , in qualitative agreement with our cluster calculations.

## 5. Conclusions

Despite the number of approximations made in the calculations presented in this paper,

the results obtained appear to enable us to make several qualitative conclusions regarding the magnitudes and significance of the lattice relaxation and charge-transfer effects on the mixing energies  $Q$  and the configurational interactions  $V_i$ .

First, our results substantiate previous remarks [9–11, 15] that LRE can significantly affect  $Q$  and  $V_i$  values in substitutional alloys, particularly when the components have a significant mismatch of atomic sizes. At the same time, our microscopic estimates for BCC Ti–V alloys have shown that the conventional phenomenological estimates of deformational contributions  $Q_d$  and  $V_i^d$ , neglecting not-nearest-neighbour Kanzaki forces, seem to noticeably overestimate the magnitudes of  $Q_d$  and  $V_i^d$ . We have also presented qualitative considerations regarding the possible connection of this overestimation with the neglect of distant Kanzaki forces.

The conclusion regarding the probable overestimation of deformational terms  $V_i^d = V_d(R_i)$  in the phenomenological estimates may be even more important for the interstitial alloys, where these terms (being quite strong and of long range) are usually supposed to dominate the interstitial atom interactions [14, 26–30]. We mention in this connection the known estimate of  $V_d$  for the NbH<sub>x</sub>-type alloys suggested by Horner and Wagner [26] and used by a number of authors [27–30]. In analogy with the mentioned truncation of Kanzaki forces at nearest neighbours, Horner and Wagner supposed that the forces  $f_s$  (in our notation) between H and Nb atoms to be non-zero only in two shells of the H impurity and estimated  $f_1$  and  $f_2$  using experimental data about the H-induced distortions of the BCC lattice of Nb. In particular, for the ratio  $r = f_2/f_1$  they obtained  $r \simeq 13/35 \simeq 0.4$ . A significant value for this  $r$  may hint that the quantities  $f_s$  actually decrease with  $s$  rather slowly, thus sums over  $s$  in (16b) and (16c) can include many terms of similar order. As was discussed in section 3, we can then expect an overestimation of  $V_d$  in Horner–Wagner-type estimates. Therefore, the magnitudes of deformational interactions  $V_d$  found in [26–30] and in similar estimates in [14] may be significantly exaggerated.

The latter can help, in particular, to resolve a long-discussed problem in interstitial alloy physics: the so-called ‘blocking’ effect in NbH<sub>x</sub>-type (and many other) alloys. Interstitial sites near each impurity atom (2–3 shells for the NbH<sub>x</sub> type alloys) cannot be occupied by other impurities [26–28]. Microscopic estimates [28] for total H–H interactions  $V_i^{HH} = V_i^d + V_i^e$  in these hydrides (in which deformational terms  $V_i^d$  were estimated according to [26] and ‘electronic’ terms  $V_i^e$  were estimated using a number of plausible models) failed to explain the blocking effect: the deformational attraction for the first three shells was too strong,  $(-V_i^d) \gtrsim (1-3)10^3$  K, to obtain ‘blocking’ values  $V_i^{HH} \gtrsim T_c \sim 500$  K at reasonable  $V^e$  (see table 2 in [28]). Therefore, an abnormally strong anharmonic repulsion was invoked to explain the blocking effect [28]. However, if the Horner–Wagner  $V_i^d$  should actually be lowered by several times, then the repulsive terms  $V_i^e$  presented in [28] can be quite sufficient to obtain blocking values  $V_i \gg T_c$  at  $i = 1$  and 2, as well as the value  $V_3 \sim 800$  K estimated from thermodynamical data in [30].

Therefore, the overestimation of deformational interactions  $V_i^d$  in phenomenological estimates neglecting distant Kanzaki forces may occur for both substitutional and interstitial alloys, and then one can naturally explain blocking effects observed in a number of interstitial alloys. In this connection, first-principles estimates of the  $R$  dependence of Kanzaki forces  $F(R)$  seem to be highly desirable.

The second main conclusion of this work concerns the charge transfer effect on mixing energies and configurational interactions in alloys. As mentioned above, in a number of recent works these effects are supposed to be insignificant [1–3, 8]. Our results for the Ni–Al alloys show that for certain quantities, in particular for the second constant  $V_2$  in these alloys, taking into account CTE is of crucial importance, while these quantities can determine



even the type of ordering. This work also shows that the cluster methods employed here and in [9–11] enable us to describe CTE in dilute alloys both consistently and relatively simply. An extension of these methods to the ordered phases with a narrow homogeneity region (i.e. almost stoichiometric phases) seems to be straightforward. Therefore, these cluster methods can provide an effective tool for consistent calculations of thermodynamics and phase equilibria for alloy phases with narrow homogeneity regions, which are characteristic for many intermetallic systems.

### Acknowledgments

The authors are very grateful to Dr A Zunger and Dr B Schonfeld for sending us preprints of papers [7] and [21], respectively, before their publication. This work was supported by the Russian Fund of Fundamental Research, under grant No 93-02-14776.

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