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Calculated elastic constants of dilute alloys based on bcc metals

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Abstract. The elastic constants of dilute alloys based on bcc metals have been calculated using the Green's function method obtaining explicit expressions for change in elastic constants in terms of t-matrix. The crystal impurity problem is discussed within an impurity model containing central and non-central force constant changes extended up to second neighbours of the impurity. The effect of volume change on elastic constants and a contribution from electron pressure term are considered. Numerical results for changes in three elastic moduli have been presented for a number of dilute alloys based on Mo, Nb, W, Ta and V.

Keywords. Green's function; t-matrix; force constant changes.

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1. Introduction

Impurity induced changes in elastic constants provide an useful tool for studying the dynamics of imperfect lattices. In comparison to some popular methods for investigating the defect lattice dynamics e.g., neutron scattering and lattice specific heat, which involve all kinds of vibrational modes, the elastic constants couple only vibrational modes with even symmetry and may provide information pertaining to individual symmetry modes. Although the elastic constant is a macroscopic property of the crystal and is determined by an effective coupling between atoms and that extent it is not very suitable for investigating the characteristic defect modes (localized and resonance modes), it may nevertheless provide important information on the interatomic force constants near the defects referring to a particular symmetry mode. As a matter of fact in cubic systems such as dilute alloys based on cubic metals the three independent elastic constants couple to A_{1g}, E_g and F_{2g} symmetry modes and as such the symmetry dependence of the force constant changes may be studied.

Although there is an extensive experimental study regarding elastic constants of dilute alloys, there seems to be little theoretical effort at calculating the elastic constants in these systems (Dederichs and Zeller 1979). In a recent paper (Ram and Semalty 1987) we have calculated elastic constants of dilute alloys using Green's function. The numerical results were presented for the dilute alloys of fcc metals Cu, Ag and Au. In the present paper we calculate the changes in elastic constants of dilute alloys of bcc transition metals Mo, Nb, Ta, W and V.

In a metal the interatomic interaction can be divided into two parts (i) central interaction depending on pair potential and (ii) a volume dependent part coming from conduction electrons which is interprated as a 'pressure' in terms of uniform electron gas. The total energy in the metal is expressed as

$$E = \sum \phi(R^{mn}) + U_e(V),$$

where U_e is a function of volume only. The presence of the alloying element in the host metal gives rise to changes in interatomic force constants leading to changes in pair potential term. In the calculation of changes a defect model extending up to second-neighbour of the impurity containing changes in longitudinal and transverse force constants has been employed. In addition to changes due to local perturbation near the defects a volume-dependent contribution is further obtained as a result of lattice expansion or contraction. Part of this volume change is related to so-called "image forces" which is a homogeneous change throughout the crystal. The other part is related to the change of the lattice distance in the average. As regards the electronic contribution it is restricted to bulk modulus only and is evaluated taking different *s*-like electron concentration for host metals and impurities. In § 2 we briefly present the theory giving explicit expressions for the change in elastic constants in terms of *t*-matrix pertaining to bcc lattice. In § 3 we calculate the change in elastic constants in different dilute alloys. The result obtained is discussed in the light of available experimental results.

2. Theory

2.1 *Change in elastic constants*

As indicated earlier the presence of defects affects the elastic constants in the following ways: (i) a lattice part due to changes in interatomic force constants near the defects (ii) a volume part due to volume expansion or contraction as a result of alloying (iii) an electronic contribution to the bulk modulus due to the presence of excess number of conduction electrons. Thus the change in elastic constants is expressed as

$$\Delta C = \Delta C^{\text{lattice}} + \Delta C^{\text{volume}} + \Delta C^{\text{elc.}}. \tag{1}$$

The change in elastic constants due to force constant changes is given by (Dederichs and Zeller 1979; Ram and Semalty 1987)

$$\Delta C_{ijkl} = \frac{c}{V_c} \sum_{mn} R_j^m t_{ik}^{mn}(0) R_l^n, \tag{2}$$

with

$$t(0) = \Delta\phi(1 + G(0)\Delta\phi)^{-1}. \tag{3}$$

Here $\mathbf{R}^m$ is the position vector of the atom m, c is the concentration of defects, V_c is the volume of a unit cell in the lattice, $\Delta\phi$ is the change in the force constant matrix due to a single defect and $G(0)$ is the static lattice Green's function. Instead of individual elastic constants the calculation of eigenvalues of the elasticity tensor C_{ijkl} is more convenient. For cubic crystals the use of appropriate eigen strains (Leibfried and Breuer 1978) result in the change in elastic moduli $\Delta C^{(\rho)}$ as

$$\Delta C^{(\rho)} = \frac{c}{V_c} \langle \varepsilon^{(\rho)} \mathbf{R} | t | \varepsilon^{(\rho)} \mathbf{R} \rangle. \tag{4}$$

Thus the calculation of $\Delta C^{(\rho)}$ involves essentially the expectation value of t-matrix with the normalized displacement $\varepsilon^{(\rho)}R$. The use of lattice symmetry further simplifies the calculation e.g., for defects with inversion symmetry only even symmetry modes contribute to the elastic constants (see § 2).

The change in elastic constants due to volume change is (Ram and Semalty 1987; Leibfried and Breuer 1978)

$$\Delta C^{\mathrm{vol}} = -\frac{\delta V^{\infty}}{3V_c}C - c\frac{\delta V^{im}}{V_c}\cdot\frac{C_{11}+2C_{12}}{3}\cdot\frac{\partial C}{\partial P}, \tag{5}$$

where change in volume is $\Delta V = N_d \delta V$, N_d being the total number of defects in the lattice and δV is the change in volume due to a single defect and is given by

$$\delta V = \delta V^{\infty} + \delta V^{im} \tag{6}$$

where δV^{∞} corresponds to displacement field in an infinite crystal whereas δV^{im} corresponds to image expansion. Here C is the perfect lattice elastic constant and $\partial C/\partial P$ is its pressure derivative. In (5) the first term arises due to a change of the lattice parameter in the average whereas the second term arises due to image term which is a homogeneous expansion or contraction in the lattice.

Following Harrison (Harrison 1980; Wills and Harrison 1983) the electronic structure of a transition metal we consider Z_d of Z valence electron as localized and non-overlapping d-states centered on each ion site and the remaining $Z_s = Z - Z_d$ electrons to be in free electron like states. Further, it is assumed that there is no overlapping between the s- and d-states. The calculation of the total energy is then simplified as for the simple metal and we take the total energy of the electron gas in Hartree-Fock approximation

$$U_e = NZ_s\left(\frac{3}{5}\frac{\hbar^2 k_f^2}{2m_s} - \frac{3e^2 k_f}{4\pi}\right), \tag{7}$$

where k_f is the fermiwave vector, NZ_s is the number of free electrons and m_s is the effective mass of the electron given by $m_s = m/\{1 + 5r^3 d/\pi r_0^3\}$, r_0 being the radius of atomic sphere (Wigner-Seitz) and r_d is the d-static radius characterizing the free atom of the transition metal. The expression for bulk modulus in terms of the density of free electrons, n, in different metals and alloys is

$$B_e = \frac{\hbar^2}{3m_s}(3\pi^2)^{2/3}n^{5/3} - \frac{e^2}{3\pi}(3\pi^2)^{1/3}n^{4/3}. \tag{8}$$

2.2 *Calculation for the substitutional impurity in bcc lattice*

For the crystal impurity problem in bcc lattice we take a second-neighbour interaction model in which changes in central and non-central force constants between the impurity and its neighbours are considered. The defect space spans 15 atoms, i.e., the impurity, its eight nearest-neighbours and six second neighbours. With the use of symmetry O_h of the defect the defect space is decomposed as follows

$$\Gamma = 2A_{1g} + 2E_g + 2F_{1g} + 3F_{2g} + A_{2u} + E_u + 5F_{14} + 2F_{24}. \tag{9}$$

The perturbation and Green's function matrices are block diagonalized using proper symmetry coordinates. The symmetry coordinates have been presented by Dettmann and Ludwig (1964). The change in three elastic moduli $C_{11}+2C_{12}$, and $C_{11}-C_{12}$ and C_{44} involve A_{1g}, E_g and F_{2g} irreducible representations, respectively. It is clear that for A_{1g} and E_g we have 2×2 matrices while for F_{2g} modes we have 3×3 matrix. In terms of symmetry adapted t-matrix the elastic moduli are given by

$$\Delta C^{(\rho)}=\frac{c}{V_c}\langle\varepsilon^{(\rho)}\mathbf{R}|\Gamma\rangle t^{\Gamma}\langle\Gamma|\varepsilon^{(\rho)}\mathbf{R}\rangle, \tag{10}$$

where $|\Gamma\rangle$ are column vectors of symmetry coordinates and t^{Γ} are t-matrices in different irreducible representations. The inner products $\langle\varepsilon^{(\rho)}\mathbf{R}|\Gamma\rangle$ appearing in (10) are given by

$$\begin{aligned}
&\langle\varepsilon^{1}\mathbf{R}|A_{1g}\rangle=[a(2)^{1/2},a(2)^{1/2}],\\
&\langle\varepsilon^{2}\mathbf{R}|E_g^{1}\rangle=[-a(2)^{1/2},-a(2)^{1/2}],\\
&\langle\varepsilon^{2}\mathbf{R}|E_g^{2}\rangle=[(3)^{1/2}a/2,-(3)^{1/2}a/2],\\
&\langle\varepsilon^{4}\mathbf{R}|F_{2g}^{1}\rangle=\langle\varepsilon^{4}\mathbf{R}|F_{2g}^{2}\rangle=(0,0,0),\\
&\langle\varepsilon^{4}\mathbf{R}|F_{2g}^{3}\rangle=[0,a(2)^{1/2},a(2)^{1/2}].
\end{aligned} \tag{11}$$

Utilizing these inner products we get the change in elastic moduli as

$$\begin{aligned}
\Delta(C_{11}+2C_{12})&=\frac{8c}{a}(t_{11}^{A_{1g}}+2t_{12}^{A_{1g}}+t_{22}^{A_{1g}}),\\
\Delta(C_{11}-C_{12})&=\frac{8c}{a}(t_{11}^{E_g}-t_{12}^{E_g}+t_{22}^{E_g}),\\
\Delta(2C_{44})&=\frac{8c}{a}(t_{22}^{F_{2g}}+2t_{23}^{F_{2g}}+t_{33}^{F_{2g}}).
\end{aligned} \tag{12}$$

where t_{ij} is the ij element of the t-matrix t^{Γ} and a is the lattice parameter.

3. Numerical results and discussion

To evaluate the volume induced changes in elastic constants the volume change ΔV, has been taken from King (1966). The calculation of individual volume change δV^{∞} and δV^{im} has been described in our earlier paper (Ram and Semalty 1987). The values of pressure derivatives of the elastic constants are taken from Katahara *et al* (1979). The experimental values of elastic constants of host metals are from Davidson and Brotzen (1968); Hubbell and Brotzen (1972); Anderson and Brotzen (1982) and Lenkkeri and Latheenkorva (1978). In order to calculate the electronic contribution to the bulk modulus the value of Z_s, r_0 and r_d are taken from Harrisen (1980). In the alloy the Z_s is calculated as

$$Z_s=cZ_s(\text{impurity})+(1-c)Z_s(\text{host}). \tag{13}$$

Using the values of Z_s and volume of the alloy $V'(= V + \Delta V)$ in (8), the electronic contribution to the impurity induced change in the bulk modulus is determined.

In order to calculate the change in elastic constants due to localized perturbation we need static lattice Green's functions and the force constant changes in different host metals. The necessary static lattice Green's functions are used from MacGillivray and Scholl (1983). These authors have calculated the static Green's functions utilizing the force constants obtained by Born–Von-Karman fits to the vibration spectra measured by inelastic neutron scattering except V, in which X-ray results were used. Subsequently, we have calculated the static Green's functions for bcc metals (Ram 1989) using modified method of Gilat and Raubenheimer (1966). The calculated values are similar to that of MacGillivray and Scholl (1983).

Because of widespread use of empirical pair potentials like Born-Mayer and Morse for the discussion of defect properties of metals (Johnson 1973) it is tempting to employ such potentials to calculate the force-constant changes. In such a scheme the equilibrium distances between the impurity and its neighbours are found by calculating the static displacements of the atoms around the impurity using the lattice statics method of Kanzaki (1957) or through computer simulation (see e.g., Johnson 1964). However, as the empirical potentials do not describe the materials exactly any such calculation is still subject to some uncertainities. Therefore in the discussion of elastic constants of dilute alloys based on fcc metals (Ram and Semalty 1987) the distance between the impurity and the neighbours were taken as the respective distances in the host lattice plus the difference of atomic radii of impurity and host atoms. Such a procedure has been tried with Born-Mayer potential and in some cases with Morse potential as well but the calculated change of elastic constants on the basis of calculated force-constant changes do not agree with experimental results, a result already known from the dilute alloys based on fcc metals (Ram and Semalty 1987).

In view of the above, we have followed the usual procedure in such a Green's function treatment employing a localized perturbation model and treated the force-constant changes as free parameters in the theory. We have tried different sets of force-constant changes assuming $\Delta f_2^1 = 0$. The calculated results with contributions from different terms which are in best agreement with the experimental values are given in table 1. The experimental values are generally available at higher concentration; therefore, the values included in table 1 are estimated on the basis of these measurements. In the case of $\underline{\text{Nb}}$Mo and $\underline{\text{Mo}}$Nb (Hubbell and Brotzen 1972), $\underline{\text{Mo}}$Re (Lenkkeri and Latheenkorva 1978) and $\underline{\text{V}}$ Cr (Davidson and Brotzen 1968) we have estimated the values from the given graphs between elastic constants and concentration of impurities. In the case of $\underline{\text{Ta}}$W and $\underline{\text{W}}$Ta (Anderson and Brotzen 1982) the experimental values were taken at the lowest concentration of impurities.

From table 1 we see that the electronic contribution to the impurity induced change in bulk modulus is very small. The contributions due to volume change and force-constant changes are comparable in most of the cases. However, the case of shear modulus, $2C_{44}$ the effect of froce-constant changes is much more dominant than the volume effect.

The resulting force-constant changes giving the best agreement with the experimental results are given in table 2. It is found that for a given impurity-host system no single set of force constants is able to explain all the three elastic moduli. Thus the force-constant changes in different symmetry modes are different. This result regarding

Table 1. Calculated relative change in elastic constants due to unit concentration of impurities. The first change (ele.press.): due to electron pressure (i) volume induced change (ii) due to force constant change (iii) total change (iv) experimental values.

		$\Delta(C_{11}+2C_{12})/c(C_{11}+2C_{12})$				$\Delta(C_{11}-C_{12})/c(C_{11}-C_{12})$				$\Delta C_{44}/cC_{44}$			
Alloys	ele.press.	(i)	(ii)	(iii)	(iv)	(i)	(ii)	(iii)	(iv)	(i)	(ii)	(iii)	(iv)
MoRe	−0·023	0·105	0·111	0·193	0·379	0·066	0·028	0·094	−0·466	0·082	0·201	0·283	0·692
MoNb	−0·032	−0·242	−0·348	−0·622	−0·289	−0·150	−0·088	−0·238	−0·379	−0·189	−0·644	−0·833	−0·832
NbMo	−0·020	0·239	0·465	0·684	0·284	0·178	0·210	0·388	1·266	0·122	2·022	2·144	0·2615
TaW	−0·005	0·184	0·433	0·612	0·350	0·186	0·247	0·433	1·902	0·128	0·782	0·910	0·209
WTa	−0·012	−0·214	−0·407	−0·633	−0·363	−0·143	−0·118	−0·261	−0·809	−0·161	−0·596	−0·757	−0·075
VCr	−0·053	0·227	0·444	0·618	0·079	0·177	0·209	0·386	1·20	0·068	1·171	1·239	0·192

Table 2. Relative change in force constants obtained by matching the experimental results of different elastic moduli.

	From $\Delta(C_{11}+2C_{12})$		From $\Delta(C_{11}-C_{12})$		From ΔC_{44}	
Alloys	$\Delta f_1/f_1$	$\Delta f_2/f_1$	$\Delta f'_1/f_1$	$\Delta f_2/f_1$	$\Delta f_1/f_1$	$\Delta f'_1/f_1$
MoRe	0·203	0·0402	−0·17	0·015	0·21	−0·008
MoNb	−0·010	0·0024	0·012	−0·08	−0·217	0·0228
NbMo	0·040	0·006	−0·014	0·149	0·065	−0·04
TaW	0·095	0·08	0·05	0·152	0·06	−0·04
WTa	−0·065	0·013	−0·059	−0·085	0·05	0·012
VCr	−0·028	0·013	0·08	0·08	0·04	−0·009

the symmetry dependence of force-constant changes is in agreement with the dilute alloys based on fcc metals (Ram and Semalty 1987).

Symmetry dependence apart, some comments about the force-constant changes obtained would seem to be in order. As it stands the forces in a metal are generally long ranged and in any discussion of force-constant changes a proper account of electron-phonon interaction has to be included. Further in the context of elastic constants the distant force-constant changes could be as important as the changes in the force constants near the impurity and to that extent force-constant changes obtained on the basis of localized perturbation model would be effective changes in force constants. Nevertheless it is well known from lattice dynamical studies that the near-neighbour forces are dominant than long range forces and as such an impurity model with force-constant changes extending up to second-neighbours of impurity seems to be adequate and an inquiry regarding parameter characterizing near-neighbour force-constant changes is useful and interesting. In all the systems studied here the host and the impurity belong to one or the other transition metal series and have partially filled *d*-shell. An unfilled electronic shell has a significant effect on the interatomic force system. Since the short-range interaction depends on the electron configuration the force-constant changes would certainly depend on the electronic structure of the constituent metal. As a matter of fact, the velocity of long wavelength sound waves is proportional to $N(E_F)^{-1/2}$, $N(E_F)$ being the electronic density of states at the fermi surface, which is indicative of the frequency level and thereby of interatomic forces. If we assume a rigid-band model for the tansition metals an estimate of $N(E_F)$ in alloys can be made and some insight into force constant changes could be obtained. The rigid-band model seems to be reasonable for transition metal alloys with same crystal structures (McMillan 1968; Matthies 1966). McMillan (1968) has estimated $N(E_F)$ for a number of metals and alloys which are in good agreement with band structure (Matthies 1966, 1965). From McMillan's estimate it is clear that in NbMo, TaW and VCr, $N(E_F)$ decreases whereas in MoNb and WTa it increases. The decrease (increase) in $N(E_F)$ indicates an increase (decrease) in interatomic force constant of alloys compared with the host. From table 2 we observe that in NbMo and TaW we indeed get increase in nearest neighbour central force-constant whereas in MoNb we get decrease in it. In the case of WTa and VCr the situation is not very clear, when it is determined with the help of $\Delta(C_{11}+2C_{12})$ the nearest neighbour force constant decreases but when it is determined from ΔC_{44} the result is opposite. In this context we note that the change in bulk-modulus as it is given in (12) involves only A_{1g} mode, thus is determined by longitudinal forces only while shear modulus involves change in transverse force constants as well. If we consider the force constant changes $\Delta f_1/f_1$ determined from $\Delta(C_{11}+2C_{12})$ the obtained result in WTa is in agreement with the qualitative trend based on electronic structure. Thus except VCr the obtained force-constant changes are as expected from electronic structure consideration. In the case of MoRa no such simple qualitative explanation based on band structures could be possible because it is not clear whether rigid-band model is valid for an alloy of metals with different crystal structures. We note that the present result of an increase in nearest neighbour central force constant in NbMo and MoRe is in agreement with that of Hubbell and Brotzen (1972) and Davidson and Brotzen (1968) who have discussed its dependent on the concentration of alloying elements. In conclusion, we have calculated elastic constants of dilute alloys based on bcc metals. The obtained force constants changes the qualitative trend based on electronic structure considerations.

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