Mechanism of elastic shear coefficients of dilute copper alloys

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With the use of the Green's-function method, explicit expressions for the exchange energy contributions to elastic shear coefficients of α-phase dilute alloys have been obtained in terms of local changes of central and noncentral force constants around an impurity atom. The results are utilized to compute the Fermi-energy contributions to the elastic constants of Cu—4.1 at. % Al and Cu—2.8 at. % Au alloys.

I. INTRODUCTION

The elastic constants of a crystal are useful in understanding the mechanical and thermal properties of a solid. The principal lattice energy contributions to the elastic shear coefficients of copper and its dilute alloys are from electrostatic energy, exchange interaction energy of nearest-neighbor ion cores, and Fermi energy of conduction electrons. Actually, their sum does not give the complete account of the internal energy of a solid because of the exchange and correlation effects for the conduction electrons, certain electrostatic terms, etc. However, their effect on the total energy is considered to be small. One can, therefore, write the total energy per atom as

$$W = W_0 + W_E + W_R + W_F , \qquad (1)$$

where W_0 is the total energy of the lowest conduction-electron state, W_E is the electrostatic energy, W_R is the exchange energy between the ion cores, and W_F is the Fermi energy of the conduction electrons.

The determination of the repulsive and Fermi-energy contributions to shear elastic constants of copper and its alloys is a difficult problem from a theoretical, as well as, experimental point of view. An attempt to calculate the Fermi-energy contribution to shear elastic constants of α-phase copper and silver based alloys was made by Collins[1] by using a rigid-band model and measured Fermi-surface parameters. However, the calculated results were found to be in poor agreement with the measured elastic constants because of the neglect of the ion-core contribution and the serious approximations involved in the calculation of the Fermi-energy contribution. Even in the case of pure copper, the Fermi-energy contributions calculated by Collins exhibit a large difference from the results of Sinha,[2] obtained by using a local-pseudopotential approach, and it is difficult to say at the present state of knowledge which of the two results might be most accurate. Another effort for the evaluation of the change in Fermi-energy contribution to the shear elastic constants due to alloying was made by Cain and Thomas.[3] In their calculations, the ion-core contribution was considered to be directly proportional to the number of modified ion-interaction pairs, and the value of the proportionality constant was chosen in an arbitrary manner. However, the effects due to force constant change around the solute

atoms were not taken into account in their calculations.

An alternative approach for estimating the Fermi-energy contribution lies in the calculation of the ion-core contribution by determining the pair potential after utilizing the pressure derivatives of second-order elastic constants and measured third-order and calculated fourth-order elastic constants. But the agreement between the different calculations is generally poor for the pure metals. However, such calculations for the α-phase dilute alloys are not available. Due to this, a reasonable decomposition of the shear elastic constants of the α-phase alloy remained an intractable problem.

For the calculation of the ion-core contribution, the present paper adopts a different approach, i.e., the Green's-function method[4] which takes into account in a natural way the discreteness of the lattice structure and, thus, has an added advantage over the pair-potential method. The calculated ion-core contribution is finally used to extract out the information about the change in the Fermi-energy contribution to shear elastic constants of dilute copper alloys. The only attempt so far to explain the elastic constants of dilute Cu-Au alloys by utilizing the Green's-function method was made by Taylor.[5] However, they were unable to find any combination of nearest-neighbor force constant changes to fit the experimental results because of the neglect of the electrostatic and Fermi-energy contributions. This paper represents the first attempt to interpret the experimental results on any dilute face-centered-cubic alloy by following the Green's-function approach. The explicit expressions for the ion-core contribution to the elastic constant of imperfect lattice have been derived in Sec. II and are utilized to calculate the Fermi-energy contributions to the elastic constants of Cu—4.1 at. % Al and Cu—2.8 at. % Au alloys in Sec. III.

II. THEORY

For a solid containing a low concentration p of similar substitutional defects, the averaged perturbed Green's function may be written as

$$\langle \underline{G}(z) \rangle = \underline{G}^0(z) - \underline{G}^0(z) \underline{\Sigma} \langle \underline{G}(z) \rangle , \qquad (2)$$

where the self-energy $\underline{\Sigma}$ has the same periodicity as the perfect phonon propagator $\underline{G}^0(z)$, and $z = \omega^2 + 2i\omega\eta^+$ is the complex squared frequency in the limit $\eta^+ \to 0$. In

writing Eq. (2), a statistical average over all the possible configurations of defects has been taken.

In normal mode representation, the averaged perturbed Green's function may be written as

$$\langle G(\mathbf{k})\rangle = [\omega_{\mathbf{k},s}^2 \underline{I} + \underline{\Sigma}(\mathbf{k},s) - z\underline{I}]^{-1} , \qquad (3)$$

where $\omega_{\mathbf{k},s}^2$ are the squared frequencies of the host lattice corresponding to the wave vector $\mathbf{k}$ of the polarization branch s.

If we consider only the scattering of phonons off single impurities and neglect the scattering off clusters of impurities, the self-energy $\underline{\Sigma}(\mathbf{k},s)$ may be written as

$$\underline{\Sigma}(\mathbf{k},s) = \langle \mathbf{k}s \mid \underline{\Sigma}(z) \mid \mathbf{k},s \rangle , \qquad (4)$$

with

$$\underline{\Sigma}(z) = p\underline{p}(\omega^2)[\underline{I} + (1-p)\underline{g}^0(z)\underline{P}(\omega^2)]^{-1} . \qquad (5)$$

Here $\underline{P}(\omega^2)$ is the perturbation matrix due to a single defect and $\underline{g}^0(z)$ is the Green's-function matrix in the subspace of a single defect (of dimension $3b \times 3b$; b is the number of atoms directly affected by the defect including the defect itself). The real part of the self-energy $\underline{\Sigma}(\mathbf{k},s)$ yields the information about the shift in the squared frequencies which may be written as

$$\widetilde{\omega}_{\mathbf{k},s}^2 - \omega_{\mathbf{k},s}^2 = \mathrm{Re}\langle \mathbf{k},s \mid \underline{\Sigma}(z) \mid \mathbf{k},s \rangle , \qquad (6)$$

where $\widetilde{\omega}_{\mathbf{k},s}$ is the perturbed phonon frequency.

The group velocities in an imperfect lattice are defined as

$$\widetilde{v}_{\mathbf{k},s} = \frac{\partial \widetilde{\omega}_{\mathbf{k},s}}{\partial \mathbf{k}} \qquad (7)$$

and are related to host lattice group velocity $v_{\mathbf{k},s}$ as

$$\widetilde{\rho}\widetilde{v}_{\mathbf{k},s}^2 = \rho v_{\mathbf{k},s}^2 \left[1 + \left[\frac{\partial}{\partial \omega_{\mathbf{k},s}^2}\right] \mathrm{Re}\langle \mathbf{k},s \mid \underline{\Sigma}(z) \mid \mathbf{k},s \rangle \right.$$

$$\left. + p\frac{\Delta M}{M} \right] , \qquad (8)$$

where $\widetilde{\rho}$ and ρ are the imperfect and host lattice densities which are related as

$$\widetilde{\rho} = \rho \left[1 + p\frac{\Delta M}{M}\right] . \qquad (9)$$

Here, ΔM is the change of mass at the site of the impurity and M is the mass of the host lattice atom.

For a cubic crystal, only three elastic constants $\widetilde{C}_{11}$, $\widetilde{C}_{12}$, and $\widetilde{C}_{44}$ are needed to describe the group velocities in any direction. The relations between the bulk elastic constants and $(\widetilde{v}_{\mathbf{k},s})_{\mathbf{k}\to 0}$, used in the present calculations, are as follows:

$$\widetilde{C}_{11} = \widetilde{\rho}\widetilde{v}_{100,\mathrm{LA}}^2 ,$$

$$\widetilde{C}_{44} = \widetilde{\rho}\widetilde{v}_{100,\mathrm{TA}}^2 , \qquad (10)$$

$$\widetilde{C}_{12} = 2\widetilde{\rho}\widetilde{v}_{110,\mathrm{LA}}^2 - \widetilde{C}_{11} - 2\widetilde{C}_{44} .$$

For a substitutional impurity in a fcc lattice, the perturbation matrix is of dimension 39×39 if changes in the central and noncentral force constants are considered only up to the nearest neighbors. The point-group symmetry of the defect site is O_h, and irreducible representations occurring in the problem are F_{1u}, F_{2u}, F_{1g}, F_{2g}, E_g, E_u, A_{2u}, A_{1g}, and A_{2g}. The perturbation and Green's-function matrices in different irreducible representations have been determined by Agrawal[6] for a diatomic fcc lattice. For a monatomic fcc lattice, one can easily deduce the necessary results. In the limit $\mathbf{k}_0 \equiv 2\pi k_0 a \to 0$, where a is the lattice parameter, various components of the symmetrized $\underline{\Sigma}(z)$ matrix in different irreducible representations appearing in Eq. (8) are

$$(\mathbf{k},s \mid \underline{\Sigma}_{F_{1u}} \mid \mathbf{k},s) = -p\frac{\Delta M}{M}\omega^2 \mathbf{k},s ,$$

$$(\mathbf{k},\mathrm{LA} \mid \underline{\Sigma}_{A_{1g}} \mid \mathbf{k},\mathrm{LA}) = \frac{2p}{3M}\frac{\lambda}{1+(1-p)\lambda/f_{1g}}k_0^2 ,$$

$$(\mathbf{k},\mathrm{LA} \mid \underline{\Sigma}_{E_g} \mid \mathbf{k},\mathrm{LA}) = \frac{p}{3M}\delta_{12}\left[k_0^2 - \frac{3(k_{0x}^2 k_{0y}^2 + \mathrm{c.p.})}{k_0^2}\right] ,$$

$$(\mathbf{k},\mathrm{LA} \mid \underline{\Sigma}_{F_{2g}} \mid \mathbf{k},\mathrm{LA}) = \frac{2p}{M}\delta_{25}\left[\frac{k_{0x}^2 k_{0y}^2 + \mathrm{c.p.}}{k_0^2}\right] ,$$

$$(k_{00},\mathrm{TA} \mid \underline{\Sigma}_{F_{2g}} \mid k_{00},\mathrm{TA}) = \frac{p}{2M}\delta_{25}k_0^2 ,$$

$$(\mathbf{k},\mathrm{TA} \mid \underline{\Sigma}_{A_{1g}} \mid \mathbf{k},\mathrm{TA}) = 0 , \qquad (11)$$

$$(k_{00},\mathrm{TA} \mid \underline{\Sigma}_{E_g} \mid k_{00},\mathrm{TA}) = 0 ,$$

$$(\mathbf{k},s \mid \underline{\Sigma}_{F_{2u}} \mid \mathbf{k},s) = 0 ,$$

$$(\mathbf{k},s \mid \underline{\Sigma}_{E_u} \mid \mathbf{k},s) = 0 ,$$

$$(\mathbf{k},s \mid \underline{\Sigma}_{A_{2u}} \mid \mathbf{k},s) = 0 ,$$

$$(\mathbf{k},s \mid \underline{\Sigma}_{A_{2g}} \mid \mathbf{k},s) = 0 ,$$

where c.p. denotes the cyclic permutations. In the above calculation of the matrix elements, only terms up to the order of k_0^2 have been considered. The matrix elements associated with F_{1g} irreducible representation have not been included because the strains due to F_{1g} irreducible representation are asymmetric.

The quantities f_{1g}, δ_{12}, and δ_{25} are defined as

$$f_{1g} = M(g_1 + 2g_3 + 2g_4 + g_5 - g_6 - g_7$$

$$+ g_9 - 2g_{10} + 4g_{12} + 2g_{13})^{-1} ,$$

$$\delta_{12} = \frac{p}{D_{E_g}(z)}\left[\lambda + 3\lambda' + (1-p)\frac{\lambda\lambda'}{M}(g_{E_g}^{22} - 2\sqrt{3}g_{E_g}^{12} + 3g_{E_g}^{11})\right] ,$$

with

$$D_{E_g}(z) = 1 + \frac{(1-p)}{M}(\lambda g_{E_g}^{11} + \lambda' g_{E_g}^{22})$$

$$+ (1-p)^2\frac{\lambda\lambda'}{M^2}[g_{E_g}^{11}g_{E_g}^{22} - (g_{E_g}^{12})^2] ,$$

and

$$\delta_{25} = \frac{p}{D_{F_{2g}}(z)}\left[\lambda + \lambda' + (1-p)\frac{\lambda\lambda'}{M}(g_{F_{2g}}^{11} + g_{F_{2g}}^{22} - 2g_{F_{2g}}^{12})\right] ,$$

with

$$D_{F_{2g}}(z) = 1 + \frac{(1-p)}{M}(\lambda' g_{F_{2g}}^{11} + \lambda g_{F_{2g}}^{22})$$
$$+ (1-p)^2 \frac{\lambda\lambda'}{M^2}[g_{F_{2g}}^{11} g_{F_{2g}}^{22} - (g_{F_{2g}}^{12})^2] . \quad (12)$$

Here, λ and λ' are the local changes of central and non-central force constants, respectively. The different Green's-function matrix elements appearing in Eq. (12) are readily obtained from Ref. 6.

In deriving the various matrix elements [Eq. (11)], the effects due to changed repulsive interaction between impurity and only its nearest neighbors have been taken into account. Using Eqs. (8)—(11), one therefore obtains the change in ion-core contributions to the elastic constants of the imperfect lattice due to substitution of impurity atoms as

$$\Delta C_{11}^R = \frac{8p}{3a}\left[\frac{\lambda}{1+(1-p)\lambda/f_{1g}} + \frac{\delta_{12}}{2}\right],$$

$$\Delta C_{12}^R = \frac{8p}{3a}\left[\frac{\lambda}{1+(1-p)\lambda/f_{1g}} - \frac{\delta_{12}}{4}\right], \quad (13)$$

$$\Delta C_{44}^R = \frac{2p}{a}\delta_{25} .$$

The change in bulk modulus ΔK_R and the change in shear elastic constants ΔC_R and $\Delta C_R'$ due to fractional concentration of defects p is given by

$$\Delta K_R = \frac{8p}{3a}\frac{\lambda}{1+(1-p)\lambda/f_{1g}} ,$$

$$\Delta C_R = \frac{2p}{a}\delta_{25} , \quad (14)$$

and

$$\Delta C_R' = \frac{p}{a}\delta_{12} .$$

III. NUMERICAL CALCULATIONS AND RESULTS

The changes in shear elastic constants ΔC and $\Delta C'$ upon alloying is assumed to consist of two separate effects: (i) the change ΔC_L and $\Delta C_L'$ due to modification of the lattice parameter and (ii) the explicit change due to the addition of the impurity in the expanded (or contracted) lattice ΔC_I and $\Delta C_I'$. The values of ΔC_I and $\Delta C_I'$ are determined from the following equation:

$$\Delta C = \Delta C_I - 3B_T\left[\frac{\partial C}{\partial P}\right]_{p=0}\frac{d(\ln a)}{d(\ln p)} , \quad (15)$$

where B_T is the isothermal bulk modulus and $(\partial C/\partial P)_{p=0}$ is the hydrostatic pressure derivative of the elastic constant of the solvent. A similar equation can be written for the change in shear elastic constant C'.

The explicit change due to the addition of impurity ΔC_I consists of three separate contributions, i.e., from (i) electrostatic energy ΔC_E, (ii) exchange interaction energy of the nearest-neighbor ion cores ΔC_R, and (iii) Fermi en-

ergy of the conduction electrons ΔC_F. Therefore, one can write

$$\Delta C_I = \Delta C_E + \Delta C_R + \Delta C_F . \quad (16)$$

In order to understand the mechanism of shear elastic constants, the numerical calculations have been performed in the case of Cu—2.8 at. % Au and Cu—4.1 at. % Al alloys. The different Green's-function matrix elements appearing in Eq. (13) have been calculated by using the lattice dynamics of copper in the model by Krebs.[7] The values of pressure derivatives of the elastic constants of copper are taken from the work of Daniels and Smith[8] and the value of B_T used in the calculations is 1.332×10^{12} dyn/cm^2.

The changes in the electrostatic contribution to shear elastic constants of an α-phase alloy due to the addition of the impurity atoms are determined by closely following the results of Fuchs[9] and are written as

$$\Delta C_E = 1.8956(Z^2 - 1)\frac{e^2}{a^4} ,$$
$$\quad (17)$$
$$\Delta C_E' = 0.2116(Z^2 - 1)\frac{e^2}{a^4} ,$$

where $Z = 1 + pq$ is the effective valence of the imperfect lattice with q as the excess valence of the solute, and e is the electronic charge.

The measurements of the elastic constants of Cu—2.8 at. % Au alloy have been performed by O'hara and Marshall.[10] The values of λ and λ' for a Cu—3.0 at. % Au alloy have been determined by Kesharwani and Agrawal[11] from the study of impurity induced phonon shifts and widths in the alloy.[12] These values of λ and λ' are not expected to be altered much for a Cu—2.8 at. % Au alloy and are, therefore, used to calculate the ion-core contribution. The results are summarized in Table I.

The elastic constants of the dilute Cu-Al alloys have

TABLE I. Impurity induced changes in different lattice energy contributions to shear elastic constants of dilute copper alloys in units of 10^{11} dyn/cm^2. For pure copper, $C = 7.54 \times 10^{11}$ dyn/cm^2 and $C' = 2.37 \times 10^{11}$ dyn/cm^2.

	Cu—4.1 at. % Al	Cu—2.8 at. % Au
ΔC		
Experiment	0.12[a]	−0.15[b]
Lattice expansion correction	−0.28	−0.04
Electrostatic contribution	0.44	
Ion-core contribution	0.13	0.17
Fermi contribution	−0.17	−0.28
$\Delta C'$		
Experiment	−0.08[a]	−0.10[b]
Lattice expansion correction	−0.07	−0.01
Electrostatic contribution	0.02	
Ion-core contribution	0.06	0.08
Fermi contribution	−0.09	−0.17

[a]Reference 3.
[b]Reference 10.

been measured by Cain and Thomas[3] for the different low concentrations of Al. However, the value of λ is available only for a Cu—4.1 at. % Al alloy.[13] The value has been obtained by analyzing the phonon spectra[14] of the alloy which exhibits a localized vibrational mode at the frequency 8.78 THz. The shear elastic constants for a Cu—4.1 at. % Al alloy have been determined by interpolation of the experimental results. The calculated values are again presented in Table I.

From Table I, one can observe that ΔC_F and $\Delta C_F'$ for both types of alloys are negative. The results in the case of a Cu—4.1 at. % Al alloy are quite different from those of Cain and Thomas,[3] because of the assumption that ΔC_R and $\Delta C_R'$ do not depend on the nature of the impurity and are directly proportional to C_R and C_R', respectively ($\Delta C_R = \sigma C_R$ and $\Delta C_R' = \sigma C_R'$; the value of σ has been taken to be negative[3]). Due to this, ΔC_R and $\Delta C_R'$ in Ref. 3 turned out to be negative which, in turn, yielded the positive values for ΔC_F and $\Delta C_F'$. For a Cu—2.8 at. % Au alloy, the results from the other authors are not available for comparison.

The effect of zone boundaries on W_F is significant. The energies of the various electron states are altered due to the distortion of a filled zone in reciprocal space These changes when averaged over the zone cancel to the first order in strain but contribute positively in the second order. For a partially filled zone, the first-order terms are positive over some part of the Fermi surface and negative over the others while second-order terms continue to remain positive. This results in shifting of the electronic population from the parts where the change is positive, to the parts where it is negative. This shift lowers the stress energy and the related elastic modulus.

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