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Elastic Constants of Dilute Mo-Re Alloys: A Second-Neighbor Model

K. M. Kesharwani and Bal K. Agrawal
Physics Department, Allahabad University, Allahabad-211002, India

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The effects of a relatively high concentration of point defects on the elastic properties of a bcc crystal in the Elliott–Taylor approximation have been studied by using a defect perturbation model extending up to second neighbors. Numerical calculations have been performed for two experimentally studied Mo-Re (7 and 7.4%) alloys. It is observed that the changes in the second-neighbor force constants are very small and the perturbation may well be described by a nearest-neighbor defect model. The results obtained in the Elliott–Taylor approximation are seen to be very near to those obtained in the lowest-order concentration theory.

In earlier papers, the authors have used the low-concentration Green's-function theory to study the elastic properties of doped cesium halides[1,2] and dilute Mo-Re alloys[3] (hereafter referred to as I) after employing a nearest-neighbor perturbation model. In transition metals, two types of interactions[4] are considered to be important: (a) the short-range exchange interaction, which may be significant up to some neighbors, and (b) the Coulombic interaction between the positive heavy ions and the free electrons. However, it has been observed that in transition metals, the elastic constants are mainly determined by short-range exchange interaction.[5,6] Both the molybdenum and rhenium contain incompletely filled *d* shells and form transition-metal alloys. The short-range interaction between the positive ions is assumed to be important up to next-nearest neighbors. If a rhenium atom is substituted at a lattice site in molybdenum metal, the perturbation may well extend up to second neighbors of the impurity. Thus, a perturbation model which incorporates also the interactions beyond the first neighbors may be more realistic.

In the present Note, we have considered a second-neighbor perturbation model for the defect to determine the effects of a low concentration of randomly distributed point defects on the bulk elastic constants of crystals of bcc structure in the framework of Elliott and Taylor's approximation.[7] The theoretical formalism is similar to I. The elastic constants of the perfect and the imperfect lattice are related by

$$\tilde{C}_{11}=C^{0}_{11}+(4c/3a)(A+2B),$$
$$\tilde{C}_{12}=C^{0}_{12}+(4c/3a)(A-B), \qquad (1)$$
$$\tilde{C}_{44}=C^{0}_{44}+2D/a,$$

where

$$A=\frac{1}{D_{A_{1g}}(0)}\left(\lambda_1+\lambda_2+(1-c)\,\frac{\lambda_1\lambda_2}{M}\,[g^{11}_{A_{1g}}(0)+g^{22}_{A_{1g}}(0)-2g^{12}_{A_{1g}}(0)]\right),$$

$$B=\frac{1}{D_{E_g}(0)}\left(\lambda'_1+\lambda_2+(1-c)\,\frac{\lambda'_1\lambda_2}{M}\,[g^{11}_{E_g}(0)+g^{22}_{E_g}(0)+2g^{12}_{E_g}(0)]\right), \qquad (2)$$

and

$$D=M(\Sigma^{22}_{F_{2g}}+2\Sigma^{23}_{F_{2g}}+\Sigma^{33}_{F_{2g}})_{\omega=0}.$$

Here *c* denotes the fractional concentration of impurity in the crystal, *a* is the lattice parameter, and $\lambda_1=\Delta\alpha_1$ $(\lambda'_1=\Delta\beta_1)$ is the change in the central (noncentral) force constants for first neighbors, whereas $\lambda_2=\Delta\alpha_2$ stands for the change in the second-neighbor central force constant. In these expressions, $D_{A_{1g}}(0)$ and $D_{E_g}(0)$ are the resonance denominators in the A_{1g} and E_g irreducible representations and are of the form

$$D_{A_{1g}}(0)=1+\frac{1-c}{M}\,[\lambda_1 g^{11}_{A_{1g}}(0)+\lambda_2 g^{22}_{A_{1g}}(0)]+\frac{(1-c)^2\lambda_1\lambda_2}{M^2}$$
$$\times\{g^{11}_{A_{1g}}(0)\,g^{22}_{A_{1g}}(0)-[g^{12}_{A_{1g}}(0)]^2\}, \qquad (3)$$

$$D_{E_g}(0)=1+\frac{1-c}{M}\,[\lambda'_1 g^{11}_{E_g}(0)+\lambda_2 g^{22}_{E_g}(0)]+\frac{(1-c)^2\lambda'_1\lambda_2}{M^2}$$
$$\times\{g^{11}_{E_g}(0)\,g^{22}_{E_g}(0)-[g^{12}_{E_g}(0)]^2\},$$

where *M* is the mass of the host-lattice atom and $g^{ij}_{\nu}(0)$ are the elements of the Green's-function matrix $g_{\nu}(0)$ at $\omega=0$ and are given by

$$g^{11}_{A_{1g}}(0)=(g_1-2g_4+g_5+2g_6-g_7+2g_8-g_9+2g_{10})_{\omega=0},$$

$$
\begin{aligned}
g^{12}_{A_{1g}}(0) &= (g_1+4g_6-g_{11})_{\omega=0}, \\
g^{22}_{A_{1g}}(0) &= 2(g_2+2g_3-g_{13}+2g_{15})_{\omega=0}, \\
g^{11}_{E_g}(0) &= (g_1-2g_4+g_5-g_6-g_7-g_8-g_9+2g_{10})_{\omega=0}, \\
g^{12}_{E_g}(0) &= (g_1-2g_6-g_{11})_{\omega=0}, \\
g^{22}_{E_g}(0) &= -2(g_2-g_3-g_{13}+2g_{15})_{\omega=0}\,.
\end{aligned}
\qquad (4)
$$

The $\Sigma^{ij}_{F_{2g}}$ are the matrix elements of the self-energy projected in F_{2g} space given by

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

where $\underline{I}$ is the unit matrix, and $\underline{p}_{F_{2g}}(\omega^2)$ and $\underline{g}^0_{F_{2g}}(z)$ have the explicit forms

$$
\underline{p}_{F_{2g}}(\omega^2) = \frac{1}{3M}\begin{pmatrix} \lambda_1+2\lambda_1' & (\sqrt{2})(\lambda_1-\lambda_1') & 0 \\ (\sqrt{2})(\lambda_1-\lambda_1') & 2\lambda_1+\lambda_1' & 0 \\ 0 & 0 & 3\lambda_2' \end{pmatrix},
$$
$$
\underline{g}^0_{F_{2g}}(z) = \begin{pmatrix} \begin{matrix} g_1+2g_4+g_5-g_7 \\ -g_9-2g_{10} \end{matrix} & -(\sqrt{2})(g_6-g_8) & -(\sqrt{8})(g_3-g_{16}) \\ -(\sqrt{2})(g_6-g_8) & g_1-g_5+g_6-g_7+g_8+g_9 & 2(g_2+g_3-g_{14}+g_{15}) \\ -(\sqrt{8})(g_3-g_{16}) & 2(g_2+g_3-g_{14}+g_{15}) & g_1+2g_6-g_{12} \end{pmatrix}, \qquad (6)
$$

with complex squared frequency $z=\omega^2+2i\omega\eta^+$ in the limit $\eta^+\to 0$, and $\lambda_2'=\Delta\beta_2$ as the change in second-neighbor noncentral force constant. The various Green's functions g_1–g_{16} have been defined by Ram and Agrawal[8] in one of their recent papers.

The expressions for nearest-neighbor perturbation[9] are easily determined by assuming λ_2 and λ_2' equal to zero. One can also obtain the results for lowest order in concentration by replacing $1-c$ by 1.

In order to perform the numerical computations, the results of the lattice dynamics of molybdenum (discussed in I) are utilized to evaluate the six new Green's functions [Eq. (21) of I] appearing in the present calculation. A set of four force-constant-change parameters (λ_1, λ_1', λ_2, and λ_2') is determined using the three relations for the elastic constants given by Eqs. (1) and the experimentally measured elastic constants[10] for the Mo-Re alloys (7 and 7.4 at. % Re). These values of λ_1, λ_1', λ_2, and λ_2' are presented in Table I along with the corresponding force constants in pure molybdenum. Davidson and Brotzen[10] have also evaluated the force constant changes in Mo-Re alloys after utilizing the distributed perturbation model of Niu and Shimizu.[11] In this model, the force constants between the host-

TABLE I. Force-constant changes incurred by the substitution of a rhenium atom in a molybdenum lattice in a localized perturbation model and the distributed perturbation model in units of 10^4 g sec^{-2}. The force constants for pure crystal have been obtained by using the data of elastic constants (Ref. 10) and the zone-boundary frequency $\omega_T=4.147\times 10^{13}$ sec^{-1} in the (ξ,ξ,ξ) direction.

	Localized perturbation model				Distributed perturbation model
	Second-neighbor perturbation model		First-neighbor perturbation model		
Changes in force constants	lowest-order concentration theory	Elliott and Taylor's approx.	lowest-order concentration theory	Elliott and Taylor's approx.	Niu-Shimizu model (Ref. 11)
λ_1	2.753	2.721	2.625	2.605	0.328
λ_1'	−0.957	−0.968	−1.053	−1.057	−0.038
λ_2	−0.102	−0.094	⋯	⋯	−0.083
λ_2'	−0.089	−0.084	⋯	⋯	⋯

α_1 (first-neighbor central force constant) = 8.229×10^4 g sec^{-2}

β_1 (first-neighbor noncentral force constant) = 1.806×10^4 g sec^{-2}

α_2 (second-neighbor central force constant) = 3.387×10^4 g sec^{-2}

β_2 (second-neighbor noncentral force constant) = -2.224×10^4 g sec^{-2}

host atoms and those between host-impurity atoms are taken to be similar. In order to have a comparison, we present their results in Table I.

From Table I, we observe that the changes in the next-neighbor force constants are too small. In fact, their magnitudes are only of the order of 3–4%. The results obtained earlier on the basis of a nearest-neighbor perturbation model are not altered much, although there are slight alterations in the force constant changes. These values for the changes in the central and noncentral force constants are supported by lattice specific-heat data[12] of Mo-Re alloys recently analyzed by Tiwari and Agrawal.[13] These authors have obtained good agreement between theory and experiment after using similar values for λ_1 and λ_1' in the nearest-neighbor perturbation model. The present values are in complete disagreement with those obtained by Davidson and Brotzen, who have seen very small changes in the nearest-neighbor force constants but a comparatively appreciable change in the second-neighbor central force constant.

The replacement of a molybdenum atom by a rhenium atom will increase the electron-per-atom ratio of the crystal because the electronic configurations of Mo and Re atoms are $4d^5 5s^1$ and $5d^5 6s^2$, respectively. As pointed out earlier, since the short-range interaction mainly determines the magnitudes of the elastic constants, the long-range Coulombic interaction, because of the increased electron-per-atom ratio, will not induce significant changes in the elastic constants of an alloy. The important role of the short-range interaction led Zener[14] to assume an antiferromagnetic arrangement of the ions in molybdenum and its alloys. In this arrangement an antiparallel spin alignment is assumed for nearest neighbors, whereas a parallel spin alignment is taken for next-nearest neighbors. The exchange energy arises only because of the interactions of *d* shells of next-nearest neighbors; consequently, an attractive interaction will be seen between nearest neighbors, while a repulsive interaction will be observed between the next-nearest neighbors. It means that the nature of interactions should be totally different for the nearest and the next-nearest neighbors. The values of the perturbation parameters obtained in the present model support this contention. However, we have found very small changes in the next-nearest-neighbor interactions around rhenium in the Mo matrix.

Further, we note that the results obtained in Elliott and Taylor's approximation are very similar to those obtained in the lowest concentration approximation. The differences in the evaluated force constants in two approximations are within 5%.

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[1] K. M. Kesharwani and Bal K. Agrawal, in *Proceedings of Nuclear Physics and Solid State Physics Symposium*, Madurai (Department of Atomic Energy, Bombay, 1970), Vol. 3, p. 469.

[2] K. M. Kesharwani and Bal K. Agrawal, Phys. Rev. B **4**, 4623 (1971).

[3] K. M. Kesharwani and Bal K. Agrawal, Phys. Rev. B **5**, 2130 (1972).

[4] K. Fuchs, Proc. R. Soc. A **153**, 622 (1936).

[5] D. I. Bolef, J. Appl. Phys. 32, 100 (1961).

[6] F. H. Featherton and J. R. Neighbours, Phys. Rev. **130**, 1324 (1963).

[7] R. J. Elliott and D. W. Taylor, Proc. R. Soc. A **296**, 161 (1967).

[8] P. N. Ram and Bal K. Agrawal (unpublished).

[9] The Eqs. (17) of Ref. 3 are in error by a factor of 2 on the right-hand side. They are obtained if we replace 1-*c* by 1 and put $\lambda_2 = \lambda_2' = 0$ in Eqs. (1)–(3) of the present paper. The values of λ and λ' reported there are also modified.

[10] D. L. Davidson and F. R. Brotzen, J. Appl. Phys. **39**, 5768 (1968).

[11] H. Niu and M. Shimizu, J. Phys. Soc. Jap. **22**, 437 (1967).

[12] F. H. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).

[13] M. D. Tiwari and Bal K. Agrawal, Phys. Rev. B 8, 1397 (1973).

[14] C. Zener, Phys. Rev. **71**, 846 (1947).