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Elastic Constants of Dilute Mo-Re Alloys

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The *T*-matrix method has been used for determining the effects of a low concentration of randomly distributed point defects on the elastic constants of a crystal of bcc structure. The expressions for the bulk elastic constants have been obtained in terms of the local changes in the central and noncentral force constants. The lattice dynamics of molybdenum have been discussed in Kreb's model with interactions up to second neighbors. The obtained eigenfrequencies and the eigenvectors are used to evaluate the different Green's-function matrix elements. Numerical estimates have been made for molybdenum crystal containing two different concentrations (7 and 7.4%) of rhenium. The results are compared with the experimentally measured elastic constants of the dilute alloys. An almost exact agreement between the theory and the experiment is observed.

I. INTRODUCTION

The elastic properties of a crystal containing a finite concentration of defects are significantly altered. The local strains around the defect are seen to be different from those of the host lattice. A knowledge of these strains, induced locally by the applied stress, is required to interpret a number of experimental measurements of the effects of elastic strains[1–4] and electric fields[5] on the properties of crystals containing point defects. In recent years, some experiments have also been done to study the effect of defects on the bulk elastic properties of metals.[6–8] Several theories[9,10] have been proposed to account for these effects, but none of them takes into consideration the local behavior of defects and the discrete nature of the lattice. The *T*-matrix method takes into account, in a natural way, the peculiarities of the discrete nature of the lattice. A different theory has been developed by Ludwig[11] and Pistorious.[12] Earlier, the present authors applied a *T*-matrix method to determine the effect of substituted point defects on the elastic properties of the crystals of CsCl structure.[13,14]

In the present paper, we use the *T*-matrix method for determining the effects of a low concentration of randomly distributed point defects on the elastic properties of the crystals of bcc structure. Expressions for the bulk elastic constants have been obtained in terms of local changes of central and noncentral force constants in Sec. III. Numerical estimates have been made in Sec. IV for the case of molybdenum containing rhenium impurity ions. The calculated values are compared with the available experimental results.[15]

II. THEORY

Consider a solid containing a low concentration of similar substitutional point defects. In order to understand the lattice dynamics of the imperfect solid, one evaluates the perturbed phonon propagator as a Green's function which is given by

$$\underline{G}(z)=[\underline{L}_0+\underline{P}_{sc}(\omega^2)-z\underline{I}\,]^{-1}\,, \qquad (1)$$

where $\underline{L}_0$ is the mass-reduced dynamical matrix of the perfect host lattice and $\underline{P}_{sc}(\omega^2)$ is the perturbation matrix caused by a specific configuration of the defects. For the explicit forms of these matrices, we refer to an earlier paper.[16] $z=\omega^2+2i\omega\xi^+$ is the complex squared frequency in the limit as $\xi^+\rightarrow 0^+$. The propagator defined by Eq. (1)

has been written for a single specific configuration of defects and the averaged perturbed Green's function is given by

$$\langle \underline{G}(z)\rangle = \underline{G}_0(z) - \underline{G}_0(z)\,\underline{\Sigma}\,\langle \underline{G}(z)\rangle\ , \tag{2}$$

where the self-energy $\underline{\Sigma}$ is periodic like the perfect phonon propagator $\underline{G}_0$. On account of the configuration average we can, therefore, go to the normal-mode representation and write

$$\langle \underline{G}(\vec{k})\rangle = [\omega^2_{\vec{k},s} + \underline{\Sigma}(\vec{k}, s) - z\underline{I}\,]^{-1}\ , \tag{3}$$

where $\omega^2_{\vec{k},s}$ denotes the squared frequency of the host lattice corresponding to the wave vector $\vec{k}$ in the polarization branch s. If we consider only multiple scatterings by the same defect and limit ourselves only up to the first order of concentration of defects, there is no mixing in the polarization branches along certain symmetry directions and, therefore, the self-energy $\underline{\Sigma}(\vec{k}, s)$ can be written as[17,18]

$$\underline{\Sigma}(\vec{k}, s) = c\,\langle \vec{k}, s \mid \underline{T}(z) \mid \vec{k}, s\rangle\ , \tag{4}$$

where c is the fractional concentration of defects and $\underline{T}(z)$ is the T matrix for the single site and is defined by

$$\underline{T}(z) = \underline{P}(\omega^2)\,[\,\underline{I} + \underline{g}^0(z)\,\underline{P}(\omega^2)\,]^{-1}\ . \tag{5}$$

Here $\underline{P}(\omega^2)$ is the perturbation matrix due to single defect and $\underline{g}^0(z)$ is Green's-function matrix in the impurity space. The poles of the propagator given by Eq. (3) in the complex z plane give us the squared frequencies and the phonon widths for the perturbed phonons. The shift in the squared frequency is given by the real part of the self-energy defined by Eq. (4). The squared frequencies of the perturbed phonons are, thus, given by

$$\tilde{\omega}^2_{\vec{k}} = \omega^2_{\vec{k},s} + c\,\mathrm{Re}\,\langle \vec{k}, s \mid \underline{T}(z) \mid \vec{k}, s\rangle\ , \tag{6}$$

where the tilde over $\omega_{\vec{k},s}$ specifies the perturbed phonon frequency. After considering the symmetric properties of the perturbation matrix, the T matrix can be written as

$$\langle \vec{k}, s \mid \underline{T}(z) \mid \vec{k}, s\rangle = \textstyle\sum_\nu \langle \vec{k}, s \mid \underline{T}_\nu(z) \mid \vec{k}, s\rangle\ , \tag{7}$$

where $\underline{T}_\nu(z)$ is the projected T matrix in the νth irreducible representation occurring in the defect problem.

III. BULK ELASTIC CONSTANTS

The group velocities for the imperfect lattice are determined by

$$\tilde{\vec{v}}_{\vec{k},s} = \frac{\partial \tilde{\omega}_{\vec{k},s}}{\partial \vec{k}}\ . \tag{8}$$

TABLE I. Group velocities along symmetry directions.

$\rho v^2_{\vec{k},s}$	⟨100⟩	⟨111⟩	⟨110⟩
L	C_{11}	$\frac{1}{3}(C_{11}+2C_{12}+4C_{44})$	$\frac{1}{2}(C_{11}+C_{12})+C_{44}$
T_1	C_{44}	$\frac{1}{3}(C_{11}-C_{12}+C_{44})$	C_{44}
T_2	C_{44}	$\frac{1}{3}(C_{11}-C_{12}+C_{44})$	$\frac{1}{2}(C_{11}-C_{12})$

It has been seen that only three independent elastic constants, i.e., $\tilde{C}_{11}$, $\tilde{C}_{12}$, and $\tilde{C}_{44}$ are required to give a complete account of the group velocities in any direction.[19] In Table I, these relations are given for the three symmetry directions. The density of the imperfect crystal, $\tilde{\rho}$, is determined by

$$\tilde{\rho} = \rho(1 + c\Delta M/M)\ , \tag{9}$$

where M is the mass of the host lattice unit cell, ΔM is the local change of mass when defects are introduced, and ρ is the density of the pure solid. To first order in c,

$$\begin{aligned}\tilde{\rho}\,\tilde{v}^2_{\vec{k},s} &= \rho v^2_{\vec{k},s}\left(1 + c\,\frac{\partial}{\partial \omega^2_{\vec{k},s}}\,\langle \vec{k}, s \mid \underline{T}(\omega^2_{\vec{k},s} + i0^+) \mid \vec{k}, s\rangle \right.\\ &\qquad \left. + c\,\frac{\Delta M}{M}\right)\ ,\end{aligned} \tag{10}$$

where $\vec{v}_{\vec{k},s}$ is the group velocity in the host crystal lattice. From Table I, the bulk elastic constants are seen to be related to $(\vec{v}_{\vec{k},s})_{\vec{k}\to 0}$ as

$$\begin{aligned}\tilde{C}_{11} &= \tilde{\rho}\,\tilde{v}^2_{100,\mathrm{LA}}\ ,\\ \tilde{C}_{44} &= \tilde{\rho}\,\tilde{v}^2_{100,\mathrm{TA}}\ ,\\ \tilde{C}_{12} &= \tilde{\rho}\,\tilde{v}^2_{100,\mathrm{LA}} - \tilde{C}_{11} - 2\tilde{C}_{44}\ .\end{aligned} \tag{11}$$

The point group symmetry of a substitutional defect in a cubic lattice is O_h. The perturbation matrix is of 27×27 dimension if we consider only nearest-neighbor interactions. The symmetry coordinates transform according to A_{1g}, A_{2u}, E_g, E_u, F_{1g}, $2F_{2g}$, $3F_{1u}$, and F_{2u} irreducible representations. The necessary expressions for the T matrix for various irreducible representations have been obtained in an earlier paper[16] (for a diatomic bcc lattice). The results may easily be used for a monatomic bcc lattice where the number of independent Green's functions is further reduced to 10.

We now consider the components $\underline{T}_\nu$ of the symmetrized T matrix which transforms according to the irreducible representation ν. When we work in the limit $\vec{k}_0 \equiv 2\pi\vec{k}_0 a \to 0$ where a is the interionic distance, only a few matrix elements $\underline{T}_\nu$ are involved in Eqs. (10); they are[16]

$$\langle \vec{k}, s \mid \underline{T}_{F_{1u}} \mid \vec{k}, s\rangle = -(\Delta M/M)\,\omega^2_{\vec{k},s}\ ,$$

$$\langle \vec{k}, \mathrm{LA} \mid \underline{T}_{A_{1g}} \mid \vec{k}, \mathrm{LA}\rangle = \frac{2}{3M}\,\frac{\lambda}{1+\lambda/f_{1g}}\,k_0^2\ ,$$

$$\langle \vec{k}, \mathrm{LA} \mid \underline{\mathrm{T}}_{E_g} \mid \vec{k}, \mathrm{LA}\rangle = \frac{4}{3M}\,\frac{\lambda'}{1+\lambda'/f_g}\left(k_0^2 - \frac{3(k_{0x}^2 k_{0y}^2 + \mathrm{c.\,p.})}{k_0^2}\right) ,$$

$$\langle \vec{k}, \mathrm{LA} \mid \underline{\mathrm{T}}_{F_{2g}} \mid \vec{k}, \mathrm{LA}\rangle = \frac{4}{3M}\left(\frac{2\lambda+\lambda'+3\lambda\lambda'/f_{2g}^1}{1+\lambda/f_{2g}^2}\right) \times \left(\frac{k_{0x}^2 k_{0y}^2 + \mathrm{c.\,p.}}{k_0^2}\right) ,$$

$$\langle k00, \mathrm{TA} \mid \underline{\mathrm{T}}_{F_{2g}} \mid k00, \mathrm{TA}\rangle = \frac{1}{3M}\left(\frac{2\lambda+\lambda'+3\lambda\lambda'/f_{2g}^1}{1+\lambda/f_{2g}^2}\right) k_0^2 ,$$

$$\langle \vec{k}, \mathrm{TA} \mid \underline{\mathrm{T}}_{A_{1g}} \mid \vec{k}, \mathrm{TA}\rangle = 0 ,$$

$$\langle k00, \mathrm{TA} \mid \underline{\mathrm{T}}_{E_g} \mid k00, \mathrm{TA}\rangle = 0 ,$$

$$\langle \vec{k}, s \mid \underline{\mathrm{T}}_{E_u} \mid \vec{k}, s\rangle = f_1(k^4) ,$$

$$\langle \vec{k}, s \mid \underline{\mathrm{T}}_{F_{2u}} \mid \vec{k}, s\rangle = f_2(k^4) ,$$

$$\langle \vec{k}, s \mid \underline{\mathrm{T}}_{A_{2u}} \mid \vec{k}, s\rangle = f_3(k^4) , \tag{12}$$

where c. p. denotes cyclic permutations. λ and λ' are the local changes in the central and noncentral force constants, respectively, and

$$f_{2g}^1 = M\,[g_1(0) + 2g_4(0) + g_5(0) - g_7(0) - g_9(0) - 2g_{10}(0)]^{-1} ,$$

$$\begin{aligned} f_{2g}^2 = 3M\,(&[3g_1(0) + 2g_4(0) - g_5(0) - 2g_6(0) - 3g_7(0) + 6g_8(0) + g_9(0) - 2g_{10}(0)] \\ &+ (\lambda'/\lambda)\,[3g_1(0) + 4g_4(0) + g_5(0) + 5g_6(0) - 3g_7(0) - 3g_8(0) - g_9(0) - 4g_{10}(0)] \\ &+ (3\lambda'/M)\,\{[g_1(0) + 2g_4(0) + g_5(0) - g_7(0) - g_9(0) - 2g_{10}(0)]\,[g_1(0) - g_5(0) + g_6(0) - g_7(0) + g_8(0) + g_9(0)] \\ &- 2[g_6(0) - g_8(0)]^2\})^{-1} . \end{aligned} \tag{13}$$

In Eq. (12), f_{1g} and f_g are the effective force constants for the A_{1g} and E_g modes. They are defined in terms of the zero-frequency Green's functions as

$$\begin{aligned} f_{1g} &= M[g_1(0) - 2g_4(0) + g_5(0) + 2g_6(0) - g_7(0) + 2g_8(0) - g_9(0) + 2g_{10}(0)]^{-1} , \\ f_g &= M[g_1(0) - 2g_4(0) + g_5(0) - g_6(0) - g_7(0) - g_8(0) - g_9(0) + 2g_{10}(0)]^{-1} . \end{aligned} \tag{14}$$

Note that the F_{1u} symmetry coordinates transform like the elements of a vector, so that they must not enter the elastic strain; indeed the F_{1u} matrix elements cancel out with the change-of-density term [Eqs. (9) and (10)]. Also the F_{2u}, E_u, and A_{2u} terms, which are of the order of k^4, do not contribute to the elastic constants. These facts are consistent with group analysis assignment of irreducible representations to the components of the fourth-order elastic tensor.[14]

The Green's-function matrix elements $g_\mu(z)$ for a monatomic lattice are defined as

$$g_\mu(z) = \frac{\Omega}{(2\pi)^3} \sum_{s=1}^{3} \int_{\mathrm{Bz}} \frac{J_\mu(\vec{k} \mid s)}{\omega_{\vec{k},s}^2 - z}\, d\vec{k} , \tag{15}$$

where Ω is the volume of unit cell (Bz represents the Brillouin zone) and $J_\mu(\vec{k} \mid s)$'s for $\mu = 1$ to 10 are the following expressions:

$$J_1(\vec{k} \mid s) = \mid e_x(\vec{k} \mid s) \mid^2 ,$$

$$J_2(\vec{k} \mid s) = \mid e_x(\vec{k} \mid s)\mid^2 \cos(2\pi k_x \tfrac{1}{2}a)\cos(2\pi k_y \tfrac{1}{2}a) \times \cos(2\pi k_z \tfrac{1}{2}a) ,$$

$$J_3(\vec{k} \mid s) = e_x(\vec{k} \mid s) e_y(\vec{k} \mid s) \sin(2\pi k_x \tfrac{1}{2}a)\sin(2\pi k_y \tfrac{1}{2}a) \times \cos(2\pi k_z \tfrac{1}{2}a) ,$$

$$J_4(\vec{k} \mid s) = \mid e_x(\vec{k} \mid s) \mid^2 \cos(2\pi k_x a)\cos(2\pi k_y a) ,$$

$$J_5(\vec{k} \mid s) = \mid e_x(\vec{k} \mid s) \mid^2 \cos(2\pi k_y a)\cos(2\pi k_z a) ,$$

$$J_6(\vec{k} \mid s) = e_x(\vec{k} \mid s)\, e_y(\vec{k} \mid s) \sin(2\pi k_x a)\sin(2\pi k_y a) ,$$

$$J_7(\vec{k} \mid s) = \mid e_x(\vec{k} \mid s)\mid^2 \cos(2\pi k_x a)\cos(2\pi k_y a) \times \cos(2\pi k_z a) ,$$

$$J_8(\vec{k} \mid s) = e_x(\vec{k} \mid s) e_y(\vec{k} \mid s) \sin(2\pi k_x a) \times \sin(2\pi k_y a)\cos(2\pi k_z a) ,$$

$$J_9(\vec{k} \mid s) = \mid e_x(\vec{k} \mid s)\mid^2 \cos(2\pi k_x a) ,$$

$$J_{10}(\vec{k} \mid s) = \mid e_x(\vec{k} \mid s) \mid^2 \cos(2\pi k_y a) . \tag{16}$$

Using Eqs. (10)–(12), we find

$$\begin{aligned} \tilde{C}_{11} &= C_{11}^0 + \frac{2c}{3a}\left(\frac{\lambda}{1+\lambda/f_{1g}} + \frac{2\lambda'}{1+\lambda'/f_g}\right) , \\ \tilde{C}_{12} &= C_{12}^0 + \frac{2c}{3a}\left(\frac{\lambda}{1+\lambda/f_{1g}} - \frac{\lambda'}{1+\lambda'/f_g}\right) , \\ \tilde{C}_{44} &= C_{44}^0 + \frac{c}{3a}\left(\frac{2\lambda+\lambda'+3\lambda\lambda'/f_{2g}^1}{1+\lambda/f_{2g}^2}\right) . \end{aligned} \tag{17}$$

The change in the bulk modulus $\Delta K = \Delta(1/\beta)$, where β is the compressibility, turns out to be

$$\Delta K = \frac{2c}{3a} \; \frac{\lambda}{1+\lambda/f_{1g}} \quad . \tag{18}$$

For central forces only, Eqs. (17) reduce to

$$\begin{aligned} \tilde{C}_{11} &= C_{11}^0 + \frac{2c}{3a} \; \frac{\lambda}{1+\lambda/f_{1g}} \quad , \\ \tilde{C}_{12} &= C_{12}^0 + \frac{2c}{3a} \; \frac{\lambda}{1+\lambda/f_{1g}} \quad , \\ \tilde{C}_{44} &= C_{44}^0 + \frac{2c}{3a} \; \frac{\lambda}{1+\lambda/f_{2g}} \quad , \end{aligned} \tag{19a}$$

where

$$f_{2g} = 3M[3g_1(0) + 2g_4(0) - g_5(0) - 2g_6(0) - 3g_7(0) + 6g_8(0) + g_9(0) - 2g_{10}(0)]^{-1} \; . \tag{19b}$$

The expression for the change in the bulk modulus turns out to be unaffected.

From Eq. (19a), we note that for central forces only, the elastic constants of the pure lattice obey Cauchy's relation, but the same is not true for the case of imperfect solids. The change in the elastic constants due to presence of defects is similar for C_{11} and C_{12}, but they are different for C_{44}.

IV. NUMERICAL ESTIMATES AND RESULTS

A. Lattice Dynamics

Molybedenum is a transition metal and crystallizes in a body-centered-cubic structure with one atom per unit cell. The electronic configuration of its atoms is $(4d)^5(5s)^1$. According to Fuchs,[20] the resistance to shear in metals stems from two types of interactions: (a) the Coulomb interactions between positive ions and negative conduction electrons and (b) the exchange interaction between ions assumed to be significant only between nearest and next-nearest neighbors. Woods and Chen[21] have computed the dispersion curves for molybdenum with the help of a seven-force-constant model. Mahesh and Dayal[22] have calculated the dispersion curves with the help of three force constants in Kreb's model.[23] The extra parameter involved in their calculation is obtained by using the experimentally observed frequency at the Brillouin zone boundary in the $[\xi\xi\xi]$ direction. Since the ionic interactions in molybdenum are of short-range type, we feel that the ion-ion interactions may extend to second neighbors only. In the present work we have studied the lattice dynamics of molybdenum

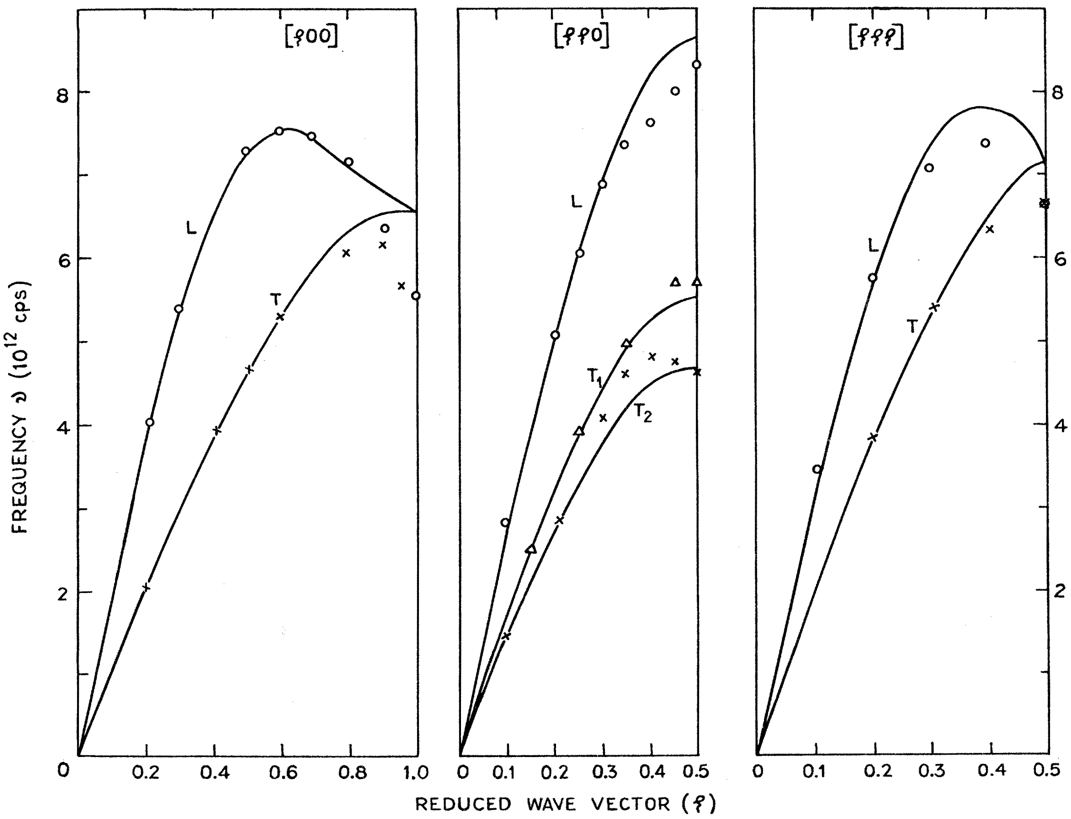

FIG. 1. Dispersion curves for molybdenum. Experimental data of Woods and Chen (Ref. 21) are marked as ○, Δ, and × for the longitudinal and the first and second transverse branches, respectively.

TABLE II. Values of the Green's-function matrix elements for molybdenum at zero frequency in the units of 10^{-27} sec^2 at room temperature (15 °C).

Green's function	Value
g_1	1.02005
g_2	0.24538
g_3	−0.04729
g_4	0.11037
g_5	0.10282
g_6	−0.22011
g_7	0.10202
g_8	−0.02180
g_9	0.33902
g_{10}	0.15259

at room temperature in the Kreb's model after taking into account the next-neighbor ion-ion interactions. In this calculation we have used the recently measured elastic constants.[15] The values of the elastic constants are $C_{11}=4.66\times10^{12}$, $C_{12}=1.626\times10^{12}$, and $C_{44}=1.095\times10^{12}$ dyn/cm^2. The values of effective charge Z and of the Bohm-Pines parameter β are taken to be 2 and 0.353, respectively. We have also considered the factor $f(t)$ in the calculation of the screening parameter k_c. The factor is wave-vector dependent and is given by

$$f(t)=\frac{1}{2}+\frac{1-t^2}{4t}\ln\left|\frac{1+t}{1-t}\right| , \tag{20}$$

where

$$t=k/2k_F .$$

Here $\vec{k}$ is the wave vector and k_F is the Fermi momentum. This factor has been approximated by unity in the calculation of the parameter A (which represents electron-gas contribution) by Mahesh and Dayal. The results for the symmetry directions $[\xi00]$, $[\xi\xi0]$, and $[\xi\xi\xi]$ are presented in Fig. 1. An over-all good agreement is seen with experimental data of Woods and Chen,[21] except for some discrepancies at zone boundaries. In the $[\xi00]$ direction the agreement is complete up to approximately $\xi=0.7$ ($\xi=k/k_m$).

In the $[\xi\xi0]$ direction there are some deviations near the zone boundary, but they are not large as compared to the calculations of Mahesh and Dayal[22] with Kreb's model. From the two calculations in Kreb's model, we conclude that it is unnecessary to start with a sophisticated model for the lattice dynamics of molybdenum. One can reproduce the dispersion curves by considering interactions only up to second neighbors.

B. Green's Functions

In order to compute the Green's functions of molybdenum at zero frequency, Eq. (15) can be written as

$$g_\mu(z)=\frac{1}{N}\sum_{s=1}\sum_{\vec{k}}\frac{J_\mu(\vec{k}\mid s)}{\omega^2_{\vec{k},s}} , \tag{21}$$

where N is the number of atoms in the crystal. All the numerical calculations were carried out in the first Brillouin zone. The necessary eigenfrequencies and eigenvectors were obtained by diagonalizing the dynamical matrix for a bcc lattice of molybdenum by the Jacobi method. Different mesh sizes were tried and a grid which yielded 8000 points in the first Brillouin zone was chosen because it yielded maximum accuracy in a reasonable computer time. The eigenfrequencies and eigenvectors so calculated were used in Eq. (21) to calculate the zero-frequency Green's functions. The results are presented in Table II.

C. Elastic Constants

Using Eqs. (16)–(18), the bulk elastic constants and bulk modulus $\tilde{K}$ were calculated for molybdenum containing 7% and 7.4% of rhenium as impurity ions. A unique choice of changes in the central and noncentral force constants, i.e., $\lambda=5.9131\times10^4$ g sec^{-2} and $\lambda'=-1.9986\times10^4$ g sec^{-2} was made. The calculated elastic constants along with the experimental results are presented in Table III. From the table it is clear that for 7% and 7.4% concentrations of Re, the calculated values are in almost complete agreement with the experimental ones. For 7.4% of rhenium, we have also estimated the values of $\tilde{C}_{12}$ and $\tilde{K}$ which have not been measured by Davidson and Brotzen.[15]

From these calculations we infer that introduction of rhenium into molybdenum enhances the first-neighbor central and noncentral interactions. Ap-

TABLE III. Values of the elastic constants of pure Mo and Mo-Re alloys at 25 °C in the units of 10^{12} dyn/cm^2: $\lambda=5.9131\times10^4$ g sec^{-2} and $\lambda'=-1.9986\times10^4$ g sec^{-2}.

Concentration of	$\tilde{C}_{11}$		$\tilde{C}_{12}$		$\tilde{C}_{44}$		$\tilde{K}$	
Re in Mo	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
0%	...	4.660	...	1.626	...	1.095	...	...
7%	4.665	4.665	1.729	1.729	1.147	1.148	2.708	2.708
7.4%	4.665	4.665	1.828	...	1.149	1.151	2.774	...

proximately similar results have been obtained by Davidson and Brotzen[15] with a different type of calculation. The values of central and noncentral force constants for a pure molybdenum crystal in the force-constant model are 6.005×10^4 g sec^{-2} and -0.418×10^4 g sec^{-2}, respectively. These changes are somewhat higher than those obtained by Davidson and Brotzen. The present situation may be improved if one starts with a more extended perturbation due to a point defect.

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Thermal Coefficient of Expansion of an Activated Vacancy in Zinc from High-Pressure Self-Diffusion Experiments*†

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The coefficient of self-diffusion along the principal axes in zinc was obtained over the temperature range 300–400 °C, and over the pressure range 0–9 kbar. The unusually high precision of 2% in the measurement of the vacancy activation volumes was achieved by means of a novel technique that insured temperature reproducibility in the diffusion zone of ± 0.2 °C at high pressure. The activation volumes for diffusion, associated with the basal and nonbasal vacancy mechanisms are found to be temperature dependent, isotropic, and approximately proportional to T. Hence the thermal coefficient of expansion of an activated vacancy is given by $\alpha_v = T^{-1}$, and is about 15 times larger than the thermal coefficient of expansion of the perfect lattice. The activation entropy is pressure dependent, whereas the activation enthalpy is pressure independent to within the experimental uncertainty.

I. INTRODUCTION

A vacancy in a crystalline lattice is characterized by a set of properties that relate to its formation and motion under conditions of thermodynamic equilibrium. Considered as an entity undergoing reversible thermodynamic processes in both its formation and motion, the vacancy's properties are obviously embodied in a knowledge of the temperature and pressure dependence of $\Delta G_f(T,p)$ and $\Delta G_m(T,p)$, the changes in the Gibbs free energy of the crystal associated with the formation and motion of the vacancy, respectively. Thus, the formation enthalpy ΔH_f and entropy ΔS_f are respectively given by $[\partial(\Delta G_f/T)/\partial(1/T)]_p$ and $-(\partial \Delta G_f/\partial T)_p$, whereas similar temperature