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Elastic Constants of the CsCl Structure Containing Impurity Ions

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The *T*-matrix method has been used in determining the effect of point defects on the elastic properties of the crystals having a CsCl structure. The expressions for the bulk elastic constants have been obtained in terms of the local changes in the central- and the noncentral-force constants. A numerical estimate has been made in the case of CsI containing some impurity ions such as Rb^+, K^+, Tl^+, and In^+. The necessary force-constant changes have been taken from the results of the infrared lattice-absorption experiments. The calculated elastic constants have been tentatively compared with the experimentally measured elastic constants of a dilute alloy Mo-Re which has a bcc structure. Agreement is seen in the relative magnitudes of change in the elastic constants.

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 that 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. The bulk elastic constants are also modified.[6,7] The *T*-matrix method includes in a natural way the peculiarities of the discrete structure of the lattice. The method was discussed with a statistical approach by Elliott *et al.*,[8] who showed that the results obtained were similar to those of the dynamical approach.[9] Benedek and Nardelli[10] have applied the *T*-matrix method to discuss the influence of defects in alkali halides; however, they did not make any numerical estimate for the modified bulk elastic constants.

In the present paper, we use the *T*-matrix method for determining the effect of substantial point defects on the elastic properties of the crystals of CsCl structure. Expressions for the bulk elastic constants have been obtained in terms of local change of central- and noncentral-force constants. Numerical estimates have been made in the case of CsI containing some impurity ions such as Rb^+, K^+, Tl^+, and In^+. They are compared with the available experimental measurements of elastic constants of a bcc dilute Mo-Re alloy. The changes in the central- and noncentral-force constants deduced from the infrared lattice-absorption data[11,12] have been used.

II. THEORY

Let us consider a solid containing a low fractional concentration p of similar substitutional point defects. In order to understand the lattice dynamics of the imperfect solid, one must evaluate the perturbed phonon propagator or Green's function which is defined by

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

where $\underline{L}_0$ is the mass-reduced dynamical matrix of the perfect host lattice and $\underline{P}_{s.c.}(\omega^2)$ is the perturbation matrix caused by a specific configuration of defects. For the explicit forms of these matrices, we refer to an earlier paper.[13] $z=\omega^2+2i\omega\zeta^+$ is the complex squared frequency in the limit as $\zeta^+\rightarrow 0^+$. The propagator defined by Eq. (1) has been written for a single specific configuration of defects. If a statistical average over all the possible configurations of defects is taken, 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 $\underline{G}_0$. Because of the configuration average, we can, therefore, go to the normal-mode representation and write

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

where $\omega^2_{\vec{k},s}$ denotes the squared frequency of the host lattice corresponding to the wave vector $\vec{k}$ of the polarization branch s. If we consider only multiple scattering by the same defect, and limit ourselves only up to the first order of concentration of defects, the self-energy $\Sigma(\vec{k}, s)$ can be written as[12, 13]

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

where $\underline{T}(z)$ is the T matrix for that 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 a single defect and $\underline{g}^0(z)$ is the 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

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

where the tilde over $\omega_{\vec{k},s}$ specifies the perturbed phonon frequency.

The symmetry properties of the T matrix for substitutional impurity in the CsCl structure have been discussed in detail elsewhere.[13] In this crystal structure the T matrix, constituted by a substitutional defect and its eight neighbors, is 27×27. The point-group symmetry of the defect is O_h and the 27 symmetry coordinates transform according to A_{1g}, A_{2u}, E_g, E_u, F_{1g}, $2F_{2g}$, $3F_{1u}$, and F_{2u} irreducible representations. In order to consider the symmetric strains which are pertinent in the present problem, we consider only the symmetrized combinations for the T matrix. Since the strains associated with F_{1g} irreducible representations are asymmetric, we shall not consider the F_{1g} component in the symmetrized T matrix.

III. BULK ELASTIC CONSTANTS

Consider the group velocities for the imperfect lattice

$$\vec{\tilde{v}}_{\vec{k},s} = \frac{\partial \tilde{\omega}_{\vec{k},s}}{\partial \vec{k}} . \tag{7}$$

TABLE I. Group velocities along symmetry directions.

$\rho v^2_{\vec{k},s}$	$\langle 100\rangle$	$\langle 111\rangle$	$\langle 110\rangle$
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}	$\frac{1}{3}(C_{11}-C_{12}+C_{44})$	$\frac{1}{2}(C_{11}-C_{12})$

TABLE II. Force-constant changes from infrared lattice-absorption data (Refs. 11 and 17).

System	λ/M_+ (10^{26} sec^{-1})	λ (10^4 g sec^{-1})	$\lambda'/M_\mp$ (10^{26} sec^{-1})	λ' (10^4 g sec^{-1})
CsI : Rb$^+$	-0.07	-0.154	0.030	0.066
CsI : K$^+$	-0.11	-0.243	0.023	0.051
CsI : Tl$^+$	-0.33	-0.728	⋯	⋯
CsI : In$^+$	-0.35	-0.766	⋯	⋯

It can be shown 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, according to the usual relations.[14] In Table I, these relations are given for the symmetry directions; $\tilde{\rho}$ denotes the density of the imperfect crystal which is related to the host-lattice density ρ by

$$\tilde{\rho} = \rho(1 + p\Delta M_\pm/M) , \tag{8}$$

where $M = M_+ + M_-$ is the mass of the host-lattice unit cell and $\Delta M_\pm$ is the local change of mass [the upper (lower) sign is to be used when positive (negative) defects are considered]. To first order in p, we can write

$$\tilde{\rho}\tilde{v}^2_{\vec{k},s} = \rho v^2_{\vec{k},s}\left[1 + p\left(\frac{\partial}{\partial\omega^2_{\vec{k},s}}\right)\right. \\ \left. \times (\vec{k}, s|\underline{T}(\omega^2_{\vec{k},s} + i0^+)|\vec{k}, s) + p\frac{\Delta M_\pm}{M}\right] , \tag{9}$$

where $v_{\vec{k},s}$ is the host-lattice group velocity. From Table I, the bulk elastic constants are seen to be related to $(\tilde{v}_{\vec{k},s})_{\vec{k}\to0}$ by

$$\begin{aligned} \tilde{C}_{11} &= \tilde{\rho}\tilde{v}^2_{100,\mathrm{LA}} , \\ \tilde{C}_{44} &= \tilde{\rho}\tilde{v}^2_{100,\mathrm{TA}} , \\ \tilde{C}_{12} &= 2\tilde{\rho}\tilde{v}^2_{110,\mathrm{LA}} - \tilde{C}_{11} - 2\tilde{C}_{44} . \end{aligned} \tag{10}$$

Consider now the components T_Γ of the symmetrized T matrix which transforms according to the irreducible representation Γ. When we consider the limit $\vec{k}_0 \equiv 2\pi k_0 r_0 \to 0$, where r_0 is the interionic distance, only a few matrix elements T_Γ are involved in Eq. (9). They are[13]

$$(\vec{k}, s|T_{F_{1u}}|\vec{k}, s) = -(\Delta M_\pm/M)\omega^2_{\vec{k},s} ,$$

TABLE III. Atomic constants.

Element	Atomic weight	Ionic radii (Å)
Cs	132.91	1.69
I	126.91	2.16
Rb	85.48	1.48
K	39.10	1.33
Tl	204.39	0.95
In	114.76	0.81

$$(\vec{k},\,\mathrm{LA}|\,T_{A_{1g}}|\vec{k},\,\mathrm{LA}) = \frac{2}{3M}\,\frac{\lambda}{1+\lambda/f_{1g}}\,k_0^{\,2}\ ,$$

$$(\vec{k},\,\mathrm{LA}|\,T_{E_g}|\vec{k},\,\mathrm{LA}) = \frac{4}{3M}\,\frac{\lambda'}{1+\lambda'/f_g}$$

$$\times\left(k_0^{\,2} - \frac{3(k_{0x}^{\;2}k_{0y}^{\;2}+\mathrm{c.p.})}{k_0^{\,2}}\right)\ ,$$

$$(\vec{k},\,\mathrm{LA}|\,T_{F_{2g}}|\vec{k},\,\mathrm{LA}) = \frac{4}{3M}\left(\frac{2\lambda+\lambda'+3\lambda\lambda'/f_{2g}^{1}}{1+\lambda/f_{2g}^{2}}\right)$$

$$\times\,\frac{k_{0x}^{\;2}k_{0y}^{\;2}+\mathrm{c.p.}}{k_0^{\,2}}\ , \qquad (11)$$

$$(k00,\,\mathrm{TA}|\,T_{F_{2g}}|k00,\,\mathrm{TA}) = \frac{1}{3M}\left(\frac{2\lambda+\lambda'+3\lambda\lambda'/f_{2g}^{1}}{1+\lambda/f_{2g}^{2}}\right)k_0^{\,2}\ ,$$

$$(\vec{k},\,\mathrm{TA}|\,T_{A_{1g}}|\vec{k},\,\mathrm{TA}) = 0\ , \quad (\vec{k}00,\,\mathrm{TA}|\,T_{E_g}|k00,\,\mathrm{TA}) = 0\ ,$$

$$(\vec{k},\,s|\,T_{F_{2u}}|\vec{k},\,s) = f_1(k^4)\ , \quad (\vec{k},\,s|\,T_{E_u}|\vec{k},\,s) = f_2(k^4)\ ,$$

$$(\vec{k},\,s|\,T_{A_{2u}}|\vec{k},\,s) = f_3(k^4)\ ,$$

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

$$f_{2g}^{1} = M_{\mp}[g_4^{\pm}(0) - g_5^{\pm}(0) + g_6^{\pm}(0) + 2g_7^{\pm}(0) - 2g_8^{\pm}(0)]^{-1}\ ,$$

$$\begin{aligned} f_{2g}^{2} = 3M_{\mp}\{&[2g_3^{\pm}(0) + g_4^{\pm}(0) - 3g_5^{\pm}(0) - g_6^{\pm}(0) + 2g_7^{\pm}(0) - 2g_8^{\pm}(0) - 2g_9^{\pm}(0) + 6g_{10}^{\pm}(0)] \\ &+ (\lambda'/\lambda)\,[g_3^{\pm}(0) + 2g_4^{\pm}(0) - 3g_5^{\pm}(0) + g_6^{\pm}(0) + 4g_7^{\pm}(0) - 4g_8^{\pm}(0) + 5g_9^{\pm}(0) - 3g_{10}^{\pm}(0)] \\ &+ (3\lambda'/M_{\mp})\,\{[g_4^{\pm}(0) - g_5^{\pm}(0) + g_6^{\pm}(0) + 2g_7^{\pm}(0) - 2g_8^{\pm}(0)] \\ &\times[g_3^{\pm}(0) - g_5^{\pm}(0) - g_6^{\pm}(0) + g_9^{\pm}(0) + g_{10}^{\pm}(0)] - 2[g_9^{\pm}(0) - g_{10}^{\pm}(0)]^2\}\}^{-1}\ . \end{aligned} \qquad (12)$$

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. (8) and (9)]. 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 the group analysis assignment of irreducible representations (irr. reps.) to the components of the fourth-order elastic tensor:

C_{11} may contain A_{1g}, A_{2g}, E_g irr. reps. ,

C_{12} may contain A_{1g}, A_{2g}, E_g irr. reps. ,

C_{44} may contain A_{1g}, A_{2g}, F_{2g} irr. reps.

Note that A_{2g} irr. rep. does not appear in our defect model. In Eqs. (11), 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 similar to those of Benedek and Nardelli.[15] We obtain

$$\begin{aligned} f_{1g} &= M_{\mp}[g_4^{\pm}(0) - g_5^{\pm}(0) + g_6^{\pm}(0) - 2g_7^{\pm}(0) + 2g_8^{\pm}(0) \\ &\qquad + 2g_9^{\pm}(0) + 2g_{10}^{\pm}(0)]^{-1}\ , \\ f_g &= M_{\mp}[g_4^{\pm}(0) - g_5^{\pm}(0) + g_6^{\pm}(0) - 2g_7^{\pm}(0) + 2g_8^{\pm}(0) \\ &\qquad - g_9^{\pm}(0) - g_{10}^{\pm}(0)]^{-1}\ . \end{aligned} \qquad (13)$$

The definitions of $g_u^{\pm}(z)$ are given in Ref. 13. Using Eqs. (9)–(11), we find

$$\tilde{C}_{11} = C_{11}^{0} + \frac{2p}{3r_0}\left(\frac{\lambda}{1+\lambda/f_{1g}} + \frac{2\lambda'}{1+\lambda'/f_g}\right)\ ,$$

$$\tilde{C}_{12} = C_{12}^{0} + \frac{2p}{3r_0}\left(\frac{\lambda}{1+\lambda/f_{1g}} - \frac{\lambda'}{1+\lambda'/f_g}\right)\ ,$$

$$\tilde{C}_{44} = C_{44}^{0} + \frac{p}{3r_0}\,\frac{2\lambda+\lambda'+3\lambda\lambda'/f_{2g}^{1}}{1+\lambda/f_{2g}^{2}}\ . \qquad (14)$$

The change in the bulk modulus $\Delta K = 3\Delta(1/\beta)$ (where β is the compressibility) turns out to be

$$\Delta K = \frac{2p}{r_0}\,\frac{\lambda}{1+\lambda/f_{1g}}\ . \qquad (15)$$

For central forces only, Eqs. (14) reduce to

$$\tilde{C}_{11} = C_{11}^{0} + \frac{2p}{3r_0}\,\frac{\lambda}{1+\lambda/f_{1g}}\ ,$$

$$\tilde{C}_{12} = C_{12}^{0} + \frac{2p}{3r_0}\,\frac{\lambda}{1+\lambda/f_{1g}}\ , \qquad (16)$$

TABLE IV. Values of the Green's-function matrix elements for CsI at zero frequency in units of 10^{-26} sec^2 at 4.2 °K.

Green's function	Value
g_0^{+}	1.64560
g_1^{+}	0.50280
g_2^{+}	−0.14280
g_3^{+}	2.10640
g_4^{+}	1.37920
g_5^{+}	0.27120
g_6^{+}	0.16800
g_7^{+}	0.28240
g_8^{+}	0.37720
g_9^{+}	−0.08900
g_{10}^{+}	−0.09996

TABLE V. $p = 0.05\%$ change in elastic constants.

System	λ' (10^4g sec^{-1})	$\tilde{C}_{11} - C_{11}^0$	$\tilde{C}_{12} - C_{12}^0$	$\tilde{C}_{44} - C_{44}^0$	ΔK
CsI : Rb$^+$	0.066	− 0.2	− 2.8	− 1.5	−1.1
	0.000	− 0.6	− 2.1	− 1.8	−1.1
CsI : K$^+$	0.051	− 0.7	− 4.1	− 2.9	−1.9
	0.000	− 1.0	− 3.5	− 3.2	−1.9
CsI : Tl$^+$	⋯	− 4.6	−16.5	−17.5	−8.9
CsI : In$^+$	⋯	− 5.2	−18.4	− 20.0	−9.9

$$\tilde{C}_{44} = C_{44}^0 + \frac{2p}{3r_0} \frac{\lambda}{1 + \lambda/f_{2g}} ,$$

where

$$f_{2g} = 3M_{\mp}[2g_3^{\pm}(0) + g_4^{\pm}(0) - 3g_5^{\pm}(0) - g_6^{\pm}(0) + 2g_7^{\pm}(0) - 2g_8^{\pm}(0) - 2g_9^{\pm}(0) + 6g_{10}^{\pm}(0)]^{-1} .$$

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

From Eqs. (16), 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 changes in the elastic constants due to the presence of defects are similar in the case of C_{11} and C_{12}, but they are different for C_{44}.

IV. CALCULATIONS AND RESULTS

Using Eqs. (14)–(16), the bulk elastic constants and bulk modulus are calculated for a CsI crystal containing impurity ions Rb$^+$, K$^+$, Tl$^+$, and In$^+$. The central- and noncentral-force-constant changes have been recently determined by our group[12] by explaining the infrared lattice-absorption experiments.[11,16] These changes for different impurity ions are presented in Table II. From Tables II and III we note that the central-force constant between the impurity and host ion decreases as the radius of the substituted impurity ion becomes smaller compared to the host-lattice ion. Results are also computed for central-force-constant changes only. The Green's-function matrix elements $g(z)$ for CsI have been computed by Ram and Agrawal[12] in the breathing shell model.[17] The breathing shell model has been used successfully recently in explaining the lattice dynamics of NaCl.[18,19] However, no experiment has been performed to measure the phonon frequencies of CsI. The values of $g(0)$ are presented in Table IV and are utilized for the calculation of the parameters f. The results for all the impurity systems are presented in Table V. The elastic constants for pure CsI are taken from Marshall and Kunkel.[20] The fractional atomic concentration of impurities is taken to be 0.05 and the value of interionic distance r_0 is taken to be 3.95 Å. From Table V we observe that the changes in the elastic constants are enhanced as the changes in the force constants due to impurity ions are increased. For moderate changes in the force constants, the elastic constants are altered within 3–4%. For large alterations in the lattice interaction around the impurity, the changes are as high as 15–20%. The effect of the impurities on the elastic constants of the pure crystal is seen to be minimal for the case of C_{11} because of the changes in central- and noncentral-force constants in opposite directions.

TABLE VI. Percentage changes in the elastic constants for Mo-Re(7%) alloy at 83 °K (Ref. 21).

System	$\tilde{C}_{11} - C_{11}^0$	$\tilde{C}_{12} - C_{12}^0$	$\tilde{C}_{44} - C_{44}^0$	ΔK
Mo-Re	0.4	6.3	4.9	2.8

The experimental measurements of the elastic constants for CsI containing impurity ions are not available. For the sake of a tentative comparison we present in Table VI the changes in the elastic constants observed experimentally by Davidson and Brotzen[21] for the case of a molybdenum-rhenium alloy (rhenium 7%) which has a bcc lattice. At low concentrations, they have seen a linear concentration dependence of elastic constants due to impurities. It is interesting to note that the masses of Cs$^+$ and I$^-$ ions are approximately the same and in this restricted sense the lattice tends to a monoatomic lattice. Therefore, the calculated changes of elastic constants for the case of a monoatomic lattice will not be substantially different from those of a diatomic lattice. From Tables V and VI we observe that the relative changes in the three elastic constants in the case of CsI: Rb$^+$(5%) and Mo-Re(7%) are strikingly similar except for their signs. In the Mo-Re alloy the central host-impurity-ion interactions are stronger than that of the pure crystal, whereas the noncentral part of the interaction is weaker.

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