Bulk and Local Elastic Constants of Imperfect Crystals*

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The influence of point defects on the elastic properties of crystals is investigated by means of the T-matrix method. Both bulk and local elastic constants are expressed in terms of the local changes of central and noncentral force constants. The local elastic constants are also obtained by means of a simple phenomenological model. Numerical applications are given for the F center and some weakly bound impurities in alkali halides. The stress coefficients for either ultraviolet or infrared absorbtion bands as corrected for local strain effects are reported.

I. INTRODUCTION

THE influence of defects on the elasticity of crystals has been the subject of many theoretical investigations. The early works concern the bulk elastic properties of imperfect crystals, and the problem was approached in a phenomenological way, based essentially on the continuum model.[1–3] More recently, the use of stress[4–6] and ultrasonic[7] techniques in the experimental investigation of many defect-induced response functions has made it necessary to have a detailed knowledge of the local elastic behavior in the region around the defect, where it is well known that the discrete structure of the lattice plays an essential role. Starting from the recent development of the lattice dynamics of imperfect lattices, we give here a microscopic evaluation of the bulk modified elastic constants ($\tilde{c}_{ik}$, in Voigt's notation) in terms of the defect parameters, such as the local changes in central and noncentral force constants, and of the T matrix at zero frequency (Sec. II). The attention is focused on defects in alkali halides. The T-matrix method includes in a natural way the peculiarities of the discrete lattice structure. It allows us to evaluate not only the vibrational properties of a defect, but also the local strains around the defect as produced by a given external stress[8] (Sec. III). We emphasize (Sec. III) that the quantity which has physical meaning around the defect is actually the local strain and not the local elastic constant. However, because of the extensive use that has been made of the latter concept in the interpretation of the experimental data, we think it useful to present a simple phenomenological approach for the local elastic constants $\tilde{c}_{ik}$ themselves. The local elastic constants introduced in such a way enable one to find the local strain as deduced by the T-matrix approach. Numerical applications are reported (Sec. IV) for F centers and weakly bound impurities in alkali halides, and are discussed in connection with recent experimental data.

II. BULK ELASTIC CONSTANTS

Up to the first order in the fractional concentration p of defects, the dispersion relation of randomly distributed defects of the imperfect crystal reads[9]

$$\tilde{\omega}_{\mathbf{q}j}^2=\omega_{\mathbf{q}j}^2+p(\mathbf{q}j|T(\omega_{\mathbf{q}j}^2+i0^+)|\mathbf{q}j), \qquad (1)$$

where $\omega_{\mathbf{q}j}$ and $\tilde{\omega}_{\mathbf{q}j}$ are the host-lattice and imperfect-lattice eigenfrequencies, respectively, for wave vector $\mathbf{q}$ and branch index j.

In Ref. 10 we have given the definition and properties of the T matrix for the system constituted by a substitutional defect and its six nearest neighbors in alkali halides. As usual, we describe this 21-dimensional system by means of the set of 21 symmetry coordinates (as given in Ref. 9) which transform according to Γ_1, Γ_{12}, Γ_{25}', Γ_{15}', Γ_{25}, and Γ_{15}, irreducible representations (irr. rep.) of the O_h point group. In the present problem we wish to treat symmetric strains only. Then we shall use the symmetrized combination for the T matrix, i.e., $T=\frac{1}{2}(T_+ + T_-)$, where the subscript $+$ or $-$ denotes the sign of the eventual rotational component of the strain. As this component transforms according

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TABLE I. Group velocities along symmetry directions.[a]

ρv_{qj}^2	⟨100⟩	⟨111⟩	⟨110⟩
L	c_{11}	$\frac{1}{3}(c_{11}+2c_{12}+4c_{44})$	$\frac{1}{2}(c_{11}+c_{12})+c_{44}$
$T1$	c_{44}	$\frac{1}{3}(c_{11}-c_{12}+c_{44})$	c_{44}
$T2$	c_{44}	$\frac{1}{3}(c_{11}-c_{12}+c_{44})$	$\frac{1}{2}(c_{11}-c_{12})$

[a] See Ref. 11.

to the Γ_{15}' irr. rep., it turns out that

$$[T_+^{(\Gamma_{15}')}+T_-^{(\Gamma_{15}')}]|\mathbf{q}j)=0, \tag{2}$$

so we shall not consider any Γ_{15}' component in the symmetrized T matrix.

Consider now the group velocities for the imperfect lattice

$$\tilde{\mathbf{v}}_{qj}=\partial\tilde{\omega}_{qj}/\partial\mathbf{q}. \tag{3}$$

It can be shown that just 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.[11] 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

$$\tilde{\rho}=\rho(1+p\Delta M_\pm/M), \tag{4}$$

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 in (4) when positive (negative) defects are considered. To first order in p, we can write

$$\tilde{\rho}\tilde{v}_{qj}^2=\rho v_{qj}^2[1+p(\partial/\partial\omega_{qj}^2)(\mathbf{q}j|T(\omega_{qj}^2+i0^+)|\mathbf{q}j) +p(\Delta M_\pm/M)], \tag{5}$$

where $\mathbf{v}_{qj}$ is the host-lattice group velocity. From Table I the bulk elastic constants are seen to be related to $(\tilde{\mathbf{v}}_{qj})_{q\to 0}$ by

$$\begin{aligned}\tilde{c}_{11}&=\tilde{\rho}\tilde{v}^2{}_{100,\mathrm{LA}},\\ \tilde{c}_{44}&=\tilde{\rho}\tilde{v}^2{}_{100,\mathrm{TA}},\\ \tilde{c}_{12}&=2\tilde{\rho}\tilde{v}^2{}_{110,\mathrm{LA}}-\tilde{c}_{11}-2\tilde{c}_{44}.\end{aligned} \tag{6}$$

Consider now the components $T^{(\Gamma)}$ of the symmetrized T matrix which transform according to the irr. rep. Γ. When we consider the limit $\mathbf{q}_0\equiv 2\pi r_0\mathbf{q}\to 0$, where r_0 is the interionic distance, only a few matrix elements of $T^{(\Gamma)}$ are involved in Eqs. (6); they are[9,10]

$$\begin{aligned}&(\mathbf{q}j|T^{(\Gamma_{15})}|\mathbf{q}j)=-(\Delta M_\pm/M)\omega_{qj}^2,\\ &(\mathbf{q},\mathrm{LA}|T^{(\Gamma_1)}|\mathbf{q},\mathrm{LA})=\frac{1}{3M}\frac{\lambda}{1+\lambda/f_1}q_0^2,\\ &(\mathbf{q},\mathrm{LA}|T^{(\Gamma_{12})}|\mathbf{q},\mathrm{LA})\\ &\qquad=\frac{2}{3M}\frac{\lambda}{1+\lambda/f_{12}}\left(q_0^2-\frac{q_{0x}^2q_{0y}^2+\mathrm{c.p.}}{q_0^2}\right),\\ &(\mathbf{q},\mathrm{LA}|T^{(\Gamma_{25}')}|\mathbf{q},\mathrm{LA})=\frac{2}{M}\frac{\lambda'}{1+\lambda'/f_{25}'}\frac{q_{0x}^2q_{0y}^2+\mathrm{c.p.}}{q_0^2},\\ &(q00,\mathrm{TA}|T^{(\Gamma_{25}')}|q00,\mathrm{TA})=\frac{1}{2M}\frac{\lambda'}{1+\lambda'/f_{25}'}q_0^2,\\ &(q00,\mathrm{TA}|T^{(\Gamma_1)}|q00,\mathrm{TA})\\ &\qquad=(q00,\mathrm{TA}|T^{(\Gamma_{12})}|q00,\mathrm{TA})=0,\\ &(\mathbf{q}j|T^{(\Gamma_{25})}|\mathbf{q}j)=O(q^4),\end{aligned} \tag{7}$$

where by c.p. we denote cyclic permutations. $\frac{1}{2}\lambda$ and $\frac{1}{2}\lambda'$ are the local changes of the nearest-neighbor central and noncentral force constants, respectively. Note that the Γ_{15} symmetry coordinates transform like the components of a vector, so that they must not enter the elastic strain; indeed the Γ_{15} matrix elements cancel out with the change-of-density term [Eqs. (4) and (5)]. Also, the Γ_{25} term [which is $O(q^4)$] does not contribute to the elastic constants. These facts are consistent with the group-analysis assignment of irreducible representations to the components of the fourth-order elastic tensor:

c_{11} may contain Γ_1, Γ_2, Γ_{12} irr. rep.,
c_{12} may contain Γ_1, Γ_2, Γ_{12} irr. rep.,
c_{44} may contain Γ_1, Γ_{12}, Γ_{25}' irr. rep.

Note that Γ_2 irr. rep. does not appear in our defect model.[9] In Eqs. (7), f_1, f_{12}, and f_{25}' are the effective force constants for the Γ_1, Γ_{12}, and Γ_{25}' modes: They are defined in terms of the zero-frequency Green's functions $\mathcal{G}_\mu^\pm(0)$, and can be approximately related to some macroscopic quantities (in our case the host-lattice elastic constants c_{ij}^0), in analogy to what we have done for the Γ_{15} modes in Ref. 10. We obtain

$$\begin{aligned}f_1&=M\mp[\mathcal{G}_4^\pm(0)+2\mathcal{G}_5^\pm(0)]^{-1}\cong 4r_0(c_{11}^0+2c_{12}^0),\\ f_{12}&=M\mp[\mathcal{G}_4^\pm(0)-\mathcal{G}_5^\pm(0)]^{-1}\cong 4r_0(c_{11}^0-c_{12}^0),\\ f_{25}'&=M\mp[\mathcal{G}_6^\pm(0)+2\mathcal{G}_5^\pm(0)]^{-1}\cong 8r_0c_{44}^0.\end{aligned} \tag{8}$$

The definitions of $\mathcal{G}_\mu^\pm(z)$ are given in Ref. 12. Use of

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Eqs. (5)–(7) gives

$$\tilde{c}_{11}=c_{11}^0+\frac{p\lambda}{6r_0}\left(\frac{1}{1+\lambda/f_1}+\frac{2}{1+\lambda/f_{12}}\right),$$
$$\tilde{c}_{12}=c_{12}^0+\frac{p\lambda}{6r_0}\left(\frac{1}{1+\lambda/f_1}-\frac{1}{1+\lambda/f_{12}}\right), \quad (9)$$
$$\tilde{c}_{44}=c_{44}^0+\frac{p\lambda'}{4r_0}\frac{1}{1+\lambda'/f_{25'}}.$$

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

$$\Delta K=\frac{p\lambda}{2r_0}\frac{1}{1+\lambda/f_1}. \quad (10)$$

III. LOCAL ELASTIC CONSTANTS

The problem of calculating the local strain around a defect, as produced by an external stress, is similar to the elastic-relaxation problem around the defect itself without external stress. According to the Green's-function method used by Elliott, Krumhansl, and Merrett,[8] the displacement field $\mathbf{u}$ can be written as

$$|\mathbf{u})=(1+\Phi^{-1}\varphi)^{-1}|\mathbf{u}^0), \quad (11)$$

where $\mathbf{u}^0$ is the host-lattice uniform displacement field, Φ is force-constant tensor matrix for the host lattice, and φ is the change of Φ due to the defects. We consider a single defect; then group analysis greatly simplifies the calculation of $\mathbf{u}$ for each irr. rep. When we are interested only in the nearest-neighbor displacement, say $u_{\rm nn}$, we can work in the subspace of the perturbation φ and get in a trivial way the results for each irr. rep. involved:

$$(u_{\rm nn}/u_{\rm nn}^0)_{\Gamma_1}=(\tilde{\epsilon}/\epsilon^0)_{\Gamma_1}=\frac{1}{1+\lambda/f_1},$$
$$(u_{\rm nn}/u_{\rm nn}^0)_{\Gamma_{12}}=(\tilde{\epsilon}/\epsilon^0)_{\Gamma_{12}}=\frac{1}{1+\lambda/f_{12}}, \quad (12)$$
$$(u_{\rm nn}/u_{\rm nn}^0)_{\Gamma_{25'}}=(\tilde{\epsilon}/\epsilon^0)_{\Gamma_{25'}}=\frac{1}{1+\lambda'/f_{25'}},$$

where we have introduced the notations $\tilde{\epsilon}$ and ϵ^0 for the strain tensors at the defect and in the perfect lattice, respectively. They are connected to the displacement field by the usual relation

$$\begin{pmatrix}u_\alpha(l)\\ u_\alpha^0(l)\end{pmatrix}=\sum_\beta x_\beta(l)\begin{pmatrix}\epsilon_{\beta\alpha}(l)\\ \epsilon_{\beta\alpha}^0(l)\end{pmatrix}, \quad (13)$$

where $\mathbf{x}(l)$ denotes the lattice vector for lth ion. $\epsilon_{\beta\alpha}(l)$ is the perturbed strain field; $\epsilon_{\beta\alpha}(l)=\tilde{\epsilon}_{\beta\alpha}$ when l is one of the ions involved in the defect perturbation.

The above equations solve the local problem. We give now a simple phenomenological approach, which can be alternatively used, particularly when we are concerned with extended perturbations. Denote by $\bar{v}$ a suitably chosen volume associated with the one-defect perturbation φ, and assume the perturbed strain field $\epsilon_{\alpha\beta}(l)$ to be uniform inside $\bar{v}$ and equal to $\tilde{\epsilon}$ for each defect, while it equals ϵ^0 in the remaining lattice, i.e., in the remaining volume $N(v-p\bar{v})=V(1-p\bar{v}/v)$. V is the crystal volume, and $v=V/N=2r_0^3$ the cell volume. This assumption enables us to write the bulk average strain $\bar{\epsilon}(\Gamma)$, which is defined by

$$\sigma_{\rm ext}(\Gamma)=\bar{c}(\Gamma)\bar{\epsilon}(\Gamma),$$

for each irr. rep. Γ in terms of the external stress $\sigma_{\rm ext}$, in the following way:

$$\bar{\epsilon}(\Gamma)=(1-p\bar{v}/v)\epsilon^0(\Gamma)+p\bar{v}/v\tilde{\epsilon}(\Gamma). \quad (14)$$

For each irr. rep. we specify elastic constants and strains as follows:

$$(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz})(c_{11}+2c_{12})\equiv 3^{-1/2}\epsilon(\Gamma_1)c(\Gamma_1),$$
$$(\epsilon_{xx}-\epsilon_{yy})(c_{11}-c_{12})\equiv 2^{-1/2}\epsilon(\Gamma_{12}\text{ rhombic})c(\Gamma_{12}),$$
$$(2\epsilon_{xx}-\epsilon_{yy}-\epsilon_{zz})(c_{11}-c_{12}) \quad (15)$$
$$\equiv 6^{-1/2}\epsilon(\Gamma_{12}\text{ tetragonal})c(\Gamma_{12}),$$
$$\epsilon_{xy}c_{44}\equiv\epsilon(\Gamma_{25'};z)c(\Gamma_{25'}).$$

Defining the local elastic constants $\bar{c}(\Gamma)$ in such a way that the equilibrium condition for the lattice reads

$$\tilde{c}(\Gamma)\tilde{\epsilon}(\Gamma)=c^0(\Gamma)\epsilon^0(\Gamma)=\bar{c}(\Gamma)\bar{\epsilon}(\Gamma) \quad (16)$$

for each Γ, from Eqs. (14) and (16), to first order in p, we obtain the following nonlinear relation among $\tilde{c}$, c^0, and $\bar{c}$:

$$\tilde{c}(\Gamma)=c^0(\Gamma)+p(\bar{v}/v)[\bar{c}(\Gamma)-c^0(\Gamma)]c^0(\Gamma)/\bar{c}(\Gamma). \quad (17)$$

In the particular case of a substitutional impurity in a NaCl-type lattice with short-range perturbation φ, we can associate with every defect a volume $\bar{v}$ with the shape of an fcc Brillouin zone, centered at the defect site and with the nearest neighbors at the centers of the six square faces. For this choice we have $\bar{v}=2v$. Then the use of Eqs. (8), (9), and (17) gives

$$\bar{c}(\Gamma_1)-c^0(\Gamma_1)\cong\lambda/4r_0,$$
$$\bar{c}(\Gamma_{12})-c^0(\Gamma_{12})\cong\lambda/4r_0, \quad (18)$$
$$\bar{c}(\Gamma_{25'})-c^0(\Gamma_{25'})\cong\lambda'/8r_0.$$

These expressions lead to the same result for the local strain as given by Eqs. (12). The Voigt components of the elastic tensor are then

$$\bar{c}_{11}\cong c_{11}^0+\lambda/4r_0,$$
$$\bar{c}_{12}\cong c_{12}^0, \quad (19)$$
$$\bar{c}_{44}\cong c_{44}^0+\lambda'/8r_0.$$

In the case in which the host-lattice elastic constants satisfy the Cauchy relation, we note that the introduc-

TABLE II. Local elastic constants, force constant changes, and stress coefficients for some uv and IR active centers, at 0°K and $\lambda'=0$. f^* is the Γ_{15} effective force constant for the host lattice. A, B, and C are given in eV for uv and in 10^{13} sec^{-1} for IR absorption peaks.

System	$\bar{c}_{11}$ 10^{12} dyn cm^{-2}	c_{11}^0	$-\lambda/f^*$ $(\lambda'=0)$	A	B	C
uv: NaCl: (F)	0.352	0.575	~0.8	3.12	0.10	0.89
KCl: (F)	0.357	0.486	~0.6	2.17	0.31	0.60
KBr: (F)	0.344	0.419	~0.4	2.13	0.22	0.32
KI: (F)	0.258	0.338	~0.5	1.84	0.25	0.37
IR: KBr:Li$^+$	0.227	0.419	0.985	9.05	5.88	2.71
KI:Ag$^+$	0.246	0.338	0.933	4.25	4.64	5.03

tion of defects makes the Cauchy relation no longer to hold in the whole crystal as well as locally. Notice also that the local c's are just equal to the elastic constants of our impurity–six-neighbor system, whose nearest-neighbor central and noncentral force-constant changes are $\frac{1}{2}\lambda$ and $\frac{1}{2}\lambda'$, respectively. This shows that Eqs. (19) could have been directly obtained in a very trivial way.

It is perhaps worth noting that the equivalence between the expressions (12) and (18) comes from the particular choice $\bar{v}=2v$. If we had made another choice, a different result would have been obtained. This is due to the fact that in Eq. (12) the strain refers to nearest-neighbor ions, and this is consistent with the choice $\bar{v}=2v$ in (18). With another choice of $\bar{v}$, Eq. (18) would give the average strain inside this new volume.

IV. NUMERICAL APPLICATIONS

Recently, the electron-phonon coupling of F centers[4] and the local anharmonicity of impurity ions[5,6] in alkali halides have been investigated by means of stress experiments on their respective ultraviolet uv and infrared IR resonant absorption bands. Of course, the quantitative interpretation of these experiments needs a knowledge of the local strain around the defect. However, as the local strain depends on the local changes of force constants, which are unknown in practice, it seems hard to deduce it starting from first principles. We have proceeded in the following way: under the simplifying assumption $\lambda'=0$, we have first fitted λ to the available optical data, and deduced the values of $\bar{c}_{ij}$ from Eqs. (19). Then the values of $\bar{c}_{ij}$ so deduced have been tested by evaluating some other properties of the defect and by comparing them with the experimental data.

For the F center we have fitted λ to the Raman data[12]; we have then obtained from the stress-experiment data[4] the correct values of the stress coefficients A, B, and C, which are defined in Ref. 5 (although in a different context), and which now play the role of electron-phonon coupling constants in the optical transition.[13] By using these values of A, B, and C, given in Table II, we obtained the theoretical temperature-dependent half-width and Huang-Rhys factor of the uv absorption band in excellent agreement with the experimental data; these results are extensively discussed in Ref. 13. For the systems KBr:Li$^+$ and KI:Ag$^+$ we have fitted λ to the IR absorption peak[10] due to the low-lying resonant mode.[14] In the case of resonant modes, the stress coefficients A, B, and C play the role of anharmonic coupling constants of the resonant mode itself with the continuum modes of the lattice. Again we have derived the values of A, B, and C, also reported in Table II, from the stress-experiment data of Nolt and Sievers[5,15] as corrected for local-strain effects on the basis of Eqs. (19). In this case also, quite good agreement was found between the values in Table II and the values of A, B, and C as predicted by lattice-dynamic calculations based on the quasi-harmonic approximation for the modification of the resonance condition induced by an external stress. Notice that the relation $A+C=2B$ given in Ref. 16 is fairly well satisfied by the values in Table II, while it is not satisfied when A, B, and C are not corrected for local-strain effects.

In Table II the local elastic constants and the values of λ as obtained from the above-mentioned fitting procedure are also reported, in the case $\lambda'=0$ and for zero absolute temperature.

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