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Influence of Force-Constant Changes on the Lattice Dynamics of Cubic Crystals with Point Defects*

PHILIP D. MANNHEIM†
Department of Nuclear Physics, Weizmann Institute of Science, Rehovoth, Israel

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The crystal-point impurity problem is examined for the case of changes in nearest-neighbor forces around the defect site. Using the recently developed group-theoretical techniques, expressions are found for the frequencies of the perturbed modes due to impurities in face-centered and body-centered cubic crystals, assuming only central forces. By solving coupled equations for double-time Green's functions, expressions are also obtained for the defect mean-square displacement and its amplitude of vibration in each perturbed mode. Applications are then made to recent optical and Mössbauer measurements.

I. INTRODUCTION

It is well known[1] that in the presence of defects great changes in the dynamical properties of a crystal may be obtained. The subject has been treated by many authors and solutions have been given for the determination of localized modes produced by a point mass defect. The method is to use the localized nature of the perturbation to the pure crystal and solve using the lattice Green's functions. This is possible because we have only added a source term to the pure-crystal equations of motion. By the same method it is also possible to calculate the amplitude of vibration of the defect in each of the normal modes of the perturbed crystal. This is very useful because in optical measurements, neutron scattering, and Mössbauer experiments, it is the defect motion which determines the process.

Though the isotopic impurity has been very popular for illustrative purposes, not too much attention has been given to considerations of the influence of changes in force constants in the vicinity of the defect. This is somewhat unreasonable since in actual experiments forces are usually changed as well. There have been some calculations performed for changes of force in a nearest-neighbor simple cubic lattice.[2] This however is an unphysical situation in which the polarizations of the phonons are ignored and the lattice becomes one-dimensional. An important development was the introduction of the matrix partitioning techniques,[3] which admit of changes in the force constants and also take into account the polarizations of the phonons. In the last two years group-theoretical techniques have become generally available[4] so that it is possible to solve for crystals with a more complicated lattice structure. The use of symmetry adapted coordinates is now thought to be the most convenient approach to the problem, and applications are now appearing regularly in the literature.[5-9]

In this paper we shall examine the defect problem for changes in nearest-neighbor forces due to impurities substitutionally inserted into face-centered and body-centered cubic lattices. We obtain conditions for the determination of the position of localized and resonance modes, and the defect amplitude of vibration $|\chi^2(0,\omega)|$ as a function of the normal mode frequency ω [Eqs. (32) and (55), respectively].

For the case of central forces only, a simple formula (32) is given which only requires knowledge of the pure-crystal density of states for solution. It contains two free parameters, the mass change M/M', and the change in the force constant at the defect site $A_{xx}(0,0)/A_{xx}'(0,0)$.

We discuss first, in Sec. II, properties of the pure crystal which are necessary for solving the impurity problem. We then examine in Sec. III the cluster of atoms around the defect where changes take place. For instance, for a face-centered cubic lattice we have 13 atoms in the cluster and hence 39 degrees of freedom. Thus to get the frequencies we have to diagonalize a 39 dimensional matrix. This is treated in Sec. IV. We make a block diagonalization of this matrix using the lattice site symmetry and isolate the F_{1u} mode in which the defect moves. We then have a four-dimensional matrix containing a large number of lattice Green's functions. We next derive relations between the Green's functions to reduce their number. The perturbed frequencies are derived in Secs. IV and V for the fcc and bcc crystals, respectively. To obtain the defect mean-square displacement $\langle u^2(0)\rangle$, we introduce double-time

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[1] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **273A**, 222 (1963). This and Ref. 4 contain many related references.

[2] W. M. Visscher, Phys. Rev. **129**, 28 (1963); A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

[3] G. W. Lehman and R. E. DeWames, Phys. Rev. **131**, 1008 (1963).

[4] A. A. Maradudin, Rept. Progr. Phys. **28**, 331 (1965).

[5] T. P. Martin, Phys. Rev. **160**, 686 (1967).

[6] W. M. Hartmann and R. J. Elliott, Proc. Phys. Soc. (London) **91**, 187 (1967).

[7] Nguyen Xuan Xinh, R. A. Coldwell-Horsfall, and A. A. Maradudin, J. Phys. (Paris) **26**, 717 (1965).

[8] G. Benedek and G. F. Nardelli, Phys. Rev. **155**, 1004 (1967).

[9] T. Gethins, T. Timusk, and E. J. Woll, Jr., Phys. Rev. **157**, 744 (1967).

Green's functions.[10] $\langle u^2(0)\rangle$ is given by solving a set of four coupled equations in these Green's functions (Sec. VI). From $\langle u^2(0)\rangle$ we then derive $|\chi^2(0,\omega)|$. In Sec. VII we give a few applications of the results derived in the paper. In the Appendix we provide a method for calculating an arbitrary lattice Green's function without first having to diagonalize the dynamical matrix of the crystal.

To conclude the Introduction we briefly relate the present paper to the earlier works cited above. The block diagonalization of the F_{1u} mode for the fcc is equivalent to the calculation of Lehman and DeWames.[3] As in the case in Ref. 3, Eqs. (23) are completely general and make no assumptions on the nature of the forces. Lehman and DeWames performed a numerical diagonalization and did calculations for both isotropic changes of force $\Delta\phi'(r)/r=\Delta\phi''(r)$, and central changes of force $\Delta\phi'(r)/r=0$. A similar calculation has also been performed by Martin[5] for central force changes. The major part of the work in these two papers was in calculating all the lattice Green's functions. A certain simplification would be achieved by using the numerical method suggested in the Appendix. In the present work general relations between the Green's functions have been provided (25)–(28), such that upon restricting to central forces, it is possible to obtain an analytic solution (32) in which only one Green's function is required. For isotropic forces only it is also so be expected that an analytic solution is available, though it was not sought here. The technique is also applied to a bcc crystal, which was not considered in Refs. 3 and 5.

Lehman and DeWames further obtained expressions for the mean-square velocity and displacement of the defect by means of the linear response function, and performed numerical calculations for varying force ratios in the cases of isotropic and central force-constant changes. We use the equivalent technique of double-time Green's functions and, through the Green's functions, obtain analytic expressions for $\langle u_x^2(0)\rangle$ and $\langle v_x^2(0)\rangle$. Because the form of $\langle u_x^2(0)\rangle$ is given explicitly, it is further possible to obtain $|\chi^2(0,\omega)|$. In forthcoming papers[11,12] numerical calculations for varying central force ratios will be reported. The fcc case has also been considered by Hartmann and Elliott[6] in a study of impurity-induced infrared absorption by the F_{1u} mode. Nguyen Xuan Xinh *et al.*[7] have examined the Raman effect in impurity doped simple cubics where the A_{1g}, E_g, and F_{2g} modes are Raman active. Benedek and Nardelli[8] have looked at phonon scattering in a simple cubic by means of the linear response function.

II. LATTICE DYNAMICS OF PURE CRYSTALS

In the harmonic approximation, the Hamiltonian of a $3N$-dimensional crystal lattice is given by

$$H=\sum_{\alpha,l}\frac{P_\alpha^2(l)}{2M(l)}+\frac{1}{2}\sum_{\substack{\alpha,\beta\\ l,l'}}A_{\alpha\beta}(l,l')u_\alpha(l)u_\beta(l')\,. \tag{1}$$

The atoms are in equilibrium at the sites $\mathbf{R}(l)$, and we have a displacement from equilibrium $u_\alpha(l,t)$, where $\alpha=x$, y, z, if we restrict ourselves to monatomic lattices only. Here we have introduced the second-order force constants $A_{\alpha\beta}(l,l')$. From the Hamiltonian equations we then obtain $3N$ equations of the form

$$M(l)\ddot{u}_\alpha(l)+\sum_{\beta,l'}A_{\alpha\beta}(l,l')u_\beta(l')=0\,. \tag{2}$$

Taking the time dependence of the vibrations as

$$u_\alpha(l,t)=e^{i\omega t}u_\alpha(l,0)\,, \tag{3}$$

we have

$$\sum_{\beta,l'}[A_{\alpha\beta}(l,l')-\omega^2M(l')\delta_{\alpha\beta}\delta(l,l')]u_\beta(l')=0\,. \tag{4}$$

For pure crystals we can invoke translational invariance and introduce the wave number $\mathbf{K}$.

We define the dynamical matrix[13]

$$D_{\alpha\beta}(\mathbf{K})=\frac{1}{M}\sum_l A_{\alpha\beta}(0,l)e^{-i\mathbf{K}\cdot\mathbf{R}(l)}\,. \tag{5}$$

Its eigenvalues are the characteristic frequencies $\omega_j^2(\mathbf{K})$ of the branches, and its eigenvectors are the polarization vectors $\sigma_\alpha^j(\mathbf{K})$, where j labels each of the three acoustic branches, i.e.,

$$\sum_\beta D_{\alpha\beta}(\mathbf{K})\sigma_\beta^j(\mathbf{K})=\omega_j^2(\mathbf{K})\sigma_\alpha^j(\mathbf{K})\,. \tag{6}$$

The eigenvectors are orthogonal and normalized as

$$\sum_\alpha \sigma_\alpha^{*j}(\mathbf{K})\sigma_\alpha^{j'}(\mathbf{K})=\delta_{jj'}\,, \tag{7a}$$

$$\sum_j \sigma_\alpha^{*j}(\mathbf{K})\sigma_\beta^{j}(\mathbf{K})=\delta_{\alpha\beta}\,. \tag{7b}$$

Thus for each wave vector $\mathbf{K}$ in the first Brillouin zone we have three eigenvalues $\{\omega_j^2(\mathbf{K})\}$, determined by the crystal dispersion curves.

We now recall some general properties of the force constants which will be useful for later calculations. We assume that the forces are derivable from a two-body potential $\phi(r)$. Then by direct calculation we im-

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[10] R. J. Elliott and D. W. Taylor, Proc. Phys. Soc. (London) **83**, 189 (1964).

[11] P. D. Mannheim and H. Friedmann (to be published).

[12] P. D. Mannheim and A. Simopoulos, Phys. Rev. **165**, 845 (1968).

[13] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

mediately find

$$A_{\alpha\beta}(l,0)=-\left(\frac{\partial^2\phi(r)}{\partial u_\alpha(l)\partial u_\beta(l)}\right)_0$$
$$=-\left(\frac{\phi''(r)}{r^2}-\frac{\phi'(r)}{r^3}\right)R_\alpha(l)R_\beta(l)-\frac{\phi'(r)}{r}\delta_{\alpha\beta}, \qquad (8)$$

provided $l\neq 0$, the origin of coordinates. For $l=0$ we have[4]

$$A_{\alpha\beta}(0,0)=-\sum_{l\neq 0} A_{\alpha\beta}(l,0). \qquad (9)$$

In particular for a cubic lattice, the plane $x=0$ is a plane of reflection symmetry, and hence $A_{xy}(0,0)=0$. For the dynamical matrix we now have

$$D_{\alpha\beta}(\mathbf{K})=\frac{1}{M}\sum_{l\neq 0} A_{\alpha\beta}(0,l)\{e^{-i\mathbf{K}\cdot R(l)}-1\}. \qquad (10)$$

If we restrict $\mathbf{K}$ to be along the x axis, then

$$D_{\alpha\beta}(K_x)=-\frac{2}{M}\sum_{l\neq 0} A_{\alpha\beta}(0,l)\sin^2\tfrac{1}{2}K_xR_x(l), \qquad (11)$$

where we have again used the reflection planes. Using the specific form of $A_{\alpha\beta}(0,l)$ given in Eq. (8), we then have

$$D_{xy}(K_x)=0. \qquad (12)$$

If we now restrict the summation on l to the nearest neighbors only and take K_x at its maximum value $K_x^{\max}$, then

$$D_{xx}(K_x^{\max})=(2/M)A_{xx}(0,0)=\omega_{\max}^2, \qquad (13)$$

since we have diagonalized $D_{\alpha\beta}(\mathbf{K})$. Thus we see that the maximum lattice frequency is given by

$$\omega_{\max}^2=\text{zero}-\text{zero force constant/reduced mass}. \qquad (14)$$

All that were needed for the derivation were the planes of reflection of the cubic system and the nearest-neighbor nature of the forces.

III. LATTICE DYNAMICS OF CRYSTALS WITH POINT DEFECTS

We restrict ourselves to the case of one impurity, a point defect, occupying a substitutional lattice site which we take as the origin of coordinates. We assume that there are no changes in the lattice structure. If we separate out the changes in mass and force constants and introduce them as a perturbation

$$V_{\alpha\beta}(l,l')=-(M-M')\omega^2\delta_{\alpha\beta}\delta(l,0)\delta(l',0)+A_{\alpha\beta}(l,l')$$
$$-A_{\alpha\beta}'(l,l'), \qquad (15)$$

where the primes denote the changed parameters; then we may rewrite Eq. (4) as

$$\sum_{\beta,l'}\{A_{\alpha\beta}(l,l')-M\omega^2\delta_{\alpha\beta}\delta(l,l')\}u_\beta(l')$$
$$=\sum_{\beta,l'} V_{\alpha\beta}(l,l')u_\beta(l'). \qquad (16)$$

We introduce the lattice Green's functions

$$g_{\alpha\beta}(\omega;l,l')=\frac{1}{NM}\sum_{\mathbf{K},j}\frac{\sigma_\alpha{}^{*j}(\mathbf{K})\sigma_\beta{}^j(\mathbf{K})}{\omega_j{}^2(\mathbf{K})-\omega^2}e^{i\mathbf{K}\cdot\mathbf{R}(l')-\mathbf{R}(l)} \qquad (17)$$

so that we can formally solve Eq. (16) by

$$u_\alpha(l)=\sum_{\substack{\beta,\gamma\\ l',l''}} g_{\alpha\beta}(\omega;l,l')V_{\beta\gamma}(l',l'')u_\gamma(l''). \qquad (18)$$

In this solution we have neglected the homogeneous solution. This is because we are looking for the frequencies ω of the perturbed crystal which are to be different from the pure-crystal frequencies before we take the limit $N\rightarrow\infty$. For these frequencies Eq. (4) has no solutions, and so Eq. (18) is complete. The perturbed frequencies are given by the determinantal condition for a solution to Eq. (18), and it is this determinant that we wish to diagonalize.

IV. CALCULATION FOR A FACE-CENTERED CUBIC LATTICE

A. Diagonalization

For the face-centered cubic it has been shown that the total representation of the cluster of the 13 atoms can be decomposed into the irreducible representations of O_h, the site symmetry at the defect, as[4]

$$\Gamma_{\text{fcc}}=A_{1g}+A_{2g}+2E_g+2F_{1g}+2F_{2g}+A_{2u}+E_u$$
$$+4F_{1u}+2F_{2u}. \qquad (19)$$

We are only interested in the triply degenerate F_{1u} mode where the defect moves. A basis for the $4F_{1u}$ representations has been given[14] as

$$\alpha_0=u_x(0,0,0), \qquad (20a)$$

$$\alpha_1=u_x(1,1,0)+u_x(\bar{1},\bar{1},0)+u_x(1,0,1)+u_x(\bar{1},0,\bar{1})$$
$$+u_x(1,\bar{1},0)+u_x(\bar{1},1,0)+u_x(\bar{1},0,1)$$
$$+u_x(1,0,\bar{1}), \qquad (20b)$$

$$\alpha_2=u_y(1,1,0)+u_y(\bar{1},\bar{1},0)+u_z(1,0,1)+u_z(\bar{1},0,\bar{1})$$
$$-u_y(1,\bar{1},0)-u_y(\bar{1},1,0)-u_z(\bar{1},0,1)$$
$$-u_z(1,0,\bar{1}), \qquad (20c)$$

$$\alpha_3=u_x(0,1,1)+u_x(0,\bar{1},\bar{1})+u_x(0,1,\bar{1})+u_x(0,\bar{1},1), \qquad (20d)$$

expressed in terms of the unit displacements of the total representation. The functions $g_{\alpha\beta}(\omega;l,l')$ are transla-

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[14] K. Dettman and W. Ludwig, Physik Kondensierten Materie 2, 241 (1964).

tionally invariant so that we may write

$$g_{\alpha\beta}(l,l')=g_{\alpha\beta}(l-l',0)=g_{\alpha\beta}(l-l')\,. \tag{21}$$

Their full symmetry properties are discussed in Ref. 4. We shall also use the notation $V_{\alpha\beta}(110)$ for $V_{\alpha\beta}(1,1,0;\ 0,0,0)$ [noting that $V_{\alpha\beta}(1,1,0;\ 0)=-V_{\alpha\beta}(1,1,0;1,1,0)$], and $V_{\alpha\beta}(00)$ for $V_{\alpha\beta}(0,0,0;\ 0,0,0)$.

To simplify the writing we introduce

$$\begin{aligned}
&g_0=g_{xx}(000)\,,\\
&g_1=g_{xx}(110)\,,\\
&g_2=g_{xy}(110)\,,\\
&g_3=g_{xx}(011)\,,\\
&A=g_0+g_{xx}(020)+g_{xx}(200)+g_{xx}(220)\,,\\
&B=g_{xy}(220)+2g_{xy}(211)\,,\\
&C=g_1+g_{xx}(121)\,,\\
&D=g_{xx}(200)+g_{xx}(020)-g_x(220)-g_0\,,\\
&E=g_{xy}(211)-g_2\,,\\
&F=g_0+2g_{xx}(020)+g_{xx}(022)\,.
\end{aligned} \tag{22}$$

We can now write down four equations in the four functions:

$$\begin{aligned}
u_x(0)=&[8V_{xx}(110)g_1+8V_{xy}(110)g_2+4V_{xx}(011)g_3\\
&+V_{xx}(00)g_0]u_x(0)+V_{xx}(011)(g_0-g_3)\alpha_3\\
&+[V_{xx}(110)(g_0-g_1)-V_{xy}(110)g_2]\alpha_1\\
&+[V_{xy}(110)(g_0-g_1)-V_{yy}(110)g_2]\alpha_2\,;
\end{aligned} \tag{23a}$$

$$\begin{aligned}
\alpha_1=&4V_{xx}(011)(2g_1-C)\alpha_3\\
&+[V_{xx}(110)(8g_1-A-2C)-V_{xy}(110)B]\alpha_1\\
&+[V_{xy}(110)(8g_1-A-2C)-V_{yy}(110)B]\alpha_2\\
&+8[V_{xx}(00)g_1+V_{xx}(110)(A+2C)+V_{xy}(110)B\\
&\qquad+2V_{xx}(011)C]u_x(0)\,;
\end{aligned} \tag{23b}$$

$$\begin{aligned}
\alpha_2=&4V_{xx}(011)(g_2-E)\alpha_3\\
&+[V_{xx}(110)(8g_2-B)+V_{xy}(110)(D-2E)]\alpha_1\\
&+[V_{xy}(110)(8g_2-B)+V_{yy}(110)(D-2E)]\alpha_2\\
&+8[V_{xx}(00)g_2+V_{xx}(110)B+V_{xy}(110)(2E-D)\\
&\qquad+2V_{xx}(011)g_{xy}(211)]u_x(0);
\end{aligned} \tag{23c}$$

$$\begin{aligned}
\alpha_3=&V_{xx}(011)(4g_1-F)\alpha_3\\
&+2[V_{xx}(110)(2g_3-C)-V_{xy}(110)g_{xy}(211)]\alpha_1\\
&+2[V_{xy}(110)(2g_3-C)-V_{yy}(110)g_{xy}(211)]\alpha_2\\
&+4[V_{xx}(00)g_3+4V_{xx}(110)C+4V_{xy}(110)\\
&\qquad\times g_{xy}(211)+V_{xx}(011)F]u_x(0)\,.
\end{aligned} \tag{23d}$$

B. Relations between Green's Functions

In principle we could calculate all the required $g_{\alpha\beta}(l)$ as indicated in the Appendix and determine the frequencies directly. However, for nearest-neighbor forces and, later on, central forces only we can simplify the problem immensely. We can relate various $g_{\alpha\beta}(l)$ using the dispersion relations, Eqs. (6). We find for a fcc lattice

$$\begin{aligned}
\frac{1}{N}\sum_{\mathbf{K},j}\Bigg\{&\frac{D_{xx}(\mathbf{K})|\sigma_x{}^j(\mathbf{K})|^2}{\omega_j{}^2(\mathbf{K})-\omega^2}+\frac{D_{xy}\sigma_x{}^{*j}(\mathbf{K})\sigma_y{}^j(\mathbf{K})}{\omega_j{}^2(\mathbf{K})-\omega^2}\\
&+\frac{D_{xz}\sigma_x{}^{*j}(\mathbf{K})\sigma_z{}^j(\mathbf{K})}{\omega_j{}^2(\mathbf{K})-\omega^2}\Bigg\}=\frac{1}{N}\sum_{\mathbf{K},j}\frac{\omega_j{}^2(\mathbf{K})|\sigma_x{}^j(\mathbf{K})|^2}{\omega_j{}^2(\mathbf{K})-\omega^2}\\
&=\frac{1}{N}\sum_{\mathbf{K},j}\left\{1+\frac{\omega^2}{\omega_j{}^2(\mathbf{K})-\omega^2}\right\}|\sigma_x{}^j(\mathbf{K})|^2=1+M\omega^2g_0\,,
\end{aligned} \tag{24}$$

using the definition of g_0 given in Eq. (17). If we now use the symmetry properties of $g_{\alpha\beta}(l)$, $A_{\alpha\beta}(l)$, under O_h and expand $D_{\alpha\beta}(\mathbf{K})$, then we obtain

$$\begin{aligned}
A_{xx}(00)g_0+8A_{xx}(110)g_1&+8A_{xy}(110)g_2\\
&+4A_{xx}(011)g_3=1+M\omega^2g_0\,.
\end{aligned} \tag{25}$$

We can repeat the process multiplying (24) through by $e^{i(K_x+K_y)}$ before summing over $\mathbf{K}$ to obtain

$$\begin{aligned}
A_{xx}(00)g_1+A_{xx}(110)(A+2C)&+A_{xy}(110)B\\
&+2A_{xx}(011)C=M\omega^2g_1\,.
\end{aligned} \tag{26}$$

On the right-hand side we should have in fact obtained an additional term

$$\frac{1}{N}\sum_{\mathbf{K}}e^{i(K_x+K_y)},$$

but this is zero since

$$\begin{aligned}
\frac{1}{N}\sum_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{R}}=\Delta(\mathbf{R})&=1\quad\text{if }\mathbf{R}\text{ is a Cartesian lattice vector,}\\
&=0\quad\text{otherwise}.
\end{aligned}$$

On multiplication of (24) by $e^{i(K_x+K_z)}$ before summation we find

$$\begin{aligned}
A_{xx}(00)g_3+4A_{xx}(110)C&+4A_{xy}(110)g_{xy}(211)\\
&+A_{xx}(011)F=M\omega^2g_3\,.
\end{aligned} \tag{27}$$

Multiplication of Eq. (6) by $\sigma_y{}^{*j}(K)$ provides the extra-independent relation

$$\begin{aligned}
A_{xx}(00)g_2+A_{xx}(110)B&+A_{xy}(110)(2E-D)\\
&+2A_{xx}(011)g_{xy}(211)=M\omega^2g_2\,.
\end{aligned} \tag{28}$$

C. Determination of Frequencies

For a fcc lattice we have from Eq. (8)

$$A_{\alpha\beta}(1,1,0;0)=-\tfrac{1}{2}\begin{bmatrix}\phi''(r)+1/(r)\phi'(r)\,, & \phi''(r)-1/(r)\phi'(r)\,, & 0\\ \phi''(r)-1/(r)\phi'(r)\,, & \phi''(r)+1/(r)\phi'(r)\,, & 0\\ 0 & 0 & 2/(r)\phi'(r)\end{bmatrix}. \tag{29}$$

We shall make the simplification $\phi'(r)=0$. This is equivalent to assuming only central forces, i.e., $A_{zz}(1,1,0;0)=0$. We have thus only one parameter $\phi''(r)$ to characterize the forces, since $A_{xx}(0,0)=4\phi''(r)$.

For the changes in the forces we now have

$$\begin{aligned}
V_{xx}(1,1,0;\ 0)&=V_{xy}(1,1,0;\ 0)\\
&=-\tfrac{1}{2}[\phi''(r)_{\text{pure}}-\phi''(r)_{\text{defect}}]\,,
\end{aligned}$$

so that $V_{xx}(0;0)=-(M-M')\omega^2-8V_{xx}(1,1,0;0)$. We introduce the parameter $\lambda=V_{xx}(1,1,0;0)/A_{xx}(1,1,0;0)$. Thus

$$\lambda=1-\frac{\phi''(r)_{\text{defect}}}{\phi''(r)_{\text{pure}}}=1-\frac{A_{xx}'(00)}{A_{xx}(00)}. \tag{30}$$

We can simplify Eqs. (23) since the combinations of Green's functions that appear in them are now exactly the same as appear in Eqs. (24) to (28). After some manipulation we arrive at

$$8A_{xx}(110)(1-\lambda)[1+(M-M')\omega^2 g_0] \\ +\lambda M'\omega^2[1+M\omega^2 g_0]=0. \tag{31}$$

Using Eqs. (14) we can rewrite this in the form

$$\left[\frac{M}{M'}-1+\frac{2\omega^2}{\omega_{\max}{}^2}\left(1-\frac{A_{xx}(00)}{A_{xx}'(00)}\right)\right]^{-1} \\ =-(1+M\omega^2 g_0)=\frac{1}{3N}\sum_{\mathbf{K},j}\frac{\omega_j{}^2(\mathbf{K})}{\omega^2-\omega_j{}^2(\mathbf{K})} \\ =\int\frac{\omega'^2\nu(\omega'^2)}{\omega^2-\omega'^2}d\omega'^2, \tag{32}$$

taking the limit $N\rightarrow\infty$.

Here $\nu(\omega'^2)$ is the pure-crystal density of states per unit ω^2, and for $\omega<\omega_{\max}$ we take the principal value, so that solutions obtained give the resonance mode frequencies.

The equation has several interesting features. If $\lambda=0$, which is no change in force, we return to the usual equation for an isotopic impurity. Also we see that an increase in force has the same effect as a decrease in mass, which is to be expected qualitatively. Thus in the absence of a change in mass, an increase in force ($\lambda<0$) can give localized modes. Also the form is very useful for calculation when only the experimental density of states is known for the pure crystal. No detailed knowledge of the dispersion curves is required.

V. CALCULATION FOR A BODY-CENTERED CUBIC LATTICE

Here we have 8 neighbors in the cluster and hence 27 degrees of freedom. The decomposition of the total representation is now[4]

$$\Gamma_{\text{bcc}}=A_{1g}+E_g+F_{1g}+2F_{2g} \\ +A_{2u}+E_u+3F_{1u}+F_{2u}. \tag{33}$$

We now have a threefold basis for the F_{1u} mode which is given[14] as

$$\alpha_0=u_x(0,0,0), \tag{34a}$$

$$\alpha_1=u_x(1,1,1)+u_x(\bar{1},1,1)+u_x(\bar{1},\bar{1},1)+u_x(1,\bar{1},1)+u_x(\bar{1},\bar{1},\bar{1})+u_x(1,\bar{1},\bar{1})+u_x(1,1,\bar{1})+u_x(\bar{1},1,\bar{1}), \tag{34b}$$

$$\alpha_2=u_y(1,1,1)+u_z(1,1,1)-u_y(\bar{1},1,1)-u_z(\bar{1},1,1)+u_y(\bar{1},\bar{1},1)-u_z(\bar{1},\bar{1},1)-u_y(1,\bar{1},1)+u_z(1,\bar{1},1)+u_y(\bar{1},\bar{1},\bar{1}) \\ +u_z(\bar{1},\bar{1},\bar{1})-u_y(1,\bar{1},\bar{1})-u_z(1,\bar{1},\bar{1})+u_y(1,1,\bar{1})-u_z(1,1,\bar{1})-u_y(\bar{1},1,\bar{1})+u_z(\bar{1},1,\bar{1}). \tag{34c}$$

For the pure bcc we have

$$A(1,1,1;0)=-\tfrac{1}{3}\begin{bmatrix}\phi''(r)+2/(r)\phi'(r), & \phi''(r)-1/(r)\phi'(r), & \phi''(r)-1/(r)\phi'(r)\\ \phi''(r)-1/(r)\phi'(r), & \phi''(r)+2/(r)\phi'(r), & \phi''(r)-1/(r)\phi'(r)\\ \phi''(r)-1/(r)\phi'(r), & \phi''(r)-2/(r)\phi'(r), & \phi''(r)+2/(r)\phi'(r)\end{bmatrix}. \tag{35}$$

Our approximation now is to neglect $\phi'(r)/r$. Thus

$$8A_{xx}(1,1,1;0)=8A_{xy}(1,1,1;0)=-A_{xx}(0,0). \tag{36}$$

For the changes in forces we have

$$V=V_{xx}(110,0)=-V_{xx}(111,111)=V_{xy}(111,0) \\ =-V_{xy}(111,111)=-\tfrac{1}{3}[\phi''(r)_{\text{pure}}-\phi''(r)_{\text{defect}}] \tag{37}$$

and

$$V_{xy}(00)=0, \\ V_{xx}(00)=-(M-M')\omega^2-8V_{xx}(111,0). \tag{38}$$

To simplify the writing we introduce

$$g_0=g_{xx}(000), \\ g_1=g_{xx}(111), \\ g_2=g_{xy}(111), \\ Q=g_0+g_{xx}(222)+g_{xx}(200)+g_{xx}(022)+2g_{xx}(220) \\ +2g_{xx}(022), \\ R=g_{xx}(222)+g_{xy}(220), \\ S=g_0+g_{yy}(222)-g_{yy}(020)-g_{yy}(202), \\ T=g_{yz}(222)-g_{yz}(022). \tag{39}$$

We again write down the equations of motion of the F_{1u} mode

$$u_x(0)=[8V(g_1+2g_2)-g_0(8V+(M-M')\omega^2)]u_x(0) \\ -V(g_1+2g_2-g_0)(\alpha_1+\alpha_2), \tag{40a}$$

$$\alpha_1=8[V(Q+2R)-g_1(8V+(M-M')\omega^2)]u_x(0) \\ +V[8g_1-(Q+2R)](\alpha_1+\alpha_2), \tag{40b}$$

$$\alpha_2=16[V(R+S+T)-g_2(8V+(M-M')\omega^2)]u_x(0) \\ +2V[8g_2-(R+S+T)](\alpha_1+\alpha_2). \tag{40c}$$

To simplify we again need relations between the Green's functions. These are found to be, without neglecting $\phi'(r)$ here,

$$A_{xx}(00)g_0+8A_{xx}(111)g_1+16A_{xy}(111)g_2 =1+M\omega^2 g_0\,, \tag{41a}$$

$$A_{xx}(00)g_1+A_{xx}(111)Q+2A_{xy}(111)R =M\omega^2 g_1\,, \tag{41b}$$

$$A_{xx}(00)g_2+A_{xx}(111)R+A_{xy}(111)(S+T) =M\omega^2 g_2\,. \tag{41c}$$

By replacement we then obtain a condition for the perturbed lattice. Interestingly, we again find Eq. (31). Thus the fcc and bcc lattices give exactly the same result, indicative of one being the reciprocal lattice of the other. This may be understood in the sense that, in the harmonic approximation, momentum and position are treated equivalently.

VI. DETERMINATION OF $\langle u^2(0)\rangle$

We shall follow the method of Elliott and Taylor[10] and introduce the double-time Green's function

$$\Omega_{\alpha\beta}(l,l';t-t')=2\pi/(\hbar i)\theta(t-t') \langle[u_\alpha(l,t),u_\beta(l',t')]\rangle\,, \tag{42}$$

where the average is to be taken over the ensemble, and $\theta(t-t')$ is a step function. We denote the Fourier transform of this function by $\Omega_{\alpha\beta}(\omega;\,l,l')$. As is shown in Ref. 10 we can write down differential equations for the Green's functions of the form

$$\Omega_{\alpha\beta}(\omega;l,l')=P_{\alpha\beta}(\omega;l,l')-\sum_{\substack{\gamma,\delta\\ l_1,l_2}} P_{\alpha\gamma}(\omega;l,l_1)V_{\gamma\delta}(l_1,l_2) \times\Omega_{\delta\beta}(\omega;l_2,l')\,. \tag{43}$$

Here $V_{\gamma\delta}(l_1,l_2)$ is the function defined in Eq. (15), and $P_{\alpha\beta}(\omega;\,l,l')=-g_{\alpha\beta}(\omega;\,l,l')$ of Eq. (17).

We are interested in $\Omega_{xx}(\omega;\,0,0)$ and, using the same symmetry techniques as with $u_x(0)$, we can write down coupled equations. Unlike Eq. (18) there is also a homogeneous term $P_{\alpha\beta}(\omega;\,l,l')$, so that as well as reproduce the determinantal condition, we can also determine $\Omega_{xx}(\omega;\,0,0)$. Thus Eq. (43) contains more information than is available just by looking at the displacements. However, the similarity between the Eqs. (43) and (18) enables us to generalize equations (23) and (40) immediately. We simply attach $_x(0)$ to each $u_\alpha(l)$ to give $\Omega_{\alpha x}(l,0)$ and include a homogeneous term $P_{\alpha x}(l,0)$. The procedure is then as before, with the result for both fcc and bcc lattices being

$$\Omega_{xx}(0,0)=\frac{\lambda(1+M\omega^2 g_0)+A_{xx}(00)(1-\lambda)g_0}{[\lambda M'\omega^2(1+M\omega^2 g_0)-A_{xx}(00)(1-\lambda)(1+(M-M')\omega^2 g_0)]}\,. \tag{44}$$

The prescription for obtaining a correlation function from a Green's function is given by Zubarev[15];

$$\langle u_x^2(0)\rangle=\lim_{\delta\to 0}\frac{i\hbar}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega}{e^{\hbar\beta\omega}-1} \times[\Omega_{xx}(\omega+i\delta;0,0)-\Omega_{xx}(\omega-i\delta;0,0)]\,. \tag{45}$$

We introduce

$$\rho(\omega)=\frac{M}{M'}-1+\frac{2\omega^2}{\omega_{\max}^2}\left(1-\frac{A_{xx}(00)}{A_{xx}'(00)}\right) \tag{46}$$

and

$$S(\omega)=\int\frac{\omega'^2\nu(\omega'^2)}{\omega^2-\omega'^2}d\omega'^2\,, \tag{47}$$

so that the condition for resonance modes, Eq. (32), now reads

$$S(\omega)\rho(\omega)-1=0\,, \tag{48}$$

and finally obtain

$$\langle u_x^2(0)\rangle=\frac{\hbar}{2M}\left(\frac{M}{M'}\right)^2 \int_0^{\omega_{\max}}\left\{\frac{\coth(\frac{1}{2}\hbar\beta\omega)\nu(\omega)d\omega}{\omega[\{1-\rho(\omega)S(\omega)\}^2+\frac{1}{4}\pi^2\omega^2\nu^2(\omega)\rho^2(\omega)]}\right\}\,. \tag{49}$$

In the event of there being a localized mode we have an extra contribution given by differentiating the denominator. It is

$$\frac{\hbar}{2M}\left(\frac{M}{M'}\right)^2\frac{\coth(\frac{1}{2}\hbar\beta\omega_L)}{\omega_L}\left[\omega_L^4\rho^2(\omega_L)\int\frac{\nu(\omega^2)}{(\omega_L^2-\omega^2)^2}d\omega^2 -(\rho(\omega_L)+1)^2+\frac{M}{M'}\right]^{-1}\,, \tag{50}$$

where ω_L is the localized-mode frequency. From this we can also determine $|\chi^2(0,\omega)|$. We make a normal mode expression of $u_\alpha(0)$:

$$u_\alpha(0)=\sum_\omega \chi_\alpha(0,\omega)d(\omega)\,, \tag{51}$$

where each normal mode ω is threefold degenerate, and we quantize according to

$$d(\omega)=(\hbar/2\omega)^{1/2}[a(\omega)+a^\dagger(\omega)]\,. \tag{52}$$

Thus

$$\langle u_\alpha^2(0)\rangle=\sum_\omega |\chi_\alpha^2(0,\omega)|\,\hbar/2\omega\coth(\tfrac{1}{2}\hbar\beta\omega)\,. \tag{53}$$

We now go to an integral and equate terms in Eqs. (49) and (53), since the normal modes are independent. Thus

$$\langle u_\alpha^2(0)\rangle=3N\int\frac{\hbar}{2\omega}|\chi_\alpha^2(0,\omega)|\coth(\tfrac{1}{2}\hbar\beta\omega)\nu(\omega)d\omega\,, \tag{54}$$

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[15] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

so that

$$\sum_{\alpha} |\chi_{\alpha}{}^2(0,\omega)| = 1/MN[(M'/M)^2\{1-\rho(\omega)S(\omega)\}^2 + (M'/M)^2\, \tfrac{1}{4}\pi^2\omega^2\nu^2(\omega)\rho^2(\omega)]^{-1} \quad (55)$$

with an obvious form for $|\chi^2(0,\omega)|$ from (50) if there is a localized mode.

As before all of these formulas reduce to the standard mass defect equations.[1]

VII. COMMENTS AND APPLICATIONS

We have derived expressions for the positions of localized modes $|\chi^2(0,\omega)|$, and $\langle u^2(0)\rangle$ for the fcc and bcc impurity problem. For the case of central forces only we have been able to obtain expressions which only depend on the pure-crystal density of states. By taking different amounts of noncentral forces Eqs. (23) and (40) could be solved in general, but the solutions are not expected to be as simple. The Green's functions method is also well suited to the determination of the change in the density of states of the crystal.[4] The main problem here is that resonance modes decay into the continuum and hence broaden the distribution. An advantage of the block diagonalization is that each mode of the total representation contributes independently to the density of states, so that the decay of F_{1u} resonance modes can be calculated from Eqs. (23). The result is

$$\Delta\nu(\omega^2) = -\frac{3}{N}\left\{\frac{\rho(\omega)[1-\rho(\omega)S(\omega)]R'(\omega)+[\rho^2(\omega)S'(\omega)+\rho'(\omega)]R(\omega)}{[1-\rho(\omega)S(\omega)]^2+[\pi\rho(\omega)R(\omega)]^2}\right\},$$

where $R(\omega)=\omega^2\nu(\omega^2)$, and the primes denote differentiation with respect to ω^2.

It is usually the case that the frequency of the resonance in $|\chi^2(0,\omega)|$ is the same as the resonance in the density of states. However, this is not necessary. Consider, for instance, when there is an isotopic impurity which is slightly heavier than the host atom, such that condition (48) has no solution inside the band. In the expression for $|\chi^2(0,\omega)|$ the term $(1-\rho(\omega)S(\omega))^2$ will dominate over $\frac{1}{4}\pi^2\omega^2\nu^2(\omega)\rho^2(\omega)$, so that an apparent resonance will appear in $|\chi^2(0,\omega)|$ when approximately

$$d/(d\omega)(1-\rho(\omega)S(\omega))=0. \quad (56)$$

However, this is not a genuine resonance, so there will be no broadening in the density of states at that frequency.

Since $|\chi^2(0,\omega)|$ has been determined [Eq. (55)] we can also calculate the mean-square momentum from

$$\langle P_{\alpha}{}^2(0)\rangle = M'^2 \int \tfrac{1}{2}\hbar\omega\nu(\omega) \times \coth(\tfrac{1}{2}\hbar\beta\omega)N|\chi_{\alpha}{}^2(0,\omega)|. \quad (57)$$

The resulting expression could also be derived by using double-time momentum Green's functions.

To establish the usefulness of Eqs. (48), (49), and (55) we consider some recent optical experiments,[16] in which localized modes were observed with diatomic molecules as defects in rare-gas crystals. The complete calculation and the physical mechanism responsible for the optical activity is discussed elsewhere.[11] For the pure rare-gas crystal a model for $\phi(r)$ is available, the Lennard-Jones potential. Also, a model for the interaction between the host and the defect is available, based on the empirical combining laws for the parameters σ, ϵ, of the potential. In this model it is possible to show that $\phi'(r)/r \ll \phi''(r)$ for both the pure and impure lattices, so that the central-force approximation is valid here. Assuming the density of states determined by this $\phi(r)$,[17] we can solve condition (48).

Localized modes are predicted for HCl in Ar at 76 cm^{-1} and HBr in Ar at 75 cm^{-1}. The experimental observations are at 73 cm^{-1} and 72 cm^{-1}, respectively. Both results indicate the strength of the change in force constant, since on a mass-defect theory only there would be no localized modes. For HBr in Ar we have a big increase in force to give a localized mode. This particular result shows that the claim that we can neglect the change in force in a first approximation when there is a large change in mass is not valid.

An important feature of the changes in force is the possibility of compensating the change in mass, so that the dynamics is again that of the pure crystal, i.e., $|\chi^2(0,\omega)| = 1/MN$. This is very valuable in optical measurements, since if the introduction of a defect can make the lattice optically active without distorting the absorption spectrum, we see the whole density of states in the spectrum. This will happen approximately if Eq. (48) is solved by $\omega=\omega_{\max}$.

The functions $\langle u_x{}^2(0)\rangle$, $\langle P_x{}^2(0)\rangle$ are very important in Mössbauer experiments. Formulas (49) and (57) have been applied[12] to fit the measured recoilless Mössbauer fraction and second-order Doppler shift of Fe^{57} in V^{51}, so that the change in force could be ascertained. Interestingly, though both functions are averages over all the modes, they show a strong sensitivity to change in force. In fact, from the data we obtain definite evidence for an increase in force and for localized mode production.

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[16] J. M. P. J. Verstegen, H. Goldring, S. Kimel, and B. Katz, J. Chem. Phys. 44, 3216 (1966).

[17] J. Grindlay and R. Howard, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 129.

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APPENDIX: DETERMINATION OF AN ARBITRARY LATTICE GREEN'S FUNCTION

To obtain $g_{\alpha\beta}(\omega;l,l')$ we have to find $\sigma_\alpha{}^j(\mathbf{K})$ and $\omega_j{}^2(\mathbf{K})$. One possible method is to diagonalize the dispersion relations for each $\mathbf{K}$ (Maradudin and Kagle, Ref. 18). This requires a lot of computer time. However, using the dispersion relations we can eliminate having to find $\sigma_\alpha{}^j(\mathbf{K})$ and $\omega_j{}^2(\mathbf{K})$. We calculate everything for a particular $\mathbf{K}$, so that the index will be suppressed. Directly from Eq. (6) we have

$$\sum_j \omega_j{}^2=\sum_x D_{xx}\,, \tag{A1}$$

$$\sum_j \omega_j{}^2\omega_{j+1}{}^2=\sum D_{yy}D_{zz}-\sum D_{xy}{}^2\,, \tag{A2}$$

$$\prod_j \omega_j{}^2=\prod D_{xx}-\sum D_{xx}D_{yz}{}^2+2\prod D_{xy}\,, \tag{A3}$$

where the sums are to be taken cyclically. Further,

$$\prod_j (\omega^2-\omega_j{}^2)=\omega^6-\omega^4\Big(\sum_j \omega_j{}^2\Big)+\omega^2\Big(\sum_j \omega_j{}^2\omega_{j+1}{}^2\Big) -\prod_j \omega_j{}^2=\pi_\omega\,,\quad \text{say.} \tag{A4}$$

Extra relations may be immediately written down:

$$\sum_j \omega_j{}^2|\sigma_x{}^j|^2=D_{xx}\,, \tag{A5}$$

$$\sum \omega_j{}^2\sigma_x{}^{*j}\sigma_y{}^j=D_{xy}\,, \tag{A6}$$

$$\sum_j \omega_j{}^4\sigma_x{}^j=D_{xx}D_{xy}+D_{xy}D_{yy}+D_{xz}D_{zy}\,, \tag{A7}$$

$$\sum_j \omega_j{}^4|\sigma_x{}^j|^2=D_{xx}{}^2+D_{yy}{}^2+D_{zz}{}^2\,, \tag{A8}$$

$$\sum_j \omega_j{}^2\omega_{j+1}{}^2|\sigma_x{}^{j+2}|^2=D_{yy}D_{zz}-D_{yz}{}^2\,. \tag{A9}$$

We introduce

$$\lambda_{xy}(\mathbf{K})=\sum_j \frac{\sigma_x{}^{*j}(\mathbf{K})\sigma_y{}^j(\mathbf{K})}{\omega^2-\omega_j{}^2(\mathbf{K})}\,. \tag{A10}$$

Hence

$$\lambda_{xy}=1/\pi_\omega\{D_{xy}(\omega^2-D_{zz})+D_{xz}D_{zy}\} \tag{A11}$$

and

$$\lambda_{xx}=1/\pi_\omega\{\omega^4-\omega^2(D_{yy}+D_{zz})+D_{yy}D_{zz}-D_{yz}{}^2\}\,. \tag{A12}$$

Thus, finally,

$$g_{\alpha\beta}(\omega;l,0)=-1/NM\sum_{\mathbf{K}}\lambda_{\alpha\beta}(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{R}(l)}\,, \tag{A13}$$

giving a closed expression for g in terms of the elements of $D_{\alpha\beta}(\mathbf{K})$. It should be noticed that this is an exact result for all-neighbor interactions, and follows from the translational invariance of the lattice only.

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[18] A. A. Maradudin and B. Kagle, Westinghouse Res. Memo No. 64, 929-442-MI (unpublished).