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**INELASTIC SCATTERING OF NEUTRONS
BY LOCALIZED VIBRATIONS
OF INTERSTITIAL HYDROGEN IN METAL LATTICES
CASE OF A VANADIUM LATTICE**

by

G. BLAESSER, J. PERETTI and G. TOTH

1969



**Joint Nuclear Research Center
Ispra Establishment — Italy**

**Reactor Physics Department
Experimental Neutron Physics**

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ABSTRACT

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KEYWORDS

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FREQUENCY

1. INTRODUCTION (**)

The problem of the vibration of an impurity atom harmonically coupled to a crystal lattice has been solved in principle by the methods of Green's function due to LIFSHITZ ⁽¹⁾ and MONTROLL and POTTS ⁽²⁾. Since the publication of these papers numerous applications of the method have been made to simple systems and more realistic ones. A detailed list of references to this work are given in two recent revue articles by MARADUDIN ⁽³⁾, LIFSHITZ and KOSEVICH ⁽⁴⁾ and LUDWIG ⁽⁵⁾ to which we refer the reader. One notable problem which has not received so much attention is the case of an interstitial impurity (WAGNER ⁽⁶⁾). To this problem we devote the present work. We consider specifically the case of a hydrogen impurity, located in a tetrahedral interstitial site of the bcc lattice of vanadium. We assume for the vanadium lattice a model with central harmonic forces between first and second neighbours that reproduces well the frequency spectrum obtained experimentally by INS ^{*}, on pure vanadium ⁽⁷⁾. Experimental results have been obtained ⁽⁸⁾ on the hydrogen-vanadium system which could be compared with our theoretical calculations. We restrict ourselves to the harmonic approximation; thus we are not concerned with the line width of the localized levels (KLEMENS ⁽⁹⁾, VISSCHER ⁽¹⁰⁾, KRIVOGLAZ ⁽¹¹⁾). Our theoretical approach will be based on the formalism of the method of double-time Green's functions (ZUBAREV ⁽¹²⁾) which was already used for the treatment of a substitutional (isotopic) impurity in a simple cubic lattice by ELLIOT and TAYLOR ⁽¹³⁾. We shall, however, introduce our Green's functions in such a way that we can avoid the resolution of a secular equation which is necessary for interstitial systems in the approach of WAGNER (loc. cit.) In Part I we have developed the general formalism for the case of an harmonic oscillator coupled to a system of harmonic oscillators. We calculate the incoherent neutron scattering cross section and the position correlation function $\langle x_{\alpha}(t) x_{\beta}(0) \rangle$ of the impurity atom using the time-dependent Green's function. We write the equation giving the frequencies of the local oscillation of the interstitial.

In Part II we apply these results to the case of interstitial hydrogen in the vanadium lattice and compare the theoretical values of the localized mode frequencies with the experimental data.

^{*} INS means Inelastic Neutron Scattering; it would be convenient to use such an abbreviation to describe a method of measurement like NMR, EPR and so.

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In Appendix A we rederive some results of Part I by a special matrix partition technique.

In Appendix B and C we derive some formulae used in the text. In Appendix D we show that our partition method can be conveniently used also in the case of substitution impurities.

PART I Theory of Incoherent Neutron Scattering by Interstitial Atoms in a Regular Lattice

1.1 The Scattering Cross Section of the Interstitial Atom

The scattering cross due to a single atom is given by the well known expression (14)

$$(1) \quad \frac{d^2\sigma}{d\Omega dE} = \frac{a^2}{\hbar} \frac{k'}{k} S(\underline{\kappa}, \omega)$$

where a is the incoherent scattering cross section of the interstitial atom, $S(\underline{\kappa}, \omega)$ the scattering law for momentum transfer $\hbar \underline{\kappa}$ and energy transfer $\hbar \omega$, and $\underline{k}, \underline{k}'$ are the wave numbers of the incident and the scattered neutron. The scattering law $S(\underline{\kappa}, \omega)$ is given by (15)

$$(2) \quad S(\underline{\kappa}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \chi(\underline{\kappa}, t) \exp(i\omega t)$$

involving the "intermediate scattering function"

$$(3) \quad \chi(\underline{\kappa}, t) = \langle \exp(-i\underline{\kappa} \underline{R}(t)) \exp(i\underline{\kappa} \underline{R}(0)) \rangle$$

where $\underline{R}(t)$ is the position operator of the scattering atom at time t (in the Heisenberg picture). In the case we consider here the interstitial atoms are coupled to the rest of the lattice by harmonic forces. If we also neglect the interaction of the modes of the host lattice due to anharmonic terms (i.e. we adopt the so-called "linear approximation" of Re. (16))

the expression for $\chi(\underline{\kappa}, t)$ becomes (16)

$$(4) \quad \chi(\underline{\kappa}, t) = \exp(-W) \exp \left\{ \sum_{\alpha, \alpha'} \kappa_{\alpha} \kappa_{\alpha'} \langle q_{\alpha}(t) q_{\alpha'}(0) \rangle \right\}$$

where q_{α} is the α -component ($\alpha = 1, 2, 3$) of the displacement of the interstitial

with respect to its equilibrium position \underline{g}_I , i.e. $\underline{R}(t) = \underline{g}_I + \underline{q}(t)$. W is the Debye-Waller exponent:

$$(5) \quad W = \sum_{\alpha, \alpha'} \kappa_{\alpha} \kappa_{\alpha'} \langle q_{\alpha}(0) q_{\alpha'}(0) \rangle$$

The expression $\langle q_{\alpha}(t) q_{\alpha'}(0) \rangle$ can be written as (c.f. ZUBAREV (12))

$$(6) \quad \langle q_{\alpha}(t) q_{\alpha'}(0) \rangle = \pi \int_{-\infty}^{+\infty} d\omega \frac{\exp(-i\omega t)}{\exp(\beta\hbar\omega) - 1} A_{\alpha\alpha'}(\omega)$$

where $\beta = \frac{1}{k_B T}$ and where the function $A_{\alpha\alpha'}(\omega)$ (which is related to the spectral density of the oscillations of the interstitial atom in the host lattice) is given by

$$(7) \quad A_{\alpha\alpha'}(\omega) = i \left[G(q_{\alpha}, q_{\alpha'}; \omega + i\epsilon) - G(q_{\alpha}, q_{\alpha'}; \omega - i\epsilon) \right]$$

$G(q_{\alpha}, q_{\alpha'}; \omega)$ is the Fourier transform of the retarded Green's function of the displacement coordinate q_{α} with respect to the displacement coordinate α' .

Eqs. (6) and (7) are a form of the "fluctuation-dissipation theorem" of CALLEN and WELTON (17).

1.2 The Hamiltonian of the System

In order to be able to calculate the Green's functions in eq. (9) we have to consider the Hamiltonian of the whole system, since these functions contain the interaction of the interstitial atom with the oscillations of the host lattice. The Hamiltonian of the system can be written as the sum of three terms

$$(10) \quad H = H_0 + H_I + H_{int}$$

where H_0 is the Hamiltonian of the host lattice, H_I the Hamiltonian of the oscillations of the interstitial atom in a "frozen" host lattice, and H_{int} the term which describes the coupling between the lattice modes and the oscillations of the interstitial atom. Using the notations of MARADUDIN (13) H_0 has the form

$$(11) \quad H_0 = \sum_{\alpha} \sum_{\ell \kappa} \frac{p_{\alpha}^2(\ell \kappa)}{2M} + \frac{1}{2} \sum_{\alpha} \sum_{\ell \kappa} \sum_{\beta} \sum_{\ell' \kappa'} \phi_{\alpha\beta}(\ell \kappa; \ell' \kappa') u_{\alpha}(\ell \kappa) u_{\beta}(\ell' \kappa')$$

M is the mass of the lattice atoms.

The Hamiltonian H_I we write in terms of the normal modes of oscillation ($s = 1, 2, 3$) of the interstitial in the "frozen" lattice. Then it takes a particularly simple form

$$(12) \quad H_I = \sum_{s=1}^3 \left(\frac{p_s^2}{2m} + \frac{\omega_s^2 q_s^2}{2} \right)$$

H_{int} has the general form, for a harmonic (bilinear) interaction between the interstitial and the atoms of the host lattice.

$$(13) \quad H_{int} = \sum_{s, \alpha, \alpha'} q_s e_{s\alpha'} M_{\alpha'\alpha}(g_I, \ell\kappa) \mu_\alpha(\ell\kappa)$$

e_s is the vector of polarization of the normal modes. The interaction matrix $M_{\alpha'\alpha}(g_I, \ell\kappa)$ is defined in such a way that $M_{\alpha'\alpha}(g_I, \ell\kappa) \mu_\alpha(\ell\kappa)$ gives the α' -component of the force at the interstitial (position g_I) if the atom $\{\ell\kappa\}$ is displaced by μ_α in the α -direction. This matrix obviously depends only on the geometry of the host lattice, the equilibrium position of the interstitial with respect to the host lattice and the interaction constants between the interstitial and the lattice atoms. For a particular problem the equilibrium position of the interstitial within the host lattices is a constant, and we can drop it as argument of the matrix. Carrying out the summation over α' we write the interaction term in the form

$$(13') \quad H_{int} = \sum_{s, \alpha, g} q_s M_{s\alpha}(\ell\kappa) \mu_\alpha(\ell\kappa)$$

with

$$(14) \quad M_{s\alpha}(\ell\kappa) = \sum_{\alpha'} e_{s\alpha'} M_{\alpha'\alpha}(g_I, \ell\kappa)$$

1.3 Calculation of the Green's Function

Our problem is now the calculation of the Green's function for a system Y_1 of three oscillators coupled by a bilinear term to a second system Y_2 of a large number of harmonic oscillators. This problem can be solved exactly, for instance by the calculation of KUBO's relaxation operator ⁽¹⁸⁾ or by using the equations-of-motion method for the Green's functions ⁽¹²⁾.

In this way we determine the Green's functions $G(q_s, q_s; \omega)$ of the normal coordinate q_s with respect to the normal coordinate q_s . As the displacements q_α of the interstitial in terms of its normal modes are given by $q_\alpha = \sum_s e_{s\alpha} q_s$ we have also the relation

$$(15) \quad G(q_\alpha, q_\alpha; \omega) = \sum_{s, s'} e_{s\alpha} e_{s'\alpha} G(q_s, q_s; \omega)$$

Thus it is sufficient for the solution of our problem to determine $G(q_s, q_s; \omega)$. The Green's function $G(q_s, q_s; \omega)$ is the Fourier transform of $G^{(r)}(q_s, q_s; t)$ which is given by

$$(16) \quad G^{(r)}(q_s, q_s; t) = -\frac{i}{\hbar} \theta(t) \langle [\phi_H(t) \tilde{q}_s(t), \tilde{q}_s(0)] \rangle_1$$

where $\langle \rangle_1$ denotes an average computed with a time-dependent density matrix corresponding to the system Y_1 ; $\theta(t)$ represents the Heavyside step function and $\tilde{q}_s(t)$ is given by

$$(17) \quad \tilde{q}_s(t) = \exp\left(\frac{i}{\hbar} H_I t\right) q_s \exp\left(-\frac{i}{\hbar} H_I t\right)$$

The relaxation operator $\phi_H(t)$ is given by a time ordered exponential ($\exp_{(-T)}$ means that the time ordering is such that the larger times are written to the right)

$$(18) \quad \phi_H(t) = \exp_{(-T)} \left\{ \int_0^t dt' \int_0^{t'} dt'' \langle \Omega_H(t'') \Omega_H(t') \rangle_2 \right\}$$

$\langle \dots \rangle_2$ denotes the average over the system Y_2 and the operator $\Omega_H(t)$ is defined by

$$(19) \quad \Omega_H(t) \dots = \frac{i}{\hbar} [H_{int}(t), \dots]$$

with

$$(20) \quad H_{int}(t) = \sum_{s, \alpha, \ell\kappa} q_s(t) M_{s\alpha}(\ell\kappa) \tilde{\mu}_\alpha(\ell\kappa, t)$$

where

$$(21) \quad \tilde{\mu}_\alpha(\ell\kappa, t) = \exp\left(\frac{i}{\hbar} H_0 t\right) \mu_\alpha(\ell\kappa) \exp\left(-\frac{i}{\hbar} H_0 t\right)$$

In writing eq. (18) we made use of the fact that $\langle \Omega_H(t) \rangle_2$ vanishes since $\langle \mu_\alpha(\ell\kappa, t) \rangle$ vanishes for all $\alpha\ell\kappa$ and t . The expression (18) for the relaxation operator is exact in our case: in fact, a system of oscillators with some bilinear coupling terms leads to a Gaussian relaxation operator (18), i.e. to eq. (18).

Since we want to apply $\phi_H(t)$ on $\tilde{q}_s(t)$ we have to calculate the effect of

operating with $\langle \Omega_H(t'') \Omega_H(t') \rangle_2$ on $\tilde{q}_s(t)$.

Since higher commutators of the type $[\tilde{q}_{s''}(t''), [\tilde{q}_{s'}(t'), \tilde{q}_s(t)]]$ vanish (because the commutator $[\tilde{q}_{s'}(t'), \tilde{q}_s(t)]$ is a pure number) we obtain

$$(22) \quad \langle \Omega_H(t'') \Omega_H(t') \rangle_2 = \frac{i}{\hbar} \sum \sum M_{s'\alpha}(\ell\kappa) M_{s''\alpha'}(\ell'\kappa') G_{(0)}^r(\mu_\alpha(\ell\kappa), \mu_{\alpha'}(\ell'\kappa'); t) \times \\ \times [q_s(t) q_{s'}(t')] q_{s''}(t'')$$

where

$$(23) \quad G_o^{(r)}(\mu_\alpha(\ell\kappa), \mu_{\alpha'}(\ell'\kappa'); t) = -\frac{i}{\hbar} \theta(t) \langle [\tilde{\mu}_\alpha(\ell\kappa, t), \tilde{\mu}_{\alpha'}(\ell'\kappa', 0)] \rangle$$

is the retarded Green's function of the perfect lattice of $\mu_\alpha(\ell\kappa)$ with respect to $\mu_{\alpha'}(\ell'\kappa')$. Henceforth we shall write it simply $G_{\alpha\alpha'}(\ell\kappa, \ell'\kappa'; t)$:

$$(24) \quad 2\pi G_{\alpha\alpha'}(\ell\kappa, \ell'\kappa', t) \equiv G_{(0)}^{(r)}(\mu_\alpha(\ell\kappa), \mu_{\alpha'}(\ell'\kappa'); t)$$

The factor 2π has been introduced in such a way that the Fourier transform of $G_{\alpha\alpha'}(\ell\kappa; \ell'\kappa', t)$ is identical with the Green's function as defined by MONTROLL and POTTS (2).

Writing out explicitly the expression that defines the exponential in $\Phi_H(t) \tilde{q}_s(t)$ while noting that $[\tilde{q}_s(t), q_{s'}(t')]$ vanishes for $s \neq s'$ and that $-\frac{i\theta(t)}{\hbar} [\tilde{q}_s(t), \tilde{q}_s(0)]$ is simply the retarded Green's function $G_{(0)}^{(r)}(q_s, q_s; t)$ of the normal coordinate q_s for the isolated system Y_1 (since $[\tilde{q}_s(t), \tilde{q}_s(0)]$ is a pure number it is equal to $\langle [\tilde{q}_s(t), \tilde{q}_s(0)] \rangle_1$) we get a series which is the Neumann series corresponding to the integral equation (which is essentially the same as DYSON's equation in field theory)

$$(25) \quad G^{(r)}(q_s, q_s; t) = \delta_{ss} G_{(0)}^{(r)}(q_s, q_s; t) + \sum_{s''=1}^3 \int_0^t dt' K_{ss''}(t-t') G^{(r)}(q_s, q_{s''}; t')$$

with the kernel

$$(26) \quad K_{ss''}(t-t') = \sum_{\alpha\ell\kappa} \sum_{\alpha'\ell'\kappa'} 2\pi \int_{-\infty}^{+\infty} dt'' G_{(0)}^{(r)}(q_s, q_{s''}; t-t'') M_{s\alpha}(\ell\kappa) M_{s'\alpha'}(\ell'\kappa') \times \\ \times G_{\alpha\alpha'}(\ell\kappa, \ell'\kappa'; t''-t')$$

From eq. (25) we obtain the corresponding equations for $G(q_s, q_s; \omega)$

$$(27) \quad G(q_s, q_{s'}; \omega) = \partial_{ss'} (G_{(0)}(q_s, q_{s'}; \omega) + \sum_{s''=1}^3 K_{ss''} G(q_{s''}, q_{s'}; \omega))$$

with

$$(28) \quad K_{ss''}(\omega) = 2\pi \left\{ \sum_{\alpha l \kappa} \sum_{\alpha' l' \kappa'} M_{s\alpha}(l\kappa) M_{s''\alpha'}(l'\kappa') G(l\kappa, l'\kappa'; \omega) \right\} G_{(0)}(q_s, q_{s'}; \omega)$$

These equations yield

$$(29) \quad G(q_s, q_{s'}; \omega) = R_{ss'}(\omega)$$

where $R_{ss'}(\omega)$ is the reciprocal matrix of

$$(30) \quad U_{ss''} = \frac{\partial_{ss''}}{G_{(0)}(q_s, q_{s'}; \omega)} - 2\pi \sum M_{s\alpha}(l\kappa) M_{s''\alpha'}(l'\kappa') G_{\alpha\alpha'}(l\kappa, l'\kappa'; \omega)$$

The couple of equations (29) and (30) are also derived by an other method in Appendix A. $G_{(0)}(q_s, q_{s'}; \omega)$ has the simple form

$$(31) \quad G_{(0)}(q_s, q_{s'}; \omega) = \frac{1}{2\pi m} \frac{1}{\omega^2 - \omega_s^2}$$

while the function $G_{\alpha\alpha'}(l\kappa, l'\kappa'; \omega)$ has to be found from the analysis of the vibrations of the perfect crystal. If it is known the function (which we shall call the "interaction function")

$$(32) \quad F_{ss'}(\omega) = \sum M_{s\alpha}(l\kappa) M_{s'\alpha'}(l'\kappa') G_{\alpha\alpha'}(l\kappa, l'\kappa'; \omega)$$

can be calculated in a straight-forward manner and we obtain for

$$(33) \quad A_{ss'}(\omega) = i \left[G(q_s, q_{s'}; \omega + i\epsilon) - G(q_s, q_{s'}; \omega - i\epsilon) \right]$$

the expression

$$(34) \quad A_{SS'}(\omega) = - \sum_{S''} \frac{1}{\pi} \text{Im} F_{SS''}(\omega) Q_{S''S}^{-1}(\omega) + \sum_i \frac{1}{2\pi\omega_i} \delta(\omega - \omega_i)$$

where the matrix Q^{-1} is the reciprocal of

$$(35) \quad Q_{SS'}(\omega) = \sum_{S''} \left\{ \left[m(\omega^2 - \omega_S^2) \partial_{SS''} - \text{Re} F_{SS''}(\omega) \right] \left[m(\omega^2 - \omega_{S'}^2) \partial_{S''S'} - \text{Re} F_{S''S'}(\omega) \right] + \text{Im} F_{SS''}(\omega) - \text{Im} F_{S''S'}(\omega) \right\}$$

The real and imaginary parts of $F_{SS'}(\omega)$ are determined by the corresponding parts of $G_{\alpha\alpha}(\ell\kappa, \ell'\kappa'; \omega)$.

Since the imaginary part of $G_{\alpha\alpha}(\ell\kappa, \ell'\kappa'; \omega)$ is equal to its spectral function $A_{\alpha\alpha}(\ell\kappa, \ell'\kappa'; \omega)$ where

$$(36) \quad A_{\alpha\alpha}(\ell\kappa, \ell'\kappa'; \omega) = i \left[G_{\alpha\alpha}(\ell\kappa, \ell'\kappa'; \omega + i\epsilon) - G_{\alpha\alpha}(\ell\kappa, \ell'\kappa'; \omega - i\epsilon) \right]$$

it vanishes outside the frequencies region of oscillations of the perfect lattice (the region of band modes).

Outside that region $A_{SS'}(\omega)$ will only be different from zero of the points ω_i for which the determinant of $Q_{SS'}(\omega)$ vanishes. This implies the vanishing of the determinant

$$(37) \quad \Delta(\omega) = |m \partial_{SS'}(\omega^2 - \omega_S^2) - \text{Re} F_{SS'}(\omega)|$$

Eq. (37) is a necessary condition for the existence of (localized) oscillation modes of the interstitial outside of the region of band modes. These modes can be thought of as corresponding to the proper oscillations of the interstitial which are shifted in frequency by the term $\text{Re} F_{SS'}(\omega)$ due to the interaction with the lattice. As an example of this method we shall calculate in the following the localized modes of interstitial hydrogen in vanadium.

Part II Determination of the Localized Modes of Interstitial Hydrogen in Vanadium

2.1 The Function $G_{\alpha\alpha}(\ell\kappa, \ell'\kappa'; \omega)$ in Vanadium

We shall use the following notations and conventions: the origin of our Cartesian system of coordinates we put in the center of the elementary cube; the atom in this site (V has a bcc-lattice) will be labeled (000); the directions of the coordinates axes are along the edges of the cube. We shall measure

all coordinates in units of $\frac{a}{2}$ where a is the lattice constant. The interstitial hydrogen is supposed ⁽⁸⁾ to occupy so-called tetraedric positions; we thus choose for the H-atom one of these sites, say $g_+ = (0, \frac{1}{2}, 1)$. We consider a coupling between hydrogen and its nearest neighbours of the V-lattice only. These are the atoms (000), (002), (111) and ($\bar{1}11$). We therefore have to know the function $G_{\alpha\alpha'}(\ell\kappa, \ell'\kappa'; \omega)$ when $\ell\kappa$ and $\ell'\kappa'$ take values corresponding to these atoms. This function is calculated in the Appendix B. We take out a factor $-\frac{3}{8\alpha_1}$ for convenience. The resulting function is given in table I.

Table I : The function $G'_{\alpha\alpha'}(\ell\kappa, \ell'\kappa'; \omega) = -\frac{8\alpha_1}{3} G_{\alpha\alpha'}(\ell\kappa, \ell'\kappa'; \omega)$

$\kappa' \backslash \kappa$	(111)	($\bar{1}11$)	(000)	(002)
(111)	$g_1(\omega)$	$g_2(\omega)$	$g_3(\omega)$	$g_4(\omega)$
($\bar{1}11$)	$g_2(\omega)$	$g_1(\omega)$	$g_5(\omega)$	$g_6(\omega)$
(000)	$g_3(\omega)$	$g_5(\omega)$	$g_1(\omega)$	$g'_2(\omega)$
(002)	$g_4(\omega)$	$g_6(\omega)$	$g'_2(\omega)$	$g_1(\omega)$

The $g_i(\omega)$ in Table I are matrices in (α, α') . One finds

$$(38) \quad g_1(\omega)_{\alpha\alpha'} = G_1(\omega)\delta_{\alpha\alpha'}, \quad g_2(\omega) = \begin{pmatrix} G_2 & 0 & 0 \\ 0 & G_3 & 0 \\ 0 & 0 & G_3 \end{pmatrix}, \quad g'_2(\omega) = \begin{pmatrix} G_3 & 0 & 0 \\ 0 & G_2 & 0 \\ 0 & 0 & G_2 \end{pmatrix}$$

The other matrices involve also non-diagonal elements. They are

$$(39) \quad g_3(\omega) = \begin{pmatrix} G_4 & G_5 & G_5 \\ G_5 & G_4 & G_5 \\ G_5 & G_5 & G_4 \end{pmatrix}, \quad g_4 = \begin{pmatrix} G_4 & G_5 & -G_5 \\ G_5 & G_4 & -G_5 \\ -G_5 & -G_5 & G_4 \end{pmatrix}$$

$$g_5(\omega) = \begin{pmatrix} G_4 & -G_5 & -G_5 \\ -G_5 & G_4 & G_5 \\ -G_5 & G_5 & G_4 \end{pmatrix}, \quad g_6 = \begin{pmatrix} G_4 & -G_5 & G_5 \\ -G_5 & G_4 & -G_5 \\ G_5 & -G_5 & G_4 \end{pmatrix}$$

The functions $G_i(\omega)$, ($i = 1, 2, 3, 4, 5$) are given by (using a FINE's model ⁽⁷⁾ for vanadium):

$$\begin{aligned}
 (40) \quad G_1(\omega) &= \frac{1}{3\pi^3} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \int_0^{2\pi} d\theta_3 \frac{N}{D} \\
 G_2(\omega) &= \frac{1}{\pi^3} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \int_0^{2\pi} d\theta_3 \frac{H_{11}}{D} (2C_3^2 - 1) \\
 G_3(\omega) &= \frac{1}{\pi^3} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \int_0^{2\pi} d\theta_3 \frac{H_{33}}{D} (2C_3^2 - 1) \\
 G_4(\omega) &= \frac{1}{3\pi^3} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \int_0^{2\pi} d\theta_3 \frac{N}{D} C_1 C_2 C_3 \\
 G_5(\omega) &= \frac{1}{\pi^3} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \int_0^{2\pi} d\theta_3 \frac{H_{12}}{D} (-S_1 S_2 C_3)
 \end{aligned}$$

with

$$C_i = \cos \theta_i \quad S_i = \sin \theta_i$$

and

$$\begin{aligned}
 (41) \quad N &= 3(1 - C_1 C_2 C_3 - \Omega^2)^2 + 3\beta(1 - C_1 C_2 C_3 - \Omega^2)(S_1^2 + S_2^2 + S_3^2) + \\
 &+ \left(\frac{2\beta}{2}\right)^2 (S_1^2 S_2^2 + S_2^2 S_3^2 + S_3^2 S_1^2) - (C_1^2 S_2^2 S_3^2 + S_1^2 C_2^2 S_3^2 + S_1^2 S_2^2 C_3^2) \\
 D &= (S_1 S_2 S_3)^2 \left[2C_1 C_2 C_3 - \frac{3\beta}{2} (C_1^2 + C_2^2 + C_3^2) + \left(\frac{3\beta}{2}\right)^2 \right] + \\
 &+ (1 - C_1 C_2 C_3 - \Omega^2) \left[\left(\frac{3}{2}\beta\right)^2 (S_1^2 S_2^2 + S_2^2 S_3^2 + S_3^2 S_1^2) - \right. \\
 &- (C_1^2 S_2^2 S_3^2 + S_1^2 C_2^2 S_3^2 + S_1^2 S_2^2 C_3^2) \left. \right] + (1 - C_1 C_2 C_3 - \Omega^2)^2 \times \\
 &\times \left(\frac{3}{2}\beta\right) (S_1^2 + S_2^2 + S_3^2) + (1 - C_1 C_2 C_3 - \Omega^2)^3
 \end{aligned}$$

These expressions involve the dimensionless constants

$$(42) \quad \Omega^2 = \frac{3M\omega^2}{8\alpha_1}, \quad \beta = \frac{\alpha_2}{\alpha_1}$$

where α_1 is the force constant for the interaction between nearest neighbours in the V-lattice, and α_2 is the corresponding constant for the next-nearest-neighbour interaction.

2.2 The Coupling Matrix $M_{\alpha\alpha}(\mathbf{k}\kappa)$ for Interstitial Hydrogen in Vanadium

For the derivation of the coupling matrix $M_{\alpha\alpha}(\mathbf{k}\kappa)$ we remember that it is the negative of the coefficient of $\mu_{\alpha}(\mathbf{k}\kappa)$ in the expression for the component α'

of the force acting on the hydrogen atom. The equations for the forces acting on hydrogen are (γ = force constant for the H-V interaction)

$$\begin{aligned}
 f_1 &= -\frac{2\gamma}{5} \left[4q_1 - 2\mu_1(111) - 2\mu_1(\bar{1}11) - \mu_2(111) + \mu_2(\bar{1}11) \right] \\
 f_2 &= -\frac{\gamma}{5} \left[4q_2 - 2\mu_1(111) + 2\mu_1(\bar{1}11) - \mu_2(111) - \mu_2(\bar{1}11) - \mu_2(000) \right. \\
 (43) \quad &\quad \left. - \mu_2(002) - 2\mu_3(000) + 2\mu_3(002) \right] \\
 f_3 &= -\frac{2\gamma}{5} \left[4q_3 - \mu_2(000) + \mu_2(002) - 2\mu_3(000) - 2\mu_3(002) \right]
 \end{aligned}$$

From these equations we can draw the following conclusions:

- (i) the free oscillations of the hydrogen atom in a frozen vanadium lattice (i.e. for all $\mu_\alpha(\ell\kappa) = 0$) have the following frequencies and polarizations:

$$\begin{aligned}
 \omega_1^2 &= \frac{8\gamma}{5m} & e_1 &= (1, 0, 0) \\
 \omega_2^2 &= \frac{4\gamma}{5m} & e_2 &= (0, 1, 0) \\
 \omega_3^2 &= \frac{8\gamma}{m} & e_3 &= (0, 0, 1)
 \end{aligned}$$

- (ii) the coupling matrixes $M_{s\alpha}(\ell\kappa)$ are the same as $M_{\alpha\alpha}(\ell\kappa)$ due to the fact, noted in (i), that the polarization directions of the hydrogen modes are along the coordinate axes. The matrices $M_{s\alpha}(\ell\kappa) = M_{\alpha'\alpha}(\ell\kappa)$ can be read off eq. (43) as follows:

$$\begin{aligned}
 M_{s\alpha}(111) &= -\frac{\gamma}{5} \begin{pmatrix} 4 & 2 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 M_{s\alpha}(\bar{1}11) &= -\frac{\gamma}{5} \begin{pmatrix} 4 & -2 & 0 \\ -2 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 (45) \quad M_{s\alpha}(000) &= -\frac{\gamma}{5} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 2 \\ 0 & 2 & 4 \end{pmatrix} \\
 M_{s\alpha}(002) &= -\frac{\gamma}{5} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -2 \\ 0 & -2 & 4 \end{pmatrix}
 \end{aligned}$$

2.3 The Interaction Function $F_{ss'}(\omega)$ for the Hydrogen Atom in the Vanadium Lattice

Now we can use equation (32) to determine $F_{ss'}(\omega)$. The calculations simplify considerably because of the explicit form of the matrices $M_{sa}(\ell\kappa)$. For instance, for $F_{11}(\omega)$ the terms with $\{\ell\kappa\} = (000)$ and $= (002)$ do not contribute and we obtain

$$\frac{8\alpha_1}{3} F_{11}(\omega) = \frac{8\gamma^2}{25} (5G_1 - G_2 + 4G_3)$$

Because of the symmetry of $M_{sa}(\ell\kappa)$ and $G_{\alpha\alpha}(\ell\kappa, \ell\kappa')$ one immediately sees that $F_{33}(\omega) = F_{11}(\omega)$. For $F_{22}(\omega)$ the calculations are somewhat lengthier but can be simplified by the use of symmetry relations as shown in Appendix C.

Finally $\frac{8\alpha_1}{3} F_{22}(\omega) = -\frac{8\gamma^2}{25} (5G_1 + G_2 - 4G_3 + 2(G_4 + 8G_5))$. The $F_{ss'}(\omega)$ for $s \neq s'$ turn out to be zero. Thus the matrix $F_{ss'}(\omega)$ becomes

$$(46) \quad F_{ss'}(\omega) = -\frac{3\gamma^2}{50\alpha_1} \begin{pmatrix} 10G_1 - 2(G_2 - 4G_3) & 0 & 0 \\ 0 & 5G_1 + 3G_2 - 4G_3 + 2(G_4 + 8G_5) & 0 \\ 0 & 0 & 10G_1 - 2(G_2 - 4G_3) \end{pmatrix}$$

3.4 Localized mode Frequencies in Vanadium-hydride

Since in this case $F_{ss'}(\omega)$ is a diagonal matrix we obtain, instead of the determinant eq. (37), immediately the following equations for the double-degenerated mode and the single mode

$$(47) \quad \begin{aligned} \Omega_1^2 &= \Omega_{10}^2 - \frac{9}{200} \frac{\rho^2}{\mu} g_1(\Omega_1^2); & \Omega_{10}^2 &= \frac{3}{5} \frac{\rho}{\mu} \\ \Omega_2^2 &= \Omega_{20}^2 - \frac{9}{400} \frac{\rho^2}{\mu} g_2(\Omega_2^2); & \Omega_{20}^2 &= \frac{3}{10} \frac{\rho}{\mu} \end{aligned}$$

where we used the dimensionless frequencies definition eq. (42) and the abbreviations

$$(48) \quad \begin{aligned} \mu &= \frac{m}{M} & \rho &= \frac{\gamma}{\alpha_1} \\ g_1 &= 5G_1^* - G_2^* + 4G_3^* \\ g_2 &= 5G_1^* + G_2^* - 4G_3^* + 2G_4^* + 16G_5^* \end{aligned}$$

A superficial look on eqs. (47) would lead to think that the first term would decrease in importance with increasing M because of the factor $\mu = m/M$. This is misleading since the terms in the brackets go asymptotically with $1/\Omega^2$, i.e. with $1/M \omega^2$ while the first term goes as $\omega^2 m$. So it is really the second term which is smaller than the first by a ratio $\frac{m}{M}$. Since in our case $\frac{m}{M} \approx \frac{1}{50}$ while the functions G_i are of order unity or smaller and ρ is also of order unity, one can take as zero-th approximation

$$(49) \quad \Omega_1^2 = \Omega_{10}^2, \quad \Omega_2^2 = \Omega_{20}^2$$

and solve the eqs. (47) by iteration, i.e. take as first approximation

$$(50) \quad \begin{aligned} \Omega_{11}^2 &= \frac{3}{5} \frac{\rho}{\mu} - \frac{9}{200} \frac{\rho^2}{\mu} g_1(\Omega_{10}^2) \\ \Omega_{21}^2 &= \frac{3}{10} \frac{\rho}{\mu} - \frac{9}{400} \frac{\rho^2}{\mu} g_2(\Omega_{20}^2) \end{aligned}$$

and so on, the (n+1)-th approximation being:

$$(51) \quad \begin{aligned} \Omega_{1(n+1)}^2 &= \frac{3}{5} \frac{\rho}{\mu} - \frac{9}{200} \frac{\rho^2}{\mu} g_1(\Omega_{1n}^2) \\ \Omega_{2(n+1)}^2 &= \frac{3}{10} \frac{\rho}{\mu} - \frac{9}{400} \frac{\rho^2}{\mu} g_2(\Omega_{2n}^2) \end{aligned}$$

$n = 0, 1, 2, \dots$

The values of the Green's function relevant for our problem are tabulated for arguments $\Omega^2 = 10(10)100$ in Table II - these values have been calculated on the IBM 360 of CETIS at ISPRA.

The experimental data on the localized vibration frequencies of vanadium-hydrogen and vanadium-deuterium have been obtained by I.N.S. at the Ispra I reactor facility by Kley et al. and published in the references (8).

In fig. 1 and fig. 2 are reproduced the intensity of scattered neutrons as function of time of flight and energy transfer. Since we know that observed peaks are the superposition of two peaks at frequencies ν_1 (doubly degenerate) and ν_2 (non-degenerate) we analyse the data in assuming that the maximum of intensity corresponds to the frequency ν_1 . We read thus the experimental values

$$(52) \quad h\nu_1(H) \cong 100 \text{ meV} \quad h\nu_1(D) \cong 77 \text{ meV}$$

To compare experimental and theoretical values we proceed as follows.

We assume, for the case of deuterium, that $h\nu_1 = 77$ meV. With $\mu = 2/50.95$ we solve for ρ the first eq. (47). We have:

$$\begin{aligned} \hbar\omega_1 &= 77 \times 10^{-3} \text{ meV} \\ (53) \quad \nu_1 &= 1.862 \times 10^{13} \text{ sec}^{-1}; \quad \omega_1 = 1.170 \times 10^{14} \text{ rad/sec} \\ \Omega_1^2 &= 22.38 \quad g_1(\Omega_1^2) = -0.2338 \end{aligned}$$

which gives

$$(54) \quad \rho = 1.427$$

We, then, solve the eq. (47) for hydrogen ($\mu = 1/50.95$) by iterations for the values of Ω_1^2 and Ω_2^2 . Only two iterations are necessary to obtain the following values:

$$\begin{aligned} \Omega_1^2 &= 44.17 \\ \omega_1 &= 1.643 \times 10^{14} \text{ rad/sec}; \quad \nu_1 = 2.615 \times 10^{13} \text{ sec}^{-1} \\ h\nu_1 &= 108 \text{ meV} \\ (55) \quad \Omega_2^2 &= 22.36 \\ \omega_2 &= 1.169 \times 10^{14} \text{ rad/sec}; \quad \nu_2 = 1.860 \times 10^{13} \text{ sec}^{-1} \\ h\nu_2 &= 77 \text{ meV} \end{aligned}$$

The theoretical values of 108 meV for the doubly-degenerate frequencies and 77 meV for the non-degenerate mode are consistent with the experimental data on polycrystalline VH system, since the second calculated frequency would correspond to a peak with half the intensity of the first one and occurs at a position where scattered intensity is indeed observed. Basic to this interpretation of the data is the assumption that the two peaks at ν_1 and ν_2 are not resolved in the conditions of the experiment on polycrystalline vanadium hydrogen system. Very recent measurement⁽¹⁹⁾ on a monocrystal of α -niobium hydride have shown indeed the existence of two separated peaks for the localized mode of hydrogen. Due to the close similarity of VH and NbH systems we can say that the above analysis for VH is essentially correct.

One point worth mentioning is that the frequencies calculated for the H atom moving a rigid vanadium lattice, as given by the first terms of eq. (47) are

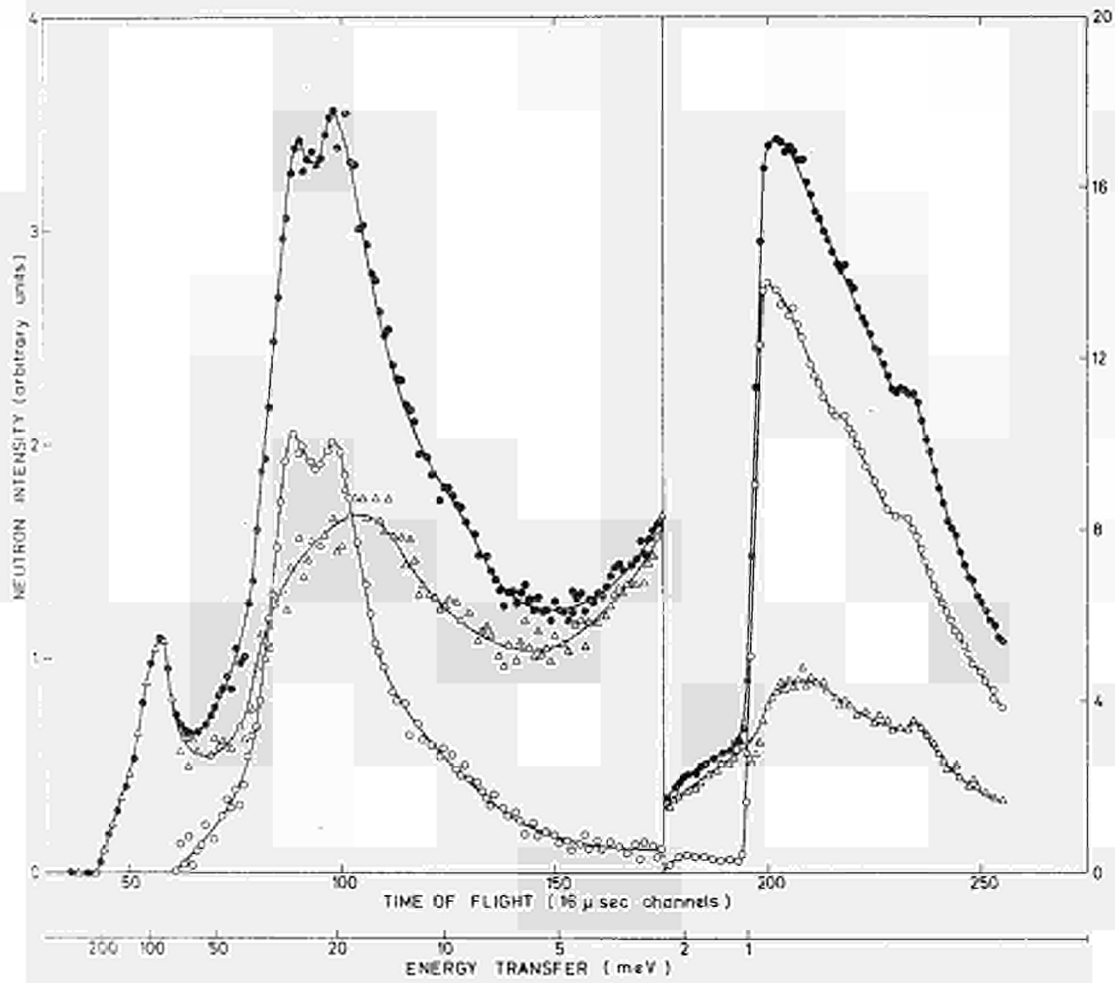
$$\Omega_{10}^2 = 43.62; \quad \hbar\omega_{10} = 107.4 \text{ meV}$$

$$\Omega_{20}^2 = 21.81; \quad \hbar\omega_{20} = 75.9 \text{ meV}$$

The coupling of this oscillator to the host lattice shift the frequency upwards by a very small amount (< 1,5%). This is due to the large mass difference between the interstitial and the host lattice and the closeness of the force constant of the vanadium-hydrogen and vanadium-vanadium interaction ($\rho = 1.427$). Experiments of the type analyzed here are therefore essentially measurements of the V-H interaction and are rather independent of the oscillation properties of the host lattice.

Table II : Numerical values of the functions G_1, \dots, G_5 in units of 10^{-3}

	G_1	G_2	G_3	G_4	G_5
10	- 120.7	1.536	1.598	1.682	- 1.960
20	- 54.57	0.3159	0.3221	0.3593	- 0.3852
30	- 35.29	0.1325	0.1342	0.1522	- 0.1592
40	- 26.08	0.0725	0.0732	0.0836	- 0.0864
50	- 20.68	0.0457	0.0460	0.0528	- 0.0542
60	- 17.14	0.0313	0.0315	0.0363	- 0.0371
70	- 14.63	0.0229	0.0230	0.0265	- 0.0270
80	- 12.76	0.0174	0.0175	0.0202	- 0.0205
90	- 11.32	0.0136	0.0137	0.0159	- 0.0161
100	- 10.17	0.0111	0.0111	0.0128	- 0.0130



Time-of-flight spectra at 50°C of VH(4 atom %) (●), V(O), and VH-V=H(Δ).

Fig.1 Time of flight spectra at 50°C of VH (4%) (●), V(o) and VH-V=H(Δ).
From ref. (8)

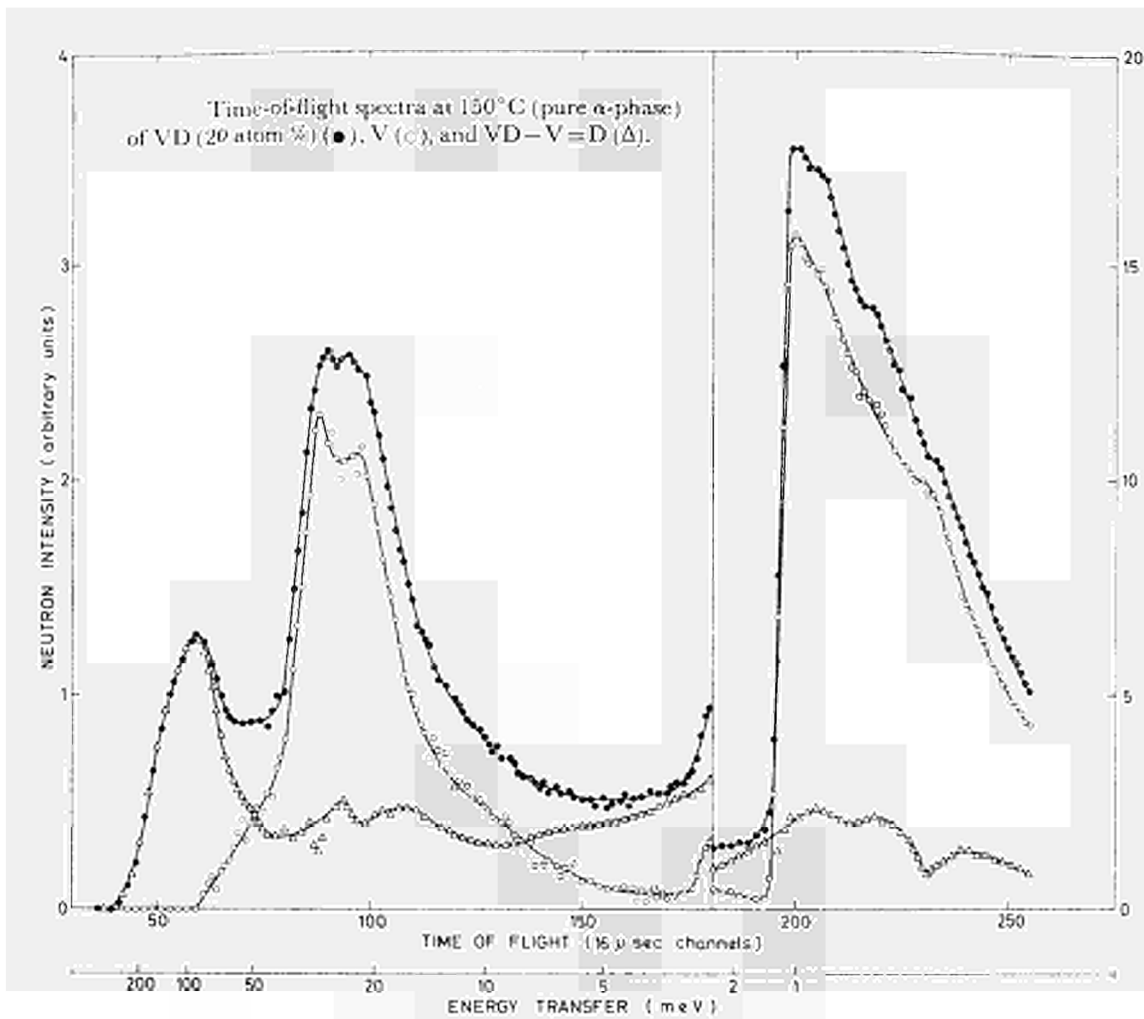


Fig. 2 Time of flight spectra at 150°C (pure α -phase) of VD (20%) (\bullet) and VD-V=D(D). From ref. (8)

Appendix A

Eqs (29) and (30) can also be derived on the basis of the identification of the Green's function $G_{\alpha\beta}(\ell\kappa)\ell'\kappa';\omega$ with the Montroll-Potts Green's function (20) For this we use a matrix partition technique analogous to the one used by Lehman and De Wames (21) and Wagner (6). That the interstitial case can be treated in this way has been remarked also by Maradudin (3) in two comprehensive articles. We refer the reader to these articles for the earlier references on the subject. We follow as closely as possible the notations of these articles.

Though analogous to the method of Wagner our partition is different, leading to specific advantages. In the method of Wagner one has to find the eigenvalues of a $3s \times 3s$ matrix $\partial I + \alpha \gamma^T$ where s is the number of atoms touched by the introduction of the impurity atom. This is done in decomposing the representation of dimension $3s$ into the irreducible representations of the point group of the impurity by the well known group-theoretical methods. In our method one has to find the eigenvalues of a 3×3 matrix, irrespective to the number s , and which in most cases is already diagonal.

We denote by $\mu_{\alpha}(\ell\kappa)$ the displacements of the crystal atoms and by μ_{α} those of the interstitial. We decompose the vector space E of the displacements of all the atoms into the direct sum of the 3-dimensional space E_3 of the displacement μ_{α} and the $3rN$ -dimensional space of the displacements $\mu_{\alpha}(\ell\kappa)$, E_{3rN} . Any matrix operating in E is partitioned accordingly.

We denote by G and L the matrices pertaining to the unperturbed crystal; by γ the "molecular" Green's matrix corresponding to the interstitial atom vibrating in a fixed host lattice; by \tilde{G} and \tilde{L} the matrices pertaining to the total system. We write the G and L matrices as

$$(A.1) \quad \tilde{G} = \begin{pmatrix} G_{11} & | & G_{12} \\ \hline G_{21} & | & G_{22} \end{pmatrix} \quad \tilde{L} = \begin{pmatrix} L_{11} & | & L_{12} \\ \hline L_{21} & | & L_{22} \end{pmatrix}$$

where the index 1 refers the space E_3 and the index 2 to the space E_{3rN} . Since $\tilde{G} = \tilde{L}^{-1}$, we have

$$(A.2) \quad \begin{aligned} L_{11} G_{11} + L_{12} G_{21} &= I \\ L_{21} G_{11} + L_{22} G_{21} &= 0 \end{aligned}$$

where I is the unit 3x3 matrix, and O the nul 3x3rN matrix.
Combining the two eq. (A2) we obtain

$$(A.3) \quad G_{11}^{-1} = L_{11} - L_{12} L_{22}^{-1} L_{21}$$

But, since:

$$(A.4) \quad \gamma = L_{11}^{-1}, \quad G = L_{22}^{-1} \quad L_{21} = L_{12}^T$$

we can write

$$(A.5) \quad \tilde{\gamma}^{-1} = G_{11}^{-1} = \gamma^{-1} - L_{12} G L_{12}^T$$

The eq. (A.5) gives the perturbed molecular Green's function $\tilde{\gamma} = G_{11}$ of the interstitial as a function of the unperturbed one γ and of the perturbation $L_{12} G L_{12}^T$ due to the crystal, through the interaction L_{12} between the interstitial and the rest of the lattice. Since the elements of the 3rNx3 matrix L_{12} are the expressions $M_{\alpha\beta}(\ell\kappa)$ of the text, we see that eq. (A.5) can be explicittely written as:

$$(A.6) \quad (\tilde{\gamma}^{-1})_{\alpha\beta} = (\gamma^{-1})_{\alpha\beta} - \sum_{\substack{\alpha'\ell\kappa \\ \beta'\ell'\kappa'}} M_{\alpha\alpha'}(\ell\kappa) G_{\alpha'\beta'}(\ell\kappa; \ell'\kappa' \omega^2) \times M_{\beta\beta'}(\ell'\kappa')$$

which is precisely equivalent to the couple of equations (29) and (30) of the text.

The perturbed frequencies are the poles of $\tilde{\gamma}$, thus the zeros of $\tilde{\gamma}^{-1}$.

Let us suppose that the axes along which the interstitial displacements μ_α are measured have been choosen so that γ is diagonal by symmetry. For example in the case treated in Part II of the text, the symmetry of the interstitial site is $D_{2d} = \bar{4}2m$ (22) and when the axes are choosen parallel to the edges of the cube, γ is diagonal and has only two independent components:

$$(A.7) \quad \gamma_{xy} = \gamma_{yz} = \gamma_{zx} = 0 \quad \gamma_{xx} = \gamma_{zz} \neq \gamma_{yy}$$

The conditions (A.7) are imposed by the symmetry D_{2d} . Since the interaction L_{12} preserves the symmetry of the problem, the perturbed matrix $\tilde{\gamma}$ should be diagonal in these axes. In this case the equations for the perturbed frequencies are the 3 scalar equations

$$(A.8) \quad \tilde{\gamma}_{\alpha\alpha}^{-1}(\omega^2) = \gamma_{\alpha\alpha}^{-1}(\omega^2) - \sum_{\substack{\beta\lambda\kappa \\ \beta'\lambda'\kappa'}} M_{\alpha\beta}(\lambda\kappa) G_{\beta\beta'}(\lambda\kappa; \lambda'\kappa'; \omega^2) \times M_{\alpha\beta'}(\lambda'\kappa') = 0$$

Thus there is no need to use advanced group-theoretical arguments to reduce the problem to scalar equations as in ref. (6) and (3).

The above argument has been put into use in the Part II of the text. Eqs (46) and (47) of the text exhibit the mere fact that $\tilde{\gamma}$ is diagonal and has two independent components, one for $[\bar{x}\bar{x}]$ and $[\bar{z}\bar{z}]$ (double degeneracy), the other for $[\bar{y}\bar{y}]$.

The above method does apply for substitutional impurities as well, with the same simplifications. This is shown on an example in Appendix D.

Appendix B

In this Appendix we derive all the independent components of the Green's functions pertaining to any pair chosen among the 4 points $A = (000)$, $B = (002)$, $C = (111)$, $D = (\bar{1}11)$.

The basis for that derivation is the fact that under any symmetry operation (S/t) which send the crystal into itself the Green's function $G_{\alpha\beta}(\underline{l}\kappa; \underline{l}'\kappa'; \omega^2)$ behaves like a second rank tensor $^{(A4)}$. Using the notations of Maradudin $^{(A4)}$ we have that:

$$(B.1) \quad G_{\alpha\beta}(\underline{l}\kappa; \underline{l}'\kappa') = \sum_{\alpha'\beta'} S_{\alpha\alpha'} S_{\beta\beta'} G_{\alpha'\beta'}(\underline{l}\kappa; \underline{l}'\kappa')$$

First when $\{\underline{l}\kappa\}$ and $\{\underline{l}'\kappa'\}$ are the same point, (S/Q) can be chosen to be any element of the point group, leaving thus the point $\{\underline{l}\kappa\}$ invariant. We obtain the well known result for the cubic symmetry:

$$G_{xy}(\underline{l}\kappa; \underline{l}'\kappa') = G_{yz}(\underline{l}'\kappa'; \underline{l}'\kappa') = G_{zx}(\underline{l}\kappa; \underline{l}'\kappa') = 0$$

$$(B.2) \quad G_{xx}(\underline{l}\kappa; \underline{l}'\kappa') = G_{yy}(\underline{l}\kappa; \underline{l}'\kappa') = G_{zz}(\underline{l}\kappa; \underline{l}'\kappa')$$

$$= \frac{1}{3N} \sum_{\underline{k}j} \frac{1}{\omega^2 - \omega_j^2(\underline{k})} = G_1$$

Second, when $\{\underline{l}\kappa\}$ and $\{\underline{l}'\kappa'\}$ are distinct, (S/t) can be chosen to be any symmetry element of the point group which leave the pair $\{\underline{l}\kappa\}$, $\{\underline{l}'\kappa'\}$ invariant (sub-group). In the following formulae the notation $G(P,Q)$ denotes the 3x3 matrix whose elements are $G_{\alpha\beta}(P,Q)$, $\alpha, \beta = 1, 2, 3$ and P, Q the lattice points $P = \{\underline{l}\kappa\}$, $Q = \{\underline{l}'\kappa'\}$.

Pair (AB) Subgroup D_{4h}

$$(B.3) \quad \left. \begin{aligned} G_{xy}(A,B) = G_{yz}(A,B) = G_{zx}(A,B) = 0 \\ G_{xx}(A,B) = G_{yy}(A,B) = G_2 \neq G_{zz}(A,B) = G_3 \end{aligned} \right| G(A,B) = \begin{pmatrix} G_2 & 0 & 0 \\ 0 & G_2 & 0 \\ 0 & 0 & G_3 \end{pmatrix}$$

Pair (CD) Same subgroup with 4 fold axis along x direction

$$(B.4) \quad \begin{array}{l} G_{xy}(C,D) = G_{yz}(C,D) = G_{zx}(C,D) = 0 \\ G_{yy}(C,D) = G_{zz}(C,D) = G'_2 \neq G_{xx}(C,D) = G'_3 \end{array} \left| \quad G(C,D) = \begin{pmatrix} G'_3 & 0 & 0 \\ 0 & G'_2 & 0 \\ 0 & 0 & G'_2 \end{pmatrix} \right.$$

Pair (AC) Subgroup C_{3v} the independent elements are found to be $G_{xx}(AC) = G_4$ and $G_{xy}(A,C) = G_5$ with the others given by

$$(B.5) \quad G(A,C) = \begin{pmatrix} G_4 & G_5 & G_5 \\ G_5 & G_4 & G_5 \\ G_5 & G_5 & G_4 \end{pmatrix}$$

Pair (AD) Subgroup C_{3v} the independent elements are $G_{xx}(A,D) = G'_4$ and $G_{xy}(A,D) = G'_5$ and the others are given by

$$(B.6) \quad G(A,D) = \begin{pmatrix} G'_4 & G'_5 & G'_5 \\ G'_5 & G'_4 & G'_5 \\ G'_5 & G'_5 & G'_4 \end{pmatrix}$$

Pair (BC) Subgroup C_{3v} the independent elements are $G_{xx}(B,C) = G''_4$; $G_{xy}(B,C) = -G''_5$ the others being given by:

$$(B.7) \quad G(B,C) = \begin{pmatrix} G''_4 & -G''_5 & -G''_5 \\ -G''_5 & G''_4 & G''_5 \\ G''_5 & G''_5 & G''_4 \end{pmatrix}$$

Pair (BD) Subgroup C_{3v} . We have $G_{xx}(B,D) = G'''_4$, $G_{xy}(B,D) = G'''_5$ and

$$(B.8) \quad G(B,D) = \begin{pmatrix} G'''_4 & G'''_5 & -G'''_5 \\ G'''_5 & G'''_4 & G'''_5 \\ -G'''_5 & G'''_5 & G'''_4 \end{pmatrix}$$

Third, (S/t) can be chosen as to exchange a pair among the four points A,B,C,D with a different pair. For example the exchange of (AB) and (CD), by the four-fold inversion axis S_4 yield

$$(B.9) \quad G'_2 = G_2 \quad \text{and} \quad G'_3 = G_3$$

In the same way the two reflections through the planes $\sigma_v : x = 0$ and $\sigma_h : z = 1$ exchange the pairs (AC), (AD), (BC), (BD) in all possible fashion, yielding

$$(B.10) \quad \begin{aligned} G_4 &= G_4' = G_4'' = G_4''' \\ -G_5 &= G_5' = G_5'' = G_5''' \end{aligned}$$

We are thus left with five independent Green's function, defined as:

$$(B.11) \quad \begin{aligned} G_1 &= G_{xx}(A,A) \quad G_2 = G_{xx}(A,B) \quad G_3 = G_{zz}(A,B) \\ G_4 &= G_{xx}(A,C) \quad G_5 = G_{xy}(A,C) \end{aligned}$$

and the other Green's function are given by the 3x3 matrices:

$$(B.12) \quad \begin{aligned} G(A,A) = \dots = G(D,D) &= \begin{pmatrix} G_1 & 0 & 0 \\ 0 & G_1 & 0 \\ 0 & 0 & G_1 \end{pmatrix} \\ G(A,B) &= \begin{pmatrix} G_2 & 0 & 0 \\ 0 & G_2 & 0 \\ 0 & 0 & G_3 \end{pmatrix} \quad G(C,D) = \begin{pmatrix} G_3 & 0 & 0 \\ 0 & G_2 & 0 \\ 0 & 0 & G_2 \end{pmatrix} \\ G(A,C) &= \begin{pmatrix} G_4 & G_5 & G_5 \\ G_5 & G_4 & G_5 \\ G_5 & G_5 & G_4 \end{pmatrix} \quad G(A,D) = \begin{pmatrix} G_4 & -G_5 & -G_5 \\ -G_5 & G_4 & G_5 \\ -G_5 & G_5 & G_4 \end{pmatrix} \\ G(B,C) &= \begin{pmatrix} G_4 & G_5 & -G_5 \\ G_5 & G_4 & -G_5 \\ -G_5 & -G_5 & G_4 \end{pmatrix} \quad G(B,D) = \begin{pmatrix} G_4 & -G_5 & G_5 \\ -G_5 & G_4 & -G_5 \\ G_5 & -G_5 & G_4 \end{pmatrix} \end{aligned}$$

We next turn to the problem of evaluating explicitly these elements in terms of the dynamical model of Fine (B1) as it was generalized by Montroll and Peaslee (B2). We define first the two Fourier matrix \tilde{M} and $\tilde{\phi}$ belonging to a certain vector \underline{k} by the equations:

$$(B.13) \quad \begin{aligned} \tilde{M}_{\alpha\beta}(\underline{k}, \underline{\kappa}, \underline{\kappa}') &= M_{\kappa} \partial_{\alpha\beta} \partial_{\kappa\kappa'} \\ \tilde{\phi}_{\alpha\beta}(\underline{k}, \underline{\kappa}, \underline{\kappa}') &= \sum_{\underline{l}} \phi_{\alpha\beta}(\underline{l}\kappa; \underline{l}\kappa') \exp \left[-i\underline{k}\underline{x}(\underline{l}\kappa) + i\underline{k}\underline{x}(\underline{l}\kappa') \right] \end{aligned}$$

In terms of these matrices the Green's functions are given by:

$$(B.14) \quad G_{\alpha\beta}(\underline{l}\kappa; \underline{l}'\kappa') = \frac{1}{N} \sum_{\underline{k}} \left[M \omega^2 - \tilde{\phi} \right]_{\alpha\beta}^{-1} \exp \left[i\underline{k}\underline{x}(\underline{l}\kappa) - i\underline{k}\underline{x}(\underline{l}'\kappa') \right]$$

where $\left[\tilde{\phi} \right]_{\alpha\beta}^{-1}$ is the $\{\alpha\beta\}$ element of the inverse matrix $\left[M \omega^2 - \tilde{\phi} \right]^{-1}$. We can write, for a Bravais lattice, like the b.c.c. lattice

$$G_{\alpha\beta}(P, Q) = \frac{1}{N} \sum_{\underline{k}} \left[\tilde{M}\omega^2 - \tilde{\Phi} \right]_{\alpha\beta}^{-1} \exp \left[i \underline{k} \cdot \underline{QP} \right]$$

$$\tilde{\Phi}_{\alpha\beta}(\underline{k}) = \sum_{\underline{l}} \Phi_{\alpha\beta}(\underline{l}) \exp \left[-i \underline{k} \cdot \underline{x}(\underline{l}) \right]$$

and the coefficient $\tilde{\Phi}_{\alpha\beta}$ are obtained in making the substitution

$$(B.16) \quad \mu_{\alpha}(\underline{l}) = \mu_{\alpha} \exp \left[-i\omega t + i \underline{k} \cdot \underline{x}(\underline{l}) \right]$$

into the expression of the components $F_{\alpha}(\underline{l})$ of the force acting on the atom $\underline{x}(\underline{l})$ expressed as a function of the displacements. Upon substitution, one gets:

$$(B.17) \quad F_{\alpha}(\underline{l}) = - \sum_{\beta} \tilde{\Phi}_{\alpha\beta}(\underline{k}) \mu_{\beta}(\underline{l})$$

This procedure, when applied to the model defined in refs (7), (23) gives the following matrix elements:

$$(B.18) \quad \begin{aligned} \tilde{\Phi}_{11} &= - \left(\frac{8\alpha_1}{3} \right) \left[1 - C_1 C_2 C_3 + \frac{3\beta}{2} S_1 - \Omega^2 \right] \\ \tilde{\Phi}_{12} &= - \left(\frac{8\alpha_1}{3} \right) S_1 S_2 C_3 \end{aligned}$$

and circular permutations.

Where α_1 and α_2 are the central force constant for 1st and 2nd neighbours and:

$$(B.19) \quad \begin{aligned} \beta &= \frac{\alpha_2}{\alpha_1} \quad \Omega^2 = \frac{3M\omega^2}{8\alpha_1} \quad (\text{dimensionless}) \\ C_i &= \cos \left(\frac{1}{2} k_i a \right) \quad S_i = \sin \left(\frac{1}{2} k_i a \right) \quad i = 1, 2, 3 \end{aligned}$$

a is the edge of the cubic cell.

We need the cofactors H_{ij} of the matrix $(\tilde{M}\omega^2 - \tilde{\Phi})$.

We have

$$(B.20) \quad \begin{aligned} H_{11} &= \left(\frac{8\alpha_1}{3} \right)^2 \left[(1 - C_1 C_2 C_3 - \Omega^2)^2 + \frac{3\beta}{2} (S_2^2 + S_3^2) (1 - C_1 C_2 C_3 - \Omega^2) \right. \\ &\quad \left. - C_1^2 S_2^2 S_3^2 + \left(\frac{3\beta}{2} \right)^2 S_2^2 S_3^2 \right] \\ H_{12} &= \left(\frac{8\alpha_1}{3} \right)^2 \left[- C_3 S_1 S_2 (1 - C_1 C_2 C_3 - \Omega^2) + \right. \\ &\quad \left. + S_1 S_2 S_3^2 (C_1 C_2 - \frac{3\beta}{2} C_3) \right] \end{aligned}$$

and circular permutations.

We also need the following expressions:

$$\begin{aligned}
 (B.21) \quad N &= H_{11} + H_{12} + H_{33} = \left(\frac{8\alpha_1}{3}\right)^{-1} \frac{dD}{d(\Omega^2)} = \\
 &= \left(\frac{8\alpha_1}{3}\right)^2 \left[3(1 - c_1 c_2 c_3 - \Omega^2)^2 + 3\beta(1 - c_1 c_2 c_3 - \Omega^2)(s_1^2 + s_2^2 + s_3^2) + \right. \\
 &\quad \left. + \left(\frac{3\beta}{2}\right)^2 (s_2^2 s_3^2 + s_3^2 s_1^2 + s_1^2 s_2^2) - (c_1^2 s_2^2 s_3^2 + c_2^2 s_3^2 s_1^2 + c_3^2 s_1^2 s_2^2) \right].
 \end{aligned}$$

$$\begin{aligned}
 D &= \det |\tilde{M}\omega^2 - \tilde{\Phi}| = \\
 &= - \left(\frac{8\alpha_1}{3}\right)^3 \left\{ (1 - c_1 c_2 c_3 - \Omega^2)^3 + \frac{3\beta}{2} (s_1^2 + s_2^2 + s_3^2)(1 - c_1 c_2 c_3 - \Omega^2)^2 + \right. \\
 &\quad + (1 - c_1 c_2 c_3 - \Omega^2) \left[\left(\frac{3\beta}{2}\right)^2 (s_1^2 s_2^2 + s_2^2 s_3^2 + s_3^2 s_1^2) - \right. \\
 &\quad \left. - (c_1^2 s_2^2 s_3^2 + c_2^2 s_3^2 s_1^2 + c_3^2 s_1^2 s_2^2) \right] + s_1^2 s_2^2 s_3^2 \times \\
 &\quad \left. \times \left[\left(\frac{3\beta}{2}\right)^2 - \left(\frac{3\beta}{2}\right) (c_1^2 + c_2^2 + c_3^2) + 2c_1 c_2 c_3 \right] \right\}
 \end{aligned}$$

In the following the summation over \underline{k} has been replaced by an integration according to the equations:

$$\begin{aligned}
 (B.22) \quad \frac{1}{N} \sum_{\underline{k}} &\rightarrow \frac{1}{\pi^3} \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \int_0^\pi d\theta_3 = \left(\frac{1}{\pi}\right)^3 \int d^3\theta \\
 \theta_i &= \frac{1}{2} k_i a, \quad 0 < k_i \leq \frac{2\pi}{a}, \quad 0 < \theta_i \leq \pi
 \end{aligned}$$

The triple integral in eq. (B.22) can be replaced by any one in θ space over a connected domain of volume π^3 for example over the 1st Brillouin zone.

With these notations, it is obtained:

$$\begin{aligned}
 (B.23) \quad G_1 &= \frac{1}{3} \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{N}{D} & G_2 &= \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{H_{11}}{D} (2c_3^2 - 1) \\
 G_3 &= \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{H_{33}}{D} (2c_3^2 - 1) & G_4 &= \frac{1}{3} \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{N}{D} c_1 c_2 c_3 \\
 G_5 &= \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{H_{12}}{D} (-s_1 s_2 c_3)
 \end{aligned}$$

For numerical computations it is useful to consider only dimensionless quantities. We shall denote them by symbols with an asterisk. We have:

$$(B.24) \quad \begin{aligned} H_{ij} &= H_{ij}^* \left(\frac{8\alpha_1}{3}\right)^2 & D &= - \left(\frac{8\alpha_1}{3}\right)^3 D^* \\ N &= \left(\frac{8\alpha_1}{3}\right)^2 N^* & G_i &= - \left(\frac{8\alpha_1}{3}\right)^{-1} G_i^* = - \frac{3}{8\alpha_1} G_i^* \end{aligned}$$

So that

$$G_1^* = \frac{1}{3} \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{N^*}{D^*} \quad \text{and so on } \dots\dots\dots$$

With these notations one obtains the formulae eq. (38) to eq. (42) in the text.

Appendix C

In this Appendix we derive the matrix elements $M_{\alpha\beta}(\ell\kappa)$, and the interaction function MGM^\dagger .

According to Appendix A, eq. (A.6) the M's are matrix elements of L_{12} representing the interaction between the interstitial atom and the lattice. If we denote by μ_α the components of the displacements of impurity, the interaction energy is given by:

$$(C.1) \quad \phi_{int} = \sum_{\alpha\beta\ell\kappa} M_{\alpha\beta}(\ell\kappa) \mu_\alpha \mu_\beta(\ell\kappa)$$

and the α -component of the force acting on the impurity is given by:

$$(C.2) \quad - \frac{\partial \phi_{int}}{\partial \mu_\alpha} = - \sum_{\beta\ell\kappa} M_{\alpha\beta}(\ell\kappa) \mu_\beta(\ell\kappa)$$

We assume the impurity atom to be located at the point $\underline{R} = \frac{a}{2} (0, \frac{1}{2}, 1)$ (tetrahedral site), and to interact with its nearest neighbours only A,B,C,D, with a central force with a force constant γ .

We can decompose the 3×12 matrix L_{12} into 4 3×3 block matrices corresponding to the interaction of the defect with each of its 4 neighbours. We thus obtain the four matrices:

$$(C.3) \quad \begin{aligned} M(A) &= - \frac{\gamma}{5} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 2 \\ 0 & 2 & 4 \end{pmatrix} & M(B) &= - \frac{\gamma}{5} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -2 \\ 0 & -2 & +4 \end{pmatrix} \\ M(C) &= - \frac{\gamma}{5} \begin{pmatrix} 4 & 2 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} & M(D) &= - \frac{\gamma}{5} \begin{pmatrix} 4 & -2 & 0 \\ -2 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

The interaction function is defined by

$$(C.4) \quad F_{\alpha\beta} = (L_{12} G L_{21})_{\alpha\beta} = \sum_{\substack{\alpha_1 \ell \kappa \\ \beta_1 \ell' \kappa'}} M_{\alpha\alpha_1}(\ell\kappa) G_{\alpha_1\beta_1}(\ell\kappa; \ell'\kappa') M_{\beta\beta_1}(\ell'\kappa')$$

Upon introducing the matrix F, the elements of which are the $F_{\alpha\beta}$, we may write with the above mentioned definitions:

$$(C.5) \quad F = \sum_{P,Q} M(P)G(P,Q)M^\dagger(Q); \quad M^\dagger(Q) = M(Q)$$

or even:

$$(C.6) \quad F = \sum_{P,Q} F(P,Q)$$

using the short-hand notation:

$$(C.7) \quad F(P,Q) = M(P)G(P,Q)M(Q)$$

(the notation F used in this Appendix should not be confused with the same notation used for the force in Appendix B).

We can get some help for the explicit evaluation of F from group theory. Nevertheless the group theoretical results that we need are almost trivial compared to the results needed on the method of Wagner, due to the fact that all the F matrices defined in eq. (C.6) and (C.7) are 3x3 matrices.

It is easy to see that the F(P,Q) matrix transform like a second rank tensor, as G and ϕ , according to

$$(C.8) \quad F_{\alpha\beta}(LK;L'K') = \sum_{\alpha'\beta'} S_{\alpha\alpha'} S_{\beta\beta'} F_{\alpha'\beta'}(l\kappa;l'\kappa')$$

for any symmetry operation (S/O) which leaves R invariant and brings the crystal into itself.

Let us call g_R the smallest subgroup of the point group of R (around R) which has the property that upon acting on the point A, it generates the four points (A,B,C,D). In our case the point group of R is D_{2d} . We use here the notations of Hamermesh⁽²²⁾ (denoted by H). The smallest subgroup is S_4 , the 4-fold inversion axis being along the Ry direction. It is easily seen that the two matrices

$$(C.9) \quad \begin{aligned} F_s &= \sum_P F(P,P) \\ F_d &= \sum_{P \neq Q} F(P,Q) \end{aligned}$$

where in the second summation P and Q are always different points, commute with all the matrices of 3x3 representation Γ of g_R based on the vector x,y,z. If we decompose Γ into its irreducible representations, then, in each of them, we obtain a scalar matrix for F_s and F_d (Shur's second lemma). The point is, that the decomposition of Γ are trivial. They all given directly in the character tables as shown in [H. p125-127], for example. It is not necessary to have recours to the orthogonality relations.

For our case the group S_4 is abelian, i.e. it has only representations of dimension one given by the Table (C1) [H. p.126 Table 4-12]. Since F_s and F_d are real they are completely diagonal in the (x,y,z) axes, according to the Table (C1). This result was already obtained by another reasoning mentioned

above, and is central to our method. In these circumstances it is only necessary to evaluate the 2 diagonal elements of F_s and F_d corresponding to $(\alpha, \beta) = (1,1)$ and $(\alpha, \beta) = (2,2)$ since the element $(3,3)$ is identical with the element $(1,1)$ according to the table (C1) (conjugate, real representations).

Using the values given by eq. (C.3) and (B.12) we calculate explicitly the product:

$$(C.10) \quad F(A,A) = M(A)G(A,A) = \frac{\gamma^2}{5} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 2 \\ 0 & 2 & 4 \end{pmatrix} G_1$$

Using the Table (C2) which exhibits how the points and the coordinates transform in any operation of the group we obtain immediately, according to the eq. (C8) the following values:

$$(C.11) \quad \begin{aligned} F(C,C) &= \frac{\gamma^2}{5} \begin{pmatrix} 4 & 2 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} G_1 & F(B,B) &= \frac{\gamma^2}{5} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -2 \\ 0 & -2 & 4 \end{pmatrix} G_1 \\ F(D,D) &= \frac{\gamma^2}{5} \begin{pmatrix} 4 & -2 & 0 \\ -2 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} G_1 & F_s &= \frac{\gamma^2}{5} \begin{pmatrix} 8 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 8 \end{pmatrix} G_1 \end{aligned}$$

The sum F_d can be split into two parts:

$$(C.12) \quad F_d = F_{d1} + F_{d2}$$

with,

$$(C.13) \quad F_{d1} = F(A,B) + F(B,A) + F(C,D) + F(D,C)$$

which commute separately with the operations of S_4 . Therefore each separately is diagonal in the (x,y,z) axes. We need calculate only diagonal elements. We have by direct evaluation:

$$(C.14) \quad \begin{aligned} F_{11}(A,B) &= 0, & F_{22}(A,B) &= \frac{\gamma^2}{25} (G_2 - 4G_3) \\ F_{33} &= -\frac{4\gamma^2}{25} (G_2 - 4G_3) \end{aligned}$$

Upon using Table (C2) we obtain:

$$F_{33}(C,D) = 0, \quad F_{22}(C,D) = \frac{\gamma^2}{25} (G_2 - 4G_3)$$

$$F_{11}(C,D) = -\frac{4\gamma^2}{25} (G_2 - 4G_3)$$

By using the symmetry plans σ_h and σ_v defined in Appendix B (they do not belong to S_4 and when adjoined to give the full point group D_{2d}) one finds $F(P,Q) = F(Q,P)$ thus giving

$$(C.15) \quad F_{d1} = \frac{2\gamma^2}{25} \begin{pmatrix} -4(G_2 - 4G_3) & 0 & 0 \\ 0 & 2(G_2 - 4G_3) & 0 \\ 0 & 0 & -4(G_2 - 4G_3) \end{pmatrix}$$

A similar method gives

$$(C.16) \quad F_{11}(A,C) = F_{33}(A,C) = 0 \quad F_{22}(A,C) = \frac{\gamma^2}{25} (G_4 + 8G_5)$$

by direct calculation, and upon using table (C2) and the elements σ_h (or σ_v) we obtain 8 times the same contribution from other terms in F_{22} thus:

$$(C.17) \quad \begin{aligned} (F_{d2})_{11} &= (F_{d2})_{33} = 0 \\ (F_{d2})_{22} &= \frac{8\gamma^2}{25} (G_4 + 8G_5) \end{aligned}$$

The final result for the interaction function is, therefore

$$(C.18) \quad \begin{aligned} F_{12} &= F_{21} = F_{23} = F_{32} = F_{31} = F_{13} = 0 \\ F_{11} &= \frac{8\gamma^2}{5} G_1 - \frac{8\gamma^2}{25} (G_2 - 4G_3) \\ F_{22} &= \frac{4\gamma^2}{5} G_1 + \frac{4\gamma^2}{25} (G_2 - 4G_3) + \frac{8\gamma^2}{25} (G_4 + 8G_5) \\ F_{33} &= F_{11} \end{aligned}$$

In terms of dimensionless quantities needed for numerical computation, it can be written as

$$(C.19) \quad \begin{aligned} F_{11} = F_{33} &= -\frac{3\gamma^2}{50\alpha_1} \left[10G_1^* - 2(G_2^* - 4G_3^*) \right] \\ F_{22} &= -\frac{3\gamma^2}{50\alpha_1} \left[5G_1^* + (G_2^* - 4G_3^*) + 2(G_4^* + 8G_5^*) \right] \end{aligned}$$

These are the expressions used in the text

Table (C1)

Character table of the group S_4

S_4	E	S_4	S_4^2	S_4^3
A	1	1	1	1
B;y	1	-1	1	-1
E;x+iz	1	i	-1	-i
	1	-i	-1	i

Table C2)

Transformation of the points A B C D, and th coordinates x,y,z, for the group S_4

Elements	E	S_4	S_4^2	S_4^3
A'	A	C	B	D
B'	B	D	A	C
C'	C	B	D	A
D'	D	A	C	B
x'	x	z	-x	-x
y'	y	-y	y	-y
z'	z	-x	-z	x

The primed symbols represent the transformed values

Appendix D

In this Appendix we show how to treat the classical problem of a substitutional impurity in a bcc lattice by the method devised in Appendix A. It is reminded that the usual treatment of this problem involves finding the eigenvalues of a 27x27 matrix if the impurity "interacts" only with its first neighbours. In our method we have to handle a 3x3 diagonal matrix whatever the number of neighbours interacting with the defect.

We suppose that the impurity is located at the origin O, center of the cube ABCDEFGH. The coordinates of the eight points from A to H are given in the table D1. In the present Appendix we use for the points, notations differing from the notations used in preceding Appendices. We assume that the atom at O interacts with its eight neighbours through a central force, with a constant γ . Let P, with coordinates $\frac{a}{2} (\epsilon_1, \epsilon_2, \epsilon_3)$, $\epsilon_i = \pm 1$ one of the eight points A to H. The interaction matrix M(P) has the following elements:

$$(D.1) \quad M(P) = -\frac{\gamma}{3} \begin{pmatrix} 1 & \epsilon_1 \epsilon_2 & \epsilon_1 \epsilon_3 \\ \epsilon_2 \epsilon_1 & 1 & \epsilon_2 \epsilon_3 \\ \epsilon_3 \epsilon_1 & \epsilon_3 \epsilon_2 & 1 \end{pmatrix}$$

We consider now the following partition of an arbitrary matrix T with components $T_{\alpha\beta}(\ell\kappa; \ell'\kappa')$:

$$(D.2) \quad \begin{aligned} T_{11}(\alpha; \beta) &= T_{\alpha\beta}(0,0) & T_{12}(\alpha; \beta \ell\kappa) &= T_{\alpha\beta}(0; \ell\kappa) \\ T_{21} &= T_{12}^{\dagger} & T_{22}(\alpha\ell\kappa; \beta\ell'\kappa') &= T_{\alpha\beta}(\ell\kappa; \ell'\kappa') \end{aligned}$$

where the points $P = \{\ell\kappa\}$ and $Q = \{\ell'\kappa'\}$ are different from O:

$$(D.3) \quad T = \begin{pmatrix} T_{11} & T_{12} \\ \text{---} & \text{---} \\ T_{21} & T_{22} \end{pmatrix}$$

With these notations we first establish a relation between the Green's function \hat{G} of the crystal with a vacancy at the point O and the Green's function G of the unperturbed crystal. The L matrices for these crystals can be written as:

$$(D.4) \quad L = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix}; \quad \hat{L} = \begin{pmatrix} 0 & 0 \\ 0 & L_{22} \end{pmatrix}$$

where the 0's are the appropriate null-matrices. From $LG=I$ and $\hat{L}\hat{G}=\hat{I}$ we obtain the equations:

$$(D.5) \quad \begin{aligned} L_{21}G_{11} + L_{22}G_{21} &= 0 \\ L_{21}G_{12} + L_{22}G_{22} &= I \\ L_{22}\hat{G} &= \hat{I} \end{aligned}$$

In the last equation we have taken into account that G , involving only $N-1$ points of the crystal, is a $3(N-1) \times 3(N-1)$ matrix, while \hat{I} is the $3(N-1) \times 3(N-1)$ unit matrix. We can solve the first two eq. (D.5) for L_{22} and L_{21} and obtain finally:

$$(D.6) \quad \hat{G} = L_{22}^{-1} = G_{22} - G_{21}G_{11}^{-1}G_{12}$$

We can write eq. (D.6) in equivalent ways:

$$(D.7) \quad \begin{aligned} \hat{G}_{\alpha\beta}(\ell\kappa; \ell'\kappa') &= G_{\alpha\beta}(\ell\kappa; \ell'\kappa') - \sum_{\alpha'\beta'} G_{\alpha\alpha'}(\ell\kappa; 0)G_{11}^{-1}(\alpha'0; \beta'0) \times \\ &\quad \times G_{\beta'\beta}(0, \ell'\kappa') \\ \hat{G}(P, Q) &= G(P, Q) - G(P, 0)G_{11}^{-1}G(0, Q) \end{aligned}$$

Eqs (D.6) and (D.7) could be used to evaluate the frequencies of a crystal with a vacancy, but we shall not pause here to do this.

We consider the case when the vacancy is occupied by a different atom of mass m interacting with the rest of the crystal with the matrix eq. (D.1). The problem is then identical with the problem of interstitial impurity except that everywhere G should be replaced by \hat{G} . We note that the symmetry properties of \hat{G} being the same as those of G regarding the transformations $(S/0)$ which leave 0 invariant we can apply the same methods as above.

We note also that the 3×3 matrix G_{11} is diagonal for cubic symmetry and is given by

$$(D.8) \quad G_{11} = G(0,0) = G(A,A) = \begin{pmatrix} G_1 & 0 & 0 \\ 0 & G_1 & 0 \\ 0 & 0 & G_1 \end{pmatrix}$$

where G_1 is the function defined in eqs (B.11) and (B.23). Therefore eq. (D.7) is simply:

$$(D.9) \quad \hat{G}(P,Q) = G(P,Q) - \frac{1}{G_1} G(0,P)G(0,Q).$$

The interaction function \hat{F} is defined by (cf. eq.C5):

$$(D.10) \quad \hat{F} = \sum_{P,Q} M(P)\hat{G}(P,Q)M(Q) = F-J$$

where

$$(D.11) \quad F = \sum_{P,Q} M(P)G(P,Q)M(Q)$$

and

$$(D.12) \quad J = \frac{1}{G_1} \sum_{P,Q} M(P)G(0,P)G(0,Q)M(Q) = K^2/G_1$$

with

$$(D.13) \quad K = \sum_P M(P)G(0,P) \quad (\text{diagonal}) \\ = \sum_P G(0,P)M(P)$$

To evaluate the interaction function F (defined in eq. D.11) we use the same method as in Appendix C. We write F as a sum of expressions invariant with respect to small subgroups of the point group of O . For each invariant expression we calculate the first term, then, by symmetry operations we obtain all the other terms. The sum is then diagonal by the arguments already presented. We write:

$$(D.14) \quad F = F_I + F_{II} + F_{III} + F_{IV} \\ F_I = \sum_P M(P)G(P,P)M(P) \\ F_{II} = \sum_{PQ=(100)} M(P)G(P,Q)M(Q) \\ F_{III} = \sum_{PQ=(110)} M(P)G(P,Q)M(Q)$$

$$(D.14) \quad F_{IV} = \sum_{PQ=(111)} M(P)G(P,Q)M(Q)$$

where $\sum_{PQ=(hk\ell)}$ means a summation over all the points P and Q such that the vector \underline{PQ} is crystallographically equivalent to the lattice vector $(hk\ell)$, P and Q being chosen amongst the eight points A to H.

We obtain the following values:

$$(D.15) \quad F(A,A) = \frac{Y^2}{3} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} G_1$$

and using the subgroup D_{2h} :

$$(D.16) \quad F_I = \frac{8Y^2}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} G_1$$

Next is:

$$(D.17) \quad F(A,B) = \frac{Y^2}{9} \begin{pmatrix} 1 & -1 & -1 \\ 1 & -1 & -1 \\ 1 & -1 & -1 \end{pmatrix} (G_3 - 2G_2)$$

and using the subgroup T_h :

$$(D.18) \quad F_{II} = -\frac{8Y^2}{9} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} (G_3 - 2G_2)$$

To calculate F_{III} and F_{IV} we need introduce new Green's functions. They are:

$$(D.19) \quad G(A,C) = \begin{pmatrix} G_6 & G_7 & 0 \\ G_7 & G_6 & 0 \\ 0 & 0 & G_8 \end{pmatrix}, \quad G(A,G) = \begin{pmatrix} G_9 & G_{10} & G_{10} \\ G_{10} & G_9 & G_{10} \\ G_{10} & G_{10} & G_9 \end{pmatrix}.$$

where G_i , $i = 6,7,8,9,10$ are defined by:

$$(D.20) \quad \begin{aligned} G_6 &= G_{xx}(A,C) & G_7 &= G_{xy}(A,C) & G_8 &= G_{zz}(A,C) \\ G_9 &= G_{xx}(A,G) & G_{10} &= G_{xy}(A,G) \end{aligned}$$

and are calculated according to the formulae:

$$\begin{aligned}
 G_6 &= \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{H_{11}}{D} (2C_1^2-1)(2C_2^2-1) \\
 G_7 &= \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{H_{12}}{D} (-4C_1C_2S_1S_2) \\
 (D.21) \quad G_8 &= \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{H_{33}}{D} (2C_1^2-1)(2C_2^2-1) \\
 G_9 &= \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{H_{11}}{D} (2C_1^2-1)(2C_2^2-1)(2C_3^2-1) \\
 G_{10} &= \left(\frac{1}{\pi}\right)^3 \int d^3\theta \frac{H_{12}}{D} \left[-4C_1C_2S_1S_2(2C_3^2-1)\right]
 \end{aligned}$$

We have:

$$(D.22) \quad F(A,C) = \frac{Y^2}{9} \begin{pmatrix} 1 & 1 & -1 \\ 1 & 1 & -1 \\ 1 & 1 & -1 \end{pmatrix} (2G_6+2G_7-G_8)$$

and using the subgroup O_h :

$$(D.23) \quad F_{III} = \frac{8Y^2}{9} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} (2G_6+2G_7-G_8)$$

And finally:

$$(D.24) \quad F(A,G) = \frac{Y^2}{3} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} (G_9+2G_{10})$$

and using the subgroup D_{2h} :

$$(D.25) \quad F_{IV} = \frac{8Y^2}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} (G_9+2G_{10})$$

The interaction matrix F is thus diagonal and spherical, having three equal diagonal elements, as required by cubic symmetry. The non zero elements are:

$$(D.26) \quad F_{xx} = F_{yy} = F_{zz} = \frac{8Y^2}{9} \left[36G_1 - G_3 + 2G_2 + 2G_6 + 2G_7 - G_8 + 3G_9 + 6G_{10} \right]$$

We turn to the evaluation of K and J . For this we write the expression of the matrix $G(O,P)$:

$$(D.27) \quad G(O,P) = \begin{pmatrix} G_4 & \epsilon_1 \epsilon_2 G_5 & \epsilon_1 \epsilon_3 G_5 \\ \epsilon_2 \epsilon_1 G_5 & G_4 & \epsilon_2 \epsilon_3 G_5 \\ \epsilon_3 \epsilon_1 G_5 & \epsilon_3 \epsilon_2 G_5 & G_4 \end{pmatrix}$$

By direct multiplication we obtain

$$(D.28) \quad M(P)G(O,P) = -\frac{\gamma}{3} \begin{pmatrix} 1 & \epsilon_1 \epsilon_2 & \epsilon_1 \epsilon_3 \\ \epsilon_2 \epsilon_1 & 1 & \epsilon_2 \epsilon_3 \\ \epsilon_3 \epsilon_1 & \epsilon_3 \epsilon_2 & 1 \end{pmatrix} (G_4 + 2G_5)$$

and

$$(D.29) \quad K = -\frac{8\gamma}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} (G_4 + 2G_5)$$

$$J = \frac{64\gamma^2}{9} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} (G_4 + 2G_5)^2 / G_1$$

The α -component of the force acting on the impurity when displaced by the vector $\underline{\mu}$ from its equilibrium position, all the other atoms in the lattice being held at their equilibrium position has the value:

$$(D.30) \quad -\frac{\partial \phi}{\partial \mu_\alpha} = -\frac{8\gamma}{3} \mu_\alpha ; \quad \alpha = 1, 2, 3$$

The frequencies ω_s of oscillations of the impurity atom in the rigid lattice are triply degenerated and given by $m\omega_s^2 = 8\gamma/3$. The molecular Green's function matrix and inverse are:

$$(D.31) \quad \gamma_{\alpha\beta} = \delta_{\alpha\beta} (m\omega^2 - 8\gamma/3)^{-1}$$

$$(\gamma^{-1})_{\alpha\beta} = \delta_{\alpha\beta} (m\omega^2 - 8\gamma/3)$$

where m is the mass of the impurity atom.

The eq. (A.8) for the frequencies of the localized modes (and also resonances, by taking appropriate real part) are thus three times the same equation:

$$(D.32) \quad m\omega^2 = \frac{8\gamma}{3} + \frac{8\gamma^2}{9} (3G_1 - G_3 + 2G_2 + 2G_6 + 2G_7 - G_8 + 3G_9 + 6G_{10})$$

$$- \frac{64\gamma^2}{9} (G_4 + 2G_5)^2 / G_1$$

(triply degenerate root)

Eq. (D.32) has been obtained rather easily. It is not too difficult to generalize it to the case when one takes into account the relaxation of the eight atoms A to H which does not change the symmetry of the site 0, or when one takes into

account the interaction of O with its next nearest neighbours.

Table D.1

Coordinates of the cube vertices in unit $\frac{a}{2}$

	A	B	C	D	E	F	G	H
x	1	-1	-1	1	1	-1	-1	1
y	1	1	-1	-1	1	1	-1	-1
z	1	1	1	1	-1	-1	-1	-1

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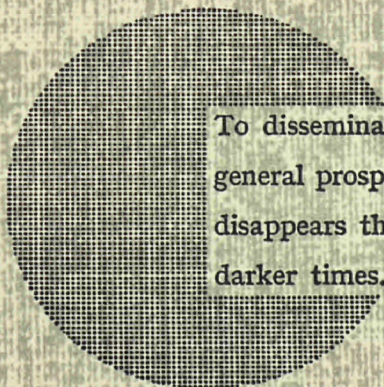
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Alfred Nobel

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