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Theory of Localized Vibrations of Interstitial Atoms in bcc Lattices

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A new method is used for the determination of the frequencies of the localized modes in the harmonic approximation which avoids the solution of a secular determinant. Explicit formulas are given for the case of an interstitial atom in a bcc lattice.

INTRODUCTION

The problem of the vibrations of an impurity atom harmonically coupled to a crystal lattice has been solved in principle by the method of Green's functions 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 recent review 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 an impurity, located in a tetrahedral interstitial site of the bcc lattice. We assume for the host lattice a model with central harmonic forces between first and second neighbors. Such a model reproduces fairly well the frequency spectrum obtained experimentally by inelastic neutron scattering (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 linewidth of the localized levels (Klemens,[9] Visscher,[10] and 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.[6]

In Sec. I we have developed the general formalism for the case of an harmonic oscillator coupled to a system of harmonic oscillators. These results can be used for a calculation of the position correlation function $\langle X_\alpha(t)X_\beta(0)\rangle$ of the impurity atom, which allows a direct comparison with incoherent neutron scattering data, using well-known techniques.[14–17] We arrive at a rather simple equation for the frequencies of the local oscillations of the interstitial.

In Sec. II we obtain explicit expressions for the case of interstitial atoms in bcc lattices and compare the theoretical values of the localized mode frequencies with the experimental data on vanadium hydride.

In Appendix A we rederive some results of Sec. I by a special matrix partition technique. In Appendix B we show that our partition method can be conveniently used also in the case of substitution impurities.

I. THEORY OF VIBRATION OF INTERSTITIAL ATOMS IN A REGULAR LATTICE

A. Hamiltonian of the System

The Hamiltonian of the system can be written as the sum of three terms

$$H=H_0+H_I+H_{\text{int}}\,, \tag{1}$$

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,[3] H_0 has the form

$$H_0=\sum_{\alpha l\kappa}\frac{p_\alpha^2(l\kappa)}{2M}+\tfrac{1}{2}\sum_{\alpha l\kappa;\,\alpha' l'\kappa'}\Phi_{\alpha\alpha'}(l\kappa;l'\kappa')u_\alpha(l\kappa)u_{\alpha'}(l'\kappa')\,, \tag{2}$$

where M is the mass of the lattice atoms.

We write the Hamiltonian H_I in terms of the normal modes of oscillation ($s=1,2,3$) of the interstitial in the

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frozen lattice. Then it takes a particularly simple form

$$H_I=\sum_{s=1}^{3}\left[\frac{p_s^2}{2m}+\tfrac{1}{2}(\omega_s^2q_s^2)\right]. \tag{3}$$

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

$$H_{\text{int}}=\sum_{s,\alpha,\alpha',l\kappa} q_s e_{s\alpha'} M_{\alpha'\alpha}(\mathbf{g}_I,l\kappa)u_\alpha(l\kappa). \tag{4}$$

$\mathbf{e}_s$ is the vector of polarization of the normal modes. The interaction matrix $M_{\alpha'\alpha}(\mathbf{g}_I,l\kappa)$ is defined in such a way that $-M_{\alpha'\alpha}(\mathbf{g}_I,l\kappa)u_\alpha(l\kappa)$ gives the α' component of the force at the interstitial (position $\mathbf{g}_I$) if the atom l is displaced by u_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 lattice is a constant, and we can drop it as an argument of the matrix. Carrying out the summation over α' we write the interaction term in the form

$$H_{\text{int}}=\sum_{s,\alpha,l,\kappa} q_s M_{s\alpha}(l\kappa)u_\alpha(l\kappa), \tag{4$'$}$$

with

$$M_{s\alpha}(l\kappa)=\sum_{\alpha'} e_{s\alpha'}M_{\alpha'\alpha}(\mathbf{g}_I,l\kappa). \tag{5}$$

B. 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 Green's functions.

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

$$G(q_\alpha,q_{\alpha'};\omega)=\sum_{s,s'} e_{s\alpha}e_{s'\alpha'}G(q_s,q_{s'};\omega). \tag{6}$$

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

$$G^{(r)}(q_s,q_{s'};t)=-(i/\hbar)\theta(t)\langle[\Phi_H(t)\tilde{q}_s(t),\tilde{q}_{s'}(0)]\rangle_1, \tag{7}$$

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

$$\tilde{q}_s(t)=\exp(iH_It/\hbar)q_s\exp(-iH_It/\hbar). \tag{8}$$

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

$$\Phi_H(t)=\exp_{(-T)}\int_0^t dt'\int_0^{t'} dt''\langle\Omega_H(t'')\Omega_H(t')\rangle_2. \tag{9}$$

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

$$\Omega_H(t)\cdots=(i/\hbar)[H_{\text{int}}(t),\cdots] \tag{10}$$

with

$$H_{\text{int}}(t)=\sum_{s,\alpha,l\kappa} q_s(t)M_{s\alpha}(l\kappa)\tilde{u}_\alpha(l\kappa,t), \tag{11}$$

where

$$\tilde{u}_\alpha(l\kappa,t)=\exp(iH_0t/\hbar)u_\alpha(l\kappa)\exp(-iH_0t/\hbar). \tag{12}$$

In writing Eq. (9) we made use of the fact that $\langle\Omega_H(t)\rangle_2$ vanishes since $\langle u_\alpha(l\kappa,t)\rangle_2$ vanishes for all $\alpha l\kappa$ and t. The expression (9) 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. (9).

Since we want to apply Φ_H 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 $[q_{s'}(t'),q_s(t)]$ is a c number) we obtain

$$\begin{aligned}\langle\Omega_H(t'')\Omega_H(t')\rangle_2\tilde{q}_s(t)=(i/\hbar)&\sum_{s',\alpha,l\kappa;s'',\alpha',l'\kappa'} M_{s'\alpha}(l\kappa)\\ &\times M_{s''\alpha'}(l'\kappa')G_0^{(r)}(u_\alpha(l\kappa),\,u_{\alpha'}(l'\kappa');t'-t'')\\ &\times[\tilde{q}_s(t),\tilde{q}_{s'}(t')]\tilde{q}_{s''}(t''),\end{aligned} \tag{13}$$

where

$$\begin{aligned}G_0^{(r)}&(u_\alpha(l\kappa),u_{\alpha'}(l'\kappa');t)\\ &=-(i/\hbar)\theta(t)\langle[\tilde{u}_\alpha(l\kappa,t),\tilde{u}_{\alpha'}(l'\kappa',0)]\rangle\end{aligned} \tag{14}$$

is the retarded Green's function of the perfect lattice of $u_\alpha(l\kappa)$ with respect to $u_{\alpha'}(l'\kappa')$. Henceforth we shall write it simply

$$2\pi G_{\alpha\alpha'}(l\kappa,l'\kappa',t)=G_0^{(r)}(u_\alpha(l\kappa),u_{\alpha'}(l'\kappa');t). \tag{15}$$

The factor 2π has been introduced in such a way that the Fourier transform of $G_{\alpha\alpha'}(l\kappa,l'\kappa',t)$ 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 $[\tilde{q}_s(t),\tilde{q}_{s'}(t')]$ vanishes for $s\neq s'$ and that $-(i/\hbar)\theta(t)\times[\tilde{q}_s(t),\tilde{q}_s(0)]$ is simply the retarded Green's function

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$G_0^{(r)}(q_s,q_s;t)$ of the normal coordinate q_s for the isolated system Y_1 (since $[\tilde{q}_s(t),\tilde{q}_s(0)]$ is a c 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)

$$G^{(r)}(q_s,q_{s'};t)=\delta_{ss'}G_0^{(r)}(q_s,q_{s'};t)+\sum_{s''}\int_0^t dt'K_{ss''}(t-t')G^{(r)}(q_{s''},q_{s'};t') \quad (16)$$

with the kernel

$$K_{ss'}(t-t')=\sum_{\alpha,l\kappa,\alpha',l'\kappa'}2\pi\int_{-\infty}^{\infty}dt''G_0^{(r)}(q_s,q_s;t-t'')M_{s\alpha}(l\kappa)\times M_{s'\alpha'}(l'\kappa')G_{\alpha\alpha'}(l\kappa,l'\kappa';t''-t'). \quad (17)$$

From Eq. (16) we obtain the corresponding equations for the Fourier transform:

$$G(q_s,q_{s'};\omega)=\delta_{ss'}G_0(q_s,q_s;\omega)+\sum_{s''}K_{ss''}(\omega)G(q_{s''},q_{s'};\omega) \quad (18)$$

with

$$K_{ss''}(\omega)=2\pi\sum_{\alpha,l\kappa,\alpha',l'\kappa'}M_{s\alpha}(l\kappa)M_{s''\alpha'}(l'\kappa')G_{\alpha\alpha'}(l\kappa,l'\kappa';\omega)\times G_0(q_s,q_s;\omega). \quad (19)$$

These equations yield

$$G(q_s,q_{s'};\omega)=R_{ss'}(\omega), \quad (20)$$

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

$$U_{ss'}(\omega)=\delta_{ss'}G_0(q_s,q_s;\omega)^{-1}-2\pi\sum_{\alpha,l\kappa;\alpha',l'\kappa'}M_{s\alpha}(l\kappa)M_{s'\alpha'}(l'\kappa')G_{\alpha\alpha'}(l\kappa,l'\kappa';\omega). \quad (21)$$

The pair of equations (20) and (21) is also derived by another method in Appendix A. $G_0(q_s,q_s;\omega)$ has the simple form

$$G_0(q_s,q_s;\omega)=(1/2\pi m)/(\omega^2-\omega_s^2) \quad (22)$$

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")

$$F_{ss'}(\omega)=\sum_{\alpha l\kappa;\alpha'l'\kappa'}M_{s\alpha}(l\kappa)M_{s'\alpha'}(l'\kappa')G_{\alpha\alpha'}(l\kappa,l'\kappa';\omega) \quad (23)$$

can be calculated in a straightforward manner and we obtain, for the spectral density function $A_{ss'}(\omega)$ defined by

$$A_{ss'}(\omega)=i[G(q_s,q_{s'};\omega+i\epsilon)-G(q_s,q_{s'};\omega-i\epsilon)], \quad (24)$$

the expression

$$A_{ss'}(\omega)=-\sum_{s''}(1/\pi)\,\mathrm{Im}F_{ss''}(\omega)Q_{s''s'}^{-1}(\omega)+\sum_i(1/2\pi\omega_i)\delta(\omega-\omega_i), \quad (25)$$

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

$$Q_{ss'}(\omega)=\sum_{s''}\{[m(\omega^2-\omega_s^2)\delta_{ss''}-\mathrm{Re}F_{ss''}(\omega)]\times[m(\omega^2-\omega_s^2)\delta_{s''s'}-\mathrm{Re}F_{s''s'}(\omega)]+\mathrm{Im}F_{ss''}(\omega)\mathrm{Im}F_{s''s'}(\omega)\}. \quad (26)$$

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

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

$$A_{\alpha\alpha'}(l\kappa,l'\kappa';\omega)=i[G_{\alpha\alpha'}(l\kappa,l'\kappa';\omega+i\epsilon)-G_{\alpha\alpha'}(l\kappa,l'\kappa';\omega-i\epsilon)], \quad (27)$$

it vanishes outside the frequency region of oscillations of the perfect lattice (the region of band modes). Outside that region $A_{ss'}(\omega)$ will only be different from zero at the points ω_i for which the determinant of $Q_{ss'}(\omega)$ vanishes. This implies the vanishing of the determinant

$$\Delta(\omega)=|m\delta_{ss'}(\omega^2-\omega_s^2)-\mathrm{Re}F_{ss'}(\omega)| \quad (28)$$

as 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 $\mathrm{Re}F_{ss'}(\omega)$ by the interaction with the lattice.

As an example of this method we shall calculate in the following the localized modes of a light impurity in a bcc lattice.

An explicit knowledge of the spectral density function is sufficient for the determination of the position autocorrelation function by means of the "fluctuation-dissipation theorem"[17]:

$$\langle q_s(t)q_{s'}(0)\rangle=\hbar\int_{-\infty}^{\infty}d\omega A_{ss'}(\omega)\times\exp(-i\omega t)/[\exp(\beta\hbar\omega)-1]. \quad (29)$$

Here, $\beta=1/k_BT$. Since the results of neutron-scattering experiments are essentially related to this function, the results of our analysis can be used directly to predict scattering cross sections. However, for the interpretation of the shape of the measured cross sections the influence of nonharmonic terms appears to be not negligible since the lines observed in such experiments are rather broad.[8] We hope, however, that the position of the center of the line will still be close to the value given by the harmonic approximation. We therefore limit our discussion to the calculation of the roots of the determinant (28).

II. DETERMINATION OF THE LOCALIZED MODES OF AN INTERSTITIAL IMPURITY IN A bcc LATTICE

A. The Function $G_{\alpha\alpha'}(l\kappa,l'\kappa';\omega)$ for a bcc Lattice

We shall use the following notations and conventions: The origin of our Cartesian system of coordinates we put

TABLE I. The function $G_{\alpha\alpha'}(0\kappa,0\kappa';\omega)$.

$l\kappa \backslash l'\kappa'$	(111)	($\bar{1}$11)	(000)	(002)
(111)	$\mathcal{G}_1(\omega)$	$\mathcal{G}_2(\omega)$	$\mathcal{G}_3(\omega)$	$\mathcal{G}_4(\omega)$
($\bar{1}$11)	$\mathcal{G}_2(\omega)$	$\mathcal{G}_1(\omega)$	$\mathcal{G}_5(\omega)$	$\mathcal{G}_6(\omega)$
(000)	$\mathcal{G}_3(\omega)$	$\mathcal{G}_5(\omega)$	$\mathcal{G}_1(\omega)$	$\mathcal{G}_2'(\omega)$
(002)	$\mathcal{G}_4(\omega)$	$\mathcal{G}_6(\omega)$	$\mathcal{G}_2'(\omega)$	$\mathcal{G}_1(\omega)$

in the center of the elementary cube. The atom in this site will be labelled (000). The directions of the coordinate axes are along the edges of the cube. We shall measure all coordinates in units of $\frac{1}{2}a$, where a is the lattice constant. The interstitial—as in the case for hydrogen in vanadium[8]—is supposed to occupy one of the so-called tetrahedral positions, say $\mathbf{g}_I=(0,\frac{1}{2},1)$. We consider a coupling between the interstitial and its nearest neighbors of the lattice only. These are the atoms (000), (002), (111), and ($\bar{1}$11). We therefore have to know the function $G_{\alpha\alpha'}(l\kappa,l'\kappa';\omega)$ for values $l\kappa$, $l'\kappa'$ corresponding to these atoms.

The calculation is straightforward and is simplified considerably if one takes into account the symmetry of the crystal. The resulting function is given in Table I.

The $\mathcal{G}_i(\omega)$ in Table I are matrices in (α,α'). One finds

$$[\mathcal{G}_1(\omega)]_{\alpha\alpha'}=G_1(\omega)\delta_{\alpha\alpha'},\quad \mathcal{G}_2(\omega)=\begin{bmatrix}G_2 & 0 & 0\\ 0 & G_3 & 0\\ 0 & 0 & G_3\end{bmatrix},$$
$$\mathcal{G}_2'(\omega)=\begin{bmatrix}G_3 & 0 & 0\\ 0 & G_2 & 0\\ 0 & 0 & G_2\end{bmatrix}. \tag{30}$$

The other matrices involve also nondiagonal elements. They are

$$\mathcal{G}_3(\omega)=\begin{bmatrix}G_4 & G_5 & G_5\\ G_5 & G_4 & G_5\\ G_5 & G_5 & G_4\end{bmatrix},$$
$$\mathcal{G}_4(\omega)=\begin{bmatrix}G_4 & G_5 & -G_5\\ G_5 & G_4 & -G_5\\ -G_5 & -G_5 & G_4\end{bmatrix},$$
$$\mathcal{G}_5(\omega)=\begin{bmatrix}G_4 & -G_5 & -G_5\\ -G_5 & G_4 & G_5\\ -G_5 & G_5 & G_4\end{bmatrix}, \tag{31}$$
$$\mathcal{G}_6(\omega)=\begin{bmatrix}G_4 & -G_5 & G_5\\ -G_5 & G_4 & -G_5\\ G_5 & -G_5 & G_4\end{bmatrix},$$

The functions $G_i(\omega)$, $i=1, 2, 3, 4, 5$ are given by (using Fine's model[7] of harmonic interaction between nearest and next-nearest neighbors)

$$G_i(\omega)=(K/\pi^3)\int_0^{\pi}d\theta_1\int_0^{\pi}d\theta_2\int_0^{\pi}d\theta_3 T_i, \tag{32}$$

where

$$\begin{aligned}T_1&=(H_{11}+H_{22}+H_{33})/3D,\\ T_2&=H_{11}(2C_3^2-1)/D,\\ T_3&=H_{33}(2C_3^2-1)/D,\\ T_4&=T_1C_1C_2C_3,\\ T_5&=-S_1S_2C_3H_{12}/D\end{aligned} \tag{32'}$$

with

$$C_i=\cos\theta_i,\quad S_i=\sin\theta_i,\quad K=-3/8\alpha_1$$

and

$$\begin{aligned}H_{ii}&=(1-C_1C_2C_3-\Omega^2)^2+(\tfrac{3}{2}\beta)\Big(\sum_{k=1}^{3}S_k^2-S_i^2\Big)(1-C_1C_2C_3-\Omega^2)+[(\tfrac{3}{2}\beta)^2-C_i^2]S_1^2S_2^2S_3^2/S_i^2,\quad i=1,2,3\\ H_{12}&=S_1S_2S_3^2[C_1C_2-(\tfrac{3}{2}\beta)C_3]-C_3S_1S_2(1-C_1C_2C_3-\Omega^2),\\ D&=(1-C_1C_2C_3-\Omega^2)^3+(1-C_1C_2C_3-\Omega^2)^2(\tfrac{3}{2}\beta)\sum_{k=1}^{3}S_k^2+(1-C_1C_2C_3-\Omega^2)[(\tfrac{3}{2}\beta)^2(S_1^2S_2^2+S_2^2S_3^2+S_3^2S_1^2)\\ &\quad-(C_1^2S_2^2S_3^2+S_1^2C_2^2S_3^2+S_1^2S_2^2C_3^2)]+S_1^2S_2^2S_3^2[2C_1C_2C_3-(\tfrac{3}{2}\beta)(C_1^2+C_2^2+C_3^2)+(\tfrac{3}{2}\beta)^2].\end{aligned} \tag{33}$$

These expressions involve the dimensionless constants

$$\Omega^2=3M\omega^2/8\alpha_1,\quad \beta=\alpha_2/\alpha_1, \tag{34}$$

where α_1 is the force constant for the interaction between nearest neighbors in the lattice, and α_2 is the corresponding constant for the next-nearest neighbor interaction.

B. Coupling Matrix $M_{s\alpha}(l\kappa)$

For the calculation of the coupling matrix $M_{\alpha\alpha'}(l\kappa)$ we remember that it is the negative of the coefficient of $u_\alpha(l\kappa)$ in the expression for the component α' of the force acting on the interstitial atom. The equations for these forces are

$$\begin{aligned}f_1&=-\tfrac{2}{5}\gamma[4q_1-2u_1(111)-2u_1(\bar{1}11)u_2-(111)+u_2(\bar{1}11)],\\ f_2&=-\tfrac{1}{5}\gamma[4q_2-2u_1(111)+2u_1(\bar{1}11)-u_2(111)-u_2(\bar{1}11)\\ &\quad-u_2(000)-u_2(002)-2u_3(000)+2u_3(002)],\\ f_3&=-\tfrac{2}{5}\gamma[4q_3-u_2(000)+u_2(002)-2u_3(000)-2u_3(002)].\end{aligned} \tag{35}$$

Here, γ denotes the force constant for the interaction between the lattice atoms and the interstitial.

From these equations we can draw the following conclusions: (i) The free oscillations of the interstitial in a "frozen" bcc lattice [i.e., for $u_\alpha(l\kappa)=0$ identically] have the following frequencies and polarizations:

$$\omega_1{}^2=8\gamma/5m\,,\quad \mathbf{e}_1=(1,0,0)\,,$$
$$\omega_2{}^2=4\gamma/5m\,,\quad \mathbf{e}_2=(0,1,0)\,,\qquad (36)$$
$$\omega_3{}^2=8\gamma/5m\,,\quad \mathbf{e}_3=(0,0,1)\,.$$

(ii) The coupling matrices $M_{s\alpha}(l\kappa)$ are the same as $M_{\alpha\alpha'}(l\kappa)$ because, as noted in (i), the polarization directions of the interstitial modes are along the coordinate axes. The matrices $M_{s\alpha}(l\kappa)=M_{\alpha\alpha'}(l\kappa)$ can be read off Eq. (35) as follows:

$$M_{s\alpha}(111)=-\tfrac{1}{5}\gamma\begin{bmatrix}4&2&0\\2&1&0\\0&0&0\end{bmatrix},$$
$$M_{s\alpha}(\bar{1}11)=-\tfrac{1}{5}\gamma\begin{bmatrix}4&-2&0\\-2&1&0\\0&0&0\end{bmatrix},$$
$$M_{s\alpha}(000)=-\tfrac{1}{5}\gamma\begin{bmatrix}0&0&0\\0&1&2\\0&2&4\end{bmatrix},\qquad (37)$$
$$M_{s\alpha}(002)=-\tfrac{1}{5}\gamma\begin{bmatrix}0&0&0\\0&1&-2\\0&-2&4\end{bmatrix}.$$

C. Interaction Function $F_{ss'}(\omega)$ for the Interstitial Atom in the bcc Lattice

Now we can use Eq. (23) to determine $F_{ss'}(\omega)$. Again, the calculations simplify considerably because of the symmetries involved. $F_{ss'}(\omega)$ turns out to be diagonal. Explicitly,

$$F_{ss'}(\omega)=(8\gamma^2/50)\begin{bmatrix}2g_1&0&0\\0&g_2&0\\0&0&2g_1\end{bmatrix}\qquad (38)$$

with

$$g_1=5G_1-G_2+4G_3\,,$$
$$g_2=5G_1+3G_2-4G_3+2G_4+16G_5\,.$$

Since in our case $F_{ss'}(\omega)$ is a diagonal matrix, we obtain immediately instead of the determinant Eq. (28) the following equations for the doubly degenerate mode and the single mode:

$$\Omega_1{}^2=\Omega_{10}{}^2-(9/200)(\rho^2/\mu K)g_1(\Omega_1{}^2)\,,\quad \Omega_{10}{}^2=3\rho/5\mu$$
$$\Omega_2{}^2=\Omega_{20}{}^2-(9/400)(\rho^2/\mu K)g_2(\Omega_2{}^2)\,,\quad \Omega_{20}{}^2=3\rho/10\mu\qquad (39)$$

where we used the dimensionless frequency definition Eq. (42) and the abbreviations

$$\mu=m/M\,,\quad \rho=\gamma/\alpha_1\,,\quad K=-3/8\alpha_1\,.$$

A superficial look at Eq. (39) would lead one 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 m/M.

In the case of a light impurity ($\mu\ll 1$) one can take as zeroth approximation

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

and solve the Eqs. (39) by iteration, the $(n+1)$th approximation being

$$\Omega_{1(n+1)}{}^2=3\rho/5\mu-(9/200)(\rho^2/\mu K)g_1(\Omega_{1n}{}^2)\,,$$
$$\Omega_{2(n+1)}{}^2=3\rho/10\mu-(9/400)(\rho^2/\mu K)g_2(\Omega_{2n}{}^2)\,,\qquad (40)$$
$$n=0,1,2,\cdots.$$

The values of the Green's functions relevant for this problem have been calculated on the IBM 360/65 of Cetis/CCR Ispra and are tabulated for arguments $\Omega^2=10(10)100$ in Table II.

TABLE II. Numerical values of the functions $G_1,\cdots,G_5$ in units of 10^{-3} ($K=3/8\alpha_1$).

Ω^2	G_1/K	G_2/K	G_3/K	G_4/K	G_5/K
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

D. Localized Mode Frequencies in Vanadium Hydride

Experimental data on the localized vibration frequencies of vanadium-hydrogen and vanadium-deuterium systems have been obtained by INS at the Ispra-I reactor by Kley *et al.* and are published in Ref. 8. The evaluation of these experiments is not quite straightforward. We summarize here the essential points discussed in these reports: Because of the lower scattering cross section of deuterium it was necessary to do the VD measurements at rather high deuterium concentrations (about 20 at.%) while the VH samples contained only 4% H. At 20% admixture the α phase is not pure below 130°C. In order to assure a pure α phase the VD experiment was performed at 150°C and the VH experiment at 50°C. For a comparison of the two experiments it was therefore necessary to correct for the different phonon occupation factors, thereby reducing the direct time-of-flight results $d^2J/dEd\Omega$ to so-called "generalized spectral distributions" $G(E)$ defined by

$$G(E)=(d^2J/dEd\Omega)8\pi kE[\exp(E/k_BT)-1]/k'x^2\,,$$

k, k' being the wave numbers of incident and scattered neutrons and $x^2=(\mathbf{k}-\mathbf{k}')^2$ while $d\Omega$ denotes the element of solid angle.

The resulting curves for $G(E)$ are rather broad and it is difficult to determine the location of the localized modes with precision. Also, the results (for polycrystalline hydrides) show only one peak. It seems therefore that the interaction between the modes (due to anharmonic effects) results in such a broadening that the two localized peaks ω_1 and ω_2 coalesce. The first (doubly degenerate) mode should have twice the intensity of the second. Therefore we base the following comparison with theory on the assumption that the experimental peak corresponds to ω_1. The position of these peaks is given in Ref. 8 as 80 meV and 100 meV for VD and VH, respectively (with an uncertainty of the order of 15%).[19]

For a comparison of our theory with these results we still have to fit the parameter ρ, i.e., the ratio of the VH force constant to the VV next-neighbor force constant. Assuming a value $\rho=1.427$ for a best fit of both data, we obtain $\hbar\omega=77$ meV for the VD system and $\hbar\omega=108$ meV for the VH system. These values are not inconsistent with the experimental results. However, the nonharmonic effects which are responsible for the broadening of the experimental peaks could have shifted also the location of the "quasimodes." Thus the value of ρ obtained as the best fit for the harmonic model can be interpreted as an "effective" or "quasiharmonic" force constant which could be used only as an order-of-magnitude estimate of the true relative VH force constant. In the light of this interpretation it is even a nontrivial fact that the same effective force constant can be used for the VD and the VH system since the anharmonic effects could well be mass-dependent.

One point worth mentioning is that the frequency calculated for the H atom moving in a rigid vanadium lattice—as given by the first terms of Eq. (47)—is

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

The coupling of this oscillator to the host lattice shifts 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 constants of the vanadium-hydrogen and vanadium-vanadium interaction. Experiments of the type analyzed here are therefore essentially measurements of the VH interaction and are rather independent of the oscillation properties of the host lattice.

APPENDIX A

Equations (20) and (21) can also be derived on the basis of the identification of the Green's function $G_{\alpha\beta}(l\kappa,l'\kappa';\omega)$ 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 his method one has to find the eigenvalues of a $3s\times 3s$ matrix $\delta L+A\gamma A^t$, 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 $u_\alpha(l\kappa)$ the displacements of the crystal atoms and by q_α those of the interstitial. We decompose the total vector space $\mathcal{E}$ of the displacements of all the atoms into the direct sum of the three-dimensional space $\mathcal{E}_3$ of the displacement q_α and $3rN$-dimensional space $\mathcal{E}_{3rN}$ of the displacements $u_\alpha(l\kappa)$. Any matrix operating in $\mathcal{E}$ is partitioned accordingly.

We denote by $\mathbf{G}$ and $\mathbf{L}$ the matrices pertaining to the unperturbed crystal, by $\boldsymbol{\gamma}$ the "molecular" Green's matrix corresponding to the interstitial atom vibrating in a fixed host lattice, and by $\mathbf{G}'$ and $\mathbf{L}'$ the matrices pertaining to the total system. We write the latter as

$$\mathbf{G}'=\begin{pmatrix}\mathbf{G}_{11} & \mathbf{G}_{12}\\ \mathbf{G}_{21} & \mathbf{G}_{22}\end{pmatrix}, \quad \mathbf{L}'=\begin{pmatrix}\mathbf{L}_{11} & \mathbf{L}_{12}\\ \mathbf{L}_{21} & \mathbf{L}_{22}\end{pmatrix}, \tag{A1}$$

where the index 1 refers to the space $\mathcal{E}_3$ and the index 2 to the space $\mathcal{E}_{3rN}$. Since $\mathbf{G}'=\mathbf{L}'^{-1}$ we have

$$\begin{aligned}\mathbf{L}_{11}\mathbf{G}_{11}+\mathbf{L}_{12}\mathbf{G}_{21}&=\mathbf{I}\,,\\ \mathbf{L}_{21}\mathbf{G}_{11}+\mathbf{L}_{22}\mathbf{G}_{21}&=\mathbf{0}\,,\end{aligned} \tag{A2}$$

where $\mathbf{I}$ is the unit 3×3 matrix and $\mathbf{0}$ the null $3\times 3rN$ matrix. Combining the two Eqs. (A2) we obtain

$$\mathbf{G}_{11}^{-1}=\mathbf{L}_{11}-\mathbf{L}_{12}\mathbf{L}_{22}^{-1}\mathbf{L}_{21}\,. \tag{A3}$$

But, since

$$\boldsymbol{\gamma}=\mathbf{L}_{11}^{-1}, \quad \mathbf{G}=\mathbf{L}_{22}^{-1}, \quad \mathbf{L}_{21}=\mathbf{L}_{12}^{t}, \tag{A4}$$

we can write

$$\boldsymbol{\gamma}'^{-1}=\mathbf{G}_{11}^{-1}=\boldsymbol{\gamma}^{-1}-\mathbf{L}_{12}\mathbf{G}\mathbf{L}_{12}^{t}\,. \tag{A5}$$

Equation (A5) gives the perturbed molecular Green's function $\boldsymbol{\gamma}'=\mathbf{G}_{11}$ of the interstitial as a function of the unperturbed one $\boldsymbol{\gamma}$ and of the perturbation $\mathbf{L}_{12}\mathbf{G}\mathbf{L}_{12}^{t}$ due to the crystal, through the interaction $\mathbf{L}_{12}$ between the interstitial and the rest of the lattice. Since the elements of the $3rN\times 3$ matrix $\mathbf{L}_{12}$ are the expressions $M_{\alpha\beta}(l\kappa)$ of the text, we see that Eq. (A5) can be explicitly written as

$$(\boldsymbol{\gamma}'^{-1})_{\alpha\beta}=(\boldsymbol{\gamma}^{-1})_{\alpha\beta}-\sum_{\alpha'l\kappa;\beta'l'\kappa'} M_{\alpha\alpha'}(l\kappa)G_{\alpha'\beta'}(l\kappa,l'\kappa';\omega) \times M_{\beta\beta'}(l'\kappa')\,, \tag{A6}$$

which is precisely equivalent to the pair of equations (20) and (21) of the text.

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

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[19] R. Rubin (private communication).

[20] J. Peretti and C. Jouanin, Nuovo Cimento **34**, 293 (1964).

[21] G. Lehman and R. E. De Wames, Phys. Rev. **131**, 1008 (1963).

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

$$\gamma_{xy}=\gamma_{yx}=\gamma_{zx}=0\,,\quad \gamma_{xx}=\gamma_{zz}\neq\gamma_{yy}\,. \tag{A7}$$

The conditions (A7) are imposed by the symmetry D_{2d}. Since the interaction L_{12} preserves the symmetry of the problem, the perturbed matrix γ' should be diagonal in these axes. In this case the equations for the perturbed frequencies are the three *scalar* equations

$$\gamma_{\alpha\alpha}{'}^{-1}(\omega^2)=\gamma_{\alpha\alpha}{}^{-1}(\omega^2)-\sum_{\beta l\kappa;\beta' l'\kappa'} M_{\alpha\beta}(l\kappa) \times G_{\beta\beta'}(l\kappa,l'\kappa';\omega^2)M_{\alpha\beta'}(l'\kappa')=0\,. \tag{A8}$$

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

These arguments have been applied in Sec. II of the text. Equations (38) and (39) of the text exhibit the fact that γ' is diagonal and has two independent components, one for $[xx]$ and $[zz]$ (double degeneracy), and the other for $[yy]$.

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

APPENDIX B

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 recalled that the usual treatment of this problem involves the determination of the eigenvalues of a 27×27 matrix if the impurity "interacts" only with its first neighbors. In our method we have to handle a 3 × 3 diagonal matrix whatever the number of neighbors 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 Table III. We assume that the atom at O interacts with its eight neighbors through a central force with force constant γ. Let P, with coordinates $\frac{1}{2}a(\epsilon_1,\epsilon_2,\epsilon_3)$, $\epsilon_i=\pm 1$, be one of the eight points A to H. The interaction matrix $M(P)$ has the following elements:

$$M(P)=-\tfrac{1}{3}\gamma\begin{bmatrix} 1 & \epsilon_1\epsilon_2 & \epsilon_1\epsilon_3 \\ \epsilon_2\epsilon_1 & 1 & \epsilon_2\epsilon_3 \\ \epsilon_3\epsilon_1 & \epsilon_3\epsilon_2 & 1 \end{bmatrix}. \tag{B1}$$

TABLE III. Coordinates of the cube vertices in units of $\frac{1}{2}a$.

	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

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

$$\mathbf{T}_{11}(\alpha;\beta)=T_{\alpha\beta}(0,0)\,,\quad \mathbf{T}_{12}(\alpha;\beta,l\kappa)=T_{\alpha\beta}(0,l\kappa)\,,$$
$$\mathbf{T}_{21}=T_{12}{}^t\,,\quad \mathbf{T}_{22}(\alpha,l\kappa;\beta,l'\kappa')=T_{\alpha\beta}(l\kappa,l'\kappa')\,, \tag{B2}$$

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

$$\mathbf{T}=\begin{pmatrix} \mathbf{T}_{11} & \mathbf{T}_{12} \\ \mathbf{T}_{21} & \mathbf{T}_{22} \end{pmatrix}. \tag{B3}$$

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

$$\mathbf{L}=\begin{pmatrix} \mathbf{L}_{11} & \mathbf{L}_{12} \\ \mathbf{L}_{21} & \mathbf{L}_{22} \end{pmatrix},\quad \mathbf{L}''=\begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{L}_{22} \end{pmatrix}, \tag{B4}$$

where the $\mathbf{0}$'s are the appropriate null matrices. From

$$\mathbf{LG}=\mathbf{I}\,,\quad \mathbf{L}''\mathbf{G}''=\mathbf{I}$$

we obtain the equations

$$\begin{aligned} \mathbf{L}_{21}\mathbf{G}_{11}+\mathbf{L}_{22}\mathbf{G}_{21}&=\mathbf{0}\,,\\ \mathbf{L}_{21}\mathbf{G}_{12}+\mathbf{L}_{22}\mathbf{G}_{22}&=\mathbf{I}\,,\\ \mathbf{L}_{22}\mathbf{G}''&=\mathbf{I}''\,. \end{aligned} \tag{B5}$$

In the last equation we have taken into account that $\mathbf{G}''$, involving only $N-1$ points of the crystal, is a $3(N-1)\times 3(N-1)$ matrix, while $\mathbf{I}''$ is the corresponding unit matrix. We can solve the first two of Eqs. (B5) for $\mathbf{L}_{22}$ and $\mathbf{L}_{21}$ and obtain finally

$$\mathbf{G}''=\mathbf{L}_{22}{}^{-1}=\mathbf{G}_{22}-\mathbf{G}_{21}\mathbf{G}_{11}{}^{-1}\mathbf{G}_{12}\,. \tag{B6}$$

We can write Eq. (B6) in equivalent ways:

$$G_{\alpha\beta}{''}(l\kappa,l'\kappa')=G_{\alpha\beta}(l\kappa,l'\kappa')-\sum_{\alpha'\beta'} G_{\alpha\alpha'}(l\kappa,0)G_{11}{}^{-1}(\alpha'0,\beta'0) \times G_{\beta\beta'}(0,l',\kappa')\,, \tag{B7}$$

$$\mathbf{G}''(P,Q)=\mathbf{G}(P,Q)-\mathbf{G}(P,0)\mathbf{G}_{11}{}^{-1}\mathbf{G}(0,Q)\,.$$

Equations (B6) and (B7) 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 (B1). The problem is then identical with that of an interstitial impurity except that everywhere G should be replaced by G''.

We note that the 3 × 3 matrix $\mathbf{G}_{11}$ is diagonal for cubic symmetry and is given by

$$\mathbf{G}_{11}=\mathbf{G}(0,0)=\mathbf{G}(A,A)=\begin{bmatrix} G_1 & 0 & 0 \\ 0 & G_1 & 0 \\ 0 & 0 & G_1 \end{bmatrix}, \tag{B8}$$

where G_1 is the function defined in Eq. (32). Thus Eq. (B7) becomes

$$\mathbf{G}''(P,Q)=\mathbf{G}(P,Q)-\mathbf{G}(0,P)\mathbf{G}(0,Q)/G_1. \qquad \text{(B9)}$$

The interaction function F'' is defined by

$$\mathbf{F}''=\sum_{P,Q}\mathbf{M}(P)\mathbf{G}''(P,Q)\mathbf{M}(Q)=\mathbf{F}-\mathbf{J}, \qquad \text{(B10)}$$

where

$$\mathbf{F}=\sum_{P,Q}\mathbf{M}(P)\mathbf{G}(P,Q)\mathbf{M}(Q) \qquad \text{(B11)}$$

and

$$\mathbf{J}=\sum_{P,Q}\mathbf{M}(P)\mathbf{G}(0,P)\mathbf{G}(0,Q)\mathbf{M}(Q)/G_1=\mathbf{K}^2/G_1 \qquad \text{(B12)}$$

with the diagonal matrix

$$\mathbf{K}=\sum_{P}\mathbf{M}(P)\mathbf{G}(0,P)=\sum_{Q}\mathbf{G}(0,Q)\mathbf{M}(Q). \qquad \text{(B13)}$$

To evaluate the interaction function $\mathbf{F}$ defined in Eq. (B11) we again use symmetry considerations. We write $\mathbf{F}$ 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. We write

$$\mathbf{F}=\mathbf{F}_{\mathrm{I}}+\mathbf{F}_{\mathrm{II}}+\mathbf{F}_{\mathrm{III}}+\mathbf{F}_{\mathrm{IV}} \qquad \text{(B14)}$$

with

$$\begin{aligned}\mathbf{F}_{\mathrm{I}}&=\sum_{P}\mathbf{M}(P)\mathbf{G}(P,P)\mathbf{M}(P),\\ \mathbf{F}_{\mathrm{II}}&=\sum_{\mathbf{PQ}=(100)}\mathbf{M}(P)\mathbf{G}(P,Q)\mathbf{M}(Q),\\ \mathbf{F}_{\mathrm{III}}&=\sum_{\mathbf{PQ}=(110)}\mathbf{M}(P)\mathbf{G}(P,Q)\mathbf{M}(Q),\\ \mathbf{F}_{\mathrm{IV}}&=\sum_{\mathbf{PQ}=(111)}\mathbf{M}(P)\mathbf{G}(P,Q)\mathbf{M}(Q),\end{aligned} \qquad \text{(B14}')$$

where

$$\sum_{\mathbf{PQ}=(hkl)}$$

means a summation over all the points P and Q such that the vector $\mathbf{PQ}$ is crystallographically equivalent to the lattice vector (hkl), P and Q being chosen among the eight points A to H.

The interaction matrix $\mathbf{F}$ is diagonal and spherical, having three equal diagonal elements, as required by cubic symmetry. The nonzero elements are

$$\begin{aligned}F_{xx}=F_{yy}=F_{zz}=(8\gamma^2/9)[&3G_1-G_3+2G_2+2G_6\\ &+2G_7-G_8+3G_9+6G_{10}],\end{aligned} \qquad \text{(B15)}$$

which involve the following terms in addition to the already known functions G_1, G_2, G_3:

$$\begin{aligned}&G_6=G_{xx}(A,C),\quad G_7=G_{xy}(A,C),\quad G_8=G_{zz}(A,C),\\ &G_9=G_{xx}(A,G),\quad G_{10}=G_{xy}(A,G).\end{aligned} \qquad \text{(B16)}$$

They have the explicit form

$$G_i=(K/\pi^3)\int d^3\theta T_i,\quad (i=6,\,7,\,8,\,9,\,10)$$

$$\begin{aligned}T_6&=H_{11}(2C_1^2-1)(2C_2^2-1)/D,\\ T_7&=-H_{12}(4C_1C_2S_1S_2)/D,\\ T_8&=H_{33}(2C_1^2-1)(2C_2^2-1)/D,\\ T_9&=H_{11}(2C_1^2-1)(2C_2^2-1)(2C_3^2-1)/D,\\ T_{10}&=-H_{12}(4C_1C_2S_1S_2)(2C_3^2-1)/D.\end{aligned} \qquad \text{(B17)}$$

We turn to the evaluation of $\mathbf{K}$ and $\mathbf{J}$. For this we write the expression of the matrix $\mathbf{G}(0,P)$:

$$\mathbf{G}(0,P)=\begin{bmatrix}G_4 & \epsilon_1\epsilon_2G_5 & \epsilon_1\epsilon_3G_5\\ \epsilon_2\epsilon_1G_5 & G_4 & \epsilon_2\epsilon_3G_5\\ \epsilon_3\epsilon_1G_5 & \epsilon_3\epsilon_2G_5 & G_4\end{bmatrix}. \qquad \text{(B18)}$$

By direct multiplication we obtain

$$\mathbf{M}(P)\mathbf{G}(0,P)=-\tfrac{1}{3}\gamma\begin{bmatrix}1 & \epsilon_1\epsilon_2 & \epsilon_1\epsilon_3\\ \epsilon_2\epsilon_1 & 1 & \epsilon_2\epsilon_3\\ \epsilon_3\epsilon_1 & \epsilon_3\epsilon_2 & 1\end{bmatrix}(G_4+2G_5) \qquad \text{(B19)}$$

and

$$\begin{aligned}K_{\alpha\beta}&=-(8\gamma/3)\delta_{\alpha\beta}(G_4+2G_5),\\ J_{\alpha\beta}&=(64\gamma^2/9)\delta_{\alpha\beta}(G_4+2G_5)^2G_1.\end{aligned} \qquad \text{(B20)}$$

The α component of the force acting on the impurity, when displaced by the vector $\mathbf{u}$ from its equilibrium position while all the other atoms in the lattice are held at their equilibrium positions, has the value

$$\frac{\partial\Phi_s}{\partial u_\alpha}=-(8\gamma/3)u_\alpha,\quad \alpha=1,2,3. \qquad \text{(B21)}$$

The frequencies ω_s of oscillations of the impurity atom in the rigid lattice are triply degenerate and given by

$$m\omega_s^2=8\gamma/3.$$

The molecular Green's function matrix and inverse are:

$$\begin{aligned}\gamma_{\alpha\beta}&=\partial_{\alpha\beta}(m\omega^2-8\gamma/3)^{-1},\\ (\gamma^{-1})_{\alpha\beta}&=\delta_{\alpha\beta}(m\omega^2-8\gamma/3),\end{aligned} \qquad \text{(B22)}$$

where m is the mass of the impurity atom.

Equation (A8) for the frequencies of the localized modes (and also of resonances, by taking the appropriate real part) yields now three times the same expression:

$$\begin{aligned}m\omega^2=(8\gamma/3)+(8\gamma^2/9)(&3G_1-G_3+2G_2+2G_6+2G_7-G_8\\ &+3G_9+6G_{10})-(64\gamma^2/9)(G_4+2G_5)^2/G_1\end{aligned} \qquad \text{(B23)}$$

(triply degenerate root).

Equation (B23) 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 O, or when one takes into account the interaction of site O with its next-nearest neighbors.

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Conduction-Electron Exchange and the Local Pseudopotential Form Factors in the Alkali Metals*

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We estimate the size of the error caused by omitting the exchange potential of the conduction electrons from the crystal potential when calculating the local pseudopotential form factors in the alkali metals. This error is determined by relating these approximate form factors to the true energy eigenvalues of the complete Hartree-Fock band-structure Hamiltonian. We then use this relation to deduce the approximate form factors from the measured anisotropy of the band energy at the Fermi surface. These form factors may be compared with the true form factors determined from Fermi-surface measurements. This comparison permits a prediction of the errors expected in present *a priori* calculations of the form factors due to the approximate treatment of the conduction-electron exchange potential. A numerical calculation is made for sodium, based on the formalism of this paper, which predicts that the errors in V_{110} for this metal are of the order of 15%. The possibility of extending the calculations to other alkali metals is also discussed.

I. INTRODUCTION

Recently *a priori* calculations of the pseudopotential form factors (PFF) in the alkali metals (see Sec. IV) have been based on a crystal potential which includes the self-consistent screening of the ionic potential by the conduction electrons, but which does not include a detailed treatment of the exchange potential of the conduction electrons. The purpose of this paper is to attempt to estimate the possible errors in the calculated PFF for the alkali metals when the spatially fluctuating part of the exchange potential is ignored in an *a priori* calculation.[1]

Psuedopotential theory gives us a prescription for the replacement of any given crystal potential $V(\mathbf{r})$ with a pseudopotential V_p which is possibly much weaker than the original potential, and which thus lends itself to a perturbation treatment. We will consider two model crystal potentials for the alkali metals. One of these, denoted by $V(\mathbf{r})$ will be the full Hartree-Fock potential given by the usual expression. The other, denoted by $\bar{V}(\mathbf{r})$, will be the Hartree-Fock potential excluding the conduction-electron contribution to the exchange potential [$\bar{V}(\mathbf{r})$ will be more precisely defined in Sec. II].

The pseudopotentials corresponding to $V(\mathbf{r})$ and $\bar{V}(\mathbf{r})$ will be denoted by V_p and $\bar{V}_p$, respectively. Similarly, the Fourier transforms of V_p and $\bar{V}_p$ at wave vector $\mathbf{G}$ ($\mathbf{G}$ is a reciprocal lattice vector) will be denoted by $V(G)$ and $\bar{V}(G)$. Thus the $V(G)$ are the PFF which would be obtained by a perfect *a priori* calculation starting with the full Hartree-Fock crystal potential, while the $\bar{V}(G)$ would be computed from a perfect *a priori* calculation which was based on an approximate crystal potential—one which ignored the contribution of conduction-electron exchange.

The prescription for obtaining V_p from V is not unique. The formal results of this paper are valid independent of the prescription chosen as long as it is the same for V and $\bar{V}$.

Let $E_{\mathbf{k}}$ denote the true Hartree-Fock energy of an electron in state $\mathbf{k}$ obtained from the complete Hartree-Fock Hamiltonian, including conduction-electron exchange. $E_{\mathbf{k}}$ is given in terms of the $V(G)$ by the usual expression (see Sec. II). Now, $E_{\mathbf{k}}$ may also be given in terms of the $\bar{V}(G)$ as follows. We can obtain the solutions to the Hartree-Fock equations *excluding* the conduction-exchange term in a straightforward way in terms of the $\bar{V}(G)$. If we then use the conduction exchange potential as a perturbation on the solutions to this approximate problem, we can find the *true* Hartree-Fock energies in terms of the approximate form factors $\bar{V}(G)$. It will be the purpose of Sec. II to determine the true Hartree-Fock energies $E_{\mathbf{k}}$ in terms of the approximate form factors $\bar{V}(G)$—these being the form factors relevant to the approximate problem in which the conduction exchange potential is excluded from the Hartree-Fock Hamiltonian.

We shall let $W_{\mathbf{k}}$ denote the true Hartree-Fock energy

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[1] The calculations in this paper are presented in much greater detail in an expanded version of this paper, which may be obtained from the author, and in W. D. Grobman, Ph.D. thesis, Princeton University, 1967 (unpublished). Some copies of this thesis are available from the author, and a copy may also be obtained from University Microfilms, Ann Arbor, Mich.