Dynamics of Cubic Crystals with a Local Change of Mass

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The effects of a local change of mass on lattice vibrations of cubic systems are discussed for simple Bravais lattices, on the basis of the harmonic theory of crystal dynamics. It is shown that the change of any extensive property, as well as the values of the discrete frequencies, are given in terms of simple expressions involving only the distribution function $G_0(\omega^2)$ of the square frequency for the unperturbed lattice; the theoretical expressions are found to be equivalent to those holding for linear chains, provided that the distribution function is normalized to one. Perturbative techniques are discussed in some detail; it is found that a perturbative expansion of the change of any extensive property converges to the right value, provided the fractional change of mass, $\epsilon=-(M'-M)/M$, lies inside the range from $-\infty$ to $+\frac{1}{2}$. Some applications are carried out starting from Overton's distribution function for a fcc lattice: a discrete frequency, threefold degenerate, is found to occur for $\epsilon\geqslant 0.215$, and the self-entropy of a substitutional impurity (neglecting the influence of the elastic distortion) is shown to be related only to the structure of the distribution function, in the high-temperature limit; this change of entropy is evaluated for several light impurities. Finally, arguments are presented which suggest that the contribution to the self-entropy of a vacant lattice site, arising from the loss of coupling with the neighbors, may be higher than was estimated by Huntington and coworkers.

1. INTRODUCTION

IN recent years, the influence of point defects on lattice vibrations has received particular attention.[1] The general theory has been developed by Lifschitz, Koster and Slater, Montroll, and others, and some applications have been made to linear chains or to simple-cubic lattices with nearest-neighbor interactions.

The aim of the present paper is to show that: (i) the effects of a local change of mass in cubic monatomic lattices (such as simple cubic, fcc, and bcc) with any order of neighbors interactions may be studied simply in terms of the distribution function $G_0(\omega^2)$ of the square frequency of the vibrational modes; (ii) a perturbative expansion of the change of any extensive property, which converges to the right value, can be found, provided the fractional change of mass $\epsilon=-(M'-M)/M$ lies inside the range from $-\infty$ to $+\frac{1}{2}$; (iii) the change of entropy due to the loss of coupling around a vacant lattice site may be higher than estimated by Huntington and coworkers[2] some years ago. For the applications presented here use is made of Overton's calculations[3] for the distribution function.

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2. PRELIMINARY REMARKS

For monatomic Born-von Kármán lattices the normal modes equation for the vibrational amplitudes χ is

$$\sum_{\mathbf{r}',x'} A_{xx'}(\mathbf{r}-\mathbf{r}')\chi^{x'}(\mathbf{r}')-zM_{\mathbf{r}}\chi^{x}(\mathbf{r})=0. \qquad (1)$$

$A_{xx'}(\mathbf{r}-\mathbf{r}')$ are the coupling coefficients between the nuclei at the lattice vectors $\mathbf{r}$, $\mathbf{r}'$; a lattice vector $\mathbf{r}$ is defined by $\mathbf{r}=\sum_{i=1}^{3} r_i\mathbf{a}^i$, where $\mathbf{a}^i$ are the principal translations of the Bravais lattice, and r_i are integers; $M_{\mathbf{r}}=M$ are the atomic masses, and $z\equiv\omega^2$ is the square frequency. We use $x=x^1, x^2, x^3$ to label the Cartesian components. When a foreign atom of mass M' is substituted at the lattice site $\mathbf{r}=0$, we have

$$M_{\mathbf{r}}=M(1-\epsilon\,\delta_{0,\mathbf{r}}), \qquad (2)$$

where $\epsilon\equiv(M-M')/M=-\Delta M/M$, and $\delta_{0,\mathbf{r}}$ is the Kronecker symbol. If there is no change in the coupling coefficients around the impurity, the normal-modes equation for the perturbed lattice may be written, in the matrix notation, as

$$[L-z(I-\epsilon\Delta)]\chi=0, \qquad (3)$$

where $L_{xx'}(\mathbf{r}-\mathbf{r}')\equiv(1/M)A_{xx'}(\mathbf{r}-\mathbf{r}')$, and $\Delta_{xx'}(\mathbf{r},\mathbf{r}')\equiv\delta_{xx'}\delta_{0,\mathbf{r}}\,\delta_{0,\mathbf{r}'}$. L may be treated as an unperturbed operator, and $z\epsilon\Delta$ as a local perturbation (ϵ is not supposed to be small). The eigenfunctions of L are the plane waves

$$\chi_{s,\mathbf{k}}{}^{0,x}(\mathbf{r})=(1/N)^{\frac{1}{2}}v_{s,\mathbf{k}}{}^{x}\exp(i\mathbf{k}\cdot\mathbf{r})\equiv\langle x;\mathbf{r}|\mathbf{v}_s;\mathbf{k}\rangle, \qquad (4)$$

where $v_{s,\mathbf{k}}{}^{x}$ are the scalar components of the (complex) polarization vector of the lattice wave having wave vector $\mathbf{k}$. $s=1, 2$ corresponds to transverse waves and $s=3$ corresponds to longitudinal waves. $(1/N)^{\frac{1}{2}}$ is the

normalization constant, N being the total number of atoms in the lattice. Imposing the periodic boundary conditions, the values of $\mathbf{k}$ are confined to the first Brillouin zone (B.z.). The eigenvalues of the unperturbed operator are the squares of the vibrational frequencies of the lattice $z\equiv\omega^2=\omega_s^2(\mathbf{k})$. The square frequency is then

$$\omega_s^2(\mathbf{k})=\sum_{\mathbf{r}}\sum_{xx'}(v_{s,\mathbf{k}}{}^x)^*L_{xx'}(\mathbf{r})v_{s,\mathbf{k}}{}^{x'}\exp(i\mathbf{k}\cdot\mathbf{r}). \quad (5)$$

For large crystals, as N tends to infinity, the unperturbed operator has a continuous spectrum extending from zero to a well-defined maximum $z_L{}^0$.

It is well known that the presence of a local perturbation leads to two kinds of effects: first, the elastic waves propagating in the crystal are scattered and the perturbed waves are given by the superposition of the incoming and diffusing wave; secondly, new modes of oscillation may be possible, in the sense that wave packets, localized around the impurity, could have standing character. The frequencies of these new modes lie outside the interval $(0,z_L{}^0)$ of the unperturbed spectrum.

3. DISCRETE FREQUENCIES EQUATION

When z lies outside the unperturbed spectrum, the inverse of the operator $(L-z)$ exists, and Eq. (3) may be written

$$|\chi\rangle=-z\epsilon(L-z)^{-1}\Delta|\chi\rangle, \quad (6)$$

or

$$[I+z\epsilon(L-z)^{-1}\Delta]|\chi\rangle=0. \quad (6')$$

In the present case, Δ is a third-rank operator, so that the three scalar components of the perturbed modes at the lattice site $\mathbf{r}=0$ are involved in the right-hand member of (6). We may write[4]:

$$\Delta|\chi\rangle=\sum_{s=1}^{3}(1/2\pi)^3\int_{(\mathrm{B.z.})}d\mathbf{k}\,|\mathbf{v}_s;\mathbf{k}\rangle\langle\mathbf{k};\mathbf{v}_s|\Delta|\chi\rangle, \quad (7)$$

where

$$\langle\mathbf{k};\mathbf{v}_s|\Delta|\chi\rangle=\sum_x(v_{s,\mathbf{k}})^*\chi_x(0).$$

If $|\mathbf{v}_s;\mathbf{k}\rangle\langle\mathbf{k};\mathbf{v}_s|$ indicates the direct product of the $3N$-dimensional vector $|\mathbf{v}_s;\mathbf{k}\rangle$ times its imaginary conjugate $\langle\mathbf{k};\mathbf{v}_s|$, the inverse operator $(L-z)^{-1}$ is given by the following expression:

$$(L-z)^{-1}=\sum_{s=1}^{3}(1/2\pi)^3\int_{(\mathrm{B.z.})}d\mathbf{k}\,|\mathbf{v}_s;\mathbf{k}\rangle(\omega_{s,\mathbf{k}}{}^2-z)^{-1}\langle\mathbf{k};\mathbf{v}_s|. \quad (8)$$

Remembering the orthonormality conditions for the unperturbed normal modes,

$$\langle\mathbf{k};\mathbf{v}_s|\mathbf{v}_{s'};\mathbf{k}'\rangle=\delta_{ss'}(2\pi)^3\delta(\mathbf{k}-\mathbf{k}'), \quad (9)$$

[4] Hereafter we neglect the normalization factor $(1/N)^{\frac{1}{2}}$, and we assume as unity the volume $\mathbf{a}^1\cdot\mathbf{a}^2\times\mathbf{a}^3$ of the unit cell of the lattice.

substitution of (7) and (8) into (6) gives, for the scalar components with respect to the Cartesian axes,

$$\chi^x(\mathbf{r})=-z\epsilon\sum_{x'}\chi_{x'}(0)\sum_{s=1}^{3}(1/2\pi)^3\int_{(\mathrm{B.z.})}d\mathbf{k}\,(v_{s,\mathbf{k}}{}^{x'})^*v_{s,\mathbf{k}}{}^x\times(\omega_{s,\mathbf{k}}{}^2-z)^{-1}\exp(i\mathbf{k}\cdot\mathbf{r}). \quad (10)$$

In particular, for $\mathbf{r}=0$,

$$\chi^x(0)=-z\epsilon\sum_{x'}\chi_{x'}(0)\sum_{s=1}^{3}(1/2\pi)^3\times\int_{(\mathrm{B.z.})}d\mathbf{k}\,(v_{s,\mathbf{k}}{}^{x'})^*v_{s,\mathbf{k}}{}^x(\omega_{s,\mathbf{k}}{}^2-z)^{-1}.$$

The integral in the right-hand member of the above expression may be written as

$$(1/2\pi)^3\int_{(\mathrm{B.z.})}d\mathbf{k}\,(v_{s,\mathbf{k}}{}^{x'})^*v_{s,\mathbf{k}}{}^x(\omega_{s,\mathbf{k}}{}^2-z)^{-1}=\int_0^{z_s{}^0}dz'(z'-z)^{-1}(1/2\pi)^3\times\int_{(\omega^2=z)}dS\,|\nabla\omega_s{}^2(\mathbf{k})|^{-1}(v_{s,\mathbf{k}}{}^{x'})^*v_{s,\mathbf{k}}{}^x, \quad (11)$$

where dS is the differential area on the constant-frequency surface in the $\mathbf{k}$ space, and $z_s{}^0$ is the maximum square frequency in the sth band. Taking into account the symmetry properties of $\mathbf{v}_{s,\mathbf{k}}$ in the $\mathbf{k}$ space, one can see that, for cubic lattices, the surface integration of any mixed component of the tensorial product $(\mathbf{v}_{s,\mathbf{k}})^*\mathbf{v}_{s,\mathbf{k}}$ vanishes, whereas the surface integration of the diagonal components yields the same result, for either x^1x^1, x^2x^2, or x^3x^3, owing to the equivalence of the coordinate axes. We have

$$(1/2\pi)^3\int_{(\omega_s{}^2=z)}dS\,|\nabla\omega_s{}^2(\mathbf{k})|^{-1}(v_{s,\mathbf{k}}{}^{x'})^*v_{s,\mathbf{k}}{}^x=\delta^{x'x}\tfrac{1}{3}G_0{}^s(z), \quad (12)$$

where

$$G_0{}^s(z)=\sum_x(1/2\pi)^3\int_{(\omega_s{}^2=z)}dS\,|\nabla\omega_s{}^2(\mathbf{k})|^{-1}(v_{s,\mathbf{k}}{}^x)^*v_{s,\mathbf{k}}{}^x=(1/2\pi)^3\int_{(\omega_s{}^2=z)}dS\,|\nabla\omega_s{}^2(\mathbf{k})|^{-1}$$

is the distribution function of the square normal frequency for the unperturbed sth band. Substitution of (12) into (10) yields the "discrete-frequency

equations":

$$1=\tfrac{1}{3}z\epsilon\int_0^{z_L{}^0}dz'\,G_0(z')(z-z')^{-1}, \tag{13}$$

for $x=x^1, x^2, x^3$; $G_0(z)$ is the distribution function for the entire vibrational branch, i.e.,

$$G_0(z)=\sum_{s=1}^{3}G_0{}^s(z).$$

Therefore, if there are discrete frequencies, they are threefold degenerate. The critical value ϵ_{cr} for the appearance of discrete frequencies is

$$\epsilon_{cr}=1\Big/\left[\tfrac{1}{3}z_L{}^0\int_0^{z_L{}^0}dz\,G_0(z)(z_L{}^0-z)^{-1}\right]. \tag{14}$$

If one remembers that for a three-dimensional lattice the distribution function is normalized to 3, the expressions (13), (14) are seen to be identical with those given previously by the quoted authors for simple lattices with all the oscillations polarized in one direction.

4. EFFECTS OF THE PERTURBATION IN THE RANGE OF THE CONTINUOUS SPECTRUM

It has been pointed out by I. M. Lifschitz and by M. Lax that the change of extensive properties arising from the effect of a finite-rank operator Λ on the unperturbed operator L, having a continuous spectrum, may be evaluated by means of J functions $\xi_j(z)$, $(j=1, 2, 3, \cdots, J)$, of the continuous eigenvalue z. J is the rank of the perturbing operator. The physical meaning of this set of functions is the following: Let F be an additive function of the eigenvalues of L, so that

$$\begin{aligned}F_0&=\mathrm{Sp}\,\varphi(L),\\ F\ &=\mathrm{Sp}\,\varphi(L+\Lambda),\end{aligned} \tag{15}$$

where $\varphi(z)$ is a given scalar function, and Λ is the perturbation. The change of this property is then

$$\begin{aligned}\delta F\equiv F-F_0&=\mathrm{Sp}[\varphi(L+\Lambda)-\varphi(L)]\\ &=\left\{N\int_0^{\infty}dz\,\Delta G_0(z)\varphi(z)\right\}_{N\to\infty}\\ &=\int_0^{\infty}dz\sum_{j=1}^{J}\xi_j(z)\varphi'(z).\end{aligned} \tag{16}$$

$\varphi'(z)$ is the first-order derivative of φ; by Sp$\cdots$ we mean the spur of the operator.[5] From the two last expressions it appears that

$$\sum_{j=1}^{J}\xi_j(z)=\left\{-N\int_0^{z}dz'\,\delta G_0(z')\right\}_{N\to\infty}.$$

[5] The last expression is the well-known "Trace formula" given by Lifschitz (see reference 1).

Outside the range of the continuous spectrum the functions $\xi_j(z)$ may have a step character, and this corresponds to discrete eigenvalues.

In place of the actual operator L, it is more convenient for the present purposes to work on a sequence of operators L_γ, defined by the same continuous set of eigenvectors $|\mathbf{v}_s;\mathbf{k}\rangle$ of the original operator, and by discrete eigenvalues $\lambda_n=n\gamma$, n being the integer part of $[\omega_{s,\mathbf{k}}{}^2/\gamma]$, γ is a real parameter$(\gamma>0)$. In the complex z-plane the inverse operator $(L_\gamma-z)^{-1}$ is given by

$$(L_\gamma-z)^{-1}=\sum_{n=0}^{N_\gamma}(\lambda_n-z)^{-1}\mathcal{P}_{(\lambda_n)}, \tag{17}$$

where

$$\mathcal{P}_{(\lambda_n)}\equiv\sum_{s=1}^{3}\int_{\tau_s(\lambda_n)}d\mathbf{k}\,|\mathbf{v}_s;\mathbf{k}\rangle\langle\mathbf{k};\mathbf{v}_s|$$

is the projection operator on the subset of eigenvectors for which $\lambda_n\leqq\omega_{s,\mathbf{k}}{}^2<\lambda_{n+1}$; $\tau_s(\lambda_n)$ is the correspondent region in the $\mathbf{k}$ space. The summation in the right-hand member of (17) is extended to the total number of distinct eigenvalues, $n=1, 2, \cdots, N_\gamma=[z_L{}^0/\gamma]$. The influence of the perturbation on the eigenvalues of L may be discussed by putting $z=\lambda_m+\gamma\xi(\lambda_m)$ in Eq. (6′). In the $|x;\mathbf{r}\rangle$ representation, our perturbation $z\epsilon\Delta$ is a third-rank matrix, so that the determinantal equation that one obtains from (6′) is again equivalent to a third-order equation. In the limit for $\gamma\to 0$, it then follows that

$$\begin{aligned}\det\Big\{I-z\epsilon\,\pi\cot[\pi\xi(z)]&\sum_{s=1}^{3}(1/2\pi)^3\\ &\times\int_{(\omega_s{}^2=z)}dS\,|\nabla\omega_s{}^2(\mathbf{k})|^{-1}\mathbf{v}_{s,\mathbf{k}}\mathbf{v}_{s,\mathbf{k}}{}^*\\ &+z\epsilon\,P\int_0^{z_L{}^0}dz'(z'-z)^{-1}\sum_{s=1}^{3}(1/2\pi)^3\\ &\times\int_{(\omega_s{}^2=z')}dS\,|\nabla\omega_s{}^2(\mathbf{k})|^{-1}\mathbf{v}_{s,\mathbf{k}}\mathbf{v}_{s,\mathbf{k}}{}^*\Big\}=0.\end{aligned} \tag{18}$$

By P we mean the principal value of the integral. In this determinantal equation $\cot(\pi\xi)$ plays the role of eigenvalue, and z is regarded as a real parameter; $\xi(z)$ is assumed to range from $-\frac{1}{2}$ to $+\frac{1}{2}$.

The symmetry properties of $\mathbf{v}_{s,\mathbf{k}}$ in the $\mathbf{k}$ space reduce the above determinantal equation to three equivalent scalar equations. The solutions are

$$\begin{aligned}\xi(z)=\xi_1(z)=\xi_2(z)=\xi_3(z)&\\ =\frac{1}{\pi}\arctan&\frac{\tfrac{1}{3}\pi z\epsilon G_0(z)}{1-\tfrac{1}{3}z\epsilon P\displaystyle\int_0^{z_L{}^0}dz'(z-z')^{-1}G_0(z')}.\end{aligned} \tag{19}$$

If we let

$$\tilde{G}_0(z)\equiv P\int_0^{z_L^0} dz'(z-z')^{-1}G_0(z'), \tag{20}$$

we may write, finally

$$\xi(z)=-\frac{1}{\pi}\arctan\pi\frac{\frac{1}{3}z\epsilon G_0(z)}{1-\frac{1}{3}z\epsilon\tilde{G}_0(z)}. \tag{19'}$$

This expression is still equivalent to that obtained for simple lattices with polarized oscillations.

We assume both $G_0(z)$, and $\tilde{G}_0(z)$ to be continuous functions; the points of discontinuity of $\xi(z)$ are then confined to the values of z for which the denominator in the expression in the right member of (19′) vanishes. Let ζ_i, $(i=1,\cdots,\nu)$ be the zeros of $1-\frac{1}{3}z\epsilon\tilde{G}_0(z)$ inside the range $(0,z_L^0)$ of the continuous spectrum; $\xi(z)$ shows ν jogs, respectively at $z=\zeta_1,\zeta_2,\cdots,\zeta_\nu$. We note that at every jog

$$\left.\begin{aligned}\xi(\zeta_i^+)&=-\tfrac{1}{2}, \quad (\text{or } +\tfrac{1}{2})\\ \xi(\zeta_i^-)&=+\tfrac{1}{2}, \quad (\text{or } -\tfrac{1}{2})\end{aligned}\right\};\quad |\delta\xi(\zeta_i)|=1; \tag{21}$$

in view of this property, let us call ζ_i "points of inversion" of ξ.

For a random solid solution of a finite concentration c, the perturbed distribution function could show small peaks (or small valleys) at the inversion points.

In the present paper we assume that $G_0(z)$ is represented by the function plotted in Fig. 1. This distribution function is deduced from Overton's calculations[2] for a fcc lattice with twelve nearest-neighbor central interaction. Figure 2 shows $\tilde{G}_0(z)$, as it is obtained by machine calculations from the above $G_0(z)$. Finally,

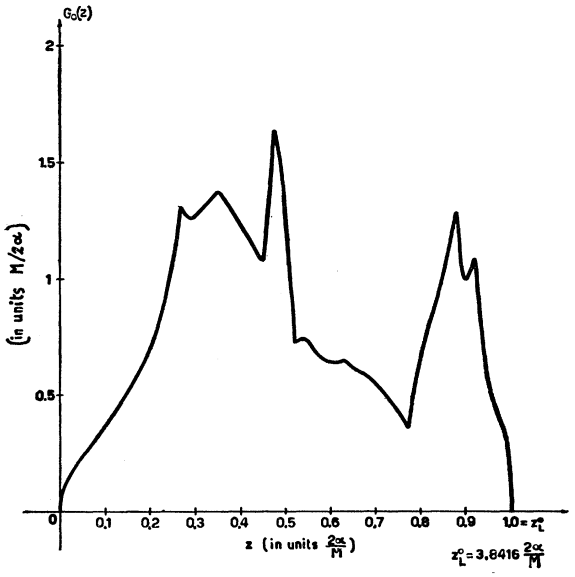

FIG. 1. Distribution function $G_0(z)$ of the square frequency $z=\omega^2$ for a fcc lattice with nearest-neighbor central interaction. (From Overton and Dent.[3])

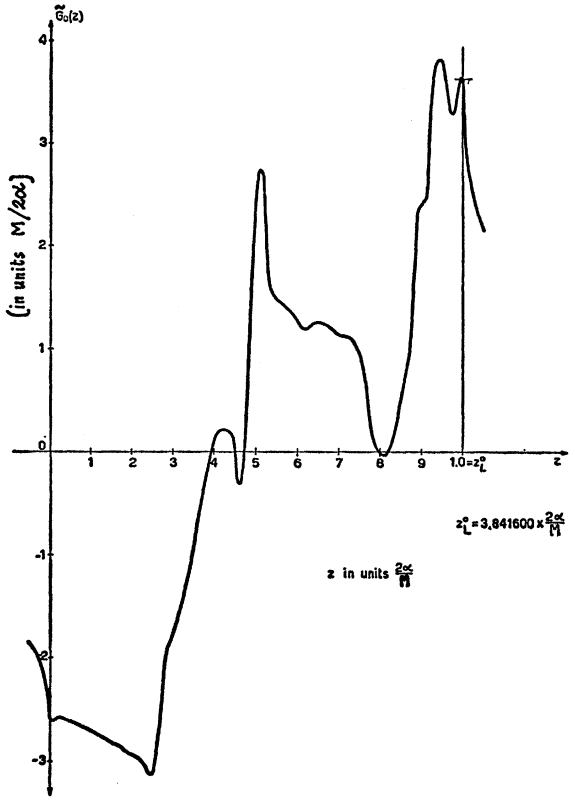

FIG. 2. Plot of $\tilde{G}_0(z)$ deduced from $G_0(z)$ with the aid of a USS 90 Remington computer.

$\frac{1}{3}z\tilde{G}_0(z)$ is plotted in Fig. 3; the zeros of $1-\frac{1}{3}z\epsilon\tilde{G}_0(z)$ are the intercepts of this curve with the line $y=1/\epsilon$ parallel to the z axis. Remembering (13), one sees that the intercept lying outside the continuous interval gives the discrete frequency. $\frac{1}{3}z\tilde{G}_0(z)$ shows several maxima and minima; the absolute maximum occurs at $z=z_L^0$, and for $0<\epsilon<\epsilon_{cr}$, $\xi(z)$ does not show inversion points. For $\epsilon_{cr}<\epsilon<0.216$, $\xi(z)$ shows an inversion point very close to z_L^0; for $0.216<\epsilon<0.242$, there are three inversion points between $0.9275z_L^0$ and z_L^0, two of which collapse when $\epsilon=0.2424$, and then disappear for $\epsilon>0.2424$. For $0.2424<\epsilon<0.5606$, $\xi(z)$ shows again a single inversion point between $0.51z_L^0$ and $0.9275z_L^0$; finally, for values of ϵ increasing from 0.5606 to 1, the number of inversion points increases up to a maximum of seven (for $\epsilon=0.971$), and then falls to five for $\epsilon=1$. For negative values of ϵ, there is always an even number of inversion points, or none, as it is expected; the number of inversion points increases from two (for $\epsilon\lesssim-1$), to six (for $\epsilon<-28.5$). Plots of $\xi(z)$ for $\epsilon=0.1$; 0.25; 0.5; 1, are shown in Fig. 4(a), (b), (c), and (d).

5. RELIABILITY OF PERTURBATION TECHNIQUES

On the basis of the present distribution function it follows that $z\tilde{G}_0(z)$ is a bounded function when z lies

on the real axis. For values of ϵ sufficiently close to zero one may suppose that the argument of the inverse trigonometric function in (19′) is smaller than one, in absolute value, for any point z in $(0,z_L{}^0)$. In this case $\xi(z)$ may be evaluated by means of a Taylor expansion; one obtains

$$\xi(z)=z\epsilon(1/3)G_0(z)+(z\epsilon)^2(1/9)G_0(z)\tilde{G}_0(x) - (z\epsilon)^3(1/27)\{G_0(z)[(\tilde{G}_0(z))^2+(\pi^2/3)(G_0(z))^2]\} +\cdots=\sum_{n=1}^{\infty}\epsilon^n\xi^{(n)}(z). \quad (22)$$

The change δF of an extensive property is then given by

$$\delta F=\sum_{n=1}^{\infty}\delta F^{(n)}, \quad (23)$$

where

$$\delta F^{(n)}=\epsilon^n\times 3\int_0^{z_L{}^0}dz\ \varphi'(z)\xi^{(n)}(z).$$

The factor three in the right-hand member of the above expression comes from the threefold degeneration of the perturbed levels. In particular

$$\delta F^{(1)}=\epsilon\int_0^{z_L{}^0}dz\ \varphi'(z)zG_0(z),$$

$$\delta F^{(2)}=\frac{\epsilon^2}{3}\int_0^{z_L{}^0}dz\ \varphi'(z)z^2G_0(z) \times P\int_0^{z_L{}^0}dz'(z-z')^{-1}G_0(z'). \quad (24)$$

The range of values of ϵ for which the expansion (23) converges to the exact expression (19′) is given by the two following conditions:

$$\left|\pi\frac{\frac{1}{3}z\epsilon G_0(z)}{1-\frac{1}{3}z\epsilon\tilde{G}_0(z)}\right|<1, \qquad |1-\tfrac{1}{3}z\epsilon\tilde{G}_0(z)|<1. \quad (24')$$

It would be interesting to compare (23) with the correspondent expression obtained by perturbative techniques. A perturbative expansion may be deduced from

$$\delta F=\frac{i}{2\pi}\oint_C\varphi(z)\ \mathrm{Sp}[(L+\Lambda-z)^{-1}-(L-z)^{-1}]dz, \quad (25)$$

expanding the inverse operator $(L+\Lambda-z)^{-1}$ in powers of the perturbation Λ. C is a counterclock-wise contour in the complex z-plane, enclosing all the eigenvalues of L and $L+\Lambda$, but none of the poles of $\varphi(z)$. Λ is defined by[6]

$$\Lambda\equiv\epsilon' L^{\frac{1}{2}}\Delta L^{\frac{1}{2}};\quad \epsilon'\equiv\epsilon/(1-\epsilon), \quad (26)$$

[6] See I. M. Lifshitz, reference 1.

where ϵ and Δ have been already defined. We expand

$$(L+\Lambda-z)^{-1}=\sum_{n=0}^{\infty}(-1)^n[(L-z)^{-1}\Lambda]^n(L-z)^{-1},$$

so that

$$(L+\Lambda-z)^{-1}-(L-z)^{-1}=-(L-z)^{-1}K(z)(L-z)^{-1},$$

where

$$K(z)\equiv\sum_{n=0}^{\infty}(-1)^n\Lambda[(L-z)^{-1}\Lambda]^n. \quad (27)$$

In the $|\mathbf{v}_s;\mathbf{k}\rangle$ representation, the matrix elements of Λ are

$$\langle\mathbf{k};\mathbf{v}_s|\Lambda|\mathbf{v}_{s'};\mathbf{k}'\rangle=\epsilon' N^{-1}\omega_{s,\mathbf{k}}\langle\mathbf{v}_{s,\mathbf{k}}|\mathbf{v}_{s',\mathbf{k}'}\rangle\omega_{s',\mathbf{k}'}. \quad (28)$$

Substitution of (28) in (27) gives:

$$\langle\mathbf{k};\mathbf{v}_s|K(z)|\mathbf{v}_{s'};\mathbf{k}'\rangle = \sum_{n=0}^{\infty}(-1)^n(\epsilon'/N)^{n+1}\omega_{s,\mathbf{k}'}\langle\mathbf{v}_{s,\mathbf{k}}|\sum_{s_1\cdots s_n}\sum_{\mathbf{k}_1\cdots\mathbf{k}_n}|\mathbf{v}_{s_1,\mathbf{k}_1}\rangle \times\omega_{s_1,\mathbf{k}_1}{}^2(\omega_{s_1;\mathbf{k}_1}{}^2-z)^{-1}\langle\mathbf{v}_{s_1,\mathbf{k}_1}|\cdots|\mathbf{v}_{s_n,\mathbf{k}_n}\rangle\omega_{s_n,\mathbf{k}_n}{}^2 \times(\omega_{s_n,\mathbf{k}_n}{}^2-z)^{-1}\langle\mathbf{v}_{s_n,\mathbf{k}_n}|\mathbf{v}_{s',\mathbf{k}'}\rangle\omega_{s',\mathbf{k}'}.$$

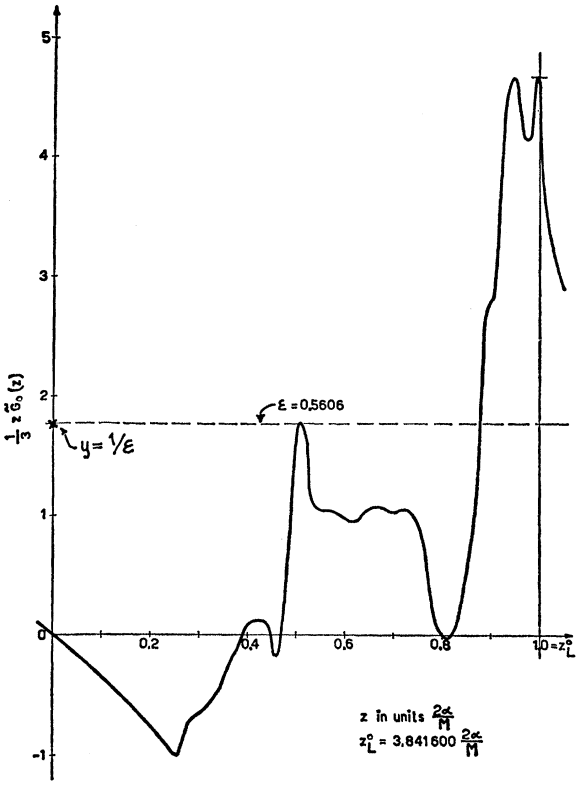

FIG. 3. Plot of $(1/3)z\tilde{G}_0(z)$.

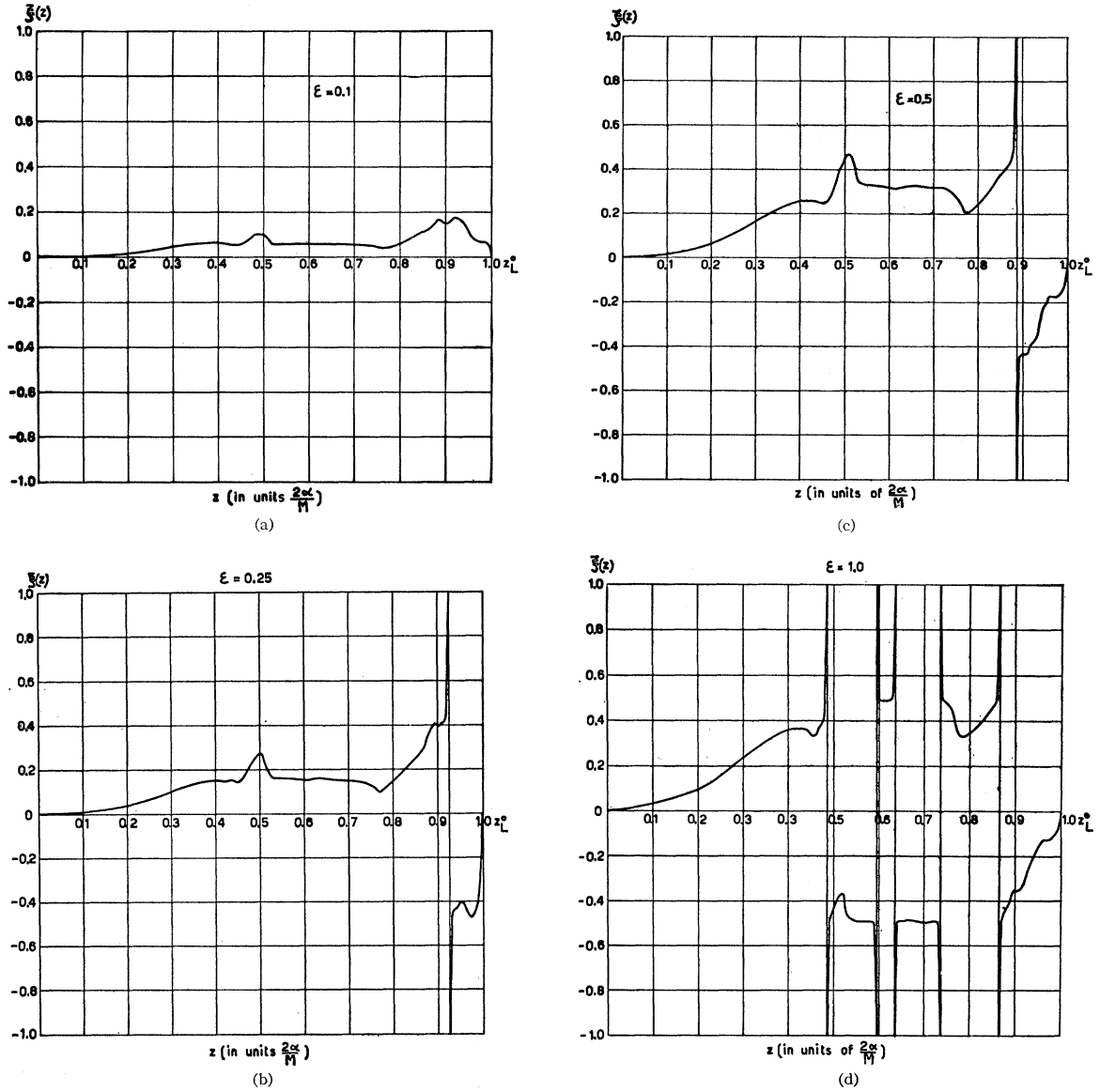

FIG. 4. Plot of $\xi(z)$ versus z, (a) for $\epsilon=0.1$; (b) for $\epsilon=0.25$; (c) for $\epsilon=0.5$; (d) for $\epsilon=1.0$.

As before, it is more convenient to work on the sequence of operators $K_\gamma(z)$:

$$K_\gamma(z)\equiv\sum_{n=0}^{\infty}(-1)^n\Lambda[(L_\gamma-z)^{-1}\Lambda]^n; \qquad (27')$$

we have:

$$\sum_{s=1}^{3}\sum_{\mathbf{k}}N^{-1}|\mathbf{v}_{s,\mathbf{k}}\rangle\omega_{s,\mathbf{k}}{}^2(\omega_{s,\mathbf{k}}{}^2-z)^{-1}\langle\mathbf{v}_{s,\mathbf{k}}| = \lim_{\gamma\to 0}\tfrac{1}{3}\sum_{i=0}^{N_\gamma}G_0(\lambda_i)\lambda_i(\lambda_i-z)^{-1}I,$$

where $NG_0(\lambda_i)$ is the degeneration factor of the λ_i eigenvalue, and we assume

$$\sum_{i=0}^{N_\gamma}G_0(\lambda_i)=3.$$

I is the unit operator in a three-dimensional space. The matrix elements of $K_\gamma(z)$ are then

$$\langle\mathbf{k};\mathbf{v}_s|K_\gamma(z)|\mathbf{v}_{s'};\mathbf{k}'\rangle = N^{-1}\epsilon'\omega_{s,\mathbf{k}}\langle\mathbf{v}_{s,\mathbf{k}}|\sum_{n=0}^{\infty}(-1)^n \times[\epsilon'(1-\tfrac{1}{3}z\sum_{i=0}^{N_\gamma}(z-\lambda_i)^{-1}G_0(\lambda_i))I]^n \times|\mathbf{v}_{s',\mathbf{k}'}\rangle\omega_{s',\mathbf{k}'}. \qquad (29)$$

The infinite series in the right-hand member of (29) may be summed, and the result is

$$\sum_{n=0}^{\infty}(-1)^n[\epsilon'(1-\tfrac{1}{3}z\sum_{i=0}^{N_\gamma}(z-\lambda_i)^{-1}G_0(\lambda_i))I]^n$$
$$=I\frac{1}{1+\epsilon'(1-\tfrac{1}{3}z\sum_{i=0}^{N_\gamma}(z-\lambda_i)^{-1}G_0(\lambda_i))}$$
$$=I\frac{\epsilon}{1-\tfrac{1}{3}z\epsilon\sum_{i=0}^{N_\gamma}(z-\lambda_i)^{-1}G_0(\lambda_i)}. \quad (30)$$

By use of (27′) and (30), the spur of the operator in the integrand of (25) is readily obtained; we have:

$$\mathrm{Sp}[(L_\gamma+\Lambda-z)^{-1}-(L_\gamma-z)^{-1}]$$
$$=-\mathrm{Sp}[(L_\gamma-z)^{-1}K_\gamma(z)(L_\gamma-z)^{-1}]$$
$$=-\sum_{j=0}^{N_\gamma}(\lambda_j-z)^{-2}\lambda_jG_0(\lambda_j)$$
$$\times\frac{\epsilon}{1-\tfrac{1}{3}z\epsilon\sum_{i=0}^{N_\gamma}(z-\lambda_i)^{-1}G_0(\lambda_i)}. \quad (31)$$

It is easy to see that the last expression in (31) behaves like

$$\sum_{j=0}^{N_\gamma}\frac{3}{z-(\lambda_j+\gamma\xi(\lambda_j))}-\sum_{j=0}^{N_\gamma}\frac{3}{z-\lambda_j}+R(z), \quad (32)$$

where $R(z)$ is a regular function, and $\xi(\lambda_j)$ are the roots ($j=0, \cdots, N_\gamma$) of

$$1-\tfrac{1}{3}z\epsilon\sum_{m=0}^{N_\gamma}(z-\lambda_m)^{-1}G_0(\lambda_m)=0, \quad (33)$$

when we put $z=\lambda_j+\gamma\xi(\lambda_j)$, and assume $|\xi|<\frac{1}{2}$ only for the values of λ_j which lie inside the continuous spectrum. Substitution of (32) in (25) gives

$$\delta F=\frac{1}{2\pi i}\oint_C\varphi(z)\Big\{\sum_{j=0}^{N_\gamma}\frac{3}{z-(\lambda_j+\gamma\xi(\lambda_j))}-\sum_{j=0}^{N_\gamma}\frac{3}{z-\lambda_j}+R(z)\Big\}dz$$
$$=\sum_{j=0}^{N_\gamma}3\varphi(\lambda_j+\gamma\xi(\lambda_j))-\sum_{j=0}^{N_\gamma}3\varphi(\lambda_j)$$
$$=3\sum_{j=0}^{(N_\gamma-1)}\varphi'(\lambda_j)\gamma\xi(\lambda_j)+3[\varphi(\bar{z})-\varphi(\lambda_{N_\gamma})].$$

Taking the limit for $\gamma\to 0$, we finally obtain

$$\delta F=3\int_0^{z_L^0}dz\,\varphi'(z)\xi(z)+3[\varphi(\bar{z})-\varphi(z_L^0)], \quad (34)$$

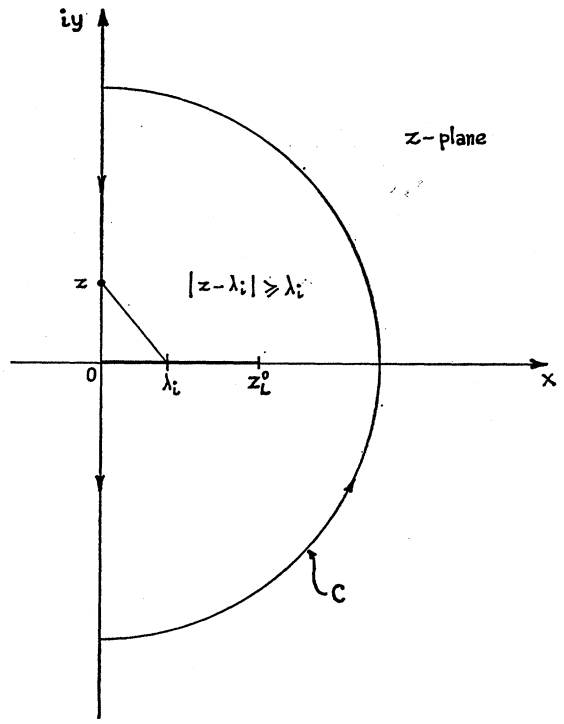

FIG. 5. Contour of integration in the z plane.

where $\bar{z}$ is the root of (33) lying outside the continuous spectrum. If one remembers that, in the present case, $\xi_1(z)=\xi_2(z)=\xi_3(z)$, (34) is seen to be nothing but the "Trace formula," (16).

In the derivation of (34) from (25), a critical point is the convergence of the infinite series in (29) to the analytical expression (30). If the contour of integration C in the complex plane is chosen as in Fig. 5, then for any point z on C we have

$$|1-\tfrac{1}{3}z\sum_{i=0}^{N_\gamma}(z-\lambda_i)^{-1}G_0(\lambda_i)|\leqslant 1,$$

and the critical point for the convergence lies at $z=0$, where the left-hand expression reaches unity. It follows that the above expansion converges to (30) if and only if

$$|\epsilon'|<1, \quad \text{or} \quad \left|\frac{\epsilon}{1-\epsilon}\right|<1. \quad (35)$$

For $\epsilon<0$, this condition is always fulfilled, while, for $\epsilon>0$, this condition holds for $\epsilon<\frac{1}{2}$.

On the other hand, substitution of (27′) in (25) gives

$$\delta F=\sum_{n=1}^{\infty}(\delta F^{(n)})_{\text{p.th.}}. \quad (36)$$

The right-hand member of (36) corresponds to an expansion in powers of ϵ'; its radius of convergence is $|\epsilon'|=1$. This corresponds to a range of values of ϵ which is always larger than the range given by (24′) for

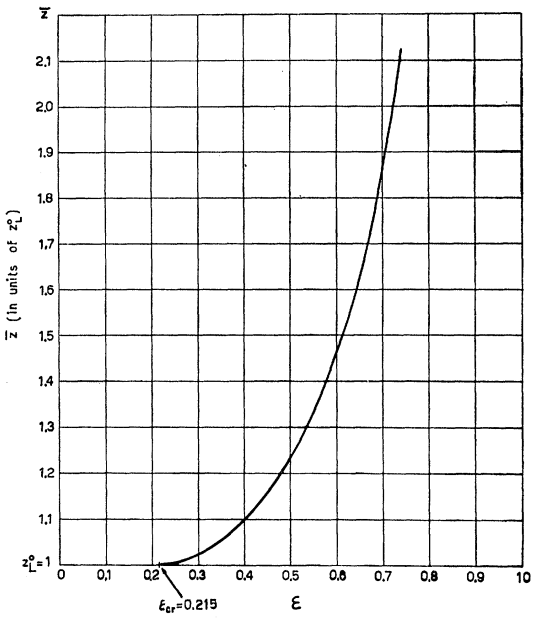

FIG. 6. Values of discrete frequency $\bar{z}$ vs values of ϵ.

the convergence of the analogous expansion (23) in powers of ϵ; one may conclude that (36) is a more useful expansion than (23). From (25), (27′), and (29) one obtains

$$\text{for } n=1, \quad (\delta F^{(1)})_{\text{p.th.}} = \epsilon' \int_0^{z_L^0} dz\, \varphi'(z) z G_0(z),$$

and,

$$\text{for } n=2, \quad (\delta F^{(2)})_{\text{p.th.}} = (\epsilon')^2 (1/3) \int_0^{z_L^0} dz\, \varphi'(z) z G_0(z) \times P \int_0^{z_L^0} dz'\, z'(z-z')^{-1} G_0(z'). \quad (37)$$

If one remembers the normalization condition for $G_0(z)$, these expressions are seen to be equivalent to (24) when powers of ϵ beyond the second are neglected.

6. APPLICATIONS

Expressions (13) and (18) solve the eigenvalues problem for a local change of mass in any monatomic cubic lattice. The solution is given in terms of the unperturbed distribution function for the square normal frequency. For numerical applications, the usefulness of the above expressions is limited by the uncertainty in our knowledge of the actual distribution function. The main difficulty concerns the principal-value integration of $(z-z')G_0(z')$; in fact, point discontinuities in the distribution function itself, or in its first derivative could affect to a large extent the value of the integral and then the denominator in the right-hand expression of (19); in this case new inversion points could occur. However, the change of extensive properties of the lattice is probably quite insensitive to this kind of effects. The present calculations are based on the distribution function plotted in Fig. 1, which was obtained by Overton and Dent[3] with the aid of an electronic computer for a fcc lattice with a twelve-nearest-neighbor central interaction. The intervals on the z axis are in units of $2\alpha/M$, where α is the force constant and M is the atomic mass. This distribution function corresponds to the superposition of three bands corresponding, respectively, to the two transverse and to the longitudinal modes of vibration.

We deduced $\tilde{G}_0(z)$ from $G_0(z)$ with the aid of a USS 90 Remington computer, dividing $(0, z_L^0)$ into hundred intervals and rectifying the profile of $G_0(z)$ by linear segments in every interval. The resulting curve is shown in Fig. 2.

a. Discrete Frequency

The discrete frequency is given by the root of (13) which lies outside the continuous spectrum; the value of ϵ_{cr} is found to be 0.215. In Table I the values of the discrete square-frequency (in units of z_L^0) are reported for some values of ϵ, and the curve discrete-frequency vs ϵ is plotted in Fig. 6. We note that for values of ϵ very close to $+1$ the square frequency approaches the asymptotic value $(1-\epsilon)^{-1}(4\alpha/M)$, which corresponds to the frequency of an uncoupled oscillator. For $\epsilon \to 1$ one obtains from (13) the asymptotic expression:

$$(\bar{z})_{\epsilon\to 1} \sim \frac{\epsilon}{1-\epsilon}(4\alpha/M); \quad (37)$$

therefore the Einstein approximation overestimates the discrete frequency.

b. Change of Extensive Properties

According to (15), (19′), and (13), the change of an extensive property is given by

$$\delta F = 3\int_0^{z_L^0} dz\, \varphi'(z)\xi(z) + 3[\varphi(\bar{z}) - \varphi(z_L^0)], \quad (38)$$

where $\bar{z}$ is the discrete square frequency. $\xi(z)$ depends on the value of ϵ; plots of $\xi(z)$ corresponding to $\epsilon=0.1$,

TABLE I. Discrete frequencies $\bar{z}$ (in units of z_L^0) for increasing values of ϵ.

$\bar{z}$	ϵ	$\bar{z}$	ϵ	$\bar{z}$	ϵ
1.000	0.2148	1.300	0.5361	2.200	0.7523
1.010	0.2756	1.350	0.5589	2.300	0.7642
1.020	0.2978	1.400	0.5792	2.400	0.7749
1.030	0.3159	1.500	0.6141	2.500	0.7848
1.040	0.3317	1.600	0.6432	3.000	0.8232
1.050	0.3459	1.700	0.6680	3.500	0.8500
1.100	0.4024	1.800	0.6893	4.000	0.8698
1.150	0.4454	1.900	0.7080		
1.200	0.4805	2.000	0.7245		
1.250	0.5103	2.100	0.7392		

TABLE II. Entropy of substitutional impurities of mass $M'=(1-\epsilon)M$.

	From the continuous spectrum	From the discrete frequency	Total	$\delta S/k$ Einstein approximation	Pert. theory[a] up to 2nd order	Pert. theory[b] up to 2nd order
$\epsilon=0.1$	−0.1578	···	−0.1578	−0.1580	−0.1575	−0.1574
$\epsilon=0.25$	−0.2437	−0.075	−0.3187	−0.4315	−0.4219	−0.4167
$\epsilon=0.5$	−0.5422	−0.3136	−0.8558	−1.0397	(−0.9375)[c]	(−0.7502)[c]
Loss of coupling ($\epsilon=1$)	Present calculation $\delta S/k=+0.978$			Huntington's estimate $\delta S/k=0.09$[d]		

[a] By use of (23) and (24).
[b] By use of (36) and (37).
[c] Parentheses are used when the perturbative expansion does not converge.
[d] See reference 2.

0.25, 0.50, 1.00 are shown in Fig. 4. $\xi(z)$ is a dimensionless function closely related to the structure of $G_0(z)$ which, in turn, depends essentially on the symmetries of the lattice. On the contrary, it does not depend on the physical constants of the lattice, i.e., the force constant α, or the atomic mass M, which give only the unit $(2\alpha/M)$ on the z scale. It then follows that the (classical) self-entropy of a substitutional impurity (neglecting the influence of the change in the local force constants) is given by a general expression which does not involve any physical constant of the lattice. The classical entropy $(T\to\infty)$ may be evaluated by use of

$$\varphi(z)\equiv\sigma(z)=-k\ln(\hbar z^{\frac{1}{2}}/kT), \tag{39}$$

where k is Boltzmann's constant and $\hbar$ is Planck's constant. We have from (38)

$$\delta S=-\tfrac{3}{2}k\int_0^{z_L{}^0}dz(1/z)\times\xi(z)-\tfrac{3}{2}k\ln(\bar{z}/z_L{}^0). \tag{38'}$$

Numerical results for $\epsilon=0.1$, 0.25, and 0.50 are reported in Table II; in the last three columns the changes of entropy according to either the Einstein approximation or the second-order perturbation theory are also reported.

c. Change of Entropy Due to the Loss of Coupling around a Vacancy

Some years ago, Huntington[2] suggested that the loss of coupling around a vacancy should not affect appreciably the self-entropy of the defect itself. On the basis of the above expressions it is now possible to estimate this contribution. When ϵ tends to unity, the discrete frequency approaches the Einstein frequency; this means that the lattice does not participate in the high-frequency localized vibrations. Let $S_0{}^{(N)}$ be the entropy of a perfect lattice of N particles, and $S_\epsilon{}^{(N)}$ be the entropy of the same lattice when one of the atomic masses is changed from M to $M'=(1-\epsilon)M$. From the above considerations it follows that $S_{\epsilon\to1}{}^{(N)}$ may be split as

$$S_{\epsilon\to1}{}^{(N)}=(S^{(N-1)})_{\text{hole}}+3\sigma(\bar{z}), \tag{40}$$

where $(S^{(N-1)})_{\text{hole}}$ does not depend on ϵ, and may be regarded as the entropy of a lattice of $N-1$ particles plus a vacant lattice site (regardless of the change in the force constants on the neighboring sites). One obtains:

$$\begin{aligned}(\delta S_h)_{\text{coupl}}&\equiv(S^{(N-1)})_{\text{hole}}-S_0{}^{(N-1)}\\&=3\int_0^{z_L{}^0}dz\,\sigma'(z)\xi_{\epsilon=1}(z)\\&\qquad+\int_0^{z_L{}^0}dz\,\sigma(z)G_0(z)-3\sigma(z_L{}^0)\\&=-\tfrac{3}{2}k\int_0^{z_L{}^0}dz\,z^{-1}\xi_{\epsilon=1}(z)\\&\qquad+\tfrac{1}{2}k\int_0^{z_L{}^0}dz\ln(z_L{}^0/z)G_0(z).\end{aligned} \tag{41}$$

The numerical result is reported on Table II.

7. COMMENTS

We have shown that the change of extensive properties of monatomic cubic lattices, as well as the discrete frequencies due to a local change of mass, can be evaluated by expressions (13), (15), (19′) involving only the distribution function $G_0(z)$ for the square frequency of the perfect lattice. This result follows from the point symmetries common to the cubic systems (sc, fcc, bcc), and its validity is subjected only to the reliability of the harmonic approximation of the interatomic potential.

The above theoretical expressions are found to be identical with those holding for linear chains, provided the distribution function $G_0(z)$ is normalized to one.

From Table II it appears that for $\epsilon>0.1$ both the perturbation theory and the Einstein approximation overestimate, in absolute value, the self-entropy of a substitutional impurity. Nevertheless the Einstein model gives a good estimate of the discrete frequency for very light substitutional impurity (i.e., $\epsilon\gtrsim0.9$), as can be seen from (37).

The last point treated here concerns the contribution to the self-entropy of a vacancy arising from the loss of coupling between the vacant site and the neighboring lattice sites. The method presented here gives this

entropic contribution when changes in the force constants are neglected at all. In a more realistic situation when both loss of coupling and elastic distortion are taken into account, it is not certain that the total self-entropy may be split into two terms which depend separately on these two kinds of perturbation. It then follows that our result cannot be added to the entropy change coming from the perturbation on the force constants only. From Table II, it appears that the present value is an order of magnitude higher than Huntington's previous estimate; this fact suggests that the usual calculations, which neglect the influence of the loss of coupling might underestimate the actual entropy of a vacancy in monatomic lattices.

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Temperature-Dependent Linewidth of Excited States in Crystals. I. Line Broadening due to Adiabatic Variation of the Local Fields*

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The effect of strains on the linewidth of the optical spectra of paramagnetic ions in ionic crystals is briefly discussed and applied to the ^2E state of ruby. A mechanism for the broadening of spectral lines in crystals at elevated temperatures is introduced. This mechanism assumes that the linewidth is due to "slow" variation in the local electric field of an individual ion. This theory should hold for states which do not interact with the crystal field to first order and is applied to the ^2E states of ruby. The agreement between theory and experiment is quite good.

A. INTRODUCTION

IT is well known that the linewidth of absorption and emission lines in paramagnetic solids is generally much larger than the inverse of the natural lifetime of these lines. This condition holds even when zero temperature is approached (0°K). To be sure, the linewidth tends to decrease with temperature at fairly high temperatures; but below some temperature, generally in the range 35–80°K, the decrease stops.

Recently Schawlow[1,2] and others have given some compelling evidence for the R_1 and R_2 lines of Cr^{3+}, that the residual linewidth is chiefly due to strains in the crystal. Strains in chromium-doped MgO have been discussed rather thoroughly in reference 2 with the conclusion that the low-temperature linewidth may be due to this cause.

Due to strains, different ions are subjected to different local crystalline fields. By annealing ruby and MgO crystals doped with Cr^{3+} the linewidth has been decreased by an order of magnitude. (Annealing can remove only macroscopic strains; that is, where many neighboring ions have identical fields but ions in distant parts of the crystal "see" different fields.) It is not clear whether the residual excess linewidth after annealing is due to remaining macroscopic strains, microscopic strains (differences in crystal field of neighboring Cr^{3+} ions) or other causes.

In the low-lying states of paramagnetic ions in crystals, the natural radiative linewidth is always negligible. However, nonradiative relaxations will often broaden lines when the states concerned interact directly with the lattice oscillators, and the energy separations are favorable. This broadening is the analog of spontaneous emission, with phonons replacing photons. As an example, it would be conceivable in ruby that the upper doublet of ^2E (the R_2 level, often designated $2A$) could be broadened by direct relaxation to the R_1 level ($\bar{E}$). This would require the spontaneous emission of phonons at low temperatures. That this does not occur is due to the fact that no vibrations couple $\bar{E}$ to $2A$ in first order. The higher order relaxation of $2A \rightarrow \bar{E}$ is discussed in reference 3.

In the rare earths, on the other hand, there are typically groups of closely spaced energy levels (the typical crystal field splitting of a Stark manifold $\sim$10–200 cm^{-1}) which are coupled directly by the crystal field. In such a case we expect direct relaxations within a Stark manifold to play a role in broadening of the lines. The $^4T_2$ state of ruby is another example of

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