

of velocity v has been estimated by Shockley¹¹ as

$$(m^*S^2/\tau_L)(m^*v^2/KT),$$

in which S is the velocity of sound and τ_L is the relaxation time for lattice scattering. When we average over the electrons in the band, we find an average energy loss for collisions with phonons, $\langle W_{ph}/\tau \rangle$

$$\langle W_{ph}/\tau \rangle = 3m^*S^2/\tau_L. \quad (18)$$

At 4°K, this loss rate is about 10^5 ev/sec. Evidently the molecular excitation process can be more important.

Since only electrons of relatively high energy are involved in the ionization process, and for these electrons the probability of energy loss by molecular excitation must be much greater than the probability of energy

gain by de-excitation, one would expect that, apart from factors of the order of unity, the cautionary statement in the previous paragraph could be discarded so that the ratio of the electric field strength at breakdown in the compensated material to that in the uncompensated samples will be about

$$[\langle W_x/\tau \rangle / \langle W_{ph}/\tau \rangle]^{1/2}.$$

It is seen, in agreement with the qualitative discussion of McWhorter and Rediker,³ that the molecular excitation mechanism considered here is capable of providing the factor of 10 to 30 increase in the breakdown field required by their experimental results.

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¹¹ W. Shockley, Bell System Tech. J. **30**, 990 (1951).

Velocity Shift of the Mössbauer Resonance

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The mean square velocity of an impurity atom in a crystal lattice has been evaluated in both the low and high temperature limits. The result for the high temperature limit includes the effect of force constant differences between solute and solvent atoms as well as the effect of mass difference. The effect of a mass difference alone is quite small in both the low temperature and high temperature regions. A determination of the Mössbauer peak position as a function of temperature in the high temperature range can be used to obtain a value of isomeric shift fully correct for the second order Doppler shift associated with the vibration of the atoms. In addition, if the experimental data are sufficiently precise, the effective stiffness with which the atoms are bound in the lattice may be determined. The calculation is illustrated with experimental data for Fe⁵⁷ dissolved in beryllium and in stainless steel.

INTRODUCTION

THE energies of the various gamma rays associated with the Mössbauer transitions in nuclei vary with the environment of the active atoms as a result of several types of interactions. These interactions fall into two classes: those which remove the m degeneracy of the nuclear levels, and those that change the mean separation between the excited and ground states. In the first class are those due to magnetic fields, which interact with the nuclear magnetic dipole moment, and to electric field gradients, which interact with the nuclear electric quadrupole moment. These effects have been treated at length elsewhere and will not be discussed here.^{1,2} In the second class are the isomeric shift and the second order Doppler shift. The isomeric shift arises from the electrostatic interaction between the nuclear charge distribution and the electronic charge density at

the nucleus. Since the nucleus charge distribution is different in the ground and excited states, this interaction changes the separation of the levels by an amount proportional to the effective electronic charge at the nucleus, which varies with the environment of the atom. The second order Doppler shift is a relativistic effect associated with the mass difference between ground and excited states, and the corresponding difference in kinetic energy. This paper is largely concerned with this latter shift, and the separation of it from the isomeric shift.

ISOMERIC SHIFT

The isomeric shift of the energy levels in either source or absorber nuclei is given approximately by³

$$\Delta E = \frac{2}{5}\pi ze^2\Delta\bar{R}^2|\psi(0)|^2,$$

where z is the atomic number, $\Delta\bar{R}^2$ is the change in

¹ S. S. Hanna, J. Heberle, C. Littlejohn, C. J. Perlow, R. S. Preston, and P. H. Vincent, Phys. Rev. Letters **4**, 177 (1960).

² O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

³ L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

square of proton radius from excited to ground state and $\psi(0)$ is the total wave function at the nucleus. Only the difference in shift between source and absorber atoms is directly observable, so that experimentally one obtains the product:

$$\Delta E' = \frac{2}{5}\pi z e^2 \Delta \bar{R}^2 [|\psi_a(0)|^2 - |\psi_e(0)|^2].$$

In the case of Fe^{57} the largest effect observed is of the order of 10^{-7} ev, for Fe^{++} in comparison with metallic iron. Using reasonable estimates for the change in wave functions at the nucleus, the apparent increase in the proton radius is of the order of 10^{-3} .⁴ In the absence of phase changes, the value of $\psi(0)$ should not change appreciably with temperature, so that the isomeric shift may usually be regarded as temperature independent. This makes it possible to separate the contributions of the isomeric shift and the second order Doppler shift.

SECOND ORDER DOPPLER SHIFT

The mass of the ground state of the nucleus differs from that of the excited state by an amount:

$$\Delta m = h\nu/c^2.$$

As a consequence, the kinetic energy of the emitting atom is increased, and the energy of the γ ray correspondingly decreased, by an amount⁵:

$$\Delta E = h\nu \langle v^2 \rangle / 2c^2,$$

where $\langle v^2 \rangle$ is the mean square velocity of the emitting atom. A corresponding shift occurs during the absorption process, so that any experiment measures only $\langle v_s^2 \rangle - \langle v_a^2 \rangle$. At reasonably high temperatures, however, $\langle v^2 \rangle$ can be predicted accurately, as discussed below. This makes it possible both to determine the isomeric shift difference between source and absorber, and to measure $\langle v^2 \rangle$ absolutely for either source or absorber at any temperature.

An approximate calculation of the mean square velocity of an impurity atom in a crystal has recently been carried out by Boyle *et al.*⁶

II. A ONE-DIMENSIONAL EXAMPLE

In order to fix our ideas and to serve as a guide for the more difficult three-dimensional calculations to follow, we present, in this section, a calculation of the mean-square velocity of an isotopic impurity atom in a one-dimensional lattice. We carry out a direct calculation of the velocity in this section to contrast this approach with the more powerful, but less direct techniques developed in the following section.

The equations of motion of the atoms in a linear chain of N atoms which contains an isotope impurity of mass

M' at the origin are

$$M\ddot{x}_n - \gamma(x_{n+1} - 2x_n + x_{n-1}) = (M - M')\delta_{n0}\ddot{x}_0; \\ n = -\frac{1}{2}N + 1, \dots, 0, \dots, \frac{1}{2}N. \quad (2.1)$$

We assume solutions of the form

$$x_n = u_n e^{-i\omega t}, \quad (2.2)$$

where it is understood that only the real part of the right-hand side has any physical significance. The equations for the time-independent amplitudes u_n become

$$Lu_n = M\omega^2 u_n + \gamma(u_{n+1} - 2u_n + u_{n-1}) = \epsilon M\omega^2 \delta_{n0} u_0, \quad (2.3)$$

where we have put

$$M' = (1 - \epsilon)M. \quad (2.4)$$

It is known⁷ that only the symmetric (i.e., $u_n = u_{-n}$) modes of the lattice are affected by the presence of the impurity, while the frequencies of the antisymmetric modes ($u_n = -u_{-n}$) are unchanged by the perturbation. However, each antisymmetric mode has a node at the position of the impurity atom so that the contribution of these modes to the mean square velocity of the impurity atom vanishes identically. In all that follows, therefore, we consider the contributions from the symmetric modes only.

Equations (2.3) can be solved formally if we introduce the Green's function $g(n)$ which satisfies the equation

$$Lg(n) = \delta_{n0} \quad (2.5)$$

and also the cyclic boundary condition

$$g(n+N) = g(n). \quad (2.6)$$

In terms of this function the solution of Eq. (2.3) is

$$u_n = \epsilon M\omega^2 g(n) u_0. \quad (2.7)$$

Since this solution is valid for all n it is valid for $n=0$, and we obtain the equation whose solutions are the normal frequencies of the perturbed lattice:

$$1 = \epsilon M\omega^2 g(0). \quad (2.8)$$

An explicit expression for $g(n)$ is⁷

$$g(n) = g(-n) = \frac{1}{N} \sum_{s=1}^N \frac{e^{(2\pi i s n / N)}}{M\omega^2 - 2\gamma + 2\gamma \cos(2\pi s / N)} \\ = \frac{1}{2\gamma \sin \phi} \left[\cot\left(\frac{N}{2}\phi\right) \cos n\phi + \sin(|n|\phi) \right], \quad (2.9)$$

where we have put

$$1 - M\omega^2 / 2\gamma = \cos \phi. \quad (2.10)$$

It will be convenient from time to time in what follows

⁴ S. De Benedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters **6**, 60 (1961).

⁵ B. D. Josephson, Phys. Rev. Letters **4**, 341 (1960).

⁶ A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, Proc. Phys. Soc. (London) **76**, 165 (1960).

⁷ R. F. Wallis and A. A. Maradudin, Progr. Theoret. Phys. **24**, 1055 (1960).

to rewrite Eq. (2.10) as

$$\omega^2/\omega_L^2 = f^2 = \sin^2(\phi/2), \quad (2.11)$$

where $\omega_L = (4\gamma/M)^{1/2}$ is the maximum frequency of the unperturbed lattice.

Since we are considering here only the symmetric modes, we restrict ϕ to lie in the interval $0 < \phi < \pi$, because we get no new normal modes in the interval $\pi < \phi < 2\pi$, and because the number of symmetric normal modes given by this restriction taken in conjunction with an equal number of anti-symmetric modes gives the correct total number of independent normal modes for the perturbed lattice.

Equations (2.8)–(2.10) lead to the following form for the eigenvalue equation

$$\tan(N\phi/2) = \epsilon \tan(\phi/2). \quad (2.12)$$

From Eq. (2.2) we see that the velocity of the n th atom is given by

$$v_n = \dot{x}_n = -i\omega u_n e^{-i\omega t} = -i\omega x_n, \quad (2.13)$$

so that

$$\langle v_n^2 \rangle_{\text{av}} = \langle (\text{Re} \dot{x}_n)^2 \rangle_{\text{av}} = \frac{1}{2} |\dot{x}_n|^2 = \frac{1}{2} \omega^2 |u_n|^2, \quad (2.14)$$

where we have used the fact that x_n and \dot{x}_n are real quantities, and $\langle \rangle_{\text{av}}$ means a time average over a time interval which is long on a microscopic scale, but short

on a macroscopic scale. Combining Eqs. (2.7) and (2.14) we find that

$$\begin{aligned} \langle v_n^2 \rangle_{\text{av}} &= \frac{1}{2} \omega^2 \epsilon^2 M^2 \omega^4 |g(n)|^2 |u_0|^2 \\ &= \epsilon^2 M^2 \omega^4 |g(n)|^2 \langle v_0^2 \rangle_{\text{av}}. \end{aligned} \quad (2.15)$$

The frequency ω which appears in this expression is any one of the $N/2$ distinct solutions of Eq. (2.8), and we indicate this by adding a subscript s , for the s th normal mode, to the relevant quantities in Eq. (2.15):

$$\langle v_n^2(s) \rangle_{\text{av}} = \epsilon^2 M^2 \omega_s^4 |g_s(n)|^2 \langle v_0^2(s) \rangle_{\text{av}}. \quad (2.16)$$

Equation (2.16) thus gives the mean-square velocity of the n th atom when it is vibrating in the s th normal mode. With the aid of this result we compute the mean kinetic energy of the s th normal mode:

$$\begin{aligned} T_s &= \frac{1}{2} \sum_{n=-\frac{1}{2}N+1}^{\frac{1}{2}N} M_n \langle v_n^2(s) \rangle_{\text{av}} = \frac{1}{2} (M' - M) \langle v_0^2(s) \rangle_{\text{av}} \\ &\quad + \frac{1}{2} M \sum_{n=-\frac{1}{2}N+1}^{\frac{1}{2}N} \langle v_n^2(s) \rangle_{\text{av}} \\ &= -\frac{1}{2} \epsilon M \langle v_0^2(s) \rangle_{\text{av}} \\ &\quad + \frac{1}{2} \epsilon^2 M^3 \omega_s^4 \langle v_0^2(s) \rangle_{\text{av}} \sum_{n=-\frac{1}{2}N+1}^{\frac{1}{2}N} |g_s(n)|^2. \end{aligned} \quad (2.17)$$

The sum in Eq. (2.17) is readily evaluated

$$\begin{aligned} \sum_{n=-\frac{1}{2}N+1}^{\frac{1}{2}N} |g_s(n)|^2 &= \frac{1}{N^2} \sum_{n=-\frac{1}{2}N+1}^{\frac{1}{2}N} \sum_{p,r} \frac{\exp[(2\pi i n/N)(p-r)]}{[M\omega_s^2 + 2\gamma - 2\gamma \cos(2\pi p/N)][M\omega_s^2 - 2\gamma + 2\gamma \cos(2\pi r/N)]} \\ &= \frac{1}{N} \sum_{p=1}^N \frac{1}{[M\omega_s^2 + 2\gamma - 2\gamma \cos(2\pi p/N)]^2} \\ &= \frac{1}{4\gamma^2 \sin^2 \phi_s} \left[\frac{N}{2} \csc^2 \left(\frac{N\phi_s}{2} \right) + \cot \left(\frac{N\phi_s}{2} \right) \cot \phi_s \right], \end{aligned} \quad (2.18)$$

in the notation of Eq. (2.10). We are thus led to the result that

$$\langle v_0^2(s) \rangle_{\text{av}} = T_s / \left\{ \frac{1}{2} \epsilon^2 M^3 \omega_s^4 \left[\frac{N}{2} \csc^2 \left(\frac{N\phi_s}{2} \right) + \cot \left(\frac{N\phi_s}{2} \right) \cot \phi_s \right] - \frac{1}{2} \epsilon M \right\}. \quad (2.19)$$

Since ϕ_s is not arbitrary but is a solution of Eq. (2.12) we can simplify Eq. (2.19) somewhat:

$$\langle v_0^2(s) \rangle_{\text{av}} = \frac{4}{NM} \frac{T_s}{1 + \epsilon^2 \tan^2(\phi_s/2) - (\epsilon/N)[1 + \tan^2(\phi_s/2)]}. \quad (2.20)$$

Furthermore, since we are working in the harmonic approximation, the expression for T_s is well known,

$$T_s = \frac{1}{4} \hbar \omega_s \coth(\hbar \omega_s / 2kT). \quad (2.21)$$

The final expression for the mean-square velocity of the impurity atom is obtained by summing Eq. (2.20) over

all the perturbed (i.e., symmetric) normal modes,

$$\langle v_0^2 \rangle = \frac{\hbar}{NM} \sum_s \frac{\omega_s \coth(\hbar \omega_s / 2kT)}{1 + \epsilon^2 \tan^2(\phi_s/2) - (\epsilon/N)[1 + \tan^2(\phi_s/2)]} \quad (2.22)$$

and we are left with this sum to evaluate.

We have not as yet considered the contribution from the localized mode of vibration which appears when $0 < \epsilon < 1$. It arises as the solution of Eq. (2.12) for complex ϕ . Putting

$$\phi = \pi + iz, \quad (2.23)$$

Eq. (2.12) becomes

$$\epsilon \coth(z/2) = 1 \quad \text{as } N \rightarrow \infty \quad (2.24)$$

and has the solution

$$z = \ln \frac{1+\epsilon}{1-\epsilon}. \quad (2.25)$$

With this result the square of the localized defect mode frequency becomes

$$f_d^2 = 1/(1-\epsilon^2). \quad (2.26)$$

Since we have from Eq. (2.11) that

$$\tan^2(\phi_s/2) = f_s^2/(1-f_s^2), \quad (2.27)$$

combining Eqs. (2.22), (2.26) and (2.27) gives us as the contribution to $\langle v_0^2 \rangle$ from the localized defect mode

$$\langle v_0^2 \rangle = \frac{\hbar\omega_L}{M} \left[\epsilon \coth \left(\frac{\hbar\omega_L}{2kT} \frac{1}{(1-\epsilon^2)^{1/2}} \right) \right] / (1-\epsilon^2)^{1/2}, \quad 0 < \epsilon < 1. \quad (2.28)$$

We now return to the evaluation of the sum in Eq. (2.22). For this purpose we need the values of ϕ_s for the perturbed lattice. As we have remarked earlier, they are the solutions to Eq. (2.12). It follows from Rayleigh's theorems,⁸ or alternatively from plotting the right- and left-hand sides of this equation as functions of ϕ , that the new values of ϕ_s are shifted from the unperturbed values,

$$\phi_s^{(0)} = 2\pi s/N, \quad (2.29)$$

by less than the distance to the next unperturbed value. This enables us to solve Eq. (2.12) by successive approximations. If we put

$$\phi_s = \phi_s^{(0)} + \delta_s, \quad (2.30)$$

where

$$|\delta_s| < 2\pi/N,$$

and expand ϕ_s in inverse powers of N , we obtain the result that to lowest order

$$\phi_s = \frac{2\pi s}{N} + \frac{2}{N} \tan^{-1} \left[\epsilon \tan \frac{\pi s}{N} \right] + o(N^{-1}). \quad (2.31)$$

We note that the second term is always of order N^{-1} smaller than the first term: for s small,

$$\phi_s \sim 2\pi s/N + 2\epsilon\pi s/N^2 + \dots;$$

for s close to $N/2$,

$$\phi_s \sim \pi + \pi/N + \dots.$$

These results mean that with an error of $O(N^{-1})$ in the final result we can replace ϕ_s in the summand of Eq. (2.22) by $\phi_s^{(0)}$. With this approximation we have

$$\langle v_0^2 \rangle_i = \frac{\hbar\omega_L}{\pi M} \int_0^{\pi/2} \frac{\coth(\hbar\omega_L \sin\theta/2kT) \cos^2\theta \sin\theta}{\epsilon^2 + (1-\epsilon^2) \cos^2\theta} d\theta, \quad (2.32)$$

where the subscript i denotes that this expression gives the contribution to $\langle v_0^2 \rangle$ from the in-band modes, and where we have omitted terms of order N^{-1} . This integral simplifies in two cases. At the absolute zero we have

$$\begin{aligned} \langle v_0^2 \rangle_i &= \frac{\hbar\omega_L}{\pi M} \int_0^{\pi/2} \frac{\cos^2\theta \sin\theta d\theta}{\epsilon^2 + (1-\epsilon^2) \cos^2\theta} \\ &= \frac{\hbar\omega_L}{\pi M} \left[\frac{1}{1-\epsilon^2} - \frac{|\epsilon|}{(1-\epsilon^2)^{3/2}} \tan^{-1} \left(\frac{(1-\epsilon^2)^{1/2}}{|\epsilon|} \right) \right], \quad 0 < \epsilon^2 < 1 \\ &= \frac{\hbar\omega_L}{\pi M} \left[\frac{|\epsilon|}{(\epsilon^2-1)^{3/2}} \tanh^{-1} \left(\frac{(\epsilon^2-1)^{1/2}}{|\epsilon|} \right) - \frac{1}{\epsilon^2-1} \right], \quad \epsilon^2 > 1. \end{aligned} \quad (2.33)$$

In the high-temperature limit we find

$$\begin{aligned} \langle v_0^2 \rangle_i &= \frac{\hbar\omega_L}{\pi M} \int_0^{\pi/2} \frac{(2kT/\hbar\omega_L) \cos^2\theta + \frac{1}{3}(\hbar\omega_L/2kT) \cos^2\theta \sin^2\theta + \dots}{\epsilon^2 + (1-\epsilon^2) \cos^2\theta} d\theta \\ &= \frac{kT}{M} \frac{1}{1+|\epsilon|} + \frac{\hbar\omega_L}{6kT} \frac{\hbar\omega_L}{M} \left[\frac{1}{4} \frac{1}{(1+|\epsilon|)^2} \right] + O(T^{-3}), \quad 0 < \epsilon^2 < 1, \quad 1 < \epsilon^2. \end{aligned} \quad (2.34)$$

These results must be combined with the contribution from the localized mode (for $0 < \epsilon < 1$) to give the final

⁸ Lord Rayleigh, *Theory of Sound* (Dover Publications, Inc., New York, 1945), Chap. IV.

results:

0°K:

$$\begin{aligned} \langle v_0^2 \rangle &= \frac{\hbar\omega_L}{\pi M} \left\{ \frac{1}{1-\epsilon^2} - \frac{\epsilon}{(1-\epsilon^2)^{3/2}} \right. \\ &\quad \times \tan^{-1} \left(\frac{(1-\epsilon^2)^{1/2}}{\epsilon} \right) + \frac{\pi\epsilon}{(1-\epsilon^2)^{3/2}} \left. \right\}, \quad 0 \leq \epsilon \leq 1 \\ &= \frac{\hbar\omega_L}{\pi M} \left\{ \frac{1}{1-\epsilon^2} - \frac{|\epsilon|}{(1-\epsilon^2)^{3/2}} \tan^{-1} \left(\frac{(1-\epsilon^2)^{1/2}}{|\epsilon|} \right) \right\}, \\ &\quad -1 \leq \epsilon \leq 0 \\ &= \frac{\hbar\omega_L}{\pi M} \left\{ \frac{|\epsilon|}{(\epsilon^2-1)^{3/2}} \tanh^{-1} \left(\frac{(\epsilon^2-1)^{1/2}}{|\epsilon|} \right) - \frac{1}{\epsilon^2-1} \right\}, \\ &\quad \epsilon \leq -1; \quad (2.35) \end{aligned}$$

$T \rightarrow \infty$:

$$\begin{aligned} \langle v_0^2 \rangle &= \frac{kT}{M} \frac{1}{1-\epsilon} + \frac{(\hbar\omega_L)^2}{24MkT} \frac{1}{(1-\epsilon)^2} + \dots, \quad 0 \leq \epsilon \leq 1 \\ &= \frac{kT}{M} \frac{1}{1+|\epsilon|} + \frac{(\hbar\omega_L)^2}{24MkT} \frac{1}{(1+|\epsilon|)^2} + \dots, \\ &\quad \epsilon \leq 0. \quad (2.36) \end{aligned}$$

We can condense both expressions in the high-temperature limit to

$$\langle v_0^2 \rangle = \frac{kT}{M'} + \frac{(\hbar\omega_L)^2}{24M'kT} \frac{M}{M'} + O(T^{-3}). \quad (2.37)$$

These results must be compared with the corresponding results for the mean square velocity of an atom in a perfect lattice:

$$\begin{aligned} 0^\circ\text{K}: \quad \langle v_0^2 \rangle &= \frac{\hbar\omega_L}{\pi M}, \\ T \rightarrow \infty: \quad \langle v_0^2 \rangle &= \frac{kT}{M} + \frac{(\hbar\omega_L)^2}{24MkT} + \dots \end{aligned} \quad (2.38)$$

In the low, but finite, temperature limit the temperature-dependent part of Eq. (2.32) becomes

$$\langle v_0^2 \rangle_T = \frac{2\hbar\omega_L}{\pi M} \sum_{n=1}^{\infty} \int_0^{\pi/2} \frac{e^{-n(\hbar\omega_L/kT) \sin\theta} \cos^2\theta \sin\theta}{\epsilon^2 + (1-\epsilon^2) \cos^2\theta} d\theta. \quad (2.39)$$

Since we are assuming that $kT \ll \hbar\omega_L$, we can use Laplace's method⁹ to evaluate this integral. We find that the leading two terms in the expansion of $\langle v_0^2 \rangle_T$ in

powers of the temperature are given by ($x = n\hbar\omega_L/kT$)

$$\begin{aligned} \langle v_0^2 \rangle_T &\sim \frac{2\hbar\omega_L}{\pi M} \sum_{n=1}^{\infty} \int_0^{\infty} e^{-x\theta} \left[\theta - \left(\frac{1}{6} + \epsilon^2\right)\theta^3 + \frac{x}{6}\theta^4 + \dots \right] d\theta \\ &= \frac{2\hbar\omega_L}{\pi M} \left\{ \frac{\pi^2}{6} \left(\frac{kT}{\hbar\omega_L} \right)^2 \right. \\ &\quad \left. - \frac{\pi^4}{90} \left(\frac{kT}{\hbar\omega_L} \right)^4 (3-6\epsilon^2) + O(T^6) \right\}. \quad (2.40) \end{aligned}$$

This result is valid for all $\epsilon < 1$. Furthermore, since the contribution from the localized mode (for $0 < \epsilon < 1$) is exponentially small in this temperature range, Eq. (2.40) gives the entire temperature-dependent contribution to $\langle v_0^2 \rangle$. We note that the leading temperature-dependent term is unaffected by the mass difference.

III. GENERAL FORMULATION OF THE PROBLEM

The method used in the preceding section to evaluate $\langle v_0^2 \rangle$ is practical for one-dimensional models because of the possibility of evaluating the Green's function, Eq. (2.9), in closed form. This has not proven to be the case thus far for three-dimensional models, although approximate methods for evaluating the analogous sum have been suggested.¹⁰ This means that if any progress is to be made in evaluating the mean-square velocity of an impurity atom in a three-dimensional lattice a more powerful and general approach must be used. In this section we present such an approach.

It is a basic result of quantum statistical mechanics that the expectation value of any operator O in the canonical ensemble is given by

$$\langle O \rangle = \text{Tr} e^{-\beta H} O / \text{Tr} e^{-\beta H}, \quad (3.1)$$

where H is the Hamiltonian for the system described by the ensemble.

We take for our system of interest a crystal, one of whose atoms is replaced by an impurity atom whose mass differs from that of the atom it replaces, and whose potential of interaction with the remaining atoms differs from that of the normal atom at that site. The Hamiltonian for the perturbed crystal takes the form

$$H = \sum_{l\alpha} \frac{(p_{\alpha}^l)^2}{2M_{\alpha}^l} + V = T + V, \quad (3.2)$$

where p_{α}^l is the α Cartesian component of the momentum of the κ th atom in the l th unit cell, and is related to the displacement amplitude u_{α}^l by

$$p_{\alpha}^l = M_{\alpha}^l \dot{u}_{\alpha}^l. \quad (3.3)$$

M_{α}^l is the mass of the κ th atom in the l th unit cell, and

⁹ A. Erdelyi, *Asymptotic Expansions* (Dover Publications, Inc., New York, 1956), p. 36.

¹⁰ M. Lax, *Phys. Rev.* **94**, 1391 (1954).

V is the potential energy of the lattice. V contains the effects of any force constant changes associated with the introduction of the impurity. In the perfect crystal M_{κ}^l is independent of l due to the perfect periodicity of the crystal. If we locate the impurity atom in the cell $l=0$ and assume (with no loss of generality) that it is the atom labeled by $\kappa=1$ in this cell, then we can rewrite the kinetic energy operator of the crystal as

$$T = \left(\frac{1}{2M_1^{(0)}} - \frac{1}{2M_1} \right) (\mathbf{p}_1^{(0)})^2 + \sum_{l\kappa} \frac{(\mathbf{p}_{\kappa}^l)^2}{2M_{\kappa}}. \quad (3.4)$$

This expression is an identity. In the second term of this equation we have dropped the now superfluous super-

script l on the masses. If we denote $M_1^{(0)}$ by

$$M_1^{(0)} = (1-\epsilon)M_1, \quad (3.5)$$

we can rewrite Eq. (3.4) as

$$T = \frac{\epsilon}{1-\epsilon} \frac{(\mathbf{p}_1^{(0)})^2}{2M_1} + \sum_{l\kappa} \frac{(\mathbf{p}_{\kappa}^l)^2}{2M_{\kappa}}. \quad (3.6)$$

The operator O in our case is

$$O = (\dot{u}_1^{(0)})^2 = \frac{(\mathbf{p}_1^{(0)})^2}{(M_1^{(0)})^2} = \frac{2}{M_1(1-\epsilon)^2} \frac{(\mathbf{p}_1^{(0)})^2}{2M_1}, \quad (3.7)$$

so that Eq. (3.1) becomes

$$\begin{aligned} \langle (\dot{u}_1^{(0)})^2 \rangle &= \frac{2}{M_1(1-\epsilon)^2} \left\{ \text{Tr} \left[\exp \left(-\beta \frac{\epsilon}{1-\epsilon} \frac{(\mathbf{p}_1^{(0)})^2}{2M_1} - \beta \sum_{l\kappa} \frac{(\mathbf{p}_{\kappa}^l)^2}{2M_{\kappa}} - \beta V \right) \right] \frac{(\mathbf{p}_1^{(0)})^2}{2M_1} \right\} / \\ &= -\frac{1}{\beta} \frac{2}{M_1(1-\epsilon)^2} \frac{d}{d[\epsilon/(1-\epsilon)]} \ln \text{Tr} \left\{ \exp \left[-\beta \frac{\epsilon}{1-\epsilon} \frac{(\mathbf{p}_1^{(0)})^2}{2M_1} - \beta \sum_{l\kappa} \frac{(\mathbf{p}_{\kappa}^l)^2}{2M_{\kappa}} - \beta V \right] \right\} \\ &= \frac{2}{M_1} \frac{d}{d\epsilon} \left\{ -\frac{1}{\beta} \ln \text{Tr} \left[\exp \left(-\beta \frac{\epsilon}{1-\epsilon} \frac{(\mathbf{p}_1^{(0)})^2}{2M_1} - \beta \sum_{l\kappa} \frac{(\mathbf{p}_{\kappa}^l)^2}{2M_{\kappa}} - \beta V \right) \right] \right\} \\ &= \frac{2}{M_1} \frac{d}{d\epsilon} F(\epsilon, T), \end{aligned} \quad (3.8)$$

where $F(\epsilon, T)$ is the Helmholtz free energy of the perturbed crystal. The free energy can be written as the sum of two contributions,

$$F = F_0(T) + \Delta F(\epsilon, T), \quad (3.9)$$

where $F_0(T)$ is the free energy of the unperturbed crystal, and $\Delta F(\epsilon, T)$ is the change in the crystal's free energy due to the introduction of the impurity. $\Delta F(\epsilon, T)$ depends on both the parameter ϵ , which characterizes the mass change, and on the parameters which characterize the force constant changes as well, although we have indicated only the former dependence explicitly. We thus arrive at the result that the mean square velocity of the impurity atom is given by

$$\langle (\mathbf{v}_1^{(0)})^2 \rangle = \frac{2}{M_1} \frac{d}{d\epsilon} \Delta F(\epsilon, T). \quad (3.10)$$

$$\begin{aligned} \langle (\mathbf{v}_{\kappa}^{(0)})^2 \rangle &= \left[\int_{-\infty}^{\infty} \cdots \int \frac{(\mathbf{p}_{\kappa}^{(0)})^2}{(M_{\kappa}^{(0)})^2} \exp \left(-\beta \sum_{l\kappa} \frac{(\mathbf{p}_{\kappa}^l)^2}{2M_{\kappa}^l} - \beta V \right) \prod_{l\kappa} d^3 \mathbf{p}_{\kappa}^l d^3 \mathbf{u}_{\kappa}^l \right] / \\ &\quad \left[\int_{-\infty}^{\infty} \cdots \int \exp \left(-\beta \sum_{l\kappa} \frac{(\mathbf{p}_{\kappa}^l)^2}{2M_{\kappa}^l} - \beta V \right) \prod_{l\kappa} d^3 \mathbf{p}_{\kappa}^l d^3 \mathbf{u}_{\kappa}^l \right], \end{aligned} \quad (3.11)$$

¹¹ J. Mahanty, A. A. Maradudin, and G. H. Weiss, *Progr. Theoret. Phys.* **20**, 369 (1958). See also, K. Yamahuzi and T. Tanaka, *Progr. Theoret. Phys.* **20**, 327 (1958); O. Litzman, *Czech. J. Phys.* **9**, 692 (1959); I. M. Lifshitz, *Suppl. Nuovo cimento* **3**, 716 (1956), and references contained therein.

where by V we denote the potential energy of the crystal. V includes the effects of any force constant changes. It is not necessary to express H in terms of normal coordinates, although in practice it is convenient to do so, since the $\{p_{\alpha k}^l\}$ and $\{u_{\alpha k}^l\}$ are conjugate variables. The integrations over coordinates and momenta factor and we can divide out the coordinate integrations since they are common to both the numerator and denominator. Similarly all but one of the momentum integrations cancel between the numerator and denominator and we are left with

$$\begin{aligned} \langle (v_k^{(0)})^2 \rangle &= \frac{1}{M_k^{(0)2}} \left\{ \left[\int_{-\infty}^{\infty} (\mathbf{p}_k^{(0)})^2 \exp\left(-\beta \frac{(\mathbf{p}_k^{(0)})^2}{2M_k^{(0)}}\right) d^3\mathbf{p}_k^{(0)} \right] \right. \\ &\quad \left. / \left[\int_{-\infty}^{\infty} \exp\left(-\beta \frac{(\mathbf{p}_k^{(0)})^2}{2M_k^{(0)}}\right) d^3\mathbf{p}_k^{(0)} \right] \right\} \\ &= (3/M_k^{(0)})kT. \end{aligned} \quad (3.12)$$

Thus in the classical limit the mean-square velocity of any atom is a function of only the mass of the atom (apart from its temperature dependence), and the truth of the original assertion follows directly. For obvious reasons we can call the result expressed by Eq. (3.12) the "equipartition value" of $\langle v_0^2 \rangle$.

We conclude this section with an illustration of the application of Eq. (3.10) in a simple one-dimensional example. In reference 11 it has been shown that the change in the high-temperature free-energy of a linear chain of atoms due to the replacement of a normal atom of mass M by an impurity atom whose mass is M' and whose force constants γ of its interaction with its nearest neighbors are altered to γ' is given by

$$\begin{aligned} \Delta F(T) &= \frac{kT}{2} \ln \frac{P^2}{Q} + \hbar\omega_L \left\{ \frac{1}{24} \left[\frac{P}{2} \left(\frac{Q+1}{Q} \right) - 1 \right] \left(\frac{\hbar\omega_L}{kT} \right) \right. \\ &\quad \left. - \frac{1}{2880} \left[\frac{P^2}{4} \left(\frac{Q+1}{Q^2} \right) + \frac{1}{8} (1+P)^2 - 1 \right] \right. \\ &\quad \left. \times \left(\frac{\hbar\omega_L}{kT} \right)^3 + \dots \right\}. \end{aligned} \quad (3.13)$$

In this equation $P = (\gamma'/\gamma)$ and $Q = (M'/M) = 1 - \epsilon$. From Eq. (3.13) we obtain the result that in the high-temperature limit

$$\begin{aligned} \langle v_0^2 \rangle &= \frac{kT}{MQ} + \frac{\hbar\omega_L}{M} \left\{ \frac{1}{24} \left(\frac{P}{Q^2} \right) \left(\frac{\hbar\omega_L}{kT} \right) \right. \\ &\quad \left. - \frac{1}{2880} \left[\frac{P^2}{2} \frac{2+Q}{Q^3} \right] \left(\frac{\hbar\omega_L}{kT} \right)^3 + \dots \right\}. \end{aligned} \quad (3.14)$$

Note that the change in force constants already affects the leading correction term to the equipartition result.

This result, Eq. (3.14), reduces to the one obtained in the last section, Eq. (2.37), when P is set equal to unity.

Although the change in the zero-point energy of the lattice due to such an impurity has been evaluated in closed form¹¹ the result is very cumbersome, and is even more so after differentiation with respect to ϵ . As a consequence we omit a discussion of the low-temperature result for $\langle v_0^2 \rangle$.

IV. A MASS-DEFECT IN A THREE-DIMENSIONAL CRYSTAL

The $3sN$ equations of motion of a three-dimensional lattice containing N unit cells can be written as

$$\begin{aligned} M_\kappa \ddot{u}_{\alpha\kappa}^l &= - \sum_{l'\beta\kappa'} \Phi_{\alpha\beta} \left(\frac{l'}{\kappa\kappa'} \right) u_{\beta\kappa'}^{l'}; \\ \alpha, \beta &= x, y, z; \quad \kappa, \kappa' = 1, 2, \dots, s, \end{aligned} \quad (4.1)$$

where $u_{\alpha\kappa}^l$ is the α component of the displacement from equilibrium of the κ th atom in the l th unit cell ($\kappa=1, 2, \dots, s$), M_κ is the mass of the κ th kind of atom, and

$$\Phi_{\alpha\beta} \left(\frac{l'}{\kappa\kappa'} \right)$$

are general force constants of the lattice.

We pick our origin at an atom corresponding to $\kappa=1$ and perturb the lattice by replacing that atom by one whose mass is M_1' . The perturbed equations of motion are

$$M_\kappa \ddot{u}_{\alpha\kappa}^l + \sum_{l'\beta\kappa'} \Phi_{\alpha\beta} \left(\frac{l'}{\kappa\kappa'} \right) u_{\beta\kappa'}^{l'} = (M_\kappa - M_1') \ddot{u}_{\alpha\kappa}^l \delta_{l0} \delta_{\kappa 1}. \quad (4.2)$$

We now introduce (time-dependent) normal coordinates $Q(\mathbf{k}j)$ through the transformation

$$u_{\alpha\kappa}^l = \frac{1}{(NM_\kappa)^{1/2}} \sum_{\mathbf{k}j} e_{\alpha}(\kappa|\mathbf{k}j) Q(\mathbf{k}j) e^{2\pi i \mathbf{k} \cdot \mathbf{x}(l)}, \quad (4.3)$$

where $\mathbf{e}(\kappa|\mathbf{k}j)$ is an eigenvector of the unperturbed dynamical matrix and $\mathbf{x}(l)$ is the position vector of the l th unit cell in the crystal. The N values of the wave vector \mathbf{k} allowed by the cyclic boundary conditions are uniformly distributed throughout the first Brillouin zone of the lattice, and j labels the $3s$ branches of the frequency spectrum.

$Q(\mathbf{k}j)$ satisfies the reality condition

$$Q(\mathbf{k}j) = Q^*(-\mathbf{k}j), \quad (4.4)$$

and has a harmonic time dependence

$$\ddot{Q}(\mathbf{k}j + \omega^2) Q(\mathbf{k}j) = 0. \quad (4.5)$$

If we substitute Eq. (4.3) into Eq. (4.2) we arrive at

the result that

$$\begin{aligned} \omega^2 \sum_j e_\alpha(\kappa | \mathbf{k}' j) Q(\mathbf{k}' j) \\ - \sum_{\beta \kappa'} D_{\alpha\beta}(\mathbf{k}' | \kappa \kappa') \sum_j e_\beta(\kappa' | \mathbf{k}' j) Q(\mathbf{k}' j) \\ = (M_\kappa - M_{\kappa'}) \frac{1}{NM_\kappa} \sum_j e_\alpha(\kappa | \mathbf{k} j) \omega^2 Q(\mathbf{k} j), \end{aligned} \quad (4.6)$$

where we have introduced the elements of the dynamical matrix

$$D_{\alpha\beta}(\mathbf{k} | \kappa \kappa') = \frac{1}{(M_\kappa M_{\kappa'})^{\frac{1}{2}}} \sum_{\tilde{l}} \Phi_{\alpha\beta} \left(\frac{\tilde{l}}{\kappa \kappa'} \right) e^{-2\pi i \mathbf{k} \cdot \mathbf{x}(\tilde{l})}, \quad (4.7)$$

where $\tilde{l} = l - l'$. The eigenvectors and eigenvalues of the dynamical matrix are defined by

$$\sum_{\beta \kappa'} D_{\alpha\beta}(\mathbf{k} | \kappa \kappa') e_\beta(\kappa' | \mathbf{k} j) = \omega_j^2(\mathbf{k}) e_\alpha(\kappa | \mathbf{k} j) \quad (4.8)$$

and satisfy the conditions

$$\sum_{\alpha \kappa} e_\alpha^*(\kappa | \mathbf{k} j) e_\alpha(\kappa | \mathbf{k} j') = \delta_{jj'}, \quad (4.9)$$

$$\sum_j e_\alpha^*(\kappa | \mathbf{k} j) e_\beta(\kappa' | \mathbf{k} j) = \delta_{\alpha\beta} \delta_{\kappa\kappa'}. \quad (4.10)$$

In view of these conditions we can write Eq. (4.6) as

$$\begin{aligned} \sum_j [\omega^2 - \omega_j^2(\mathbf{k}')] e_\alpha(\kappa | \mathbf{k}' j) Q(\mathbf{k}' j) \\ = \frac{(M_\kappa - M_{\kappa'}) \omega^2}{M_\kappa} \frac{\delta_{\kappa 1}}{N} \sum_j e_\alpha(\kappa | \mathbf{k} j) Q(\mathbf{k} j). \end{aligned} \quad (4.11)$$

If we multiply both sides of this equation by $e_\alpha^*(\kappa | \mathbf{k}' j')$ and sum over α and κ , in view of Eq. (4.9) we obtain finally

$$\begin{aligned} Q(\mathbf{k}' j') &= \frac{\omega^2}{\omega^2 - \omega_{j'}^2(\mathbf{k}')} \sum_{\alpha \kappa} \sum_j \frac{(M_\kappa - M_{\kappa'})}{M_\kappa} \frac{\delta_{\kappa 1}}{N} \\ &\quad \times e_\alpha^*(\kappa | \mathbf{k}' j') e_\alpha(\kappa | \mathbf{k} j) Q(\mathbf{k} j) \\ &= \frac{\omega^2}{\omega^2 - \omega_{j'}^2(\mathbf{k}')} \sum_{\alpha \kappa} \frac{(M_\kappa - M_{\kappa'})}{(NM_\kappa)^{\frac{1}{2}}} \delta_{\kappa 1} \\ &\quad \times e_\alpha^*(\kappa | \mathbf{k}' j') u_{\alpha\kappa}^{(0)}. \end{aligned} \quad (4.12)$$

Substituting this result back into Eq. (4.3) leads to the result that

$$\begin{aligned} u_{\alpha\kappa}^{(l)} &= \sum_{\beta \kappa'} \left\{ \frac{1}{N(M_\kappa M_{\kappa'})^{\frac{1}{2}}} \sum_j \frac{e_\alpha(\kappa | \mathbf{k} j) e_\beta^*(\kappa' | \mathbf{k} j)}{\omega^2 - \omega_j^2(\mathbf{k})} e^{2\pi i \mathbf{k} \cdot \mathbf{x}(l)} \right\} \\ &\quad \times (M_{\kappa'} - M_{\kappa'}) \omega^2 \delta_{\kappa' 1} u_{\beta\kappa'}^{(0)}. \end{aligned} \quad (4.13)$$

If we denote the expression in brackets by $G_{\alpha\beta}(l; \omega; \kappa \kappa')$, our result reads

$$u_{\alpha\kappa}^{(l)} = \sum_{\beta} G_{\alpha\beta}(l; \omega; \kappa 1) (M_1 - M_1') \omega^2 u_{\beta 1}^{(0)}. \quad (4.14)$$

This equation is the three-dimensional analog of Eq. (2.7) with $G_{\alpha\beta}(l; \omega; \kappa \kappa')$ playing the role of the Green's function. The eigenvalue equation for the perturbed lattice is obtained by setting $l=0$ and $\kappa=1$ in Eq. (4.14) and letting α assume the three values x, y, z successively.

A considerable simplification in the subsequent analysis can be achieved if we restrict the unperturbed lattice to be a cubic Bravais lattice. Then all the masses M_κ become simply M , and the summations over κ can be suppressed. The Green's function $G_{\alpha\beta}(l; \omega)$ becomes

$$G_{\alpha\beta}(l; \omega) = \frac{1}{NM} \sum_{\mathbf{k} j} \frac{e_\alpha(\mathbf{k} j) e_\beta(\mathbf{k} j)}{\omega^2 - \omega_j^2(\mathbf{k})} e^{2\pi i \mathbf{k} \cdot \mathbf{x}(l)}, \quad (4.15)$$

because $\mathbf{e}(\mathbf{k} j)$ now is real. Equation (4.14) takes the form

$$u_\alpha^{(l)} = \epsilon M \omega^2 \sum_{\beta} G_{\alpha\beta}(l; \omega) u_\beta^{(0)}. \quad (4.16)$$

The eigenvalue equation becomes

$$\begin{bmatrix} u_x^{(0)} \\ u_y^{(0)} \\ u_z^{(0)} \end{bmatrix} = \epsilon M \omega^2 \begin{bmatrix} G_{xx}(0; \omega) & G_{xy}(0; \omega) & G_{xz}(0; \omega) \\ G_{yx}(0; \omega) & G_{yy}(0; \omega) & G_{yz}(0; \omega) \\ G_{zx}(0; \omega) & G_{zy}(0; \omega) & G_{zz}(0; \omega) \end{bmatrix} \begin{bmatrix} u_x^{(0)} \\ u_y^{(0)} \\ u_z^{(0)} \end{bmatrix}. \quad (4.17)$$

Now from Eq. (4.15) we see that

$$G_{\alpha\beta}(0; \omega) = \frac{1}{NM} \sum_{\mathbf{k} j} \frac{e_\alpha(\mathbf{k} j) e_\beta(\mathbf{k} j)}{\omega^2 - \omega_j^2(\mathbf{k})} \quad (4.18)$$

$$= \frac{\delta_{\alpha\beta}}{NM} \sum_{\mathbf{k} j} \frac{e_\alpha(\mathbf{k} j) e_\alpha(\mathbf{k} j)}{\omega^2 - \omega_j^2(\mathbf{k})} \quad (4.19)$$

$$= \frac{1}{NM} \sum_{\mathbf{k} j} \frac{1}{\omega^2 - \omega_j^2(\mathbf{k})}, \quad (4.20)$$

where we have used the assumed cubic symmetry of our lattice to go from Eq. (4.18) to Eq. (4.20).

The condition that the set of homogeneous equations, Eq. (4.17), have a solution is that the determinant of the coefficients vanishes. In view of Eq. (4.20), this condition takes the form

$$\begin{vmatrix} \epsilon M \omega^2 G_{xx}(0; \omega) - 1 & 0 & 0 \\ 0 & \epsilon M \omega^2 G_{yy}(0; \omega) - 1 & 0 \\ 0 & 0 & \epsilon M \omega^2 G_{zz}(0; \omega) - 1 \end{vmatrix} = 0, \quad (4.21)$$

so that the perturbed frequencies are triply degenerate and are given by the solutions of

$$1 = \epsilon \omega^2 \sum_{\mathbf{k}j} \frac{1}{\omega^2 - \omega_j^2(\mathbf{k})}. \quad (4.22)$$

We are now in a position to calculate the mean-square velocity of the impurity atom. We denote the determinant on the left-hand side of Eq. (4.21) by $-\Delta(\omega)$:

$$\Delta(\omega) = [1 - \epsilon M \omega^2 G_{xx}(0; \omega)]^3. \quad (4.23)$$

Then, according to the general theory presented in reference 11 the function

$$\Omega(f) = (d/df) \ln \Delta(if), \quad (4.24)$$

is of fundamental importance in determining the change in the Helmholtz free energy due to the introduction of the impurity. Here we have put

$$f = \omega/\omega_L, \quad (4.25)$$

where ω_L is the maximum frequency of the unperturbed lattice. The change in zero-point energy is

$$\Delta E_0 = -\frac{\hbar \omega_L}{2\pi} \int_0^\infty f \Omega(f) df. \quad (4.26)$$

The low-temperature expansion of the change in the free energy is given by

$$\Delta F(T) \sim \Delta E_0 - \frac{\hbar \omega_L}{\pi} \left\{ \frac{\pi^2}{6} \Omega(0+) \left(\frac{kT}{\hbar \omega_L} \right)^2 - \frac{\pi^4}{90} \Omega''(0+) \left(\frac{kT}{\hbar \omega_L} \right)^4 + O(T^6) \right\}. \quad (4.27)$$

In the high-temperature limit

$$\Delta F(T) = \frac{kT}{2} \ln \left(\frac{M}{M'} \right)^3 \Delta(0) - kT \sum_{n=1}^{\infty} \frac{(-1)^n B_n}{(2n)(2n)!} \left(\frac{\hbar}{kT} \right)^{2n} (3N \Delta \mu_{2n}), \quad (4.28)$$

where B_n is the n th Bernoulli number,¹²

$$B_1 = 1/6, \quad B_2 = 1/30, \quad B_3 = 1/42, \quad \dots \quad (4.29)$$

$\Delta \mu_{2n}$ appearing in Eq. (4.28) is the change in the $2n$ th moment of the frequency spectrum of the crystal due to the impurity, and is related to $\Omega(f)$ through its large $|f|$ expansion:

$$\Omega(f) = -\frac{2}{f} (3N) \sum_{n=1}^{\infty} (-1)^n \frac{\Delta \mu_{2n}}{\omega_L^{2n} f^{2n}}. \quad (4.30)$$

¹² E. P. Adams, *Smithsonian Mathematical Formulas and Tables of Elliptic Functions* (The Smithsonian Institution, Washington, D. C., 1947), p. 140.

Thus we see that the large and small f expansions of $\Omega(f)$, and consequently of $G_{xx}(0; if)$, are of particular interest, and it is to their determination we turn first.

From Eq. (4.20) we obtain

$$\begin{aligned} G_{xx}(0; if) &= -\frac{1}{3NM} \sum_{\mathbf{k}j} \frac{1}{\omega_L^2 f^2 + \omega_j^2(\mathbf{k})} \\ &= -\frac{1}{M \omega_L^2 f^2} \frac{1}{3N} \sum_{\mathbf{k}j} \left\{ 1 - \frac{\omega_j^2(\mathbf{k})}{\omega_L^2 f^2} + \frac{\omega_j^4(\mathbf{k})}{\omega_L^4 f^4} - \dots \right\} \\ &= -\frac{1}{M \omega_L^2 f^2} \left\{ \mu_0 - \frac{\mu_2}{\omega_L^2 f^2} + \frac{\mu_4}{\omega_L^4 f^4} - \dots \right\}, \end{aligned} \quad (4.31)$$

where, by definition

$$\mu_{2n} = \frac{1}{3N} \sum_{\mathbf{k}j} \omega_j^{2n}(\mathbf{k}), \quad (4.32)$$

is the $2n$ th moment of the frequency spectrum of the unperturbed lattice. With the aid of this result we find that

$$\begin{aligned} \Omega(f) &= 3 \frac{d}{df} \ln \left\{ 1 - \epsilon \left[\mu_0 - \frac{\mu_2}{\omega_L^2 f^2} + \frac{\mu_4}{\omega_L^4 f^4} - \dots \right] \right\} \\ &= \frac{2}{f} (3N) \left\{ -\frac{1}{3N} \frac{3\epsilon}{1 - \epsilon \omega_L^2 f^2} + \frac{1}{3N} \frac{6\epsilon}{1 - \epsilon \omega_L^4 f^4} \frac{\mu_4}{\omega_L^4 f^4} \right. \\ &\quad \left. + \frac{1}{3N} \frac{3\epsilon^2}{(1 - \epsilon)^2} \frac{\mu_2^2}{\omega_L^4 f^4} + O(f^{-6}) \right\}. \end{aligned} \quad (4.33)$$

Comparing this result with Eq. (4.30) we obtain

$$\begin{aligned} \Delta \mu_2 &= \frac{1}{3N} \frac{3\epsilon}{1 - \epsilon} \mu_2, \\ \Delta \mu_4 &= \frac{1}{3N} \left[\frac{6\epsilon}{1 - \epsilon} \mu_4 + \frac{3\epsilon^2}{(1 - \epsilon)^2} \mu_2^2 \right], \end{aligned} \quad (4.34)$$

These results together with Eq. (4.28) lead to the following expansion for the change in the Helmholtz free energy in the high-temperature limit:

$$\begin{aligned} \Delta F(T) &= -\frac{kT}{2} \ln(1 - \epsilon)^3 \Delta(0) \\ &\quad - kT \left\{ \frac{-B_1}{4} \left(\frac{\hbar}{kT} \right)^2 (3N \Delta \mu_2) \right. \\ &\quad \left. + \frac{B_2}{96} \left(\frac{\hbar}{kT} \right)^4 (3N \Delta \mu_4) + O(T^{-6}) \right\}. \end{aligned} \quad (4.35)$$

$\Delta(0)$ is just unity in the present case and we find that the mean-square velocity of the impurity atom in the

high-temperature limit is given by

$$\langle v_0^2 \rangle = \frac{3kT}{M'} \left\{ 1 + \frac{1}{12} \left(\frac{\hbar}{kT} \right)^2 \frac{M}{M'} \mu_2 - \frac{1}{720} \left(\frac{\hbar}{kT} \right)^4 \left[\frac{M}{M'} \mu_4 + \epsilon \left(\frac{M}{M'} \right)^2 \mu_2^2 \right] + \dots \right\}. \quad (4.36)$$

The leading correction term to the equipartition value $3kT/M'$ can be put into a form which depends only on experimentally obtainable quantities. With the aid of the relation, due to Domb and Salter,¹³

$$\Theta_\infty = \frac{\hbar}{k} \left(\frac{5}{3} \mu_2 \right)^{\frac{1}{2}}, \quad (4.37)$$

where Θ_∞ is the limiting high-temperature value of the equivalent Debye characteristic temperature, we have finally

$$\langle v_0^2 \rangle = \frac{3kT}{M'} \left\{ 1 + \frac{1}{20} \frac{M}{M'} \left(\frac{\Theta_\infty}{T} \right)^2 + O(T^{-4}) \right\}. \quad (4.38)$$

The small $|f|$ expansion of $G_{xx}(0; if)$ is found in the Appendix to be of the form

$$G_{xx}(0; if) \sim -\frac{1}{M} [c_0 + c_1|f| + c_2f^2 + c_3|f|^3 + \dots]. \quad (4.39)$$

This expansion in conjunction with Eq. (4.24) leads to

$$\begin{aligned} \Omega(f) &= 3 \frac{d}{df} \ln \{ 1 - \epsilon \omega_L^2 f^2 [c_0 + c_1|f| + c_2f^2 + c_3|f|^3 + \dots] \} \\ &= -3 \{ 2\epsilon c_0 \omega_L^2 f + 3\epsilon c_1 \omega_L^2 f^2 \operatorname{sgn} f + 4\epsilon c_2 \omega_L^2 f^3 + 2\epsilon^2 c_0^2 \omega_L^4 f^3 + 5\epsilon c_3 \omega_L^2 f^4 \operatorname{sgn} f + 5\epsilon^2 c_0 c_1 \omega_L^4 f^4 \operatorname{sgn} f + \dots \}. \end{aligned} \quad (4.40)$$

We are thus led to

$$\begin{aligned} \Omega(0+) &= 0, \\ \Omega''(0+) &= -18\epsilon c_1 \omega_L^2, \\ \Omega'''(0+) &= -360\epsilon c_3 \omega_L^2 - 360\epsilon^2 c_0 c_1 \omega_L^4. \end{aligned} \quad (4.41)$$

The low-temperature expansion for the change in the free energy becomes

$$\begin{aligned} \Delta F(T) &= \Delta E_0 + \frac{\hbar \omega_L}{\pi} \left\{ \frac{\pi^4}{90} (-18\epsilon c_1 \omega_L^2) \left(\frac{kT}{\hbar \omega_L} \right)^4 + \frac{\pi^6}{945} (360)(\epsilon c_3 \omega_L^2 + \epsilon^2 c_0 c_1 \omega_L^4) \left(\frac{kT}{\hbar \omega_L} \right)^6 + \dots \right\}, \end{aligned} \quad (4.42)$$

so that

$$\langle v_0^2 \rangle = \frac{2}{M} \frac{d}{d\epsilon} \Delta E_0 - \frac{3\hbar}{M\pi} \left\{ \frac{2\pi^4}{15} \frac{c_1}{\omega_L} \left(\frac{kT}{\hbar} \right)^4 - \frac{16\pi^6}{63} \left(\frac{c_3}{\omega_L^3} + 2\epsilon \frac{c_0 c_1}{\omega_L} \right) \left(\frac{kT}{\hbar} \right)^6 + \dots \right\}. \quad (4.43)$$

The results of the appendix show that in terms of the coefficients $\{a_{2n}\}$ appearing in the low-frequency expansion of the frequency spectrum,

$$g(\omega) = a_2 \omega^2 + a_4 \omega^4 + a_6 \omega^6 + \dots, \quad (4.44)$$

the constants $\{c_n\}$ are given by

$$\begin{aligned} c_0 &= \mu_{-2}, \\ c_1 &= -\frac{1}{2} \pi a_2 \omega_L, \\ c_3 &= \frac{1}{2} \pi a_4 \omega_L^3, \\ c_5 &= -\frac{1}{2} \pi a_6 \omega_L^5, \end{aligned} \quad (4.45)$$

where μ_{-2} is the -2 nd moment of the unperturbed frequency spectrum. The coefficients a_2 and a_4 have been evaluated for some lattice models by Bhatia and Horton¹⁴ and by Horton and Schiff.¹⁵ Equation (4.43) can be rewritten as

$$\langle v_0^2 \rangle = \frac{2}{M} \frac{d}{d\epsilon} \Delta E_0 + \frac{3\hbar}{M} \left\{ \frac{\pi^4}{15} a_2 \left(\frac{kT}{\hbar} \right)^4 + \frac{8\pi^6}{63} (a_4 - 2\epsilon \mu_{-2} a_2) \left(\frac{kT}{\hbar} \right)^6 + O(T^8) \right\}. \quad (4.46)$$

We see that the leading temperature-dependent term is unaffected by the mass change.

The coefficient a_2 is related to the zero temperature value of the Debye characteristic temperature by

$$a_2 = 3(\hbar/k\Theta_0)^3. \quad (4.47)$$

To compute the change in the zero-point energy we need the function $\Omega(f)$ explicitly for all f in the interval $0 \leq f \leq \infty$. This in turn requires knowledge of $G_{xx}(0; if)$ over this entire range as well. From Eq. (4.31) we see that the latter function can be written as

$$G_{xx}(0; if) = -\frac{1}{M} \int_0^{\omega_L} \frac{g(\xi) d\xi}{\omega_L^2 f^2 + \xi^2}, \quad (4.48)$$

where $g(\omega)$ is the frequency spectrum (normalized to unity) of the unperturbed crystal.

For simplicity we denote the integral in Eq. (4.48) by $G(f)/\omega_L^2$

$$G(f) = \int_0^1 \frac{P(x)}{f^2 + x^2} dx, \quad (4.49)$$

¹³ C. Domb and L. Salter, Phil. Mag. **43**, 1083 (1952).

¹⁴ A. B. Bhatia and G. K. Horton, Phys. Rev. **98**, 1715 (1955).

¹⁵ G. K. Horton and H. Schiff, Phys. Rev. **104**, 32 (1956).

where we have introduced the dimensionless frequency spectrum $P(x)$ which is defined by

$$P(x) = \omega_L g(\omega_L x).$$

The expression for $\Omega(f)$ becomes

$$\begin{aligned} \Omega(f) &= 3 \frac{d}{df} \ln[1 - \epsilon f^2 G(f)] \\ &= -3\epsilon \frac{2fG(f) + f^2 G'(f)}{1 - \epsilon f^2 G(f)}. \end{aligned} \quad (4.50)$$

The change in zero-point energy becomes

$$\Delta E_0 = \frac{3\epsilon \hbar \omega_L}{2\pi} \int_0^\infty \frac{2f^2 G(f) + f^3 G'(f)}{1 - \epsilon f^2 G(f)} df. \quad (4.51)$$

From Eq. (3.10) we obtain finally that at the absolute zero of temperature

$$\begin{aligned} \langle v_0^2 \rangle_{0^\circ\text{K}} &= \frac{2}{M} \frac{d}{d\epsilon} \Delta E_0 \\ &= \frac{3\hbar \omega_L}{\pi M} \int_0^\infty \frac{2f^2 G(f) + f^3 G'(f)}{[1 - \epsilon f^2 G(f)]^2} df. \end{aligned} \quad (4.52)$$

$$\begin{aligned} \langle v_0^2 \rangle_{0^\circ\text{K}} &= \frac{9\hbar \omega_D}{\pi M} \int_0^\infty \frac{2f^2 - 3f^3 \tan^{-1}(1/f) - [f^4/(1+f^2)]}{\{1 - 3\epsilon[f^2 - f^3 \tan^{-1}(1/f)]\}^2} df \\ &= \frac{9\hbar \omega_D}{\pi M} \int_0^{\pi/2} \frac{2 \sin^2 x \cos^2 x + \sin^2 x \cos^4 x - 3x \sin x \cos^3 x}{[\sin^2 x - 3\epsilon(\sin x \cos^2 x - x \cos^3 x)]^2} dx. \end{aligned} \quad (4.57)$$

The change of variable $f = \tan(\pi/2 - x)$ has been used to obtain the second form of this integral. The value of this expression in the case $\epsilon = 0$ is

$$\langle v_0^2 \rangle_{0^\circ\text{K}} = 9\hbar \omega_D / 8M, \quad \epsilon = 0. \quad (4.58)$$

The integral in Eq. (4.57) was evaluated numerically as a function of ϵ and the results are plotted in Fig. 1.

For comparison with the predictions of the Debye approximation the expression (4.52) was computed numerically as a function of ϵ for copper. The frequency spectrum $g(\omega)$ used in these calculations was that calculated by Flinn, McManus, and Rayne¹⁶ using deLaunay's two-force constant model.¹⁷ The results of the copper calculations are plotted in Fig. 1. The value of ω_D used in the Debye spectrum has been chosen to

reproduce the zero-temperature value of the Debye Θ for copper obtained from the two-force constant model.

$$G'(f) = -2f \int_0^1 \frac{P(x)}{(f^2 + x^2)^2} dx. \quad (4.53)$$

$g(\omega)$ is known only numerically for any realistic model of a crystal. The integrals in Eqs. (4.49) and (4.53) can be evaluated by numerical integration to give $G(f)$ and $G'(f)$ as functions of f numerically. The final integration over f in Eq. (4.52) then could also be carried out numerically for different values of ϵ .

We will carry out the evaluation of $\langle v_0^2 \rangle_{0^\circ\text{K}}$ here with the use of two frequency spectra. The first of these is the Debye spectrum given by

$$g(\omega) = (3/\omega_D^3) \omega^2. \quad (4.54)$$

The Debye cutoff frequency ω_D introduced here is not, in general, equal to the true maximum frequency of the crystal being studied. It is, in fact, related to the coefficient a_2 in the expansion (4.44) by

$$\omega_D^3 = 3/a_2. \quad (4.55)$$

In this case $G(f)$ and $G'(f)$ become

$$G(f) = 3(1 - f \tan^{-1}(1/f)), \quad (4.56a)$$

$$G'(f) = 3[f/(1+f^2) - \tan^{-1}(1/f)], \quad (4.56b)$$

where we have put $f = \omega/\omega_D$, so that the mean square velocity of the impurity atom at the absolute zero of temperature is given by

reproduce the zero-temperature value of the Debye Θ for copper obtained from the two-force constant model.

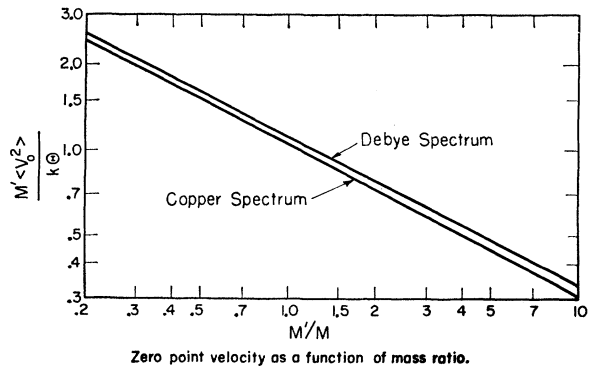


FIG. 1. The mean-square velocity at 0°K of a mass defect atom in copper as a function of the ratio of the impurity mass to the mass of a copper atom. Θ is the 0°K value of the Debye characteristic temperature for copper. One curve is calculated on the basis of a realistic frequency spectrum for copper, and the second is based on a Debye spectrum for copper.

¹⁶ P. A. Flinn, G. McManus and J. A. Rayne, Phys. Rev. **123**, 809 (1961).

¹⁷ J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 2, p. 219.

V. EFFECTS OF FORCE CONSTANT CHANGES AT HIGH TEMPERATURES

Although it is a rather difficult problem to find the mean-square velocity at low temperatures of an impurity atom whose potential of interaction with its neighbors as well as its mass differs from that of an atom in the unperturbed crystal, the calculation is feasible in the high-temperature limit. Our starting point is Eq. (4.28) and Eq. (3.12). We have that at high temperatures

$$\langle v_0^2 \rangle = \frac{3kT}{M'} + \frac{2kT}{M} \frac{d}{d\epsilon} \left\{ \frac{1}{24} \left(\frac{\hbar}{kT} \right)^2 (3N\Delta\mu_2) - \frac{1}{2880} \left(\frac{\hbar}{kT} \right)^4 (3N\Delta\mu_4) + O(T^{-6}) \right\}. \quad (5.1)$$

It is only necessary to determine the changes in the even moments of the frequency spectrum due to the introduction of the impurity to obtain $\langle v_0^2 \rangle$ in this limit. We do this by the moment-trace method.

We assume a monatomic Bravais lattice for our unperturbed lattice. We assume that the atoms interact through central forces derived from a pair potential function $\phi(r)$ which is significant only between nearest and next nearest neighbor atoms. The equations of motion of the crystal are

$$M_l \ddot{u}_x^l = \sum_{l'y} \phi_{xy}{}^{ll'} u_y^{l'}, \quad (5.2)$$

where

$$\phi_{xy}{}^{ll'} = \frac{\partial^2 \phi(r)}{\partial x \partial y} \Big|_{r=r_{ll'}}, \quad (5.3)$$

and

$$\phi_{xy}{}^{ll} = - \sum_{l'}' \phi_{xy}{}^{ll'}. \quad (5.4)$$

The prime on the sum in Eq. (5.4) means that l' does not equal l in the summation.

We introduce time-independent amplitudes V_x^l by

$$u_x^l = [V_x^l / (M_l)^{1/2}] e^{-i\omega t}, \quad (5.5)$$

in terms of which Eq. (5.2) becomes

$$\omega^2 V_x^l = - \sum_{l'y} \frac{\phi_{xy}{}^{ll'}}{(M_l M_{l'})^{1/2}} V_y^{l'}. \quad (5.6)$$

Pairing the indices as (l, x) and (l', y) we see that the normal mode frequencies are the eigenvalues of a symmetric matrix whose elements are

$$D \begin{pmatrix} ll' \\ xy \end{pmatrix} = - \frac{\phi_{xy}{}^{ll'}}{(M_l M_{l'})^{1/2}}. \quad (5.7)$$

It follows that the $2n$ th moment of the frequency spectrum is just proportional to the trace of the n th power

of this matrix:

$$\mu_{2n} = (1/3N) \text{Trace} \{ D^n \}. \quad (5.8)$$

We restrict ourselves here to computing the change in the second moment, which suffices to give the leading correction to the equipartition value of $\langle v_0^2 \rangle$. μ_2 is given by

$$\begin{aligned} \mu_2 &= \frac{1}{3N} \sum_{lx} D \begin{pmatrix} ll \\ xx \end{pmatrix} \\ &= - \frac{1}{3N} \sum_{lx} \frac{\phi_{xx}{}^{ll}}{M_l} \end{aligned} \quad (5.9)$$

$$\begin{aligned} &= \frac{1}{3N} \sum_l \frac{1}{M_l} \sum_{l'}' [\phi_{xx}{}^{ll'} + \phi_{yy}{}^{ll'} + \phi_{zz}{}^{ll'}] \\ &= \frac{1}{3N} \sum_l \frac{1}{M_l} \sum_{l'}' \nabla^2 \phi(r^{ll'}) \\ &= \frac{1}{3N} \sum_l \frac{1}{M_l} \sum_{l'}' \left\{ \phi''(r^{ll'}) + \frac{2}{r^{ll'}} \phi'(r^{ll'}) \right\}. \end{aligned} \quad (5.10)$$

We first specialize to the case of a face-centered cubic lattice with lattice parameter a_0 . There are 12 nearest neighbors at the permutations of $(\pm a_0/2, \pm a_0/2, 0)$, and 6 next nearest neighbors at the permutations of $(\pm a_0, 0, 0)$. Denoting the nearest neighbor separation $a_0/\sqrt{2}$ by r_0 , we make the following identifications

$$\begin{aligned} \alpha_1 &= \phi''(r_0), \\ \beta_1 &= (2/r_0) \phi'(r_0), \\ \alpha_2 &= \phi''(\sqrt{2}r_0), \\ \beta_2 &= (\sqrt{2}/r_0) \phi'(\sqrt{2}r_0). \end{aligned} \quad (5.11)$$

Only three of these constants are independent in view of the equilibrium condition which can be stated as

$$12\phi'(r_0) + 6\phi'(\sqrt{2}r_0) = 0. \quad (5.12)$$

In the perfect lattice every lattice point is equivalent, and we have

$$\mu_2 = \frac{1}{3M} \{ 12(\alpha_1 + \beta_1) + 6(\alpha_2 + \beta_2) \}. \quad (5.13)$$

If the atom at the origin is replaced by an impurity whose mass is M' and whose interaction potential with its nearest and next nearest neighbors is $\chi(r)$, so that

$$\begin{aligned} \alpha_1' &= \chi''(r_0), \\ \beta_1' &= (2/r_0) \chi'(r_0), \\ \alpha_2' &= \chi''(\sqrt{2}r_0), \\ \beta_2' &= (\sqrt{2}/r_0) \chi'(\sqrt{2}r_0), \end{aligned} \quad (5.14)$$

the change in the second moment is given by

$$\Delta\mu_2 = \frac{1}{3N} \left\{ \frac{1}{M'} [12(\alpha_1' + \beta_1') + 6(\alpha_2' + \beta_2')] \right. \\ - \frac{1}{M} [12(\alpha_1 + \beta_1) + 6(\alpha_2 + \beta_2)] \\ + \frac{12}{M} [(\alpha_1' + \beta_1') - (\alpha_1 + \beta_1)] \\ \left. + \frac{6}{M} [(\alpha_2' + \beta_2') - (\alpha_2 + \beta_2)] \right\}. \quad (5.15)$$

In the case of a body-centered cubic lattice with lattice parameter a_0 , there are 8 nearest neighbors at $(\pm a_0/2, \pm a_0/2, \pm a_0/2)$ and 6 second-nearest neighbors at the permutations of $(\pm a_0, 0, 0)$. Denoting the nearest-neighbor separation $\frac{1}{2}a_0\sqrt{3}$ by r_0 we have, in this case

$$\begin{aligned} \alpha_1 &= \phi''(r_0), \\ \beta_1 &= (2/r_0)\phi'(r_0), \\ \alpha_2 &= \phi''(2r_0/\sqrt{3}), \\ \beta_2 &= (\sqrt{3}/r_0)\phi'(2r_0/\sqrt{3}). \end{aligned} \quad (5.16)$$

The equilibrium condition in this case reads

$$8\phi'(r_0) + 6\phi(2r_0/\sqrt{3}) = 0. \quad (5.17)$$

The second moment for the unperturbed lattice is

$$\mu_2 = \frac{1}{3M} \{ 8(\alpha_1 + \beta_1) + 6(\alpha_2 + \beta_2) \}, \quad (5.18)$$

and the change due to the impurity becomes

$$\Delta\mu_2 = \frac{1}{3N} \left\{ \frac{1}{M'} [8(\alpha_1' + \beta_1') + 6(\alpha_2' + \beta_2')] \right. \\ - \frac{1}{M} [8(\alpha_1 + \beta_1) + 6(\alpha_2 + \beta_2)] \\ + \frac{8}{M} [(\alpha_1' + \beta_1') - (\alpha_1 + \beta_1)] \\ \left. + \frac{6}{M} [(\alpha_2' + \beta_2') - (\alpha_2 + \beta_2)] \right\}, \quad (5.19)$$

where the primed force constants are defined in a manner completely analogous to that in the fcc case.

Since in each case

$$M' = (1 - \epsilon)M,$$

we insert the expressions (5.15) and (5.19) into Eq. (5.1) and obtain the following results:

fcc:

$$\langle v_0^2 \rangle = \frac{3kT}{M'} \left\{ 1 + \frac{1}{12} \left(\frac{\hbar}{kT} \right)^2 \frac{M}{M'} \right. \\ \times \frac{12(\alpha_1' + \beta_1') + 6(\alpha_2' + \beta_2')}{3M} + \dots \left. \right\}, \quad (5.20)$$

bcc:

$$\langle v_0^2 \rangle = \frac{3kT}{M'} \left\{ 1 + \frac{1}{12} \left(\frac{\hbar}{kT} \right)^2 \frac{M}{M'} \right. \\ \times \frac{8(\alpha_1' + \beta_1') + 6(\alpha_2' + \beta_2')}{3M} + \dots \left. \right\}. \quad (5.21)$$

These results should be compared with Eq. (4.36).

VI. APPLICATION TO EXPERIMENTAL DATA

The interpretation of experimental results is most straightforward in the high-temperature region, where the effect of force constant changes as well as mass differences can be taken into account in a reasonably simple way. A comparison of Eq. (4.38) with (5.20) and (5.21) suggests that we define an effective impurity characteristic temperature θ_i by the relation:

$$\langle v_0^2 \rangle = \frac{3kT}{M'} \left\{ 1 + \frac{1}{20} \frac{M}{M'} \left(\frac{\theta_i}{T} \right)^2 + O(T^{-4}) \right\}. \quad (6.1)$$

For the fcc model considered, θ_i is given by:

$$\theta_i = \frac{\hbar}{k} \left\{ \frac{20(\alpha_1' + \beta_1') + 10(\alpha_2' + \beta_2')}{3M} \right\}^{\frac{1}{2}}. \quad (6.2)$$

In general, θ_i will be some reasonably simple function of the force constants between the impurity atom and the lattice. In the special case where the forces between impurity and solvent atoms are the same as those between solvent atoms themselves, θ_i is obviously simply Θ_∞ , for the pure solvent lattice. If θ_i is greater than Θ_∞ the impurity atom is more stiffly bound than the solvent atoms, and conversely.

The total observed Mössbauer shift includes the isomeric shift of source and absorber as well as the second-order Doppler shifts of each. For a given source at fixed temperature, and variable absorber temperature, the observed shift in the high-temperature region may be written:

$$s = s_1 - s_0 + \frac{3kT}{2M'c} \left\{ 1 + \frac{1}{20} \frac{M}{M'} \left(\frac{\theta_i}{T} \right)^2 + O(T^{-4}) \right\}, \quad (6.3)$$

where s_0 is the combined isomeric and second-order Doppler shift of the source, and s_1 is the isomeric shift of the absorber. It is convenient to rewrite this in the form:

$$\left[s - \frac{3kT}{2M'c} \right] = s_1 - s_0 + \frac{3}{40} \frac{k}{M'c} \frac{M}{M'} \frac{\theta_i^2}{T} + O(T^{-3}). \quad (6.4)$$

Clearly, a plot of $s - 3kT/2M'c$ vs $1/T$ should be a straight line, the slope of which determines θ_i , and the intercept of which is $s_1 - s_0$. If similar plots are made for two different absorbers using the same source, the

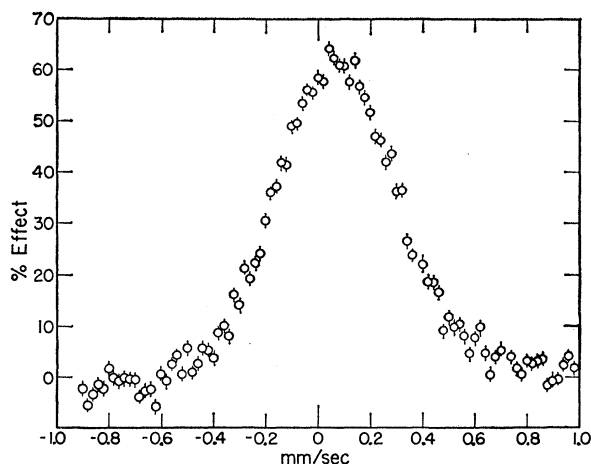


FIG. 2. A typical Mössbauer profile. Stainless steel source at 300°K; stainless steel absorber at 195°K.

difference in the two intercepts gives directly the difference in isomeric shifts for the two absorber materials, independent of the properties of the source and fully corrected for the second-order Doppler shift. It is interesting to note that the term (M/M') cancels the dependence of θ_i on the solvent mass, so that any difference in slope observed for a given solute in two different solvents must arise essentially from a difference in force constants.

To investigate a case with a large ratio of impurity to solvent mass, an absorber consisting of a dilute solution of iron in beryllium was prepared. A 0.01-in. thick Be foil was electroplated with enriched iron ($\sim 30\%$ Fe^{57}) and a solid solution produced by an anneal at 1150°C. The alloy contained of the order of one atomic percent of iron. For comparison, a standard 304 stainless steel absorber was also used. The Mössbauer peaks were determined at various temperatures using a stainless steel source and a velocity sorting Mössbauer spectrometer described previously.¹⁸ The uncertainty in the peak positions (taken as the centroids) was of the order of ± 0.01 mm/sec, and was caused largely by drift in the analyzer circuitry. A typical experimental profile is shown in Fig. 2.

It is worth emphasizing that Eq. (5.1) is independent of the details of the lattice structure and thus applies equally well to the hexagonal beryllium lattice as to the cubic stainless steel lattice. This means that Eqs. (6.1) and (6.4) hold for these two lattices equally well, with the parameter θ_i given in general by

$$\theta_i^2 = -\left(\frac{M'}{M}\right)^2 \left(\frac{\hbar}{k}\right)^2 \left(\frac{d}{d\epsilon} 3sN\Delta\mu_2\right),$$

where s is the number of atoms in a unit cell. The interpretation of θ_i in terms of changes in atomic force constants and masses is somewhat more cumbersome in the case of beryllium than it is for a cubic Bravais

¹⁸ S. L. Ruby and D. I. Bolef, Phys. Rev. Letters 5, 5 (1960).

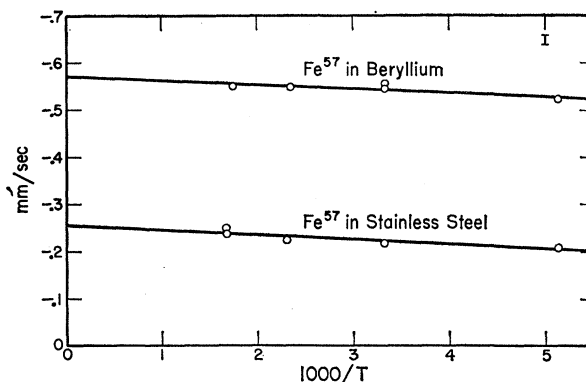


FIG. 3. The variation with temperature of the quantity $(s - 3kT/2M'c)$, where s is the total observed Mössbauer shift at high temperatures and is the sum of the isomeric shift and the second-order Doppler shift between source and observer.

lattice. In any event due to present experimental uncertainties in the determination of θ_i we did not attempt to extract information about the effective force constants between an impurity and its neighbors in either of the two cases studied.

The experimental results are plotted in Fig. 3, in the form discussed above. A least-squares fit of the data gave the results:

	$s_1 - s_0$	θ_i
Fe in beryllium	-0.570 ± 0.004 mm/sec	$1210^\circ \pm 240^\circ\text{K}$
Fe in 304 stainless	-0.253 ± 0.003 mm/sec	$510^\circ \pm 75^\circ\text{K}$
Isomeric shift Be-stainless	-0.317 ± 0.005 mm/sec	

The isomeric shift is clearly determined far more accurately than the effective characteristic temperature, since the slope of such curves is much more sensitive to errors in the data than is the intercept. The results for θ_i are, however, not unreasonable. The limiting high-temperature Debye temperature for beryllium is 900°K.¹⁹ Comparison with the result above suggests that an iron atom in a beryllium lattice is somewhat more stiffly held than are the beryllium atoms themselves, but the large uncertainty in θ_i makes this suggestion quite tentative. Unfortunately, the Debye temperature for stainless steel is not known, but since the values for the constituent elements are all in the 400° to 500°K range, our result is plausible.

VII. SUMMARY

Expressions have been obtained for the mean-square velocity of a solute atom in a three-dimensional lattice in both the high- and low-temperature regions. The low-temperature result has been obtained only for the case where solute and solvent atoms differ in mass but not in interatomic force constants. Under this restriction, changing the mass of the solvent lattice atoms has relatively little effect on the mean square velocity of the solute atom.

The low-temperature region is of limited interest for

¹⁹ R. W. Hill and P. L. Smith, Phil. Mag. (7) 44, 636 (1953).

experimental investigation at present because both the vibrational spectrum of the lattice and the force constants affect the velocity in complicated ways which preclude any simple interpretation of experimental data. In the high-temperature range, however, the combination of theory and experiment can be fruitful in two separate ways. First of all, it is now possible to determine the isomeric shift accurately by fully correcting for the second-order Doppler shift. Secondly, an average interatomic force constant between solute and solvent atoms can be obtained. To determine such constants with meaningful accuracy requires at least an order of magnitude improvement in the accuracy of measurement of line position over that obtained in the experiments reported here. Although a different experimental technique is required, such precision is possible, as shown by the red-shift measurements.²⁰

ACKNOWLEDGMENT

We would like to acknowledge the assistance given us by John Hicks in the collection of the experimental data.

APPENDIX

We obtain here the small ω^2 expansion of the integral

$$I(\omega) = \int_0^{\omega L} \frac{g(\xi)}{\omega^2 + \xi^2} d\xi, \quad (\text{A1})$$

where $g(\omega)$ is the frequency spectrum (normalized to unity) of a three-dimensional crystal. We will make use of the fact that for small ω , $g(\omega)$ has the expansion

$$g(\omega) = a_2\omega^2 + a_4\omega^4 + a_6\omega^6 + \dots \quad (\text{A2})$$

We begin by rewriting Eq. (A.1) as

$$\begin{aligned} I(\omega) &= \int_0^{\omega L} g(\xi) \int_0^\infty \exp[-t(\omega^2 + \xi^2)] dt d\xi \\ &= \int_0^\infty \exp(-t\omega^2) F(t) dt, \end{aligned} \quad (\text{A3})$$

where

$$F(t) = \int_0^{\omega L} g(\xi) \exp(-t\xi^2) d\xi. \quad (\text{A4})$$

It is now straightforward to show that any singular terms in $I(\omega)$ in the limit as $\omega^2 \rightarrow 0$ are determined by the large- t behavior of $F(t)$. We break up the range of integration into two parts $(0, T)$ and (T, ∞) where T is large enough that the large- t asymptotic expansion for $F(t)$ can be used in the latter part. Thus we have that

$$\begin{aligned} I(\omega) &= \int_0^T \exp(-t\omega^2) F(t) dt + \int_T^\infty \exp(-t\omega^2) F(t) dt \\ &= I_1 + I_2. \end{aligned} \quad (\text{A5})$$

We now expand the exponential in the first integral and integrate term by term:

$$\begin{aligned} I_1 &= \int_0^T F(t) dt - \omega^2 \int_0^T t F(t) dt \\ &\quad + \frac{1}{2} \omega^4 \int_0^T t^2 F(t) dt + \dots \end{aligned} \quad (\text{A6})$$

We see that the small- t behavior of $F(t)$ gives rise only to analytic terms in ω^2 in the small- ω^2 expansion of $I(\omega)$.

The large- t asymptotic expansion of $F(t)$ is given by

$$\begin{aligned} F(t) &\sim \int_0^\infty \exp(-t\xi^2) (a_2\xi^2 + a_4\xi^4 + \dots) d\xi \\ &= \frac{a_2}{2} \frac{\Gamma(\frac{3}{2})}{t^{\frac{3}{2}}} + \frac{a_4}{2} \frac{\Gamma(\frac{5}{2})}{t^{\frac{5}{2}}} + \frac{a_6}{2} \frac{\Gamma(\frac{7}{2})}{t^{\frac{7}{2}}} + \dots \end{aligned} \quad (\text{A7})$$

and $I_2(\omega)$ becomes

$$I_2(\omega) \sim \int_T^\infty \exp(-t\omega^2) \left\{ \frac{a_2}{2} \frac{\Gamma(\frac{3}{2})}{t^{\frac{3}{2}}} + \frac{a_4}{2} \frac{\Gamma(\frac{5}{2})}{t^{\frac{5}{2}}} + \dots \right\} dt. \quad (\text{A8})$$

The small- ω^2 behavior of this integral has been studied in great detail by Maradudin *et al.*²¹ With the aid of their results we obtain

$$\begin{aligned} I_2(\omega) &\sim \left(\frac{\pi}{T}\right)^{\frac{1}{2}} \left[\frac{1}{2} a_2 + \frac{1}{3T} \frac{1}{2} \frac{3}{2} a_4 + \frac{1}{5T^2} \frac{1}{2} \frac{5}{2} a_6 + \dots \right] \\ &\quad - \frac{\pi}{2} a_2 |\omega| + \omega^2 (\pi T)^{\frac{1}{2}} \left[\frac{1}{2} a_2 - \frac{1}{T} \frac{1}{2} \frac{3}{2} a_4 \right. \\ &\quad \left. - \frac{1}{3T^2} \frac{1}{2} \frac{5}{2} a_6 - \dots \right] + \frac{\pi}{2} a_4 |\omega|^3 + O(\omega^4). \end{aligned} \quad (\text{A9})$$

The infinite series in T^{-1} comprising the coefficients of ω^0 and ω^2 in Eq. (A9) are asymptotic, but generally converge rapidly for $T \gtrsim 10$. From Eqs. (A6) and (A9) we see that for small ω

$$\begin{aligned} I(\omega) &\sim b_0 + b_1 |\omega| + b_2 \omega^2 + b_3 |\omega|^3 + \dots \\ &= c_0 + c_1 |f| + c_2 f^2 + c_3 |f|^3 + \dots \end{aligned} \quad (\text{A10})$$

The only coefficients in the expansion (A10) which enter into the low temperature value of the mean square velocity of the impurity atom are c_0 and the odd coefficients, c_1, c_3, c_5, \dots , c_0 is nothing more than μ_{-2} , the minus 2nd moment of the frequency spectrum of the unperturbed crystal. It can be obtained experimentally from the high-temperature behavior of the Debye-Waller factor for the unperturbed crystal. The coefficients c_{2n+1} are given by

$$c_{2n+1} = (-1)^{n+1} (\pi/2) a_{2n+2} \omega L^{2n+1}. \quad (\text{A11})$$

²⁰ R. V. Pound and G. A. Rebka, Jr., Phys. Rev. Letters 4, 337 (1960).

²¹ A. A. Maradudin, E. W. Montroll, G. H. Weiss, R. Herman, and H. W. Milnes, Memoires Academie Royale de Belgique (Classe des Sciences) Tome XIV, Fascicule 7, No. 1709 (1960).