PHYSICAL REVIEW VOLUME 146, NUMBER 2 10 JUNE 1966

Analysis of Debye-Waller-Factor and Mössbauer-Thermal-Shift Measurements. I. General Theory*

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(Received 20 January 1966)

We give a simple theoretical analysis of the dynamics of an arbitrary atom in a general harmonic solid. The atom under discussion may be an impurity. Several general results are found which limit the possible temperature dependences of the mean-square displacement and mean-square velocity in a way which is described. These results are expected to be most useful in analyzing experiments involving Debye-Waller-factor and Mössbauer-thermal-shift measurements. As an illustration the allowed range of mean-square displacements at $T=0$ and $T=80°\mathrm{K}$ corresponding to a measured value at $T=298°\mathrm{K}$ is given. These results also provide strong consistency relations that experimental data or numerical calculations should satisfy. One especially interesting result indicates a possible method for determining a simple sum over atomic force constants from Debye-Waller-factor measurements. This sum, which in general is not obtainable from any other type of measurements, could be used as a convenient check on atomic-force-constant models. The dependence of the mean-square displacement and mean-square velocity on the various masses and force constants in the lattice is described. The relation between our results derived in the harmonic approximation and experimentally measurable quantities is discussed. Finally, several experiments which appear to be interesting are mentioned.

1. INTRODUCTION

In this paper we intend to accomplish two related objectives. First we want to establish as complete an understanding as possible of the important aspects of the dynamics of a particular atom in a general harmonic solid. Second we want to provide as complete a basis as possible for interpreting Debye-Waller-factor and Mössbauer-thermal-shift measurements and to suggest some areas in which further measurements would be useful. In this regard a discussion of some measurements which seem to be interesting is given in Sec. 7. We will give an analysis of some results from the literature in part II.

In Sec. 2 the dynamics of a particle in a general harmonic system is discussed. It is shown that in general two weighted mean frequencies depend only on the mass of the particular atom and are independent of the masses of the other atoms. In addition, one of the weighted mean frequencies depends on the force constants in a very simple way. Convenient formulas for the mean-square velocity and mean-square displacement of a particular particle are obtained.

In Sec. 3 the temperature dependence of the mean-square velocity and mean-square displacement when the system is in thermal equilibrium is discussed. It is found that in certain temperature ranges the results are easily expressed in terms of weighted mean frequencies. This together with the results of Sec. 2 suggests how a simple sum of atomic force constants might be measured. Formulas are also obtained for low-temperature deviation of the mean-square velocity and mean-square displacement from their values at $T=0$.

In Sec. 4 the implications of a mathematical relationship which the weighted mean frequencies must satisfy is discussed. Careful use of this relationship allows interpolation and extrapolation from known results. The relationship also provides strong consistency conditions which experimental data *or* numerical calculations must satisfy. Also in this section is a discussion of the dependence of the weighted mean frequencies on the relevant masses and force constants.

In Sec. 5 some further results especially useful in the case of pure crystals are mentioned. The relationship between our weighted mean frequencies and the moments of the frequency spectrum, which can be determined from specific-heat data, is shown.

In Sec. 6 the problem of determining the weighted mean frequencies from experimental data is discussed. In particular, a procedure for analyzing Mössbauer f measurements and for correcting for the effects of anharmonicity is suggested.

2. GENERAL DYNAMICAL PROPERTIES OF HARMONIC SYSTEMS

In this section we consider a general harmonic system of point particles. We make no assumptions about size, structure, or special boundary conditions.[1a] We only use the well-known result that there exists a unitary transformation B which transforms from the particle coordinates to a set of normal coordinates y_i in which the equations of motion are separated.[1b]

We first write the equations of motion in the form

$$M\ddot{x}+Kx=0, \tag{1}$$

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* This work is part of the research program of the Netherlands Foundation for Fundamental Research on Matter (F.O.M.), financially supported by the Netherlands Organization for Pure Research (Z.W.O.).

[1a] It has been pointed out to us by D. P. Johnson that Eq. (13) cannot be derived for a free system of particles since Eq. (11) cannot be inverted in that case. In application of the theory to solids this is not a real restriction since measurements are always made on samples clamped in some way.

[1b] See, for example, W. Hauser, *Principles of Mechanics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1965), Chap. 11.

where the elements of x are the Cartesian components of the displacements of the various particles and M and K are respectively mass and atomic force constant matrices. Since M is diagonal it is easy to see that Eq. (1) may be rewritten

$$\ddot{\bar{x}}+M^{-1/2}KM^{-1/2}\bar{x}=0\,, \tag{2}$$

where $\bar{x}=M^{1/2}x$.

Since K is a real symmetric matrix $M^{-1/2}K\,M^{-1/2}$ must also be real and symmetric. Therefore, if λ is a matrix with the squares of the normal-mode frequencies on the diagonal and zeros elsewhere, a unitary matrix B exists such that

$$B^{-1}M^{-1/2}KM^{-1/2}B=\lambda\,, \tag{3}$$

$$y=B^{-1}\bar{x}\,, \tag{4}$$

and

$$\bar{x}=By\,, \tag{5}$$

where y_i are the normal coordinates of the system.

In a normal mode all the particles move in phase along straight lines with a simple harmonic motion. If one normal mode y_i has an amplitude a_i and all the others have zero amplitude then the corresponding amplitudes A_j along the mass weighted coordinates $\bar{x}_j$ are

$$A_{ji}=b_{ji}a_i\,,$$

where the b_{ji} are the appropriate elements of B. At the instant when all the particles are passing through equilibrium the total energy in the system is kinetic. Then we have

$$E_i=\tfrac{1}{2}\sum_j b_{ji}^2a_i^2\omega_i^2=\tfrac{1}{2}a_i^2\omega_i^2\,,$$

where in obtaining the second equality we have made use of one of the two conditions

$$\sum_j b_{ji}^2=\sum_i b_{ji}^2=1\,, \tag{6}$$

which follow from the unitary nature of B. We also can see that

$$\langle\dot{\bar{x}}_{ji}^2\rangle=\tfrac{1}{2}A_{ji}^2\omega_i^2=\tfrac{1}{2}b_{ji}^2a_i^2\omega_i^2\,.$$

Therefore,

$$\langle\dot{\bar{x}}_{ji}^2\rangle=b_{ji}^2E_i \tag{7}$$

and

$$\langle\bar{x}_{ji}^2\rangle=b_{ji}^2(E_i/\omega_i^2)\,. \tag{8}$$

It is easy to see classically or from the properties of Hermite polynomials that contributions to $\langle\bar{x}_j^2\rangle$ and $\langle\dot{\bar{x}}_j^2\rangle$ from different normal modes modes are additive. It is convenient now to change notation slightly. We change from the mass-weighted coordinates back to Cartesian coordinates and at the same time replace the index j which stood for both a particle and a direction by j and k. Thus, the mean-square velocity and mean-square displacement of particle k in direction j are given in terms of the energies in the normal modes by

$$\langle v_{jk}^2\rangle=\frac{1}{m_k}\sum_i b_{jki}^2E_i \tag{9}$$

and

$$\langle x_{jk}^2\rangle=\frac{1}{m_k}\sum_i b_{jki}^2\frac{E_i}{\omega_i^2}\,. \tag{10}$$

While it is easy to see that equations similar to (9) and (10) should hold the preceding treatment which identifies the constants b_{jki}^2 as squares of elements of the unitary transformation matrix allows two important theorems to be proved. The first follows from Eq. (3) by rewriting it in the form

$$K=M^{1/2}B\lambda B^{-1}M^{1/2} \tag{11}$$

and multiplying out the right-hand side. If we then equate corresponding terms on the diagonal we have

$$\phi_{jkjk}=m_k\sum_i b_{jki}^2\omega_i^2\,, \tag{12}$$

where ϕ_{jkjk} gives the j component of the restoring force on particle k if it is displaced in the j direction and all the other particles held fixed. Since the above is physically indistinguishable from holding particle k fixed and displacing all the other particles in the minus j direction ϕ_{jkjk} can also be written as a sum over force constants connecting the particle k to the other particles of the system. The relationship given in Eq. (12) is potentially very valuable since, as will be shown in Sec. 3, the sum on the right might in suitable circumstances be determined experimentally. For any material more complicated than a monatomic cubic crystal Eq. (12) will then give information on the atomic force constants not obtainable by other means. (For a cubic monatomic crystal the same information can be obtained from specific-heat measurements.)

Our second theorem follows by rewriting Eq. (11) in the inverse form

$$K^{-1}=M^{-1/2}B\lambda^{-1}B^{-1}M^{-1/2}$$

and again multiplying out the right-hand side and setting equivalent terms on the diagonal equal. We get

$$\sum_i b_{jki}^2\frac{1}{\omega_i^2}=\frac{1}{m_k}g(\{\phi_{jkj'k'}\})\,, \tag{13}$$

where g is an unspecified function of the force constants alone.

3. STATISTICAL MECHANICS

If we now assume our harmonic system is in thermodynamic equilibrium it is well known that the mean energy E_i in a mode of frequency ω_i is

$$E_i=\left[\frac{1}{2}+\frac{1}{e^{\hbar\omega_i/kT}-1}\right]\hbar\omega_i\,.$$

Using this result, Eqs. (9) and (10) become

$$\langle v_{jk}^2\rangle = \frac{\hbar}{m_k}\sum_i \left[\frac{1}{2}+\frac{1}{e^{\hbar\omega_i/kT}-1}\right] b_{jki}^2\omega_i \tag{14}$$

and

$$\langle x_{jk}^2\rangle = \frac{\hbar}{m_k}\sum_i \left[\frac{1}{2}+\frac{1}{e^{\hbar\omega_i/kT}-1}\right] \frac{b_{jki}^2}{\omega_i}. \tag{15}$$

Each term in (14) and (15) has the following properties: The slope and curvature are zero at $T=0$. The slope and curvature are both always $\geqq 0$. The slope approaches a constant value as $T\to\infty$. Since they are finite sums of such terms $\langle v_{jk}^2\rangle$ and $\langle x_{jk}^2\rangle$ must also have these properties, therefore their temperature dependences must be qualitatively similar to those shown by curves 1 and 2 in Fig. 1.

Further insight into the behavior of Eqs. (14) and (15) may be obtained by considering their limiting forms. To simplify the terminology we define weighted mean frequencies $\omega_{jk}(n)$ by the relationship

$$\omega_{jk}(n) = \left[\sum_i b_{jki}^2\omega_i^n\right]^{1/n}. \tag{16}$$

Then by making a Thirring expansion of the statistical factors we get, respectively, for high temperatures

$$\langle v_{jk}^2\rangle_T = \frac{kT}{m_k}\left[1+\frac{1}{12}\left(\frac{\hbar}{kT}\right)^2\omega_{jk}^2(2) - \frac{1}{720}\left(\frac{\hbar}{kT}\right)^4\omega_{jk}^4(4)+\cdots\right] \tag{17}$$

and

$$\langle x_{jk}^2\rangle_T = \frac{kT}{m_k}\left[\frac{1}{\omega_{jk}^2(-2)}+\frac{1}{12}\left(\frac{\hbar}{kT}\right)^2 - \frac{1}{720}\left(\frac{\hbar}{kT}\right)^4\omega_{jk}^2(2)+\cdots\right], \tag{18}$$

where sums of the b_{jki}^2 occurred without any multiplying power of the ω_i they have been set equal to 1 by using Eq. (6). It can be seen that $\langle v_{jk}^2\rangle$ goes to the equipartition value in the high-temperature limit as expected. The Thirring expansion converges for $\hbar\omega_m/kT\leqq 2\pi$, where ω_m is the maximum frequency that contributes to the sum. In fact, the first two terms of the series are in error by less than 2% down to $\hbar\omega_m/kT=2$.

One of the most interesting things to be seen from these expansions is the possibility of determining $\omega_{jk}(2)$ from experimental results. As was shown in Sec. 2, $\omega_{jk}(2)$ can in turn be directly related to a sum over force constants. It is worthwhile to mention that several variations of the Thirring expansion which may be more suited to actually evaluating the $\omega_{jk}(n)$ from experimental results have been considered.[2–4]

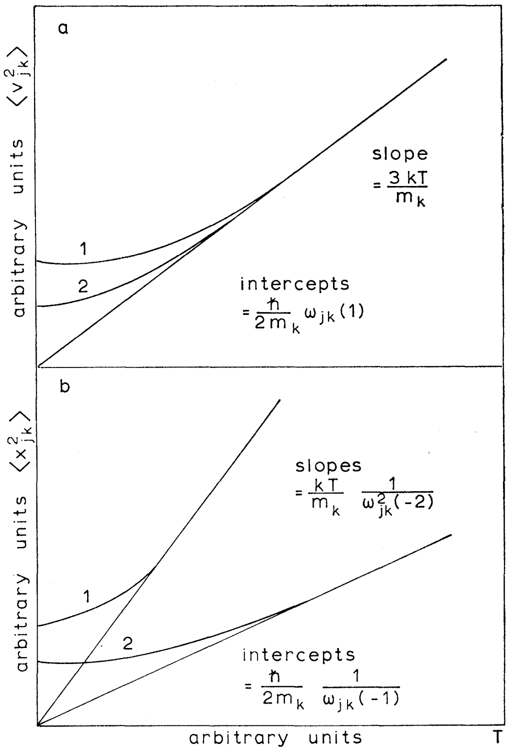

FIG. 1. (a) Two possible curves of mean-square velocity versus temperature. (b) Two possible curves of mean-square displacement versus temperature.

In the limit $T\to 0$, Eqs. (14) and (15) become

$$\langle v_{jk}^2\rangle = (\hbar/2m_k)\omega_{jk}(1) \tag{19}$$

and

$$\langle x_{jk}^2\rangle = (\hbar/2m_k)(1/\omega_{jk}(-1)). \tag{20}$$

If we now assume our harmonic system is a crystal containing a large number of atoms we can say some interesting things regarding the initial deviations from Eqs. (19) and (20) when the temperature is raised. These deviations are caused by the very long-wavelength acoustic vibrations which are the first to be excited. In these modes large groups of atoms move together so that the motion of the atom k does not depend on its mass, force constants, or local surroundings. The first deviations from (19) and (20) depend only on the bulk elastic constants of the ideal crystal. It is possible to derive formulas for these deviations by methods completely analogous to those used to derive the familiar T^3 law for the low-temperature specific heat. The results are

$$\langle v_{jk}^2\rangle_T - \langle v_{jk}^2\rangle_0 = \frac{\pi^4}{5}\frac{1}{M}k\theta_0\left(\frac{T}{\theta_0}\right)^4\gamma_j \tag{21}$$

and

$$\langle x_{jk}^2\rangle_T - \langle x_{jk}^2\rangle_0 = \frac{\pi^2}{2}\frac{1}{M}\frac{\hbar^2}{k\theta_0}\left(\frac{T}{\theta_0}\right)^2\gamma_j, \tag{22}$$

where M is the total mass in the ideal unit cell. θ_0 is the

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[2] C. Domb and L. Salter, Phil. Mag. **43**, 1083 (1952).

[3] G. K. Horton and H. Schiff, Proc. Roy. Soc. (London) **A250**, 248 (1959).

[4] R. A. Sack, A. A. Maradudin, and G. H. Weiss, Phys. Rev. **124**, 717 (1961).

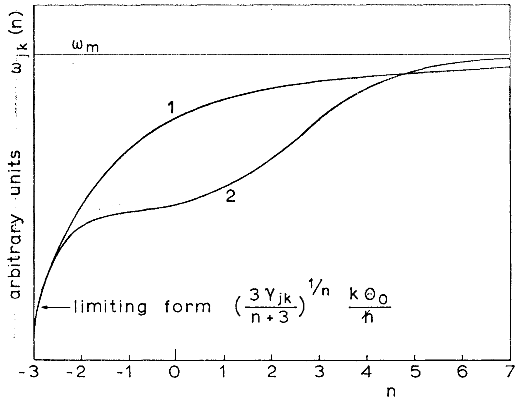

FIG. 2. Two possible curves of the weighted mean frequency $\omega_{jk}(n)$ versus n. See text for explanation.

value obtained by fitting the T^3 law to low-temperature specific-heat measurements in such a manner that the total number of modes allowed is 3 times the number of unit cells. The γ_j are dimensionless constants which depend on the anisotropy of the crystal. For a cubic crystal they are all equal to one. In general $\gamma_1+\gamma_2+\gamma_3=3$. Calculations pertinent to determining the γ_j for hexagonal crystals have been done by Zener.[5]

The expected range of validity of (21) and (22) is about $T\leqq\theta_0/50$. It can be shown by comparing these formulas with Eqs. (19) and (20) that the change in $\langle v_{jk}^2\rangle$ and $\langle x_{jk}^2\rangle$ in the range of validity of the formulas is normally less than 0.1%. This means that liquid-He-temperature results can normally be taken with confidence as low-temperature limits. At least for monatomic cubic crystals low-temperature expansions valid for somewhat higher temperatures than (21) and (22) may be derived by methods previously used in the analysis of low-temperature specific-heat data.[6]

From Eqs. (17), (18), (19), and (20), it is apparent that the information contained in both moderately high-temperature measurements and $T=0$ measurements is conveniently described in terms of the weighted mean frequencies $\omega_{jk}(n)$. In principle, additional weighted mean frequencies may be derived from measurements at intermediate temperatures. A method proposed by Hwang[7] for the analysis of specific-heat data leads to the equations

$$\int_0^\infty \frac{\langle v_{jk}^2\rangle_T-\langle v_{jk}^2\rangle_0}{T^{n+2}}dT =\frac{\hbar}{m_k}\Gamma(n+1)\zeta(n+1)\left(\frac{k}{\hbar}\right)^{n+1}\omega_{jk}^{-n}(-n) \qquad 0<n<3, \tag{23}$$

and

$$\int_0^\infty \frac{\langle x_{jk}^2\rangle_T-\langle x_{jk}^2\rangle_0}{T^{n}}dT =\frac{\hbar}{m_k}\Gamma(n-1)\zeta(n-1)\left(\frac{k}{\hbar}\right)^{n-1}\omega_{jk}^{-n}(-n) \qquad 2<n<3, \tag{24}$$

where Γ indicates the gamma function and ζ indicates the Riemann zeta function of their respective arguments. One of these formulas has been derived independently by Kagan.[8] (His result appears to contain an error of a factor of 2.) It is seen that the only new moments which can be derived from these formulas are fractional ones. In addition, very accurate low-temperature measurements and the use of Eqs. (21) and (22) would be necessary in order to evaluate the integrals with sufficient accuracy to be useful.

4. RESULTS DETERMINED BY MATHEMATICAL PROPERTIES OF $\omega_{jk}(n)$

Since we have now seen that most of the information contained in curves of $\langle v_{jk}^2\rangle$ and $\langle x_{jk}^2\rangle$ versus temperature can be conveniently expressed in terms of the $\omega_{jk}(n)$ it is interesting to inquire further into the properties of these weighted mean frequencies. It can be shown by use of the Schwarz inequality that any function of n defined by a relation like Eq. (16) where the ω_i are positive constants, and the b_{jki}^2 are positive constants whose sum is one, must be a monotonically increasing function.[9] In particular, our $\omega_{jk}(n)$ must increase monotonically with n. Further, it is apparent that $\omega_{jk}(n)$ must approach ω_m the maximum frequency con-

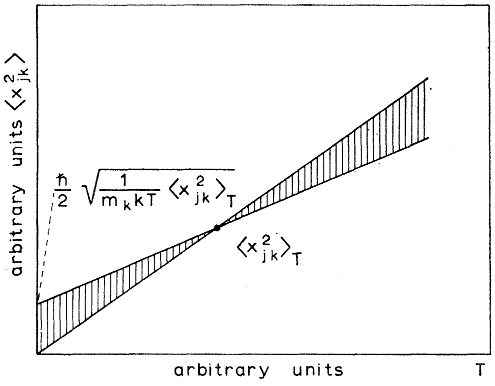

FIG. 3. If the point is the mean-square displacement at a temperature T then for any harmonic solid the mean-square displacement at higher or lower temperatures cannot lie outside the shaded region.

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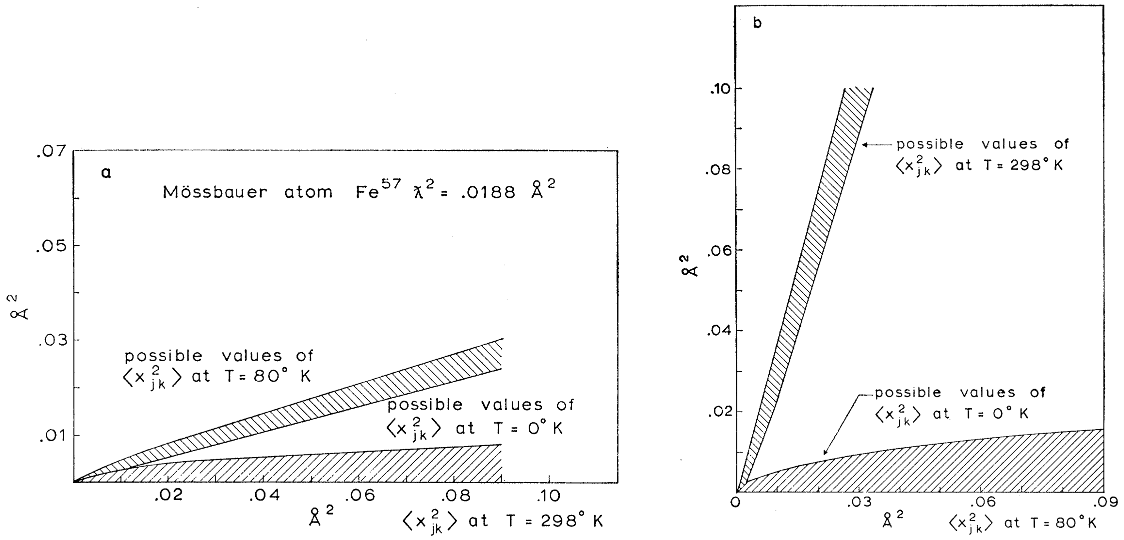
[5] C. Zener, Phys. Rev. **49**, 122 (1936).

[6] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) **A242**, 478 (1957).

[7] J. L. Hwang, J. Chem. Phys. **22**, 154 (1954).

[8] Yu. Kagan, Zh. Eksperim. i Teor. Fiz. **47**, 366 (1964) [English transl.: Soviet Phys.—JETP **20**, 243 (1965)].

[9] A proof of an even stronger result can be obtained by slightly generalizing the proof of a similar inequality in R. von Mises, *Mathematical Theory of Probability and Statistics* (Academic Press Inc., New York, 1964), Chap. 8, p. 396.



(a) (b)

FIG. 4. (a) If the mean-square displacement of Fe^{57} in a harmonic solid has been measured at $T=298$ then the values at $T=80$ and $T=0$ must lie between the appropriately labeled lines. (b) Same except measured value at $T=80$ and allowed range at $T=0$ and $T=298$.

tributing to the motion when $n\rightarrow\infty$. For a crystal the density of modes contributing to the motion can be thought of as approaching zero continuously as ω^2 when ω approaches zero. Then $\omega_{jk}(n)=0$ for $n\leqq -3$ and rises as

$$\omega_{jk}(n)=\left(\frac{3\gamma_j}{n+3}\right)^{1/n}\frac{k\theta_0}{\hbar}$$

for n just greater than -3, where the constants have all been defined previously. Two possible curves of $\omega_{jk}(n)$ versus n are shown in Fig. 2.

Since the $T=0$ intercepts of $\langle v_{jk}^2\rangle$ and $\langle x_{jk}^2\rangle$ versus T and the high-temperature slope of $\langle x_{jk}^2\rangle$ depend on the $\omega_{jk}(n)$ we can now establish two independent inequalities among them. They are

$$\langle x_{jk}^2\rangle_0\langle v_{jk}^2\rangle_0\geqq\tfrac{1}{4}(\hbar^2/m_k^2) \tag{25}$$

and

$$\langle x_{jk}^2\rangle_T\geqq\langle x_{jk}^2\rangle_0^2(4m_kkT/\hbar^2)\,. \tag{26}$$

The first, relating $\langle v_{jk}^2\rangle$ and $\langle x_{jk}^2\rangle$ at $T=0$, is as expected just the Heisenberg uncertainty relation.

One use of the second inequality is to predict the allowed limits for $\langle x_{jk}^2\rangle$ versus T if $\langle x_{jk}^2\rangle_T$ is known at one temperature. This can be done simply as follows. The high-temperature limiting slope must be $\leqq\langle x_{jk}^2\rangle_T/T$. With Eq. (26) this sets an upper limit for $\langle x_{jk}^2\rangle_0$. Then due to the established shape of $\langle x_{jk}^2\rangle$ versus T the only allowed values for $\langle x_{jk}^2\rangle$ must be between the two straight lines in Fig. 3. Using this method we have computed (for Fe^{57}) the allowed range in $\langle x_{jk}^2\rangle$ at $T=0$ and $T=80$°K for different assumed values at $T=298$°K and the allowed range at $T=0$ and 298°K for different assumed values at $T=80$°K. The results are shown in Figs. 4(a) and (b). If a maximum frequency for the lattice is assumed then a lower limit for $\langle x_{jk}^2\rangle$ at $T=0$ is also set.

The fact that $\omega_{jk}(n)$ is a monotonically increasing function can be used in a different way. Taken together with the general results of Sec. 2, and the results of model calculations by various authors it makes it possible to see how the various $\omega_{jk}(n)$, and hence the physical quantities which they determine, depend on the various masses and force constants involved.

Equations (12) and (13) show that $\omega_{jk}(-2)$ and $\omega_{jk}(2)$ are proportional to $m_k^{-1/2}$ and are independent of the masses of all the other atoms. In addition, $\omega_{jk}(2)$ is proportional to $(\phi_{jkjk})^{1/2}$ and is independent of all the other force constants of the lattice. Since $\omega_{jk}(-1)$ and $\omega_{jk}(1)$ lie between $\omega_{jk}(-2)$ and $\omega_{jk}(2)$ it is seen that they must be approximately proportional to $m_k^{-1/2}$ and approximately independent of the other masses. The extent to which $\omega_{jk}(-1)$ and $\omega_{jk}(1)$ are limited by the above approximate relationship depends on the ratio $\omega_{jk}(2)/\omega_{jk}(-2)$. This is only known for a few simple lattice models where it can be directly calculated and for a few pure cubic crystals where it has been determined from specific-heat measurements.[10] The values range from 1.25 for the Leighton model of a fcc metal to 1.77 for Ge.

Perturbation calculations by Lipkin[11] indicate that for small mass changes the proportionality of $\omega_{jk}(-1)$ and $\omega_{jk}(1)$ with $m_k^{-1/2}$ and their independence on changes in the other masses is much better than required by the above limits. Lipkin studied in detail an isotopic impurity (no force-constant change) in a

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[10] L. Salter, Advan. Phys. 14, 1 (1965).

[11] H. J. Lipkin, Ann. Phys. (N. Y.) 23, 28 (1963).

Bravais lattice. His results can be put in the form

$$\frac{d\ln\omega_{jk}(-1)}{d\ln m}=-\rho_1, \tag{27}$$

$$\frac{d\ln\omega_{jk}(-1)}{d\ln m_k}=-\tfrac{1}{2}+\rho_1, \tag{28}$$

$$\frac{d\ln\omega_{jk}(1)}{d\ln m}=-\rho_2, \tag{29}$$

$$\frac{d\ln\omega_{jk}(1)}{d\ln m_k}=-\tfrac{1}{2}+\rho_2, \tag{30}$$

where m stands for the mass of the host lattice atoms. The quantities ρ_1 and ρ_2 are weighted sums over the frequency spectrum and a plausible argument shows that they should be small at least for the pure crystal. As Lipkin mentions, it should be easily possible to generalize his calculations. Hence, the same results are expected to also apply to an arbitrary atom in a complex crystal.

The symmetrical nature of Eqs. (17) and (28), and of (29) and (30) is not accidental. Imagine that the masses of all the atoms in the crystal are slightly changed by the same fraction of their original masses. Then the $b_{jki}{}^2$ must be unchanged and all the frequencies must change as the reciprocal square root of the mass change. This small change in all the masses may be imagined to result from successive small changes in the individual masses leading to the result

$$\sum_{k'}\frac{d\ln\omega_{jk}(n)}{d\ln m_{k'}}=-\tfrac{1}{2}. \tag{31}$$

By the same reasoning applied to force constant changes we also get the result

$$\sum_{j'k'j''k''}\frac{d\ln\omega_{jk}(n)}{d\ln\phi_{j'k'j''k''}}=\tfrac{1}{2}. \tag{32}$$

Kagan and Iosilevskii[12] have studied the dynamics of an isotopic impurity in a general crystal lattice in considerable detail. They have also considered small force-constant changes by perturbation methods. For $T=0$ their results become simple in the light- and heavy-impurity limits. Expressed in terms of $\omega_{jk}(-1)$ the results are just the limiting possibilities allowed by the fact that $\omega_{jk}(n)$ is a monotonically increasing, namely

$$\omega_{jk}(-1)=\omega_{jk}(-2)\quad m_k\gg m,$$

and

$$\omega_{jk}(-1)=\omega_{jk}(2)\quad m\gg m_k.$$

A similar result for the heavy-impurity limit was also obtained by DeWames *et al.*[13] These limiting forms are physically reasonable since in either the light- or heavy-impurity limit the main amplitude of the motion is concentrated in a narrow band of frequencies.

Numerical calculations for isotopic impurities in monatomic cubic lattices have been done by Dzyub and Lubchenko[14] and by Dawber and Elliott.[15] Assuming a Debye frequency spectrum they find that the above limiting values are not approached very rapidly. In fact, for

$$0.2\leqq m_k/m\leqq 26.6,$$

$\omega_{jk}(-1)$ deviates from being proportional to $m_k{}^{-1/2}$ by less than 5%. Dawber and Elliott show also that in the same range $\omega_{jk}(1)$ deviates from proportionality with $m_k{}^{-1/2}$ by less than 10%.

Taken together the above results suggest that the functional dependences of the important $\omega_{jk}(n)$ are as listed in Table I. The only important information missing are the dependences of $\omega_{jk}(-2)$, and $\omega_{jk}(-1)$ on the various force constants. The only general information available on this is Eq. (32) and the results of Kagan and Iosilevskii.[12] The latter, however, are not in a form which leads to a simple general interpretation. Two simple models using only one force constant ϕ_{jk} for the impurity and one force constant ϕ for the host and one detailed realistic model have been studied. Visscher[16] found for a simple cubic lattice

$$\frac{d\ln\omega_{jk}(-1)}{d\ln\phi_{jk}}\approx 0.5$$

and

$$\frac{d\ln\omega_{jk}(-1)}{d\ln\phi}\approx 0.0$$

for $0.5\leqq\phi_{jk}/\phi\leqq 1.5$ and $0.5\leqq m_k/m\leqq 1.5$.

Maradudin and Flinn[17] found for a model fcc lattice that

$$\frac{d\ln\omega_{jk}(-2)}{d\ln\phi_{jk}}=0.298$$

and

$$\frac{d\ln\omega_{jk}(-2)}{d\ln\phi}=0.202,$$

where the derivatives are evaluated at $m_k/m=1$ and $\phi_{jk}/\phi=1$.

The above result is in contradiction to their statement that the mean-square displacement depends primarily on the host-lattice stiffness.

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[12] Yu. Kagan and Ya. A. Iosilevskii, Zh. Eksperim. i Teor. Fiz. **46**, 2165 (1964) [English transl.: Soviet Phys.—JETP **19**, 1462 (1964)].

[13] R. E. DeWames, T. Wolfram, and G. W. Lehman, Phys. Rev. **138**, A717 (1965).

[14] I. P. Dzyub and A. F. Lubchenko, Dokl. Akad. Nauk SSSR **147**, 584 (1962) [English transl.: Soviet Phys.—Doklady **7**, 1027 (1963)].

[15] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **A273**, 222 (1963).

[16] W. M. Visscher, Phys. Rev. **129**, 28 (1963).

[17] A. A. Maradudin and P. A. Flinn, Phys. Rev. **126**, 2059 (1962).

TABLE I. Functional dependence of $\omega_{jk}(n)$ on masses and force constants.

	m_k	Other masses	ϕ_{jkjk}	Other force constants
$\omega_{jk}(-2)$	$m_k^{-1/2}$	independent		
$\omega_{jk}(-1)$	$\approx m_k^{-1/2}$	$\approx$independent		
$\omega_{jk}(1)$	$\approx m_k^{-1/2}$	$\approx$independent	$\approx \phi_{jkjk}^{1/2}$	$\approx$independent
$\omega_{jk}(2)$	$m_k^{-1/2}$	independent	$\phi_{jkjk}^{1/2}$	independent

Lehman and DeWames[18] have developed a mathematical procedure suitable for calculating the effect of both mass and force-constant changes when an impurity is substituted into a realistic model of a crystal. They illustrated the method with a calculation of $\langle x_{jk}^2\rangle$ and $\langle v_{jk}^2\rangle$ as a function of temperature for Fe^{57} in Al. Results for no force-constant change and for 7 different changes in the nearest-neighbor force constants are listed in their Table II. (The force constant changes they list should be changed as follows: multiply $\Delta\alpha_1$ and $\Delta\gamma_1$ by 2 and $\Delta\beta_1$ by 4.)[19] The force constants used for pure Al were derived from x-ray diffraction data and hence are probably not correct; however, this does not detract from the illustrative usefulness of the calculations. We have found the values of the $\omega_{jk}(n)$ which are implied by their results for various force-constant changes. They are shown in Fig. 5, where the labels indicate the force-constant changes. For an exact explanation of their meaning the reader is referred to the paper of Lehman and DeWames. The plots suggest the qualitative conclusion that $\omega_{jk}(-2)$ decreases more rapidly with large negative force-constant changes than $\omega_{jk}(2)$ and increases more slowly with large positive changes.

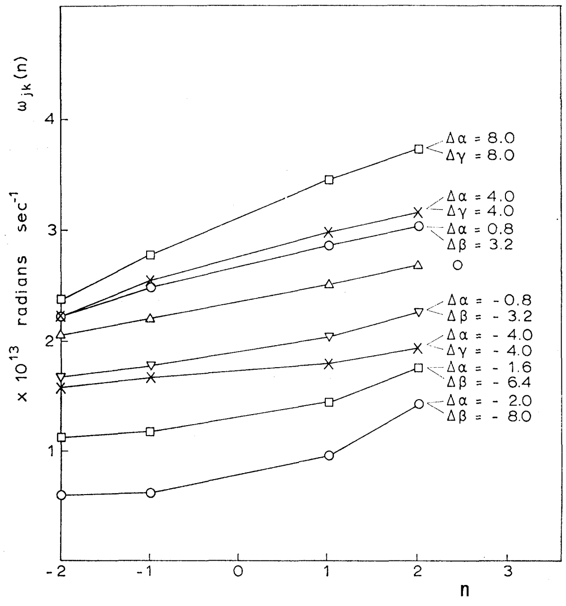

FIG. 5. Variation of $\omega_{jk}(n)$ with n for various force constant changes in a model representing Fe^{57} in Al. See Ref. 18 for an explanation of the force-constant changes.

The fact that $\omega_{jk}(2)$, which determines $\langle v_{jk}^2\rangle$ at moderately high temperatures, depends only on m_k and ϕ_{jkjk} should be of interest to chemists. It means that a shift produced by substituting a distant atom in a compound is most probably due to a change in electron density and can only be explained as due to a change in $\langle v_{jk}^2\rangle$ if long-range force constants coupling the two atoms are important. Since $\omega_{jk}(1)$ will normally depend primarily on m_k and ϕ_{jkjk} the same conclusion should generally apply to low-temperature-shift measurements as well.

5. RELATIONS BETWEEN THE MOTION OF THE ATOM *k* AND PROPERTIES OF THE WHOLE CRYSTAL

The following results follow immediately from considerations concerning the total energy of a crystal or from the mathematical properties of the b_{jki}^2.

$$\sum_{jk} m_k\langle v_{jk}^2\rangle=\sum_i\left[\frac{1}{2}+\frac{1}{e^{\hbar\omega_i/kT}-1}\right]\hbar\omega_i, \tag{33}$$

$$\sum_{jk} m_k\langle x_{jk}^2\rangle=\sum_i\left[\frac{1}{2}+\frac{1}{e^{\hbar\omega_i/kT}-1}\right]\frac{1}{\hbar\omega_i}, \tag{34}$$

and

$$\sum_{jk}\omega_{jk}^n(n)=\sum_i\omega_i^n\equiv 3N\omega^n(n), \tag{35}$$

where total number of degrees of freedom is $3N$ and the $\omega(n)$ without subscripts are the ordinary mean frequencies which can be determined from specific-heat measurements on the crystal.[10] These results should be most useful for interpreting measurements on pure crystals which are either anisotropic or contain several different kinds of atoms. For example, in a monatomic axially symmetric crystal measurement of $\omega_{jk}^2(n)$ in one direction could be combined with specific-heat results to give the value in any other direction. Similarly, in a diatomic crystal with cubic symmetry a measurement of $\langle v_{jk}^2\rangle$, $\langle x_{jk}^2\rangle$, or $\omega_{jk}(n)$ for one component can be combined with specific-heat measurements to yield the corresponding quantity for the other component.

Equation (34), which should be most useful in analysis of measurements by x-ray, neutron, or electron diffraction, was previously obtained in a different manner by Blackman.[20]

6. RELATIONSHIP TO MEASURABLE QUANTITIES

So far we have discussed the behavior of the quantities $\langle v_{jk}^2\rangle$ and $\langle x_{jk}^2\rangle$ in an ideal harmonic solid. Now we

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

[19] G. W. Lehman (private communication).

[20] M. Blackman, Acta Cryst. **9**, 734 (1956).

must consider how our results are related to experimentally measurable quantities. We will limit our discussion to measurements made by the Mössbauer effect. For discussions of the relationship between $\langle x_{jk}^2 \rangle$ and measurements made by electron, x-ray, or neutron scattering the reader is referred to the literature of those subjects.

It was realized in 1960 that there is a shift s in the energy of the sharp Mössbauer γ rays that is given by

$$s = -\langle v_k^2 \rangle / 2c^2 , \tag{36}$$

where $\langle v_k^2 \rangle \equiv \langle v_{1k}^2 \rangle + \langle v_{2k}^2 \rangle + \langle v_{3k}^2 \rangle$. This shift was explained by Pound and Rebka[21] as a relativistic second-order Doppler shift. It was suggested independently by Josephson[22] that it should result from considerations of the relativistic change in mass of the emitting nucleus. The two viewpoints seem to be equivalent.

Since at best only $\langle v_k^2 \rangle$ and not the individual $\langle v_{jk}^2 \rangle$ can be measured Eq. (25) must be modified in practice to

$$\langle v_k^2 \rangle \geqq \frac{1}{4} \frac{\hbar^2}{m_k^2} \sum_j \frac{1}{\langle x_{jk}^2 \rangle} . \tag{37}$$

At present there is considerable evidence (to be discussed in part II) to indicate that there is another contribution to the temperature shift caused by a change in electron density at the nucleus with temperature. Sufficient experimental and/or theoretical work has not been done to make it clear how well the two contributions can be separated. Therefore, the question of how much can be learned from $\langle v_k^2 \rangle$ measurements must remain open.

Fairly general considerations[23] lead to the expectation that the Mössbauer f factor will be given by

$$f = | \langle \psi_0 | \exp(-i\boldsymbol{\kappa} \cdot \mathbf{r}) | \psi_0 \rangle_T{}^2 , \tag{38}$$

where $\boldsymbol{\kappa}$ is the wave vector of the emitted γ ray, $\mathbf{r}$ is the position vector of the nucleus, ψ_0 is an initial-state wave function of the solid and the subscript T indicates a thermal average over possible initial states. For a pure harmonic crystal it is also possible to show[23] that Eq. (38) is equivalent to

$$f = e^{-\kappa^2 \langle x_{jk}^2 \rangle} . \tag{39}$$

Considerable confusion has existed concerning the case of an impurity light enough that localized vibrational modes are present. This seems to have been resolved.[24,25] If, as is always the case in practice, there is enough anharmonicity so that the local mode width is considerably larger than the width of the Mössbauer line Eq. (39) is still correct.

The explicit effect of anharmonicity has been considered by Maradudin and Flinn[26] and by Krivoglaz.[25] The former authors considered in detail a simple model of a fcc lattice. Although they could evaluate some terms only approximately they came to the conclusion that even though $\langle x_{jk}^2 \rangle$ was changed considerably by the anharmonicity Eq. (39) was still correct to a very good approximation. A derivation of this result for a more general case would be most welcome. In particular, a calculation for an atom in a position lacking inversion symmetry might prove interesting. It also might be worthwhile to investigate the possibility that in certain circumstances a decaying nucleus in a magnetic material might lose energy to the electron spin system. These questions notwithstanding we shall for the present assume that experimental f measurements can be interpreted by Eq. (39).

Of course, Eq. (38) and, hence, also (39) are only true if a thermal equilibrium distribution of initial states can be assumed. This limits us to consideration of measurements made on isotopes where the excited state of the nucleus is populated by beta decay or electron capture. For states populated by Coulomb excitation or heavy-particle reactions so much energy is lost in the vicinity of the radiating nucleus that its motion probably can not be described by a thermal equilibrium distribution of initial states.

One further point worth emphasizing since it is frequently overlooked by experimentalists concerns the case in which there are two or more Mössbauer sites in the crystal with different f values. Unless the effect from these sites is clearly resolved and the relative populations are known or unless f is so large that it may be given by $f = 1 - \kappa^2 \langle x_{jk}^2 \rangle$ for each site, no unique interpretation of the f measurements in terms of mean-square displacements is possible. This is simply because the average f is not uniquely related to the average mean-square displacement. This applies in particular to measurements made on a polycrystalline sample of an anisotropic material. These points have previously been made by Kagan.[12,8]

Finally we must consider the explicit effect of anharmonicity on the $\langle x_{jk}^2 \rangle$. The analyses previously mentioned[25,26] indicate that for temperatures $kT > \hbar\omega_m$ up to fairly high temperatures this should merely add a term proportional to T^2 to the expression for $\langle x_{jk}^2 \rangle$ versus temperature. At still higher temperatures, a term proportional to T^3 might become important. The temperature dependence of the anharmonic contribution in the lower temperature region has not been described. In the absence of better information it seems reasonable to use the quasiharmonic approximation. Hence, we tentatively assume that at least for cubic materials the $\omega_{jk}(n)$ depend on temperature at moderate temperatures only through the change in volume. To analyze measurements the $\langle x_{jk}^2 \rangle$ values obtained at temperatures

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[21] R. V. Pound and G. A. Rebka, Phys. Rev. Letters **4**, 274 (1960).

[22] B. D. Josephson, Phys. Rev. Letters **4**, 341 (1960).

[23] H. J. Lipkin, Ann. Phys. (N. Y.) **9**, 332 (1960).

[24] H. J. Lipkin, Ann. Phys. (N. Y.) **26**, 115 (1964).

[25] M. A. Krivoglaz, Zh. Eksperim. i Teor. Fiz. **46**, 637 (1964) [English transl.: Soviet Phys.—JETP **19**, 432 (1964)].

[26] A. A. Maradudin and P. A. Flinn, Phys. Rev. **129**, 2529 (1963).

greater than $kT=\hbar\omega_m/2$ should be corrected by subtracting the second term in Eq. 18. (It should be noted that this term depends only on temperature and is independent of the properties of the crystal.) Then the difference should be divided by T and the result plotted against $\Delta V/V_0$. Then the intercept will give $\omega_{jk}(-2)$ characteristic of the volume V_0 at $T=0$ and the slope will give a weighted Grüneisen parameter[27] $\gamma_{jk}(-2)$. The $\omega_{jk}(-2)$ characteristic of V_0 is generally the most suitable one to compare with other measurements and with theoretical calculations. To go from calculated $\omega_{jk}(-2)$ values to experimental predictions the inverse procedure should be used with estimated $\gamma_{jk}(-2)$ values.

The value of $\omega_{jk}(-1)$ is determined by a measurement at $T=0$ and hence needs no correction. If the effect of the temperature-dependent isomer shift can be eliminated the same is true of $\omega_k(1)$, where

$$\omega_k(n)\equiv\omega_{1k}(n)+\omega_{2k}(n)+\omega_{3k}(n).$$

In attempts to determine $\omega_{jk}(2)$ probably the best procedure would be to correct all the experimental data using the experimental $\gamma_{jk}(-2)$ value.

Since $\omega_{jk}(-1)$, $\omega_k(1)$ and the $\omega_{jk}(-2)$ as determined above all correspond to the same volume V_0 they must satisfy the relations imposed by the fact that $\omega_{jk}(n)$ is monotonically increasing. Since experimental results are frequently described by giving the θ of a Debye distribution that would lead to the same result it is useful to give the relation between these θ values and the $\omega_{jk}(n)$

$$\omega_{jk}(n)=\left(\frac{3}{n+3}\right)^{1/n}\frac{k\theta_{jk}(n)}{\hbar}. \tag{40}$$

In terms of these θ values Eqs. (25) and (26) become

$$\theta_{jk}(-1)\geqq(\sqrt{3}/2)\theta_{jk}(-2) \tag{41}$$

and

$$\theta_k(1)\geqq(8/9)\theta_k(-1). \tag{42}$$

7. SUGGESTED EXPERIMENTS

Potentially the most rewarding line of experimental research suggested by the present work is the determination of $\omega_{jk}(2)$ from f measurements. As seen in Sec. 2 these then give the sum of atomic force constants which provide the restoring force when the atom k is displaced in the direction j all other atoms remaining fixed. For a nonmagnetic monatomic cubic crystal the same information can be obtained from the analysis of specific-heat data.[10] For any more complicated case this is not so. The sum of force constants which may be found are especially useful since they provide a reference against which fundamental lattice dynamical models can be checked without detailed calculations. They also could be used as input data in phenomenological lattice dynamical calculations.

In order to determine the $\omega_{jk}(2)$ it is certain that f measurements which determine $\langle x_{jk}^2\rangle$ quite accurately over at least the temperature interval $\hbar\omega_m/4<kT<\hbar\omega_m$ are needed. It is not exactly certain what accuracy is necessary or how troublesome the anharmonicity correction will be.

Measurements sufficient to determine $\omega_{jk}(-2)$ and/or $\omega_{jk}(-1)$ for crystals more complicated than monatomic cubic ones again provide a check for lattice dynamical models independent of that provided by specific-heat measurements. The same may be said for shift measurements which determine $\omega_k(1)$, in the case of polyatomic crystals or impurities. However, in all these cases extensive calculations must be done before the comparison can be made. It should be emphasized that f measurements on polycrystalline samples of anisotropic materials are much less useful than ones made on single crystals. In materials like Fe the magnetic contribution prevents the determination of moments from specific-heat data and hence Mössbauer measurements can provide useful information.

Perhaps $\gamma_{jk}(-2)$ values will provide useful information about anharmonicity but more theoretical and/or experimental work will be needed to decide this question.

It seems that work to see if the shift due to $\langle v_k^2\rangle$ and the temperature-dependent isomer shift can be separated would be useful. In this regard a theoretical prediction of the form of the isomer shift versus temperature would help. More accurate and extensive measurements are probably also needed. An interesting experiment would be to measure the temperature shift for two different nuclear transitions in the same element. The difference would be due only to isomer shift; hence, the form of the difference versus temperature would show how the isomer shift varies with temperature.

The theoretical uncertainty about how $\langle x_{jk}^2\rangle$ depends on various force constants in the lattice suggests that a series of f measurements on isomorphous crystals might be interesting.

In simple diatomic crystals with the NaCl structure measurement of $\omega_k(2)$ for one component can be used together with specific-heat data to determine $\omega_{k'}(2)$ for the other component. The difference between them then would for example give the difference between a sum over Na-Na force constants and a sum over Cl-Cl force constants. This difference should arise only from second-neighbor overlap forces and the difference in polarizability of the ions and hence should provide some information about the importance of these quantities.

Mössbauer measurements on impurities in lattices for which the host atomic force constants are known together with an analysis of the type done by Lehman and DeWames[18] could in principle yield quantitative information on force-constant changes. If the systems studied are properly chosen, it seems likely that this could yield useful information concerning the quantities

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[27] T. H. K. Barron, J. A. Leadbetter, and J. A. Morrison, Proc. Roy. Soc. (London) A279, 62 (1964).

which are involved in attempts to calculate atomic force constants from first principles.[28] It seems likely that a systematic study of impurity systems will reveal interesting correlations even in the absence of such detailed analysis.

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[28] H. C. White, Phys. Rev. 112, 1092 (1958).

ACKNOWLEDGMENTS

We would like to acknowledge helpful discussions with Dr. K. K. Singh and with Professor B. R. A. Nijboer. One of us (RMH) would like to express his sincere thanks to Professor H. de Waard for making his stay at Groningen possible.

PHYSICAL REVIEW VOLUME 146, NUMBER 2 10 JUNE 1966

Temperature Dependence of Infrared Dispersion in Ionic Crystals LiF and MgO*

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(Received 27 December 1965)

Infrared-reflectivity measurements were made from 200 cm^{-1} to 800 cm^{-1} at temperatures ranging from 7.5 to 1060°K for LiF and from 8 to 1950°K for MgO. The reflection spectra were analyzed by means of a two-resonance damped-oscillator model, and the calculated optical properties are presented. Dielectric dispersion theory is reviewed and it is shown that all the major theories discussed give identical results for the susceptibility when evaluated at the reststrahlen frequency but differ from one another at other frequencies. The damping constant γ for LiF and MgO in the high-temperature limit ($h\nu_1<kT$) agrees reasonably well with the formula suggested by Maradudin and Wallis, but discrepancies seem to appear in the low-temperature limit ($h\nu_1>kT$). The general behavior of the extinction coefficient in the wings of the absorption region is consistent with the notion of continuous absorption produced by multiphonon processes. The shift of the long-wavelength optical-mode frequencies of LiF, MgO, and RbI with temperature is discussed in terms of the volume and other anharmonic effects. The anharmonic part of the frequency shift is found to agree qualitatively with the theory of Maradudin and Fein.

I. INTRODUCTION

IN this paper the infrared reflection spectra of single-crystal LiF and MgO are presented as functions of temperature ranging from 7.5°K to near their respective melting points. The experimental work was motivated by the fact that very few self-consistent measurements of the infrared reflectivity have been made for such wide temperature ranges. By using a two-resonance damped-oscillator model, numerical values for the high and low-frequency dielectric constants, long-wavelength optic-mode frequencies and damping constants are obtained as functions of temperature. The results are discussed in relation to the existing theoretical models used to represent the dielectric constant. The relationship between the experimentally determined dielectric constant in the infrared for an ionic crystal and that predicted by theory has been extensively discussed in the literature. A brief review of the theoretical models for representing the dielectric constant of ionic crystals is presented here. The width and shift of the one-phonon frequencies with temperature are discussed in the light of existing lattice dynamical theories of ionic crystals incorporating anharmonic forces.

II. EXPERIMENTAL PROCEDURE

Infrared-reflectivity measurement at low and high temperatures were made using a Perkin-Elmer Model 12 monochromator equipped with a cesium bromide and a cesium iodide prism. A special fore-optical system was designed and built such that both a low- and high-temperature cell could be attached to the spectrometer. The entire system was enclosed in a thick-walled plexiglass housing and could be continuously flushed with a dry inert gas. For measurements at liquid-nitrogen temperatures and above, dry nitrogen was used to flush the spectrometer. At liquid-helium temperatures high-purity helium gas was used. The reflectivities were determined by a measurement of the

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* Parts of this paper were presented at the Eighth European Congress on Molecular Spectroscopy, held in Copenhagen, Denmark, August 15–20, 1965, and the American Physical Society Meeting held in Honolulu, Hawaii, September 2, 1965. Some of the preliminary data were published in Appl. Phys. Letters, Vol. 5, No. 2 (1964).

† The experimental work and some of the analytical work was done by J. R. Jasperse while at Arthur D. Little, Inc., Cambridge, Massachusetts under contract with U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research.

‡ The analytical work done by S. S. Mitra was also supported by U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research.