Debye-Waller Factor for Mössbauer Resonant Impurity Atoms

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The probability for recoilless resonant gamma-ray emission or absorption by atoms present as impurities in a host lattice has been evaluated in the high-temperature limit. The effect of interatomic force constant differences between impurity atoms and host lattice atoms is included explicitly for a simple model. The first order quantum corrections have been calculated for the case of an isotopic impurity (no force constant difference). The Debye-Waller factor at high temperatures is determined largely by the stiffness of the host lattice, and partially by the forces between host and impurity atoms. The effects of the host and impurity masses appear only in the quantum corrections.

I. INTRODUCTION

IN many Mössbauer-effect experiments the atoms whose nuclei are resonant are present as a dilute solid solution in a crystal of some other material. In such cases, the details of the thermal vibrations of the active atoms and the effects of this motion on the observed resonance pattern are of interest for two reasons. First, one may use the Mössbauer effect as a technique for studying the dynamics of the active atoms, and to derive some information about the interatomic forces between the solute and host atoms. Secondly, if one is performing a Mössbauer experiment to investigate some other aspect of the solid, it is important to know, at least approximately, the way in which purely dynamical effects influence the experimental results.

The vibrations of the resonant atoms affect both the position and the amplitude of the observed resonance peak. The effect on peak position, the "second-order Doppler shift" which depends on the mean square velocity of the resonant atoms, has been treated by us in a previous paper[1] and will not be discussed here. The effect on peak height which depends on the amplitude of vibration of the resonant atoms was considered by Mössbauer in his original work, and has been analyzed by a number of workers since,[2] but the particular problem which concerns us, the case of the dilute impurity, has not been solved in quantitative detail. Our approach is more restricted than many others, in that we consider only the vibrations of a crystal in the harmonic approximation, and only the zero-phonon processes. Non-periodic motions of the atoms, such as diffusive jumps, are not considered in our analysis nor do we consider the displaced resonances associated with phonon emission or absorption.

The probability that resonant gamma-ray emission or absorption will occur without phonon emission or absorption (a zero-phonon process) is often referred to as the "Debye-Waller factor" by analogy with the corresponding factor for the coherent scattering of x rays. For the case of an impure crystal, the terminology is

slightly misleading, since there is an important basic difference between the phenomena. In the x-ray case, all the atoms in the crystal take part in the scattering, and the scattered intensity depends on the relative displacements of atom pairs, summed over all pairs in the crystal. In the case of gamma-ray resonance, only one nucleus is involved at a time, and the probability of a zero-phonon process depends only on the amplitude of vibration of that nucleus. Our problem, therefore, is to calculate the appropriate thermal average for the impurity atoms only.

By general arguments of momentum conservation and translational invariance, Lipkin[2] has shown that the relative probability $P(f,i)$, of a gamma-ray emission or absorption which is accompanied by a transition of the crystal lattice from state $|E_i\rangle$ to state $|E_f\rangle$ is given by

$$P(f,i) = |\langle E_f | \exp i\mathbf{\kappa} \cdot \mathbf{R}(l) | E_i\rangle|^2, \qquad (1.1)$$

where $\mathbf{\kappa}$ is the momentum vector of the gamma ray and $\mathbf{R}(l)$ is the position vector of the resonant atom. We are concerned here only with the relative probability of those events in which no phonons are emitted or absorbed, and hence, leave the lattice unchanged. This is clearly given by $P(i,i) = |\langle E_i | \exp i\mathbf{\kappa} \cdot \mathbf{R}(l) | E_i\rangle|^2$. However, we do not know the initial state of the crystal, and in the usual way express this ignorance by averaging $P(i,i)$ over an equilibrium distribution of initial states

$$f = \langle P \rangle = \frac{\sum_i e^{-\beta E_i} |\langle E_i | \exp i\mathbf{\kappa} \cdot \mathbf{R}(l) | E_i\rangle|^2}{\sum_i e^{-\beta E_i}}. \qquad (1.2)$$

As pointed out by Van Hove,[3] however, for the analogous problem of neutron scattering, the thermal average of the square of a matrix element of this sort is awkward to evaluate directly; but, fortunately, the correct result is obtained by calculating the thermal average of $\exp i\mathbf{\kappa} \cdot \mathbf{R}(l)$ itself, and then squaring it. Moreover, since $\mathbf{R}(l) = \mathbf{x}(l) + \mathbf{u}(l)$, where $\mathbf{x}(l)$ is the position vector of the equilibrium position of the lth atom, a constant, and $\mathbf{u}(l)$ is the displacement of this atom from its equilibrium position, our problem is reduced to the evaluation of the

[1] A. A. Maradudin, P. A. Flinn, and S. L. Ruby, Phys. Rev. **126**, 9 (1962).

[2] W. M. Visscher, Ann. Phys. **9**, 194 (1960); H. J. Lipkin, Ann. Phys. **9**, 332 (1960); K. S. Singwi and A. Sjölander, Phys. Rev. **120**, 1093 (1960).

[3] L. Van Hove, Technical Report No. 11, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, 1959 (unpublished).

thermal average of $\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)$, which we denote by $\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle$. The fraction of recoiless events f is then given by $|\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle|^2$.

For simplicity, we restrict our calculations to the case of cubic crystals with one atom in the primitive unit cell, and in investigating the effect of force constant changes, use the specific model of a face-centered cubic crystal with only nearest-neighbor interactions, which we have used elsewhere.[4] The generalizations to more complex crystals, and to more elaborate models, are straightforward, but such elaboration does not seem justified at present.

Finally, our calculations in this paper are restricted to the high-temperature limit, where by high temperatures we mean those of the order of, or greater than, the high-temperature Debye characteristic temperature of the host crystal. This restriction is due primarily to the simple dependence on temperature the results in this limit possess, which should make the interpretation of experimental data somewhat easier than at very low temperatures, where the temperature dependence of the results is less pronounced. In the high-temperature limit the thermal average of an operator O is given by

$$\langle O\rangle=\frac{\int\cdots\int e^{-\beta H}O\,d\Omega}{\int\cdots\int e^{-\beta H}d\Omega},\tag{1.3}$$

where H is the crystal Hamiltonian, and where $d\Omega$ is the volume element in the $6N$-dimensional phase space for the crystal.

II. A MASS DEFECT

In this section we calculate the thermal average $\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle$ in the special case that the mass of the atom at $\mathbf{x}(l)$ is changed from its normal value M to a value $M'=(1-\epsilon)M$ without any changes in the atomic forces which link it to its neighbors in the crystal.

It is easy to show that in the classical limit the change in mass of the lth atom will not change the value of $\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle$ from what it is for the perfect monatomic crystal. This conclusion follows from the explicit expression for $\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle$ in the classical limit

$$\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle$$

$$=\frac{\int\cdots\int\exp(-\beta H)\exp[i\boldsymbol{\kappa}\cdot\mathbf{u}(l)]d^{3N}p\,d^{3N}u}{\int\cdots\int\exp(-\beta H)d^{3N}p\,d^{3N}u},\tag{2.1}$$

where H is the crystal Hamiltonian,

$$H=\sum_{l\alpha}\frac{p_\alpha^2(l)}{2M_l}+\tfrac{1}{2}\sum_{l\alpha,l'\beta}\Phi_{\alpha\beta}(ll')u_\alpha(l)u_\beta(l).\tag{2.2}$$

In Eq. (2.2), $u_\alpha(l)$ is the α-Cartesian component of the displacement of the lth atom from its equilibrium position in the static lattice; $\Phi_{\alpha\beta}(ll')=\Phi_{\alpha\beta}(l-l')$ is an atomic force constant of the crystal; M_l is the mass of the lth atom; and $p_\alpha(l)$ is the α component of the momentum of the lth atom, $p_\alpha(l)=M_l\dot{u}_\alpha(l)$. If we substitute Eq. (2.2) into Eq. (2.1) and note that the integrations over the momenta are independent of the integrations over the displacements and hence cancel between the numerator and denominator of Eq. (2.1), we find that

$$\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle=\frac{\int\cdots\int\exp[-\tfrac{1}{2}\beta\sum\Phi_{\alpha\beta}(ll')u_\alpha(l)u_\beta(l')+i\boldsymbol{\kappa}\cdot\mathbf{u}(l)]d^{3N}u}{\int\cdots\int\exp[-\tfrac{1}{2}\beta\sum\Phi_{\alpha\beta}(ll')u_\alpha(l)u_\beta(l')]d^{3N}u}.\tag{2.3}$$

The atomic masses no longer appear in this expression and this establishes our initial statement.

To obtain the effect of a pure mass defect in the high-temperature limit we must, accordingly, consider the quantum corrections to the thermal average expressed by Eq. (2.1). A way of evaluating these corrections was indicated by Wigner[5] who showed that they are given correctly by Eq. (2.1), if the statistical weighting factor $\exp(-\beta H)$ is replaced by

$$e^{-\beta H}(1+\hbar^2 g_2+\hbar^4 g_4+\cdots),\tag{2.4}$$

where in our notation the coefficient g_2 is given by

[4] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. **15**, 360 (1961).
[5] E. Wigner, Phys. Rev. **40**, 749 (1932).

$$g_2=-\frac{\beta^2}{8}\sum_{l\alpha}\frac{1}{M_l}\frac{\partial^2 V}{\partial[u_\alpha(l)]^2}+\frac{\beta^3}{24}\sum_{l\alpha}\frac{1}{M_l}\left(\frac{\partial V}{\partial u_\alpha(l)}\right)^2$$

$$+\frac{\beta^3}{24}\sum_{l\alpha,l'\beta}\frac{p_\alpha(l)p_\beta(l')}{M_l M_{l'}}\frac{\partial^2 V}{\partial u_\alpha(l)\partial u_\beta(l')}\tag{2.5}$$

$$=-\frac{\beta^2}{8}\sum_{l\alpha}\frac{1}{M_l}\Phi_{\alpha\alpha}(ll)$$

$$+\frac{\beta^3}{24}\sum_{l\alpha}\frac{1}{M_l}\left[\sum_{l'\beta}\Phi_{\alpha\beta}(ll')u_\beta(l')\right]^2$$

$$+\frac{\beta^3}{24}\sum_{l\alpha,l'\beta}\frac{\Phi_{\alpha\beta}(ll')}{M_l M_{l'}}p_\alpha(l)p_\beta(l').\tag{2.6}$$

In Eq. (2.5), V represents the potential energy term of the Hamiltonian (2.2).

In this paper we will be interested in just the first quantum correction to the classical result for $\langle \exp i\mathbf{\kappa} \cdot \mathbf{u}(l) \rangle$, and from Eq. (2.4) we see that correct to order $\hbar^2$ we can rewrite the statistical weight function given by Eq. (2.4) as

$$e^{-\beta H + \hbar^2 \sigma 2}. \tag{2.7}$$

If we note that the first term of Eq. (2.6) is a constant, while the last term of this expression is a function of the momenta only, and use the fact that the integrations over coordinates and momenta factor, we are led to the result that correct to order $\hbar^2$

$$\langle \exp i\mathbf{\kappa} \cdot \mathbf{u}(l) \rangle = \frac{\int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum \Phi_{\alpha\beta}(ll')u_\alpha(l)u_\beta(l') + \frac{\hbar^2 \beta^3}{24} \sum \frac{1}{M_l}[\sum \Phi_{\alpha\beta}(ll')u_\beta(l')]^2 + i\mathbf{\kappa} \cdot \mathbf{u}(l) \right\} d^{3N}u}{\int \cdots \int \exp\left\{ -\frac{\beta}{2} \sum \Phi_{\alpha\beta}(ll')u_\alpha(l)u_\beta(l') + \frac{\hbar^2 \beta^3}{24} \sum \frac{1}{M_l}[\sum \Phi_{\alpha\beta}(ll')u_\beta(l')]^2 \right\} d^{3N}u}. \tag{2.8}$$

We now write

$$\sum_{l\alpha} \frac{1}{M_l}[\sum_{l'\beta} \Phi_{\alpha\beta}(ll')u_\beta(l')]^2$$

$$= \frac{1}{M} \sum_{l\alpha} [\sum_{l'\beta} \Phi_{\alpha\beta}(ll')u_\beta(l')]^2$$

$$+ \left(\frac{1}{M_l} - \frac{1}{M}\right)\sum_\alpha [\sum_{l'\beta} \Phi_{\alpha\beta}(ll')u_\beta(l')]^2. \tag{2.9}$$

Since $M_l = (1 - \epsilon)M$, we have that

$$\frac{1}{M_l} - \frac{1}{M} = \frac{\epsilon}{(1 - \epsilon)M} \equiv \frac{\lambda}{M}. \tag{2.10}$$

It is now convenient to transform to normal coordinates according to

$$u_\alpha(l) = \frac{1}{(NM)^{\frac{1}{2}}} \sum_{kj} e_\alpha(\mathbf{k}j)Q(\mathbf{k}j)e^{2\pi i\mathbf{k} \cdot \mathbf{x}(l)}. \tag{2.11}$$

In Eq. (2.11), N is the number of unit cells in the crystal, $e_\alpha(\mathbf{k}j)$ is the α-Cartesian component of the polarization vector for the lattice wave described by the propagation vector $\mathbf{k}$ and the branch index j. The allowed values of $\mathbf{k}$ are uniformly and densely distributed throughout a unit cell of the lattice reciprocal to that defined by the translation vector $\mathbf{x}(l)$. In order that $u_\alpha(l)$ be real, we adopt the following conventions:

$$Q(-\mathbf{k}j) = Q^*(\mathbf{k}j), \quad \mathbf{e}(-\mathbf{k}j) = \mathbf{e}(\mathbf{k}j). \tag{2.12}$$

The components of the vector $\mathbf{e}(\mathbf{k}j)$ satisfy the orthonormality and closure relations

$$\sum_\alpha e_\alpha(\mathbf{k}j)e_\alpha(\mathbf{k}j') = \delta_{jj'}, \tag{2.13a}$$

$$\sum_j e_\alpha(\mathbf{k}j)e_\beta(\mathbf{k}j) = \delta_{\alpha\beta}. \tag{2.13b}$$

If we apply this transformation to the lattice potential energy, we obtain

$$\frac{1}{2} \sum_{l\alpha, l'\beta} \Phi_{\alpha\beta}(ll')u_\alpha(l)u_\beta(l')$$

$$= \frac{1}{2} \sum_{kj} \omega_j^2(\mathbf{k})Q(\mathbf{k}j)Q(-\mathbf{k}j), \tag{2.14}$$

where $\omega_j(\mathbf{k})$ is the frequency of the vibration mode $(\mathbf{k}j)$, and is obtained from the equation

$$\omega_j^2(\mathbf{k})e_\alpha(\mathbf{k}j) = \sum_\beta D_{\alpha\beta}(\mathbf{k})e_\beta(\mathbf{k}j), \tag{2.15}$$

where

$$D_{\alpha\beta}(\mathbf{k}) = (1/M)\sum_l \Phi_{\alpha\beta}(l)e^{-2\pi i\mathbf{k} \cdot \mathbf{x}(l)}. \tag{2.16}$$

In a similar fashion, we find that

$$\sum_{l'\beta} \Phi_{\alpha\beta}(ll')u_\beta(l')$$

$$= \left(\frac{M}{N}\right)^{\frac{1}{2}} \sum_{kj} \omega_j^2(\mathbf{k})e_\alpha(\mathbf{k}j)Q(\mathbf{k}j)e^{2\pi i\mathbf{k} \cdot \mathbf{x}(l)}, \tag{2.17}$$

so that

$$\sum_{l\alpha} [\sum_{l'\beta} \Phi_{\alpha\beta}(ll')u_\beta(l')]^2$$

$$= M \sum_{kj} \omega_j^4(\mathbf{k})Q(\mathbf{k}j)Q(-\mathbf{k}j), \tag{2.18}$$

where we have used Eqs. (2.13a), (2.15), (2.16) and the relation

$$\sum_l e^{2\pi i\mathbf{k} \cdot \mathbf{x}(l)} = N\Delta(\mathbf{k}). \tag{2.19}$$

The function $\Delta(\mathbf{k})$ is unity, if $\mathbf{k} = 0$ or a reciprocal lattice vector and vanishes otherwise.

From Eq. (2.17), we obtain also the result that

$$\sum_\alpha [\sum_{l'\beta} \Phi_{\alpha\beta}(ll')u_\beta(l')]^2 = \frac{M}{N} \sum_{k_1 j_1} \sum_{k_2 j_2} \mathbf{e}(\mathbf{k}_1 j_1) \cdot \mathbf{e}(\mathbf{k}_2 j_2)\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_2)e^{2\pi i(\mathbf{k}_1 + \mathbf{k}_2) \cdot \mathbf{x}(l)}Q(\mathbf{k}_1 j_1)Q(\mathbf{k}_2 j_2). \tag{2.20}$$

Finally, we have the result that

$$\boldsymbol{\kappa}\cdot\mathbf{u}(l)=\frac{1}{(NM)^{\frac{1}{2}}}\sum_{kj}\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)Q(\mathbf{k}j)e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}=\sum_{kj}C(\mathbf{k}j)Q(\mathbf{k}j).\qquad(2.21)$$

It should be kept in mind that the coefficient $C(\mathbf{k}j)$ is a function of $\mathbf{x}(l)$.

Combining Eqs. (2.9), (2.14), (2.18), and (2.19) we find that the integral in the denominator of Eq. (2.8) becomes

$$I_0=\int\cdots\int\exp\!\left[-\frac{\beta}{2}\sum_{kj}\Omega_j{}^2(\mathbf{k})Q(\mathbf{k}j)Q(-\mathbf{k}j)+\lambda\sum_{k_1j_1}\sum_{k_2j_2}B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)Q(\mathbf{k}_1j_1)Q(\mathbf{k}_2j_2)\right]d\Omega(Q),\qquad(2.22)$$

where

$$\Omega_j{}^2(\mathbf{k})=\omega_j{}^2(\mathbf{k})-\tfrac{1}{12}\hbar^2\beta^2\omega_j{}^4(\mathbf{k}),\qquad(2.23)$$

$$B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)=\frac{\hbar^2\beta^3}{24N}[\mathbf{e}(\mathbf{k}_1j_1)\cdot\mathbf{e}(\mathbf{k}_2j_2)]\omega_{j_1}{}^2(\mathbf{k}_1)\omega_{j_2}{}^2(\mathbf{k}_2)e^{2\pi i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{x}(l)},\qquad(2.24)$$

and $d\Omega(Q)$ is the volume element of the phase space of the Q variables.

The integral in the numerator of Eq. (2.8) becomes

$$I_1=\int\cdots\int\exp\left\{-\frac{\beta}{2}\sum_{kj}\Omega_j{}^2(\mathbf{k})Q(\mathbf{k}j)Q(-\mathbf{k}j)+\lambda\sum_{k_1j_1k_2j_2}B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)Q(\mathbf{k}_1j_1)Q(\mathbf{k}_2j_2)\right.$$

$$\left.+\frac{i}{2}\sum_{kj}[C(\mathbf{k}j)Q(\mathbf{k}j)+C(-\mathbf{k}j)Q(-\mathbf{k}j)]\right\}d\Omega(Q)$$

$$=\int\cdots\int\exp\left\{-\frac{\beta}{2}\sum_{kj}\Omega_j{}^2(\mathbf{k})\left[Q(\mathbf{k}j)-i\frac{C(-\mathbf{k}j)}{\beta\Omega_j{}^2(\mathbf{k})}\right]\left[Q(-\mathbf{k}j)-i\frac{C(\mathbf{k}j)}{\beta\Omega_j{}^2(\mathbf{k})}\right]\right.$$

$$\left.-\frac{1}{2\beta}\sum_{kj}\frac{C(\mathbf{k}j)C(-\mathbf{k}j)}{\Omega_j{}^2(\mathbf{k})}+\lambda\sum_{k_1j_1k_2j_2}B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)Q(\mathbf{k}_1j_1)Q(\mathbf{k}_2j_2)\right\}d\Omega(Q).\qquad(2.25)$$

We now make a change of variables:

$$Q(\mathbf{k}j)=P(\mathbf{k}j)+iA(\mathbf{k}j),\qquad(2.26)$$

where

$$A(\mathbf{k}j)=\frac{C(-\mathbf{k}j)}{\beta\Omega_j{}^2(\mathbf{k})}=\frac{\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)}{(NM)^{\frac{1}{2}}}\frac{e^{-2\pi i\mathbf{k}\cdot\mathbf{x}(l)}}{\beta\Omega_j{}^2(\mathbf{k})}.\qquad(2.27)$$

In terms of these new variables the integral I_1 becomes

$$I_1=e^{-M}\int\cdots\int e^{-\beta(H_0+H_1+\eta H_2)}d\Omega(P)=e^{-M}I_{11},\qquad(2.28)$$

with

$$M=\frac{1}{2\beta}\sum_{kj}\frac{C(\mathbf{k}j)C(-\mathbf{k}j)}{\Omega_j{}^2(\mathbf{k})}$$

$$+\lambda\sum_{k_1j_1k_2j_2}B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)A(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2),\qquad(2.29\mathrm{a})$$

$$H_0=\tfrac{1}{2}\sum_{kj}\Omega_j{}^2(\mathbf{k})P(\mathbf{k}j)P(-\mathbf{k}j),\qquad(2.29\mathrm{b})$$

$$H_1=-\frac{\lambda}{\beta}\sum_{k_1j_1k_2j_2}B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)P(\mathbf{k}_1j_1)P(\mathbf{k}_2j_2),\qquad(2.29\mathrm{c})$$

$$H_2=-\frac{2i\lambda}{\beta}\sum_{k_1j_1k_2j_2}B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)A(\mathbf{k}_1j_1)P(\mathbf{k}_2j_2).\qquad(2.29\mathrm{d})$$

In Eq. (2.28), $d\Omega(P)$ is the volume element in the phase space of the P variables. It can be shown[6] that the P variables are completely equivalent to the Q variables for calculating thermal averages in the harmonic approximation, and if we wished we could replace the P's by Q's in Eqs. (2.28) and (2.29). The parameter η in Eq. (2.28) is merely an order parameter which we set equal to unity at the end of the calculation.

We can thus express Eq. (2.8) as

$$\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle=e^{-M}I_{11}/I_0.\qquad(2.30)$$

The integral I_0, Eq. (2.22), is recognized to be the partition function of a system whose Hamiltonian is H_0+H_1. Thus, we can write it as

$$I_0=e^{-\beta F},\qquad(2.31)$$

where F is the Helmholtz free energy of this system. Similarly, the integral I_{11} is the partition function for a system whose Hamiltonian is $H_0+H_1+\eta H_2$. Thus, we can write I_{11} as

$$I_{11}=e^{-\beta F-\beta\Delta F},\qquad(2.32)$$

where ΔF is that part of the Helmholtz free energy of this system which is at least linear in η. We thus obtain the result that

$$\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle=e^{-M-\beta\Delta F}.\qquad(2.33)$$

[6] A. A. Maradudin and P. A. Flinn (to be published).

We must now evaluate ΔF correct to order $\hbar^2$. However, we can easily show that ΔF is of order $\hbar^4$, so that to the order of the approximation to which we work we can neglect it in Eq. (2.33). We start with the relation

$$F+\Delta F=-\frac{1}{\beta}\ln Z_0$$
$$\times\int\cdots\int\frac{e^{-\beta H_0}}{Z_0}e^{-\beta(H_1+\eta H_2)}d\Omega(P), \quad (2.34)$$

where

$$Z_0=\int\cdots\int e^{-\beta H_0}d\Omega(P). \quad (2.35)$$

We thus have that

$$F+\Delta F=F_0-\frac{1}{\beta}\ln\langle e^{-\beta(H_1+\eta H_2)}\rangle_0, \quad (2.36)$$

where F_0 is $-(1/\beta)\ln Z_0$ and $\langle\cdots\rangle_0$ denotes an average over the canonical ensemble defined by the statistical weight function $Z_0^{-1}\exp(-\beta H_0)$. Expanding the loga-

rithm in Eq. (2.36) in terms of cumulants,[7] we obtain

$$F+\Delta F=F_0-\frac{1}{\beta}\left\{-\beta\langle H_1+\eta H_2\rangle_0+\frac{\beta^2}{2!}[\langle(H_1+\eta H_2)^2\rangle_0\right.$$
$$\left.-\langle H_1+\eta H_2\rangle_0^2]-\cdots\right\}. \quad (2.37)$$

Since F_0 is independent of η, we obtain for ΔF the expansion

$$\Delta F=\langle H_2\rangle_0-\tfrac{1}{2}\beta[\langle 2H_1H_2+H_2^2\rangle_0$$
$$-2\langle H_1\rangle_0\langle H_2\rangle_0-\langle H_2\rangle_0^2]+\cdots. \quad (2.38)$$

However, since $\langle H_2\rangle_0$ vanishes as does $\langle H_1H_2\rangle_0$, we see that the leading term in the expansion of ΔF is

$$\Delta F=-\tfrac{1}{2}\beta\langle H_2^2\rangle_0+\cdots, \quad (2.39)$$

and this according to Eqs. (2.29d) and (2.24) is of order $\hbar^4$.

We have obtained the result that, correct to order $\hbar^2$,

$$\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle=\exp\left\{-\frac{1}{2\beta}\sum\frac{C(\mathbf{k}j)C(-\mathbf{k}j)}{\Omega_j^2(\mathbf{k})}-\lambda\sum_{\mathbf{k}_1j_1\mathbf{k}_2j_2}B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)A(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2)\right\}. \quad (2.40)$$

With the aid of Eqs. (2.21) and (2.23), we find

$$\frac{1}{2\beta}\sum_{\mathbf{k}j}\frac{C(\mathbf{k}j)C(-\mathbf{k}j)}{\Omega_j^2(\mathbf{k})}=\frac{1}{2\beta}\sum_{\mathbf{k}j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{NM}\left[\frac{1}{\omega_j^2(\mathbf{k})}+\frac{\hbar^2\beta^2}{12}+O(\hbar^4)\right]$$
$$=\frac{kT}{2NM}\sum_{\mathbf{k}j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega_j^2(\mathbf{k})}+\frac{\hbar^2\kappa^2}{24MkT}+O(\hbar^4). \quad (2.41)$$

Similarly, we have that

$$\sum_{\mathbf{k}_1j_1\mathbf{k}_2j_2}B(\mathbf{k}_1j_1;\mathbf{k}_2j_2)A(\mathbf{k}_1j_1)A(\mathbf{k}_2j_2)=\frac{\hbar^2}{24N^2}\frac{1}{MkT}\sum_{\mathbf{k}_1j_1\mathbf{k}_2j_2}[\mathbf{e}(\mathbf{k}_1j_1)\cdot\mathbf{e}(\mathbf{k}_2j_2)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}_2j_2)]+O(\hbar^4)$$
$$=\frac{\hbar^2\kappa^2}{24MkT}+O(\hbar^4). \quad (2.42)$$

Combining Eqs. (2.40), (2.41), and (2.42), we obtain finally

$$\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle=\exp\left\{-\frac{kT}{2NM}\sum_{\mathbf{k}j}\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega_j^2(\mathbf{k})}-\frac{\hbar^2\kappa^2}{24(1-\epsilon)MkT}+O(\hbar^4)\right\}. \quad (2.43)$$

In the case of cubic crystals, this expression simplifies to

$$\langle\exp i\boldsymbol{\kappa}\cdot\mathbf{u}(l)\rangle=\exp\left\{-\frac{kT}{6NM}\kappa^2\sum_{\mathbf{k}j}\frac{1}{\omega_j^2(\mathbf{k})}-\frac{\hbar^2\kappa^2}{24(1-\epsilon)MkT}+O(\hbar^4)\right\}. \quad (2.44)$$

III. A FORCE CONSTANT CHANGE

When the Mössbauer active impurity is an atom whose potential of interaction with the atoms of the host crystal differs from that between the atoms of the host crystal, the effects of this force constant change show up in the classical limit. However, because the

effects of an accompanying mass difference will not show up in this limit, we can assume that the mass of the impurity is that of a normal atom in the crystal.

[7] M. G. Kendall and A. Stuart, *The Advanced Theory of Statistics* (Charles Griffin and Company, Ltd., London, 1943), Vol. I, Chap. 3. See also, R. Brout, Phys. Rev. **115**, 824 (1959).

The Hamiltonian for the crystal can be written

$$H = \sum_{l\alpha} \frac{p_\alpha^2(l)}{2M} + \frac{1}{2} \sum_{l\alpha, l'\beta} \Phi_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l') + \frac{1}{2} \sum_{l\alpha, l'\beta} \Delta_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l'),$$

where $\Delta_{\alpha\beta}(ll')$ represents the change in the atomic force constants due to the impurity and is nonvanishing only if either l or l' refers to the site of the impurity atom. The expectation value $\langle \exp i\mathbf{\kappa} \cdot \mathbf{u}(l) \rangle$ becomes

$$\langle \exp i\mathbf{\kappa} \cdot \mathbf{u}(l) \rangle = \frac{\int \cdots \int \exp\{-\frac{1}{2}\beta \sum \Phi_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l) - \frac{1}{2}\beta \sum \Delta_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l') + i\mathbf{\kappa} \cdot \mathbf{u}(l)\} d^{3N}u}{\int \cdots \int \exp\{-\frac{1}{2}\beta \sum \Phi_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l') - \frac{1}{2}\beta \sum \Delta_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l')\} d^{3N}u}$$

$$= J_1/J_0. \tag{3.1}$$

We now carry out the normal coordinate transformation (2.11) on the expression appearing in the exponent of the integrand in the denominator of Eq. (3.1), whereupon we obtain

$$J_0 = \int \cdots \int e^{-\beta(H_0 + H_1)} d\Omega(Q), \tag{3.2}$$

where

$$H_0 = \frac{1}{2} \sum_{\mathbf{k}j} \omega_j^2(\mathbf{k}) Q(\mathbf{k}j) Q(-\mathbf{k}j), \tag{3.3}$$

$$H_1 = \frac{1}{2} \sum_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2} C(\mathbf{k}_1 j_1; \mathbf{k}_2 j_2) Q(\mathbf{k}_1 j_1) Q(\mathbf{k}_2 j_2), \tag{3.4}$$

with

$$C(\mathbf{k}_1 j_1; \mathbf{k}_2 j_2) = \frac{1}{NM} \sum_{m\alpha, n\beta} \Delta_{\alpha\beta}(mn) e_\alpha(\mathbf{k}_1 j_1) e_\beta(\mathbf{k}_2 j_2)$$

$$\times e^{2\pi i \mathbf{k}_1 \cdot \mathbf{x}(m)} e^{2\pi i \mathbf{k}_2 \cdot \mathbf{x}(n)}. \tag{3.5}$$

We carry out the same coordinate transformation in the integral J_1, and then replace the Q variables by P variables according to

$$Q(\mathbf{k}j) = P(\mathbf{k}j) + iA(\mathbf{k}j), \tag{3.6}$$

where

$$A(\mathbf{k}j) = \frac{\mathbf{\kappa} \cdot \mathbf{e}(\mathbf{k}j)}{(NM)^{\frac{1}{2}}} \frac{e^{-2\pi i \mathbf{k} \cdot \mathbf{x}(l)}}{\beta \omega_j^2(\mathbf{k})}. \tag{3.7}$$

The result of these transformations is that

$$J_1 = e^{-M_0 + M_1} \int \cdots \int e^{-\beta(H_0 + H_1 + \eta H_2)} d\Omega(P)$$

$$= e^{-M_0 + M_1} J_{11}, \tag{3.8}$$

where

$$M_0 = \frac{1}{2\beta} \sum_{\mathbf{k}j} \frac{C(\mathbf{k}j)C(-\mathbf{k}j)}{\omega_j^2(\mathbf{k})}, \tag{3.9}$$

$$M_1 = \frac{\beta}{2} \sum_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2} C(\mathbf{k}_1 j_1; \mathbf{k}_2 j_2) A(\mathbf{k}_1 j_1) A(\mathbf{k}_2 j_2), \tag{3.10}$$

$$H_2 = i \sum_{\mathbf{k}_1 j_1 \mathbf{k}_2 j_2} C(\mathbf{k}_1 j_1; \mathbf{k}_2 j_2) A(\mathbf{k}_1 j_1) P(\mathbf{k}_2 j_2). \tag{3.11}$$

H_0 and H_1 are given by Eqs. (3.3) and (3.4). The parameter η is again merely an order parameter and will be set equal to unity at the end of the calculation. The desired thermal average can thus be written

$$\langle \exp i\mathbf{\kappa} \cdot \mathbf{u}(l) \rangle = e^{-M_0 + M_1} J_{11}/J_0 \tag{3.12}$$

$$= e^{-M_0 + M_1 - \beta \Delta F}, \tag{3.13}$$

where ΔF is that part of the Helmholtz free energy for the system whose Hamiltonian is $H_0 + H_1 + \eta H_2$ which is at least linear in η.

To obtain ΔF we proceed as before. We have that

$$F + \Delta F = F_0 - \frac{1}{\beta} \ln \langle e^{-\beta(H_1 + \eta H_2)} \rangle_0, \tag{3.14}$$

where

$$F_0 = -\frac{1}{\beta} \ln \int \cdots \int e^{-\beta H_0} d\Omega(P) = -\frac{1}{\beta} \ln Z_0 \tag{3.15}$$

and $\langle \cdots \rangle_0$ denotes an average in the canonical ensemble described by the statistical weight function $Z_0^{-1} \exp(-\beta H_0)$. From Eq. (3.14), we obtain

$$F + \Delta F = F_0 - \frac{1}{\beta}\{-\beta \langle H_1 + \eta H_2 \rangle_0 + \frac{1}{2}\beta^2$$

$$\times [\langle (H_1 + \eta H_2)^2 \rangle_0 - \langle H_1 + \eta H_2 \rangle_0^2] + \cdots\} \tag{3.16}$$

to second order in $C(\mathbf{k}_1 j_1; \mathbf{k}_2 j_2)$. Recalling the definition

of ΔF, it is readily found that to second order

$$\Delta F = -\tfrac{1}{2}\beta\langle H_2{}^2\rangle_0$$

$$= \tfrac{1}{2}\beta \sum_{k_1 j_1 k_2 j_2} \sum_{k_3 j_3 k_4 j_4} C(k_1 j_1; k_2 j_2) C(k_3 j_3; k_4 j_4) A(k_1 j_1) A(k_3 j_3) \langle P(k_2 j_2) P(k_4 j_4)\rangle_0$$

$$= \tfrac{1}{2} \sum_{k_1 j_1 k_2 j_2 k_3 j_3} C(k_1 j_1; k_2 j_2) C(k_3 j_3; -k_2 j_2) \frac{A(k_1 j_1) A(k_3 j_3)}{\omega_{j_2}{}^2(k_2)}. \qquad (3.17)$$

In obtaining Eq. (3.17), we have used the well-known result that

$$\langle P(k_1 j_1) P(k_2 j_2)\rangle_0 = \frac{1}{\beta \omega_{j_1}{}^2(k_1)} \Delta(k_1 + k_2) \delta_{j_1 j_2}, \quad (3.18)$$

where $\Delta(k)$ is unity when k is zero or a reciprocal lattice vector and vanishes otherwise.

Equations (3.13), (3.9), (3.10), and (3.17) give us a result for $\langle \exp i\kappa \cdot u(l)\rangle$, which is correct to the second order in the departure of the impurity force constants from those of a perfect lattice. It only remains to evaluate M_0, M_1, and ΔF. From Eqs. (2.41) and (3.9), we see that

$$M_0 = \frac{kT}{2NM} \sum_{kj} \frac{[\kappa \cdot e(kj)]^2}{\omega_j{}^2(k)}. \qquad (3.19)$$

To evaluate M_1 and ΔF we need a model for our crystal. We choose the simplest nontrivial model of a three-dimensional crystal: a face-centered cubic crystal with nearest-neighbor central force interactions. In this case the force constant $\Phi_{\alpha\beta}(ll')$ becomes

$$\Phi_{\alpha\beta}(ll') = -\frac{\partial^2\phi(r)}{\partial x_\alpha \partial x_\beta}\Big|_{r=r^{ll'}}$$

$$= -\frac{x_\alpha x_\beta}{r^2}\phi''(r)\Big|_{r=r^{ll'}}, \qquad (3.20)$$

where $\phi(r)$ is the interaction energy between a pair of atoms separated by a distance r, and $r^{ll'}$ is the distance between atoms l and l'. If the interaction energy be-

tween the impurity atom and an atom of the host crystal is denoted by $\theta(r)$, then the coefficient $\Delta_{\alpha\beta}(ll')$ becomes

$$\Delta_{\alpha\beta}(ll') = \Big[-\frac{x_\alpha x_\beta}{r^2}\theta''(r) + \frac{x_\alpha x_\beta}{r^3}\theta'(r) - \frac{\delta_{\alpha\beta}}{r}\theta'(r)$$

$$+ \frac{x_\alpha x_\beta}{r^2}\phi''(r)\Big]_{r=r^{ll'}}, \qquad (3.21)$$

and vanishes unless either l or l' corresponds to the defect position. For our nearest-neighbor model, we can write Eq. (3.21) as

$$\Delta_{\alpha\beta}(ll') = [x_\alpha x_\beta A + \delta_{\alpha\beta} B]_{r=r^{ll'}}, \qquad (3.22)$$

where

$$A = -\frac{\theta''(r_0)}{r_0{}^2} + \frac{\theta'(r_0)}{r_0{}^3} + \frac{\phi''(r_0)}{r_0{}^2}, \qquad (3.23a)$$

$$B = -\frac{\theta'(r_0)}{r_0}, \qquad (3.23b)$$

and r_0 is the nearest-neighbor separation between atoms. r_0 equals $a_0/\sqrt{2}$, where a_0 is the lattice parameter.

In what follows we will make use of the relation

$$\Delta_{\alpha\beta}(mm) = -\sum_n{}' \Delta_{\alpha\beta}(mn), \qquad (3.24)$$

where the prime on the sum excludes the term with $m=n$.

Equation (3.5) for $C(k_1 j_1; k_2 j_2)$ becomes

$$C(k_1 j_1; k_2 j_2) = \sum_{mn}{}' \{ A[(x(n) - x(m)) \cdot e(k_1 j_1)][(x(n) - x(m)) \cdot e(k_2 j_2)]$$

$$+ Be(k_1 j_1) \cdot e(k_2 j_2) \} e^{2\pi i(k_1 + k_2)\cdot x(m)} \{ e^{2\pi i k_2 \cdot [x(n) - x(m)]} - 1 \}, \qquad (3.25)$$

where it should be kept in mind that the lattice points m and n refer to the defect and its nearest neighbors.

We are now in a position to evaluate M_1 and ΔF. The expression for M_1 is explicitly

$$M_1 = \frac{1}{2N^2 M^2 \beta} \sum_{k_1 j_1 k_2 j_2} \sum_{mn}{}' \frac{[\kappa \cdot e(k_1 j_1)][\kappa \cdot e(k_2 j_2)]}{\omega_{j_1}{}^2(k_1)\omega_{j_2}{}^2(k_2)} e^{2\pi i(k_1 + k_2)\cdot [x(m) - x(l)]}$$

$$\times \{ A[(x(n) - x(m)) \cdot e(k_1 j_1)][(x(n) - x(m)) \cdot e(k_2 j_2)] + Be(k_1 j_1) \cdot e(k_2 j_2) \} \{ e^{2\pi i k_2 \cdot [x(n) - x(m)]} - 1 \}. \qquad (3.26)$$

In order to simplify the analysis past this point, we make an approximation in the evaluation of M_1 and ΔF. This approximation, due to Ludwig[8] consists of replacing the squared frequencies in the denominator of the summand in

[8] W. Ludwig, J. Phys. Chem. Solids 4, 283 (1958).

Eq. (3.26) by their average value

$$\langle \omega_j{}^2(\mathbf{k}) \rangle = \frac{1}{3N} \sum_{\mathbf{k}j} \omega_j{}^2(\mathbf{k})$$

$$= \tfrac{1}{2}\omega_L{}^2 = \mu_2, \tag{3.27}$$

where μ_2 is the second moment of the unperturbed frequency spectrum, and ω_L the maximum frequency of the host lattice is given by $\omega_L{}^2 = 8\phi''(r_0)/M$. With this approximation all the summations can be carried out in closed form. In the Appendix we show that the error incurred by the use of Ludwig's approximation is 31% in the evaluation of M_1.

We begin by evaluating the sums over j_1 and j_2:

$$M_1 = \frac{kT}{2N^2M^2\mu_2{}^2} \sum_{\mathbf{k}_1\mathbf{k}_2} \sum_{mn}{}' \{A[\mathbf{\kappa}\cdot(\mathbf{x}(n)-\mathbf{x}(m))]^2 + B\kappa^2\} e^{2\pi i(\mathbf{k}_1+\mathbf{k}_2)\cdot[\mathbf{x}(m)-\mathbf{x}(l)]} \{e^{2\pi i\mathbf{k}_2\cdot[\mathbf{x}(n)-\mathbf{x}(m)]} - 1\}, \tag{3.28}$$

where we have used the closure property of the eigenvectors Eq. (2.13b). The sums over the wave vectors are evaluated with the aid of the relation

$$\sum_{\mathbf{k}} e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)} = N\delta_{\mathbf{x}(l),0}, \tag{3.29}$$

where $\delta_{\mathbf{x}(l),0}$ is unity if $\mathbf{x}(l)=0$ and vanishes otherwise. We thus find

$$M_1 = \frac{kT}{2\mu_2{}^2N^2M^2} \sum_{mn}{}' \{A[\mathbf{\kappa}\cdot(\mathbf{x}(n)-\mathbf{x}(m))]^2 + B\kappa^2\} N^2\{\delta_{\mathbf{x}(m)-\mathbf{x}(l),0}\delta_{\mathbf{x}(n)-\mathbf{x}(l),0} - \delta_{\mathbf{x}(m)-\mathbf{x}(l),0}\}$$

$$= -\frac{kT}{2\mu_2{}^2M^2} \sum_{mn}{}' \{A[\mathbf{\kappa}\cdot(\mathbf{x}(n)-\mathbf{x}(m))]^2 + B\kappa^2\}\delta_{\mathbf{x}(m)-\mathbf{x}(l),0}. \tag{3.30}$$

The sum over $\mathbf{x}(m)$ vanishes unless $\mathbf{x}(m)$ equals $\mathbf{x}(l)$, the position vector of the impurity atom. This means that the summation over $\mathbf{x}(n)$ extends over the twelve nearest-neighbors to the defect site. We obtain finally

$$M_1 = -\frac{kT}{2\mu_2{}^2M} \sum_{n}{}' \{A[\mathbf{\kappa}\cdot(\mathbf{x}(n)-\mathbf{x}(l))]^2 + B\kappa^2\}$$

$$= -\frac{kT}{2\mu_2{}^2M^2}\kappa^2\{2Aa_0{}^2 + 12B\}. \tag{3.31}$$

The expression for ΔF becomes explicitly

$$\Delta F = \frac{1}{2N^3M^3\beta^2} \sum_{\mathbf{k}_1j_1} \sum_{\mathbf{k}_2j_2} \sum_{\mathbf{k}_3j_3} \sum_{mn}{}' \sum_{rs}{}' \frac{[\mathbf{\kappa}\cdot\mathbf{e}(\mathbf{k}_1j_1)][\mathbf{\kappa}\cdot\mathbf{e}(\mathbf{k}_3j_3)]}{\omega_{j_1}{}^2(\mathbf{k}_1)\omega_{j_2}{}^2(\mathbf{k}_2)\omega_{j_3}{}^2(\mathbf{k}_3)}$$

$$\times e^{-2\pi i(\mathbf{k}_1+\mathbf{k}_3)\cdot\mathbf{x}(l)} \{A[(\mathbf{x}(n)-\mathbf{x}(m))\cdot\mathbf{e}(\mathbf{k}_1j_1)][(\mathbf{x}(n)-\mathbf{x}(m))\cdot\mathbf{e}(\mathbf{k}_2j_2)] + B\mathbf{e}(\mathbf{k}_1j_1)\cdot\mathbf{e}(\mathbf{k}_2j_2)\}$$

$$\times \{e^{2\pi i[\mathbf{k}_1\cdot\mathbf{x}(m)+\mathbf{k}_2\cdot\mathbf{x}(n)]} - e^{2\pi i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{x}(m)}\} \{A[(\mathbf{x}(s)-\mathbf{x}(r))\cdot\mathbf{e}(\mathbf{k}_3j_3)][(\mathbf{x}(s)-\mathbf{x}(r))\cdot\mathbf{e}(\mathbf{k}_2j_2)] + B\mathbf{e}(\mathbf{k}_3j_3)\cdot\mathbf{e}(\mathbf{k}_2j_2)\}$$

$$\times \{e^{2\pi i[\mathbf{k}_3\cdot\mathbf{x}(r)-\mathbf{k}_2\cdot\mathbf{x}(s)]} - e^{2\pi i(\mathbf{k}_3-\mathbf{k}_2)\cdot\mathbf{x}(r)}\}. \tag{3.32}$$

In Ludwig's approximation it becomes

$$\Delta F = \frac{(kT)^2}{2N^3M^3\mu_2{}^3} \sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3} \sum_{mn}{}' \sum_{rs}{}' e^{-2\pi i(\mathbf{k}_1+\mathbf{k}_3)\cdot\mathbf{x}(l)} \{e^{2\pi i[\mathbf{k}_1\cdot\mathbf{x}(m)+\mathbf{k}_2\cdot\mathbf{x}(n)]} - e^{2\pi i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{x}(m)}\}$$

$$\times \{e^{2\pi i[\mathbf{k}_3\cdot\mathbf{x}(r)-\mathbf{k}_2\cdot\mathbf{x}(s)]} - e^{2\pi i(\mathbf{k}_3-\mathbf{k}_2)\cdot\mathbf{x}(r)}\} \{A^2(\mathbf{\kappa}\cdot\mathbf{x}_{nm})(\mathbf{\kappa}\cdot\mathbf{x}_{sr})(\mathbf{x}_{nm}\cdot\mathbf{x}_{sr}) + AB[(\mathbf{\kappa}\cdot\mathbf{x}_{nm})^2 + (\mathbf{\kappa}\cdot\mathbf{x}_{sr})^2] + B^2\kappa^2\} \tag{3.33}$$

$$= \frac{(kT)^2}{2\mu_2{}^3M^3} \sum_{mn}{}' \sum_{rs}{}' \{\delta_{\mathbf{x}_{ml},0}\delta_{\mathbf{x}_{ns},0}\delta_{\mathbf{x}_{rl},0} + \delta_{\mathbf{x}_{ml},0}\delta_{\mathbf{x}_{mr},0}\delta_{\mathbf{x}_{rl},0}\}$$

$$\times \{A^2(\mathbf{\kappa}\cdot\mathbf{x}_{nm})(\mathbf{\kappa}\cdot\mathbf{x}_{sr})(\mathbf{x}_{nm}\cdot\mathbf{x}_{sr}) + AB[(\mathbf{\kappa}\cdot\mathbf{x}_{nm})^2 + (\mathbf{\kappa}\cdot\mathbf{x}_{sr})^2] + B^2\kappa^2\} \tag{3.34}$$

$$= \frac{(kT)^2}{2\mu_2{}^3M^3} \sum_{\substack{n \\ \text{n.n.}}} \{A^2(\mathbf{\kappa}\cdot\mathbf{x}_{nl})^2(\mathbf{x}_{nl}\cdot\mathbf{x}_{nl})+2AB(\mathbf{\kappa}\cdot\mathbf{x}_{nl})^2+B^2\kappa^2\}$$

$$+\frac{(kT)^2}{2\mu_2{}^3M^3} \sum_{\substack{ns \\ \text{n.n.}}} \{A^2(\mathbf{\kappa}\cdot\mathbf{x}_{nl})(\mathbf{\kappa}\cdot\mathbf{x}_{sl})(\mathbf{x}_{nl}\cdot\mathbf{x}_{sl})+AB(\mathbf{\kappa}\cdot\mathbf{x}_{nl})^2+AB(\mathbf{\kappa}\cdot\mathbf{x}_{sl})^2+B^2\kappa^2\} \quad (3.35)$$

$$=\frac{(kT)^2}{2\mu_2{}^3M^3}\kappa^2[5A^2a_0{}^4+52ABa_0{}^2+168B^2]. \tag{3.36}$$

In these equations, we have used the abbreviation $\mathbf{x}_{nm}=\mathbf{x}(n)-\mathbf{x}(m)$.

Combining Eqs. (3.13), (3.19), (3.31), and (3.36), we obtain finally

$$\langle\exp i\mathbf{\kappa}\cdot\mathbf{u}(l)\rangle=\exp\left\{-\frac{kT}{6NM}\kappa^2\sum_{\mathbf{k}j}\frac{1}{\omega_j{}^2(\mathbf{k})}-\frac{kT}{2\mu_2{}^2M^2}\kappa^2[2Aa_0{}^2+12B]\right.$$

$$\left.-\frac{kT}{2\mu_2{}^3M^3}\kappa^2[5A^2a_0{}^4+52BAa_0{}^2+168B^2]+\cdots\right\}. \tag{3.37}$$

IV. DISCUSSION

In the Debye approximation the thermal average $\langle\exp i\mathbf{\kappa}\cdot\mathbf{u}(l)\rangle$ is given in the classical limit by

$$\langle\exp i\mathbf{\kappa}\cdot\mathbf{u}(l)\rangle=\exp\left\{-\frac{3}{2}\frac{\hbar^2\kappa^2}{Mk}\frac{T}{\Theta_M{}^2}\right\}, \tag{4.1}$$

where Θ_M is the so-called x-ray Debye characteristic temperature. We can convert Eq. (3.37) into the same form by defining an appropriate effective characteristic temperature Θ_E:

$$\frac{1}{\Theta_E{}^2}=\frac{k^2}{\hbar^2}\left\{\frac{1}{3}\mu_{-2}+\frac{2}{3}\frac{Aa_0{}^2+6B}{M\mu_2{}^2}\right.$$

$$\left.+\frac{5A^2a_0{}^4+52BAa_0{}^2+168B^2}{3M^2\mu_2{}^3}+\cdots\right\}, \tag{4.2}$$

where we introduce the notation

$$\mu_{-2}=(3N)^{-1}\sum_{\mathbf{k}j}\omega_j{}^{-2}(\mathbf{k}).$$

Using Eq. (4.2), we have in place of Eq. (3.37)

$$\langle\exp i\mathbf{\kappa}\cdot\mathbf{u}(l)\rangle=\exp\left\{-\frac{3}{2}\frac{\hbar^2\kappa^2}{Mk}\frac{T}{\Theta_E{}^2}\right\}. \tag{4.3}$$

We see that the effective Debye temperature depends primarily on the inverse second moment of the frequency spectrum of the unperturbed lattice, and that the correction terms depend in a relatively complicated way on the forces acting on the impurity atom. The physical significance of the correction terms can be more easily appreciated if two additional approximations are introduced. First, let us assume that $\theta'(r_0)=0$. This will be a reasonable approximation when the impurity atom is roughly the same size as the host lattice atom. By

using Eq. (3.23), we now have

$$B=0 \tag{4.4}$$

and

$$A=[\phi''(r_0)-\theta''(r_0)]/r_0{}^2.$$

Since $r_0{}^2=a_0{}^2/2$, using the notation $\alpha=\phi''(r_0)$, $\alpha'=\theta''(r_0)$, we have

$$Aa_0{}^2=2(\alpha-\alpha'). \tag{4.5}$$

Second, we use the nearest-neighbor central force approximation for evaluating μ_{-2} and μ_2. These calculations have been carried out elsewhere,[9] with the results that

$$\mu_{-2}=1.68/\mu_2 \tag{4.6}$$

and

$$\mu_2=4\alpha/M. \tag{4.7}$$

Using Eqs. (4.4), (4.5), (4.6), and (4.7), we can reduce Eq. (4.2) to the substantially simpler form:

$$\frac{1}{\Theta_E{}^2}=0.140\frac{k^2}{\hbar^2}\frac{M}{\alpha}\left\{1+0.596\left(\frac{\alpha-\alpha'}{\alpha}\right)\right.$$

$$\left.+0.744\left(\frac{\alpha-\alpha'}{\alpha}\right)^2+\cdots\right\}. \tag{4.8}$$

Since α is a measure of the stiffness of the crystal lattice [$(4/3)(\alpha/a_0)$ equals the bulk modulus in this approximation], it is clear that the effective characteristic temperature depends in the usual way on the stiffness of the lattice and the mass of the host atoms. The correction terms have the expected effect: If $\alpha'>\alpha$, the restoring forces acting on the impurity are stiffer than those acting in the pure crystal, and the effective characteristic temperature is raised by the correction; the converse is true for $\alpha'<\alpha$.

To obtain f, the fraction of recoiless events, we must

[9] P. A. Flinn and A. A. Maradudin, Ann. Phys. 18, 81 (1962).

square $\langle \exp i\mathbf{\kappa} \cdot \mathbf{u}(l) \rangle$ as discussed in the introduction. At the same time we introduce the energy of the gamma ray directly, using the relation,

$$\kappa^2 = E^2/\hbar^2 c^2. \tag{4.9}$$

Finally, using (4.3), (4.8), and (4.9), we have

$$f = \langle \exp i\mathbf{\kappa} \cdot \mathbf{u}(l) \rangle^2$$

$$= \exp \left\{ -0.420 \frac{E^2}{\hbar^2 c^2} \frac{kT}{\alpha} \left[1 + 0.596 \left(\frac{\alpha - \alpha'}{\alpha} \right) \right. \right.$$

$$\left. \left. + 0.744 \left(\frac{\alpha - \alpha'}{\alpha} \right)^2 + \cdots \right] \right\}. \tag{4.10}$$

We can now consider the application of (4.10) to the experimental situation. First, we note that in this approximation neither the mass of the impurity nor that of the host lattice enters. It is clear, then, that in choosing a host lattice to obtain a large resonant fraction, the appropriate parameter to consider is the bulk modulus rather than the Debye temperature. Second, we can consider the possible usefulness of measurements of the resonant fraction as a function of temperature to obtain information about the crystal. In principle, from such measurements one could determine α' by using Eq. (4.10). Such a procedure, however, would not be very satisfactory. The derivation of Eq. (4.10) assumes that $[(\alpha - \alpha')/\alpha]$ is moderately small; this leads to two sorts of problems. One is experimental: f must be determined with great accuracy, which is difficult, since it depends on a measurement of peak intensity. The other difficulty arises from the use of the approximation of Eq. (4.6). The error in using an approximate rather than the true frequency spectrum of the unperturbed crystal (generally unknown) may not be negligible in comparison with the $[(\alpha - \alpha')/\alpha]$ terms. Since essentially the same information can be obtained in a more straightforward way by accurate measurement of peak position,[1] there does not appear to be any great value in using intensity measurements for this purpose.

In the case of a mass defect, we find from Eq. (2.44)

that f can be written as

$$f = \exp \left\{ -\frac{kT}{3NM} \kappa^2 \sum_{\mathbf{k}j} \frac{1}{\omega_j^2(\mathbf{k})} - \frac{\hbar^2 \kappa^2}{12M'kT} + O(\hbar^4) \right\}$$

$$= \exp \left\{ -\left(\frac{kT}{M} \kappa^2 \mu_{-2} \right) \right.$$

$$\left. \times \left[1 + \frac{1}{20} \frac{M}{M'} \frac{1}{\mu_2 \mu_{-2}} \left(\frac{\Theta_\infty}{T} \right)^2 + O(\hbar^4) \right] \right\}, \tag{4.11}$$

where we have introduced the limiting high-temperature value of the Debye characteristic temperature of the host crystal by[10]

$$\Theta_\infty^2 = (5/3)\mu_2 \hbar^2/k^2. \tag{4.12}$$

The product $\mu_2 \mu_{-2}$ for our model of a face-centered cubic crystal with nearest-neighbor central-force interactions is 1.68. In the Debye approximation it is 1.8. The result, Eq. (4.11), shows that the classical result for the Debye-Waller factor for a perfect, cubic, host crystal

$$f = \exp[-(kT/M)\kappa^2 \mu_{-2}], \tag{4.13}$$

is a good approximation for the f factor of a mass impurity as long as the temperature T satisfies the inequality

$$T \gg \frac{\Theta_\infty}{(20\mu_2 \mu_{-2} M'/M)^{\frac{1}{2}}} \approx \frac{\Theta_\infty}{5.8(M'/M)^{\frac{1}{2}}}, \tag{4.14}$$

where the last expression follows on setting $\mu_2 \mu_{-2} \approx 1.7$.

If the Mössbauer active impurity is heavier than the atoms of the host crystal, Eq. (4.13) can be used over a greater temperature range than if the impurity mass is the same as or lighter than that of the host atoms. Apart from this qualitative conclusion, Eq. (4.11) provides no other information about the dynamics of the impurity atom.

ACKNOWLEDGMENT

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

APPENDIX

We write Eq. (3.26) for M_1 as

$$M_1 = \frac{kT}{2N^2 M^2} \{ AS_1 + BS_2 \}, \tag{A1}$$

where

$$S_1 = \sum_{\mathbf{k}_1 j_1} \sum_{\mathbf{k}_2 j_2} \sum_{mn}{}' \frac{[\mathbf{\kappa} \cdot \mathbf{e}(\mathbf{k}_1 j_1)][\mathbf{\kappa} \cdot \mathbf{e}(\mathbf{k}_2 j_2)]}{\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_2)} e^{2\pi i(\mathbf{k}_1 + \mathbf{k}_2) \cdot [\mathbf{x}(m) - \mathbf{x}(l)]}$$

$$\times \{ e^{2\pi i \mathbf{k}_2 \cdot [\mathbf{x}(n) - \mathbf{x}(m)]} - 1 \} \{ [(\mathbf{x}(n) - \mathbf{x}(m)) \cdot \mathbf{e}(\mathbf{k}_1 j_1)][(\mathbf{x}(n) - \mathbf{x}(m)) \cdot \mathbf{e}(\mathbf{k}_2 j_2)] \}, \tag{A2}$$

$$S_2 = \sum_{\mathbf{k}_1 j_1} \sum_{\mathbf{k}_2 j_2} \sum_{mn}{}' \frac{[\mathbf{\kappa} \cdot \mathbf{e}(\mathbf{k}_1 j_1)][\mathbf{\kappa} \cdot \mathbf{e}(\mathbf{k}_2 j_2)]}{\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_2)} e^{2\pi i(\mathbf{k}_1 + \mathbf{k}_2) \cdot [\mathbf{x}(m) - \mathbf{x}(l)]} \{ e^{2\pi i \mathbf{k}_2 \cdot [\mathbf{x}(n) - \mathbf{x}(m)]} - 1 \}. \tag{A3}$$

We consider each of the sums in turn.

We begin by evaluating the sums over m and n in Eq. (A2). We first set $\mathbf{x}(m)$ equal to $\mathbf{x}(l)$, the position vector of the impurity atom. The vector $\mathbf{x}(n)$ then runs over the twelve nearest neighbors to the impurity site. We then let $\mathbf{x}(m)$ run over the twelve neighbors to $\mathbf{x}(l)$ in turn while in each case $\mathbf{x}(n)=\mathbf{x}(l)$. The result is

$$S_1 = \sum_{k_1 j_1} \sum_{k_2 j_2} \frac{1}{\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_2)}\left(\frac{a_0}{2}\right)^2 \times 2 \times [2\kappa_x^2 e_{1x}e_{2x} + 2\kappa_y^2 e_{1y}e_{2y} + 2\kappa_z^2 e_{1z}e_{2z}]$$

$$\times \{(e_{1x}+e_{1y})(e_{2x}+e_{2y})[\sin[\pi a_0(k_{1x}+k_{1y})]\sin[\pi a_0(k_{2x}+k_{2y})] - 4\sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})]\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]]$$

$$+ (e_{1y}+e_{1z})(e_{2y}+e_{2z})[\sin[\pi a_0(k_{1y}+k_{1z})]\sin[\pi a_0(k_{2y}+k_{2z})] - 4\sin^2[\tfrac{1}{2}\pi a_0(k_{1y}+k_{1z})]\sin^2[\tfrac{1}{2}\pi a_0(k_{2y}+k_{2z})]]$$

$$+ (e_{1z}+e_{1x})(e_{2z}+e_{2x})[\sin[\pi a_0(k_{1z}+k_{1x})]\sin[\pi a_0(k_{2z}+k_{2x})] - 4\sin^2[\tfrac{1}{2}\pi a_0(k_{1z}+k_{1x})]\sin^2[\tfrac{1}{2}\pi a_0(k_{2z}+k_{2x})]]\}. \quad \text{(A4)}$$

In obtaining Eq. (A4) we have used the fact that the eigenvector $\mathbf{e}(\mathbf{k}j)$ transforms as the vector $\mathbf{k}$. For convenience, we have also written $e_x(k_1 j_1)$ as e_{1x}.

It follows from the form of Eq. (A4) as a function of $\mathbf{k}_1$ and $\mathbf{k}_2$ and the transformation properties of the eigenvectors that S_1 is isotropic in the vector $\boldsymbol{\kappa}$. Thus, S_1 can be written as

$$S_1 = \frac{a_0^2}{3}\kappa^2 \sum_{k_1 j_1} \sum_{k_2 j_2} \frac{e_{1x}e_{2x} + e_{1y}e_{2y} + e_{1z}e_{2z}}{\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_2)}$$

$$\times \{(e_{1x}+e_{1y})(e_{2x}+e_{2y})[\sin[\pi a_0(k_{1x}+k_{1y})]\sin[\pi a_0(k_{2x}+k_{2y})] - 4\sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})]\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]]$$

$$+ (e_{1y}+e_{1z})(e_{2y}+e_{2z})[\sin[\pi a_0(k_{1y}+k_{1z})]\sin[\pi a_0(k_{2y}+k_{2z})] - 4\sin^2[\tfrac{1}{2}\pi a_0(k_{1y}+k_{1z})]\sin^2[\tfrac{1}{2}\pi a_0(k_{2y}+k_{2z})]]$$

$$+ (e_{1z}+e_{1x})(e_{2z}+e_{2x})[\sin[\pi a_0(k_{1z}+k_{1x})]\sin[\pi a_0(k_{2z}+k_{2x})] - 4\sin^2[\tfrac{1}{2}\pi a_0(k_{1z}+k_{1x})]\sin^2[\tfrac{1}{2}\pi a_0(k_{2z}+k_{2x})]]\}. \quad \text{(A5)}$$

The next simplification we can effect in this expression follows from the fact that each of the three terms in the curly brackets contributes equally to the sum. This means that S_1 becomes

$$S_1 = a_0^2\kappa^2 \sum_{k_1 j_1} \sum_{k_2 j_2} \frac{e_{1x}e_{2x} + e_{1y}e_{2y} + e_{1z}e_{2z}}{\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_2)}(e_{1x}+e_{1y})(e_{2x}+e_{2y})$$

$$\times \{\sin[\pi a_0(k_{1x}+k_{1y})]\sin[\pi a_0(k_{2x}+k_{2y})] - 4\sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})]\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]\} \quad \text{(A6)}$$

$$= a_0^2\kappa^2 \sum_{k_1 j_1} \sum_{k_2 j_2} \frac{e_{1x}e_{2x} + e_{1y}e_{2y}}{\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_2)}(e_{1x}+e_{1y})(e_{2x}+e_{2y})$$

$$\times \{\sin[\pi a_0(k_{1x}+k_{1y})]\sin[\pi a_0(k_{2x}+k_{2y})] - 4\sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})]\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]\} \quad \text{(A7)}$$

$$= a_0^2\kappa^2\left\{\sum_{k_1 j_1} \frac{e_{1x}(e_{1x}+e_{1y})}{\omega_{j_1}^2(\mathbf{k}_1)}\sin[\pi a_0(k_{1x}+k_{1y})]\sum_{k_2 j_2}\frac{e_{2x}(e_{2x}+e_{2y})}{\omega_{j_2}^2(\mathbf{k}_2)}\sin[\pi a_0(k_{2x}+k_{2y})]\right.$$

$$-4\sum_{k_1 j_1}\frac{e_{1x}(e_{1x}+e_{1y})}{\omega_{j_1}^2(\mathbf{k}_1)}\sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})]\sum_{k_2 j_2}\frac{e_{2x}(e_{2x}+e_{2y})}{\omega_{j_2}^2(\mathbf{k}_2)}\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]$$

$$+\sum_{k_1 j_1}\frac{e_{1y}(e_{1x}+e_{1y})}{\omega_{j_1}^2(\mathbf{k}_1)}\sin[\pi a_0(k_{1x}+k_{1y})]\sum_{k_2 j_2}\frac{e_{2y}(e_{2x}+e_{2y})}{\omega_{j_2}^2(\mathbf{k}_2)}\sin[\pi a_0(k_{2x}+k_{2y})]$$

$$\left.-4\sum_{k_1 j_1}\frac{e_{1y}(e_{1x}+e_{1y})}{\omega_{j_1}^2(\mathbf{k}_1)}\sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})]\sum_{k_2 j_2}\frac{e_{2y}(e_{2x}+e_{2y})}{\omega_{j_2}^2(\mathbf{k}_2)}\sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]\right\}. \quad \text{(A8)}$$

The summands in the first and third terms are odd functions of the wave vector so that these terms sum to zero

We are left with

$$S_1 = -4a_0^2\kappa^2 \left\{ \sum_{kj} \frac{e_x(kj)[e_x(kj)+e_y(kj)]}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] \right\}^2$$

$$-4a_0^2\kappa^2 \left\{ \sum_{kj} \frac{e_y(kj)[e_x(kj)+e_y(kj)]}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] \right\}^2. \quad (A9)$$

It is clear, however that

$$\sum_{kj} \frac{e_x(kj)[e_x(kj)+e_y(kj)]}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] = \sum_{kj} \frac{e_y(kj)[e_x(kj)+e_y(kj)]}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)]. \quad (A10)$$

Our expression for S_1 finally becomes

$$S_1 = -8a_0^2\kappa^2 \left\{ \frac{1}{2} \sum_{kj} \frac{[e_x(kj)+e_y(kj)]^2}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] \right\}^2. \quad (A11)$$

The sum over k and j in the curly brackets has been evaluated elsewhere for this model[4] and has the value

$$\sum_{kj} \frac{[e_x(kj)+e_y(kj)]^2}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] = \frac{NM}{4\phi''(r_0)} = \frac{N}{\mu_2}. \quad (A12)$$

With the aid of this result, S_1 can be written as

$$S_1 = -2a_0^2\kappa^2 N^2/\mu_2^2. \quad (A13)$$

Turning now to the sum S_2, we begin its evaluation by performing the sums over m and n, with the result that

$$S_2 = 4 \sum_{k_1 j_1} \sum_{k_2 j_2} \frac{e(k_1 j_1) \cdot e(k_2 j_2)}{\omega_{j_1}^2(k_1)\omega_{j_2}^2(k_2)} [\kappa_x^2 e_{1x}e_{2x} + \kappa_y^2 e_{1y}e_{2y} + \kappa_z^2 e_{1z}e_{2z}]$$

$$\times \{ \sin[\pi a_0(k_{1x}+k_{1y})] \sin[\pi a_0(k_{2x}+k_{2y})] - 4 \sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})] \sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})]$$

$$+ \sin[\pi a_0(k_{1y}+k_{1z})] \sin[\pi a_0(k_{2y}+k_{2z}) - 4 \sin^2[\tfrac{1}{2}\pi a_0(k_{1y}+k_{1z}) \sin^2[\tfrac{1}{2}\pi a_0(k_{2y}+k_{2z})]$$

$$+ \sin[\pi a_0(k_{1z}+k_{1x})] \sin[\pi a_0(k_{2z}+k_{2x})] - 4 \sin^2[\tfrac{1}{2}\pi a_0(k_{1z}+k_{1x}) \sin^2[\tfrac{1}{2}\pi a_0(k_{2z}+k_{2x})] \}. \quad (A14)$$

We again make use of the facts that S_2 is isotropic in the vector κ and that each of the three terms in the curly brackets contributes equally to the sum. We thus obtain

$$S_2 = 4\kappa^2 \sum_{k_1 j_1} \sum_{k_2 j_2} \frac{[e(k_1 j_1) \cdot e(k_2 j_2)]^2}{\omega_{j_1}^2(k_1)\omega_{j_2}^2(k_2)} \{ \sin[\pi a_0(k_{1x}+k_{1y})] \sin[\pi a_0(k_{2x}+k_{2y})]$$

$$-4 \sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})] \sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})] \}. \quad (A15)$$

The first term in the curly brackets gives a vanishing contribution to S_2, because it is odd in the vectors k_1 and k_2. The expression for S_2 becomes

$$S_2 = -16\kappa^2 \sum_{k_1 j_1 k_2 j_2} \frac{[e(k_1 j_1) \cdot e(k_2 j_2)]^2}{\omega_{j_1}^2(k_1)\omega_{j_2}^2(k_1)} \sin^2[\tfrac{1}{2}\pi a_0(k_{1x}+k_{1y})] \sin^2[\tfrac{1}{2}\pi a_0(k_{2x}+k_{2y})] \quad (A16)$$

$$= -32\kappa^2 \left\{ \sum_{kj} \frac{e_x^2(kj)}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] \right\}^2 - 16\kappa^2 \left\{ \sum_{kj} \frac{e_z^2(kj)}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] \right\}^2$$

$$-32\kappa^2 \left\{ \sum_{kj} \frac{e_x(kj)e_y(kj)}{\omega_j^2(k)} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] \right\}^2. \quad (A17)$$

The three sums appearing in this expression have been evaluated elsewhere for the present model.[9] They have the values

$$\sum_{\mathbf{k}j} \frac{e_x^2(\mathbf{k}j)}{\omega_j^2(\mathbf{k})} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] = \frac{N}{\mu_2}(0.5811),$$

$$\sum_{\mathbf{k}j} \frac{e_z^2(\mathbf{k}j)}{\omega_j^2(\mathbf{k})} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] = \frac{N}{\mu_2}(0.6323), \quad (A18)$$

$$\sum_{\mathbf{k}j} \frac{e_x(\mathbf{k}j)e_y(\mathbf{k}j)}{\omega_j^2(\mathbf{k})} \sin^2[\tfrac{1}{2}\pi a_0(k_x+k_y)] = \frac{N}{\mu_2}(-0.0811).$$

With these results, we can finally express S_2 as

$$S_2 = -\frac{N^2\kappa^2}{\mu_2^2}(17.414). \quad (A19)$$

Combining Eqs. (A1), (A13), and (A18), we find that M_1 equals

$$M_1 = -\frac{kT}{2\mu_2^2 M^2}\kappa^2[2Aa_0^2+17.414B]. \quad (A20)$$

If we compare this result with that obtained using Ludwig's approximation,

$$M_1 = -\frac{kT}{2\mu_2^2 M^2}\kappa^2[2Aa_0^2+12B], \quad (A21)$$

we see that the coefficient of Aa_0^2 is given exactly by Ludwig's approximation, while the coefficient of B is 31% low in this approximation. These results are consistent with those obtained elsewhere[4] in cases where exact calculations could also be carried out. In all cases studied so far, Ludwig's approximation gives results which are somewhat smaller than the true values.

Certain General Order-Disorder Models in the Limit of Long-Range Interactions*

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We investigate in the limit as the range of the interparticle interactions becomes indefinitely great, but is still small compared to the size of the system, the behavior of a large class of order-disorder models. This class includes, for example, the Ising model, the spherical model, and the Gaussian model. We show that when certain general conditions hold and the interparticle interaction is chosen to be the same for all models, but otherwise arbitrary, the energy per particle above the critical temperature has the same limiting value through terms of order $1/R$, where R is a measure of the number of spins in the range of the interaction. We further show why the behavior above the critical point in this limit does not necessarily provide information about the behavior below the critical point. Some examples are worked out which illustrate the above results.

1. INTRODUCTION

THE purpose of this paper is to investigate the behavior of a certain class of order-disorder models as a function of the range of the interaction. We investigate the limiting behavior of these models as the range of interaction becomes indefinitely great, but is still much smaller than the total size of the system. In the second section of this paper we show that above the critical point, when certain general conditions are met, the details of the model (probability distribution of the various states of the system) but not the shape of the interaction are unimportant in the limit of indefinitely long-range forces. The class of models considered is general enough to contain the Ising model, the spherical model, and the Gaussian model. Below the critical

point no such general result is obtained. We see that in this region the details of the model affect the energy per spin in leading order.

In the third section we compute the energy per spin for the one-dimensional spherical model (and Gaussian model) with exponential interactions between spins. We verify explicitly the results of the second section for this type of interaction by comparing the results of the third section with the previously known results for the Ising model. We also verify explicitly that the behavior below the critical point is different for the spherical and Ising models.

In the last section of this paper we evaluate the energy per spin of the three-dimensional spherical model as a function of the range of a force which drops off approximately exponentially with distance. Here we may follow the behavior of the known third-order transition with range.