

## Some Dynamical Properties of Surface Atoms

A. A. MARADUDIN AND J. MELNGAILIS

*Westinghouse Research Laboratories, Pittsburgh, Pennsylvania*

(Received 4 October 1963)

Expressions for the mean-square velocity and mean-square amplitude of an atom in the surface layers of a simple cubic crystal are obtained using double-time Green's functions. They are evaluated explicitly in the high-temperature limit. The Hamiltonian of the unperturbed crystal is taken in the harmonic approximation with nearest- and next-nearest-neighbor central force interactions between the atoms. The perturbation produces free surfaces by subtracting off all the interactions (or bonds) which cross a certain plane. The exponential in the Debye-Waller factor for a surface atom, calculated to lowest order in inverse temperature, is twice as large as its bulk value for  $\gamma$ -ray emission perpendicular to the surface and about 30% larger than the bulk value for emission parallel to the surface. These surface corrections decay very rapidly as one goes into the crystal from the surface. In the fifth atomic layer the exponential in the Debye-Waller factor is within 5% of the bulk value. In the second-order Doppler shift the effect of the surface is to reduce the second-order term in inverse temperature (first quantum correction) by about 30%. The lowest-order term is unaffected. If the crystal is made isotropic in the long wavelength, continuum limit surface waves which are the classical Rayleigh waves appear.

**D**IFFERENCES between the dynamical properties of atoms in the surface of a crystal and those in the bulk might be observable by means of the Mössbauer effect<sup>1,2</sup> and have, in fact, been observed by low-energy electron diffraction.<sup>3</sup> Using double-time Green's functions we calculate in this note the mean-square amplitude and the mean-square velocity of an atom in the surface layers of a simple cubic crystal with nearest- and next-nearest neighbor interactions, which, unlike the model used by Rich,<sup>2</sup> gives rise to surface modes. In the long wavelength, continuum limit these modes correspond to the classical Rayleigh waves. The formal expressions obtained for the exponential in the Debye-Waller factor and for the second-order Doppler shift are evaluated explicitly in the high-temperature limit.

We make free surfaces of the planes  $x_3=0$  and  $x_3=a$ , where  $a$  is the lattice parameter, by setting equal to zero all of the interactions between these two planes. In the approximation of central forces the crystal Hamiltonian for the cut crystal is

$$H = \sum_{1\alpha} \frac{p_{\alpha}^2(\mathbf{l})}{2M} + \frac{1}{4} \sum_{1\alpha 1'\beta} \phi_{\alpha\beta}(\mathbf{l}') \\ \times [u_{\alpha}(\mathbf{l}) - u_{\alpha}(\mathbf{l}')] [u_{\beta}(\mathbf{l}) - u_{\beta}(\mathbf{l}')] - \frac{1}{2} \sum_{1\alpha 1'\beta} \phi_{\alpha\beta}(\mathbf{l}') \\ \times \delta_{i_3,0} \delta_{i_3',1} [u_{\alpha}(\mathbf{l}) - u_{\alpha}(\mathbf{l}')] [u_{\beta}(\mathbf{l}) - u_{\beta}(\mathbf{l}')], \quad (1)$$

where  $u_{\alpha}(\mathbf{l})$  is the  $\alpha$ -Cartesian component of the displacement of equilibrium of the atom located at  $\mathbf{a}\mathbf{l} = a(\mathbf{i}_1 l_1 + \mathbf{i}_2 l_2 + \mathbf{i}_3 l_3)$   $a$  is the lattice parameter,  $M$  is the mass of an atom,  $\phi_{\alpha\beta}(\mathbf{l}')$  are the atomic force constants, and  $l_1, l_2, l_3$  are three integers, each of which ranges between  $-L/2+1$  and  $L/2$ . The factor  $\frac{1}{4}$  enters in the second term because each interaction is counted twice.

<sup>1</sup> R. F. Wallis and D. C. Gazis, *Phys. Rev.* **128**, 106 (1962).

<sup>2</sup> M. Rich, *Phys. Letters* **4**, 153 (1963).

<sup>3</sup> A. U. MacRae and L. H. Germer, *Phys. Rev. Letters* **8**, 489 (1962).

For  $\phi_{\alpha\beta}(\mathbf{l}')$  we will use the following expression:

$$\phi_{\alpha\beta}(\mathbf{l}') = \frac{x_{\alpha}(\mathbf{l}') x_{\beta}(\mathbf{l}')}{r^2(\mathbf{l}')} \phi''(r(\mathbf{l}')), \quad (2)$$

where  $\phi(r)$  is the interatomic potential function,  $x_{\alpha}(\mathbf{l}')$  is  $x_{\alpha}(\mathbf{l}) - x_{\alpha}(\mathbf{l}')$  and  $r(\mathbf{l}') = |\mathbf{x}(\mathbf{l}) - \mathbf{x}(\mathbf{l}')|$ . Since  $\phi_{\alpha\beta}(\mathbf{l}')$  depends on  $\mathbf{l}' - \mathbf{l}$ , only one index is necessary to characterize the interaction. For nearest- and next-nearest neighbor interactions  $r(\mathbf{l}')$  has only two possible values,  $a$  and  $\sqrt{2}a$ .

By comparing the small  $\mathbf{k}$  form of the dynamical matrix for our crystal model with the corresponding matrix for the vibrations of a cubic elastic medium, we obtain the following relations between the potential derivatives  $\phi''(a)$  and  $\phi''(\sqrt{2}a)$  on the one hand, and the elastic constants on the other:

$$aC_{11} = \phi''(a) + 2\phi''(\sqrt{2}a) \quad (3) \\ aC_{12} = aC_{44} = \phi''(\sqrt{2}a).$$

If we set

$$\phi''(a) = \phi''(\sqrt{2}a), \quad (4)$$

the elastic constants satisfy the isotropy condition

$$C_{11} = 3C_{12} \quad (5)$$

for a cubic crystal for which the Cauchy relation on the elastic constants holds as well. Although the assumption of the condition expressed by Eq. (4) does not lead to any great simplifications in the numerical evaluation of the exponent in the Debye-Waller factor and of the second-order Doppler shift, it enables us to show analytically rather than numerically that our crystal model gives rise to surface modes of vibration in the long wavelength or continuum limit. Therefore, we have assumed Eq. (4) in all the calculations that follow.

We now express the crystal Hamiltonian in terms of the phonon field variables according to the

transformations

$$u_{\alpha}(\mathbf{l}) = \left( \frac{\hbar}{2NM} \right)^{1/2} \sum_{\mathbf{k}j} \frac{e_{\alpha}(\mathbf{k}j)}{(\omega(\mathbf{k}j))^{1/2}} e^{2\pi i \mathbf{a} \cdot \mathbf{k} \cdot \mathbf{l}} A_{\mathbf{k}j}$$

$$p_{\alpha}(\mathbf{l}) = \frac{1}{i} \left( \frac{\hbar M}{2N} \right)^{1/2} \sum_{\mathbf{k}j} e_{\alpha}(\mathbf{k}j) (\omega(\mathbf{k}j))^{1/2} e^{2\pi i \mathbf{a} \cdot \mathbf{k} \cdot \mathbf{l}} B_{\mathbf{k}j},$$
(6)

where  $\omega(\mathbf{k}j)$  is the frequency of the normal mode of the unperturbed crystal with wave vector  $\mathbf{k}$  and polarization  $j$ ,  $e_{\alpha}(\mathbf{k}j)$  is the  $\alpha$  component of the associated polarization vector, and  $N$  is the number of atoms in the uncut crystal. The operators  $A_{\mathbf{k}j}$  and  $B_{\mathbf{k}j}$  are related to the usual phonon creation and destruction operators  $a_{\mathbf{k}j}^{\dagger}$  and  $a_{\mathbf{k}j}$  by

$$A_{\mathbf{k}j} = a_{\mathbf{k}j} + a_{-\mathbf{k}j}^{\dagger} = A_{-\mathbf{k}j}^{\dagger},$$

$$B_{\mathbf{k}j} = a_{\mathbf{k}j} - a_{-\mathbf{k}j}^{\dagger} = -B_{-\mathbf{k}j}^{\dagger}.$$
(7)

In terms of the new operators the Hamiltonian becomes

$$H = \frac{1}{4} \sum_{\mathbf{k}j} \hbar \omega(\mathbf{k}j) [B_{\mathbf{k}j} B_{0j}^{\dagger} + A_{\mathbf{k}j} A_{\mathbf{k}j}^{\dagger}]$$

$$+ \sum_1 \sum_{\mathbf{k}j\mathbf{k}'j'} \delta(k_1 + k_1') \delta(k_2 + k_2')$$

$$\times f_1(\mathbf{k}j) f_1(\mathbf{k}'j') A_{\mathbf{k}j} A_{\mathbf{k}'j'}, \quad (8)$$

with  $\delta(k_1 + k_1') = 1$ , for  $k_1 + k_1' = 0$ ,  $\delta(k_1 + k_1') = 0$  otherwise, and

$$f_1(\mathbf{k}j) = \frac{1}{2} i \delta_{l_3, 1} \left( \frac{1}{2N^{1/3}M} \right)^{1/2} \left( \frac{\phi''(r(\mathbf{l}))}{r^2(\mathbf{l})\omega(\mathbf{k}j)} \right)^{1/2}$$

$$\times \sum_{\alpha} e_{\alpha}(\mathbf{k}j) x_{\alpha}(\mathbf{l}) (1 - e^{2\pi i \mathbf{a} \cdot \mathbf{k} \cdot \mathbf{l}}). \quad (9)$$

The sum over  $\mathbf{l}$  extends over the nearest and next nearest neighbors of a given atom.

The double-time temperature-dependent Green's function is defined by<sup>4</sup>

$$G(\mathbf{k}j; \mathbf{k}'j'; t) = \langle \langle A_{\mathbf{k}j}(t); A_{\mathbf{k}'j'}(0) \rangle \rangle. \quad (10)$$

The differential equation for  $G$  is found in the usual way<sup>4</sup> by differentiating both sides of this equation with respect to time twice and by using the relation  $(i\hbar)dA/dt = AH - HA$  for quantum mechanical operators. It is

$$\frac{d^2 G(\mathbf{k}j; \mathbf{k}'j'; t)}{dt^2}$$

$$= 2\omega(\mathbf{k}j) \delta(t) \Delta(\mathbf{k} + \mathbf{k}') \delta_{jj'} + \omega^2(\mathbf{k}j) G(\mathbf{k}j; \mathbf{k}'j'; t)$$

$$+ 4\omega(\mathbf{k}j) \sum_1 \sum_{\mathbf{h}s} \delta(h_1 - k_1) \delta(h_2 - k_2)$$

$$\times f_1(\mathbf{h}s) f_1(-\mathbf{k}j) G(\mathbf{h}s; \mathbf{k}'j'; t). \quad (11)$$

If we define the Fourier transform of  $G$  by

$$G(t) = \int_{-\infty}^{\infty} G(E) e^{-iEt} dE, \quad (12)$$

the equation satisfied by  $G(\mathbf{k}j; \mathbf{k}'j'; E)$  is

$$G(\mathbf{k}j; \mathbf{k}'j'; E) = \frac{1}{\pi} \frac{\omega(\mathbf{k}j)}{E^2 - \omega^2(\mathbf{k}j)} \Delta(\mathbf{k} + \mathbf{k}') \delta_{jj'} + \frac{4\omega(\mathbf{k}j)}{E^2 - \omega^2(\mathbf{k}j)}$$

$$\times \sum_1 \sum_{\mathbf{h}s} f_1(k_1 k_2 h_3 s) f_1(-\mathbf{k}j) G(k_1 k_2 h_3 s; \mathbf{k}'j'; E). \quad (13)$$

Let us define a function  $g_1(k_1 k_2; \mathbf{k}'j'; E)$  by

$$g_1(k_1 k_2; \mathbf{k}'j'; E) = \sum_{\mathbf{k}s} f_1(\mathbf{k}j) G(\mathbf{k}j; \mathbf{k}'j'; E). \quad (14)$$

If we multiply Eq. (13) by  $f_1(\mathbf{k}j)$  and sum over  $\mathbf{k}s$  we have

$$g_1(k_1 k_2; \mathbf{k}'j'; E)$$

$$= \frac{\omega(\mathbf{k}'j') \delta(k_1 + k_1') \delta(k_2 + k_2')}{\pi(E^2 - \omega^2(\mathbf{k}'j'))} f_1(k_1 k_2 - k_3' j')$$

$$+ \sum_1 \left[ \sum_{\mathbf{k}s} 4 f_1(\mathbf{k}j) \frac{\omega(\mathbf{k}j)}{E^2 - \omega^2(\mathbf{k}j)} f_1(-\mathbf{k}j) \right]$$

$$\times g_1(k_1 k_2; \mathbf{k}'j'; E). \quad (15)$$

The expression in the brackets defines a  $(5 \times 5)$  matrix  $\mathbf{M}(E)$ , since each set of  $l$ 's runs over 5 sets of values corresponding to the one nearest-neighbor and 4 next-nearest neighbor interactions per atom being cut by the perturbation. Equation (15) can be solved formally provided the inverse of  $\mathbf{I} - \mathbf{M}$  exists. The result for  $g$  can then be substituted in Eq. (13), and we obtain finally

$$G(\mathbf{k}j; \mathbf{k}'j'; E) = \frac{\omega(\mathbf{k}j) \Delta(\mathbf{k} + \mathbf{k}') \delta_{jj'}}{\pi(E^2 - \omega^2(\mathbf{k}j))}$$

$$+ \frac{4\omega(\mathbf{k}j) \omega(\mathbf{k}'j') \delta(k_1 + k_1') \delta(k_2 + k_2')}{\pi(E^2 - \omega^2(\mathbf{k}j))(E^2 - \omega^2(\mathbf{k}'j'))}$$

$$\times \sum_{\mathbf{l}l'} f_1(-\mathbf{k}j) [\mathbf{I} - \mathbf{M}]_{\mathbf{l}l'}^{-1} f_1(-\mathbf{k}'j'). \quad (16)$$

The Fourier transform of the Green's function defined by

$$G'(\mathbf{k}j; \mathbf{k}'j'; t) = \langle \langle B_{\mathbf{k}j}(t); B_{\mathbf{k}'j'}(0) \rangle \rangle \quad (17)$$

can be obtained in a similar manner. The result is

$$G'(\mathbf{k}j; \mathbf{k}'j'; E) = - \frac{\omega(\mathbf{k}j) \Delta(\mathbf{k} + \mathbf{k}') \delta_{jj'}}{\pi(E^2 - \omega^2(\mathbf{k}j))}$$

$$\frac{4E^2 \delta(k_1 + k_1') \delta(k_2 + k_2')}{\pi(E^2 - \omega^2(\mathbf{k}j))(E^2 - \omega^2(\mathbf{k}'j'))}$$

$$\times \sum_{\mathbf{l}l'} f_1(-\mathbf{k}j) [\mathbf{I} - \mathbf{M}]_{\mathbf{l}l'}^{-1} f_1(-\mathbf{k}'j'). \quad (18)$$

<sup>4</sup> V. L. Bonch-Bruевич and S. V. Tyablikov, *The Green Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962); D. N. Zubarev, Usp. Fiz. Nauk. 71, 71 (1960) [translation: Sov. Phys.—Uspekhi 3, 320 (1960)].

The Debye-Waller factor and the second-order Doppler shift have been related to these Green's functions elsewhere.<sup>5</sup> The exponent in the Debye-Waller factor for an atom located at  $\mathbf{al}$  is given by

$$2M = -\frac{8\pi^3}{2NM\beta} \sum_{\mathbf{kj}\mathbf{k}'j'} \frac{(\mathbf{K} \cdot \mathbf{e}(\mathbf{k}j))(\mathbf{K} \cdot \mathbf{e}(\mathbf{k}'j'))}{(\omega(\mathbf{k}j)\omega(\mathbf{k}'j'))^{1/2}} \times e^{2\pi i a(\mathbf{k}+\mathbf{k}') \cdot \mathbf{l}} \sum_{n=-\infty}^{\infty} G(\mathbf{k}j; \mathbf{k}'j'; i\omega_n), \quad (19)$$

where  $\mathbf{K}$  is the wave vector of the emitted photon (or  $\hbar^{-1} \times$  change in momentum of the electron for the electron diffraction case),  $\beta = 1/kT$  and  $E$  has been replaced by  $i\omega_n = i(2\pi n/\beta\hbar)$  in the expression for  $G$  Eq. (16).

The second-order Doppler shift is similarly expressed by<sup>5</sup>

$$\left(\frac{\delta E}{E}\right) = \frac{2\pi}{4NMc^2\beta} \sum_{\mathbf{kj}\mathbf{k}'j'} \mathbf{e}(\mathbf{k}j) \cdot \mathbf{e}(\mathbf{k}'j') (\omega(\mathbf{k}j)\omega(\mathbf{k}'j'))^{1/2} \times e^{2\pi i a(\mathbf{k}+\mathbf{k}') \cdot \mathbf{l}} \sum_{n=-\infty}^{\infty} G'(\mathbf{k}j; \mathbf{k}'j'; i\omega_n), \quad (20)$$

where  $G'$  is the  $B-B$  Green's function, Eq. (18).

The computation of both of these quantities is considerably simplified if the high temperature limit is considered, i.e., if  $G$  and  $G'$  are expanded in powers of  $T^{-1}$ , which enters through  $\omega_n$ . In fact to first order in  $T^{-1}$ ,  $(\delta E/E)$  can be computed analytically as follows:

Taking the first term in  $G'$ , Eq. (18) (the term corresponding to the uncut crystal), we have

$$\left(\frac{\delta E}{E}\right)_0 = \frac{kT}{2NMc^2} \sum_{\mathbf{k}j} \left[ 1 + 2 \sum_{n=1}^{\infty} \frac{\omega^2(\mathbf{k}j)}{\omega_n^2 + \omega^2(\mathbf{k}j)} \right], \quad (21)$$

$$= \frac{3kT}{2Mc^2} + \frac{kT}{NMc^2}$$

$$\times \sum_{\mathbf{k}j} \sum_{n=1}^{\infty} \left[ \frac{\omega^2(\mathbf{k}j)}{\omega_n^2} - \left(\frac{\omega^2(\mathbf{k}j)}{\omega_n^2}\right)^2 + \dots \right]. \quad (22)$$

Using the relations  $\sum_{n=1}^{\infty} n^{-2} = \pi^2/6$  and  $\sum_{\mathbf{k}j} \omega^2(\mathbf{k}j) = 18N\phi''(a)/M$  we obtain

$$\left(\frac{\delta E}{E}\right)_0 = \frac{3kT}{2Mc^2} + \frac{3\hbar^2\phi''(a)}{4(Mc)^2kT} + \dots \quad (23)$$

The contribution of the second, surface term, in  $G'$  to  $(\delta E/E)$  is simplified by the fact that the  $n=0$  term vanishes and that the matrix  $\mathbf{M}$  is proportional to  $T^{-2}$ . Hence, the inverse of  $\mathbf{I} - \mathbf{M}$  to order  $T^{-1}$  is just the unit

matrix, and we obtain

$$\left(\frac{\delta E}{E}\right)_1 = \frac{4kT}{NMc^2} \sum_{\mathbf{kj}\mathbf{k}'j'} \mathbf{e}(\mathbf{k}j) \cdot \mathbf{e}(\mathbf{k}'j') \times (\omega(\mathbf{k}j)\omega(\mathbf{k}'j'))^{1/2} e^{2\pi i a(\mathbf{k}+\mathbf{k}') \cdot \mathbf{l}} \times \sum_{l'} \delta(k_1+k_1')\delta(k_2+k_2') f_{l'}(-\mathbf{k}j) f_{l'}(-\mathbf{k}'j') \times \sum_{n=1}^{\infty} \frac{1}{\omega_n^2} \left[ 1 - \frac{\omega^2(\mathbf{k}j) + \omega^2(\mathbf{k}'j')}{\omega_n^2} + \dots \right]. \quad (24)$$

To lowest order in  $T^{-1}$  this reduces to

$$\left(\frac{\delta E}{E}\right)_1 = -\frac{\hbar^2\phi''(a)}{24N^{4/3}(Mc)^2kT} \times \sum_{\mathbf{k}\mathbf{k}'} \sum_{l'} \delta(k_1+k_1')\delta(k_2+k_2') e^{2\pi i a(\mathbf{k}+\mathbf{k}') \cdot \mathbf{l}} \times \delta_{l_3,1} (1 - e^{-2\pi i a\mathbf{k} \cdot \mathbf{l}'})(1 - e^{-2\pi i a\mathbf{k}' \cdot \mathbf{l}'}), \quad (25)$$

where we have performed the sum over  $j$  and  $j'$  using the closure relation  $\sum_j e_\alpha(\mathbf{k}j)e_\beta(\mathbf{k}j) = \delta_{\alpha\beta}$ . Since the sums over  $\mathbf{k}$  and  $\mathbf{k}'$  vanish except when  $l_3=0, 1$ , and since the  $l'$ 's run over the 5 bonds that are cut between the  $x_3=0$  and  $x_3=a$  plane, the result becomes

$$\left(\frac{\delta E}{E}\right)_1 = -\frac{5\hbar^2\phi''(a)}{24(Mc)^2kT} [\delta_{l_3,0} + \delta_{l_3,1}] + \dots, \quad (26)$$

i.e., with this approximation  $(\delta E/E)_1=0$  except for atoms in the two surface layers. Adding Eqs. (23) and (26), we have

$$\left(\frac{\delta E}{E}\right) = \frac{3kT}{2Mc^2} + \frac{\hbar^2\phi''(a)}{24(Mc)^2kT} \times [18 - 5(\delta_{l_3,1} + \delta_{l_3,0})] + O(T^{-3}). \quad (27)$$

Thus the effect of the surface is to reduce the first quantum correction to  $(\delta E/E)$  when the resonant nucleus is in the surface layers only.

Unfortunately, the high-temperature calculation for  $2M$  cannot be done analytically as it was for  $(\delta E/E)$ . Taking the first term for  $G$  in Eq. (16) and substituting it in Eq. (19) we obtain

$$2M_0 = \frac{4\pi^2kT}{NM} \sum_{\mathbf{k}j} (\mathbf{K} \cdot \mathbf{e}(\mathbf{k}j))^2 \times \left[ \frac{1}{\omega^2(\mathbf{k}j)} + 2 \sum_{n=1}^{\infty} \frac{1}{\omega_n^2 + \omega^2(\mathbf{k}j)} \right] \quad (28)$$

$$= \frac{(2\pi K)^2kT}{3NM} \sum_{\mathbf{k}j} \frac{1}{\omega^2(\mathbf{k}j)} + \frac{\hbar^2(2\pi K)^2}{12Mc^2kT} + O(T^{-3}), \quad (29)$$

where the cubic symmetry of the unperturbed crystal has been used to simplify the first term.

<sup>5</sup> A. A. Maradudin, P. A. Flinn, and J. M. Radcliffe, Ann. Phys. (N. Y.) (to be published).

The sum

$$\frac{1}{3N} \sum_{\mathbf{k}j} \frac{1}{\omega^2(\mathbf{k}j)} = 0.462 \frac{M}{2\phi''(a)}$$

has been evaluated on a computer. Thus Eq. (29) takes the form

$$2M_0 = \frac{0.462(2\pi K)^2 kT}{2\phi''(a)} + \frac{\hbar^2(2\pi K)^2}{12MkT} + O(T^{-3}). \quad (30)$$

If the second term in  $G$ , Eq. (16), which includes the effect of the surface is substituted in Eq. (19), we have

$$2M_1 = -\frac{16\pi^2 kT}{NM} \sum_{\mathbf{k}j\mathbf{k}'j'} \frac{(\mathbf{K} \cdot \mathbf{e}(\mathbf{k}j))(\mathbf{K} \cdot \mathbf{e}(\mathbf{k}'j'))}{(\omega(\mathbf{k}j)\omega(\mathbf{k}'j'))^{3/2}} \\ \times \delta(k_1 + k_1') \delta(k_2 + k_2') e^{2\pi i a(\mathbf{k} + \mathbf{k}') \cdot \mathbf{l}} \\ \times \sum_{l_1 l_1'} f_{l_1 l_1'}(-\mathbf{k}j) [\mathbf{I} - \mathbf{M}(0)]_{l_1 l_1'}^{-1} \\ \times f_{l_1 l_1'}(-\mathbf{k}'j') + O(T^{-3}). \quad (31)$$

In the final result  $2M = 2M_0 + 2M_1$ , the main effect of the surface is to increase the coefficient of the term proportional to  $kT$ . The expression given by Eq. (31) was evaluated on a computer for various positions of the vibrating atom,  $\mathbf{l}$ . (Actually the result depends only on the distance from the surface,  $l_z$ , as is to be expected.) The mean-square amplitude of atoms approaches the bulk value very rapidly as one goes into the crystal from the surface, as shown in Fig. 1. By the time that the atom is four atomic layers into the crystal  $2M$  is within 5% of its value in the interior of the crystal. Note the marked anisotropy of  $2M$  as a function of  $\mathbf{K}$  for the resonant nucleus in the surface layers of a crystal. For an atom in the surface itself  $2M$  is twice as large as its bulk value for  $\gamma$ -ray emission perpendicular to the

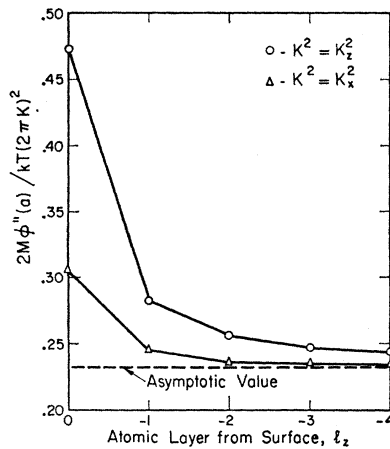


FIG. 1. A plot of the exponent in the Debye-Waller factor (divided by a dimensionless quantity) for an atom in various atomic layers going in from the surface, calculated in the high-temperature limit. The surface correction is larger for vibration perpendicular to the surface than for vibration parallel to the surface and decays very rapidly within a few atomic spacings from the surface.

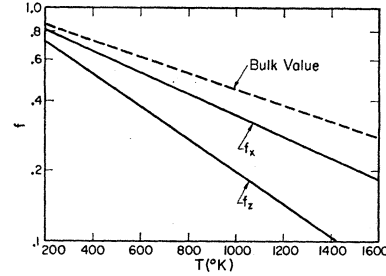


FIG. 2. A plot of  $f = \exp(-2M)$  as a function of temperature in the high-temperature limit for values of the model parameters corresponding to  $\text{Fe}^{57}$  in Fe. The Mössbauer active atom is in the surface layer. The effect of the surface on  $f$  is larger when the  $\gamma$  ray is emitted perpendicular to the surface  $f_z$  than when it is emitted parallel to the surface  $f_x$ . The Debye-Waller factor for an atom in the bulk of a crystal is shown dashed.

crystal surface  $[\mathbf{K} = (0, 0, K_z)]$  and about 30% larger than the bulk value for  $\gamma$ -ray emission parallel to the crystal surface  $[\mathbf{K} = (K_x, 0, 0)]$ .

The fraction of recoilless emissions for an atom in the surface, shown in Fig. 2, is calculated from the sum of Eqs. (30) and (31). The numerical values for  $\text{Fe}^{57}$  in Fe are used. We pretend that Fe is simple cubic and choose  $a$  and  $\phi''(a)$  so that the crystal has the correct density and shear wave speed for Fe. Using the relation  $a^3 = M/\rho$ , where  $\rho$  is the mass density, together with  $\phi''(a) = a\rho c_t^2$ , where  $c_t$  is the speed of pure transverse waves in Fe,<sup>6</sup> we obtain the values  $a = 2.28 \times 10^{-8}$  cm and  $\phi''(a) = 1.8 \times 10^4$  dyn/cm.

Since the momentum of the 14.4 keV  $\gamma$ -ray from  $\text{Fe}^{57}$  is of the same order of magnitude as the change in momentum of the electrons scattered from surface atoms by MacRae and Germer,<sup>3</sup> and since mechanically Ni and Fe are quite similar, the results of Fig. 2 should agree with the electron scattering results on Ni surfaces. However, only the rough agreement we obtain can be expected, since Ni is face-centered cubic, not simple cubic.

The Green's functions  $G$  and  $G'$  both contain the matrix elements of  $[\mathbf{I} - \mathbf{M}]^{-1}$ . These matrix elements are, in turn, all proportional to the reciprocal of the determinant,  $|\mathbf{I} - \mathbf{M}|$ . If this determinant vanishes, the Green's functions have a pole. The same determinant appears also in another context. If  $d^2 A_{\mathbf{k}j}(t)/dt^2$  is determined in the same way as  $d^2 G/dt^2$  was determined, then the vanishing of  $|\mathbf{I} - \mathbf{M}|$  is just the condition for a nontrivial solution of the resulting (Fourier transformed) equations of motion. The matrix elements of  $\mathbf{M}$  are

$$M_{l_1 l_1'} = -\frac{[\phi''(r(\mathbf{l}))\phi''(r(\mathbf{l}'))]^{1/2}}{2N^{1/3}M} \delta_{l_1 l_1'} \delta_{l_3, l_3'} \\ \times \sum_{\mathbf{k}j} (1 - e^{2\pi i \mathbf{a} \cdot \mathbf{k} \cdot \mathbf{l}}) (1 - e^{-2\pi i \mathbf{a} \cdot \mathbf{k} \cdot \mathbf{l}'}) \\ \times \frac{(\mathbf{e}(\mathbf{k}j) \cdot \mathbf{l})(\mathbf{e}(\mathbf{k}j) \cdot \mathbf{l}')}{E^2 - \omega^2(\mathbf{k}j)}. \quad (32)$$

<sup>6</sup> *A.I.P. Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 3-80.

If we require that the crystal be isotropic and take the long wavelength (continuum) limit, we can simplify the expression given by Eq. (32). The sum over  $j$  is done explicitly using the dispersion curves

$$\begin{aligned} \omega^2(\mathbf{k}1) &= 4\pi^2 c_l^2 k^2 \\ \omega^2(\mathbf{k}2) &= \omega^2(\mathbf{k}3) = 4\pi^2 c_t^2 k^2, \end{aligned} \quad (33)$$

which obtain in the long wavelength limit.  $c_l$  and  $c_t$  in Eq. (33) are the speeds of sound for longitudinal and transverse waves, respectively. The result then depends on the eigenvector components only through the combination  $e_\alpha(\mathbf{k}1)e_\beta(\mathbf{k}1)$  because we can eliminate the products  $e_\alpha(\mathbf{k}j)e_\beta(\mathbf{k}j)$  for  $j=2, 3$  by the use of the closure relation

$$\sum_{j=1}^3 e_\alpha(\mathbf{k}j)e_\beta(\mathbf{k}j) = \delta_{\alpha\beta}. \quad (34)$$

This is a convenient feature of the isotropic continuum

$$M_{l_1'l_2'; l_1l_2} = \frac{a}{2} \int_{-1/2a}^{1/2a} dk_3 \left\{ \frac{(k_1l_1 + k_2l_2 + k_3)^2 (k_1l_1' + k_2l_2' + k_3)^2}{r^2 + k_3^2} \times \left[ \frac{1}{3(\mu^2 + k_3^2)} \frac{1}{\lambda^2 + k_3^2} \right] - \frac{(l_1l_1' + l_2l_2' + 1)(k_1l_1 + k_2l_2 + k_3)(k_1l_1' + k_2l_2' + k_3)}{\lambda^2 + k_3^2} \right\}, \quad (38)$$

where

$$\lambda^2 = \frac{4\pi^2 c_t^2 r^2 - E^2}{4\pi^2 c_l^2}, \quad \mu^2 = \frac{4\pi^2 c_l^2 r^2 - E^2}{4\pi^2 c_t^2}, \quad (39)$$

$r^2 = k_1^2 + k_2^2$ , and the exponentials were expanded since  $\mathbf{k}$  is small. The following relations between the matrix elements hold:

$$\begin{aligned} M_{l_1'l_2'; l_1l_2} &= M_{l_1l_2; l_1'l_2'} \\ M_{-l_1'l_2'; -l_1l_2} &= M_{l_1'l_2'; l_1l_2} \\ M_{l_1'-l_2'; l_1-l_2} &= M_{l_1'l_2'; l_1l_2}. \end{aligned} \quad (40)$$

Using these relations and proper operations on the rows and columns, the determinant  $|\mathbf{I} - \mathbf{M}|$  factors, and we have the equation

$$\begin{aligned} &\begin{vmatrix} 1 - M_{00;00} & -M_{00;10} & -M_{00;01} \\ -2M_{00;10} & 1 - M_{10;10} - M_{10;-10} & -M_{10;01} - M_{10;0-1} \\ -2M_{00;01} & -M_{10;01} - M_{10;0-1} & 1 - M_{01;0-1} - M_{01;01} \end{vmatrix} \\ &\times \begin{vmatrix} 1 - M_{10;10} + M_{10;-10} & M_{10;0-1} - M_{10;01} \\ M_{10;0-1} - M_{10;01} & 1 - M_{01;01} + M_{01;0-1} \end{vmatrix} = 0. \end{aligned} \quad (41)$$

The first factor appears to have no zeros in the long wavelength limit. The second factor reduces to

$$\left[ r^2 - \lambda^2 - \frac{8\lambda}{3(\mu + \lambda)} r^2 \right] = 0. \quad (42)$$

because the eigenvector  $\mathbf{e}(\mathbf{k}1)$  in this case has the simple form

$$\mathbf{e}(\mathbf{k}1) = (k_1/k, k_2/k, k_3/k). \quad (35)$$

The speeds of sound  $c_l$  and  $c_t$  are given explicitly by

$$\begin{aligned} c_l^2 &= 3\phi''(a)/a\rho \\ c_t^2 &= \phi''(a)/a\rho, \end{aligned} \quad (36)$$

for the present model, where  $\rho$  is the mass density.

Putting all the preceding results together, and replacing the sum over  $k_3$  in Eq. (32) by an integral according to

$$\sum_{k_3} = aN^{1/3} \int_{-1/2a}^{1/2a} dk_3, \quad (37)$$

we can finally express the matrix elements of  $\mathbf{M}$  as (recalling that  $l_3$  and  $l_3'$  are required to equal  $+1$ )

The integrations in the matrix elements Eq. (38), give rise to terms containing  $\tan^{-1}(1/2a\lambda)$  which can be taken as equal to  $\pi/2$  since  $a \rightarrow 0$  in the continuum limit. Letting  $\zeta = E^2/4\pi^2 c_l^2 r^2$  and remembering the definitions of  $\mu$  and  $\lambda$  we can reduce Eq. (42) to

$$\zeta^3 - 8\zeta^2 + (56/3)\zeta - (32/3) = 0. \quad (43)$$

This equation has three roots:

$$\begin{aligned} \zeta_1 &= 4, \\ \zeta_2 &= 2 + \frac{2}{3}\sqrt{3} = 3.154701, \end{aligned} \quad (44)$$

and

$$\zeta_3 = 2 - \frac{2}{3}\sqrt{3} = 0.845299.$$

In defining  $\mu^2$  and  $\lambda^2$  we implicitly assumed that  $E^2 < 4\pi^2 c_l^2 r^2$ , since the integrals in Eq. (38) are not defined otherwise. Thus only  $\zeta_3$  is an acceptable root. Taking its square root we obtain for the location of a pole of the Green's function  $G$ ,

$$E = 2\pi(0.9194 \dots) c_l r. \quad (45)$$

This is the famous dispersion relation first obtained by

Lord Rayleigh<sup>7,8</sup> for the surface vibration modes in a semi-infinite isotropic elastic continuum which bear his name. These modes are waves which propagate over the boundary surface of a solid but penetrate only a small distance into its interior. This result shows that

<sup>7</sup>L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Inc., New York, and Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1959), p. 108.

<sup>8</sup>A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), pp. 307-309.

our expressions for  $2M$  and  $(\delta E/E)$  contain contributions from the surface vibration modes. This is in contrast with the results obtained by Rich,<sup>2</sup> because the crystal model used by him in his work is too simple to give rise to surface modes.

#### ACKNOWLEDGMENT

We wish to thank Brenda Kagle for programming the sums in the expression for  $2M$  for the computer.

## Photochemical Study of $F$ and $M$ Centers in Additively Colored Alkali Halides\*†‡

I. SCHNEIDER§ AND M. E. CASPARI

*Laboratory for Research on the Structure of Matter, Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania*

(Received 20 September 1963)

A study of absorption changes in the visible and near infrared spectral region, produced by  $F$ -band irradiation at 77°K which recover spontaneously when the  $F$  light is removed was made in additively colored KCl, KBr, and KI crystals containing  $M$  bands. These temporary changes are caused by a superposition of two processes. In crystals containing small  $M$ -center concentrations the tunneling of excited  $F$ -center electrons to nearby  $F$  centers could account for the temporary process. In crystals containing large  $M$ -center concentrations, the dominant process involves the transformation of  $M$  centers to related centers. In KCl, the principal  $M$ -center transitions at 801 and 546  $m\mu$  are changed to 685 and 505  $m\mu$ , respectively. Studies in crystals containing polarized  $M$  bands in which the temporary changes were produced with polarized light, show that this irradiation is not absorbed by  $M$  centers, but probably by  $F$  centers. The  $F$ -center excitation energy is then transferred locally to nearby  $M$  centers. The consistent interpretation of both processes requires the occurrence of  $F$ -center clustering during the early stages of room temperature irradiation and the formation of  $F$  and  $M$  centers in close proximity during later stages. The possible nature of the transformed  $M$  center is discussed and may involve  $F_2^+$ -center formation or the excitation of the  $M$  center into a metastable state. The recovery involves two channels: a temperature-independent process dominant below 100°K and one involving a thermal activation energy of about 0.035 eV dominant at higher temperatures.

### I. INTRODUCTION

IT is well known that  $F$ -band irradiation at room temperature of additively colored alkali halide crystals results in the formation of the  $M$  band.<sup>1,2</sup> Recent experiments have established that the  $M$  center, which gives rise to this band, consists of two nearest-neighbor  $F$  centers.<sup>3-8</sup> Moreover, room-temperature

irradiation of crystals containing  $M$  centers with  $M$  light polarized along a  $[011]$  direction produces a dichroic  $F$ ,<sup>9</sup> as well as  $M$  band indicating that  $M$ -center optical transitions may exist in the  $F$ -band region ( $M_2$ ,  $M_3$ , etc., bands).<sup>10</sup>

Studies concerning  $M$ -center formation have led to the conclusion that  $F$ -center migration and clustering occurs during the earliest stages of  $F$  irradiation.<sup>11</sup> During subsequent stages,  $M$  centers form probably in close proximity to  $F$  centers. Effects which have been attributed to the interaction of near lying color centers include the large reduction in  $F'$  yields and  $F$ -center fluorescence in crystals which had received relatively small exposure to  $F$  irradiation near room temperature. Energy transfer from  $F$  to  $M$  centers has been proposed as a possible interpretation for the observed  $M$ -center

\* This work was supported by a contract with the Electronic Technology Laboratory, Wright Air Development Division, U. S. Air Force.

† This work was presented in part at the Color Center Symposium, Stuttgart, Germany (August 1962) and in Solid State Communications 1, 9 (1963).

‡ Based on a thesis submitted by one of us (I.S.) to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

§ Now at Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts.

<sup>1</sup>J. P. Molnar, thesis, Massachusetts Institute of Technology, 1940 (unpublished).

<sup>2</sup>St. Petroff, *Z. Physik* **127**, 443 (1950).

<sup>3</sup>C. Z. van Doorn, *Phys. Rev. Letters* **4**, 236 (1960).

<sup>4</sup>B. J. Faraday, H. Rabin, and W. D. Compton, *Phys. Rev. Letters* **7**, 57 (1961).

<sup>5</sup>W. C. Holton, H. Blum, and C. P. Slichter, *Phys. Rev. Letters* **5**, 197 (1960).

<sup>6</sup>A. W. Overhauser and H. Rüdhardt, *Phys. Rev.* **112**, 722 (1958).

<sup>7</sup>H. Gross and H. C. Wolf, *Naturwissenschaften* **8**, 299 (1961).

<sup>8</sup>E. Sonder, *Phys. Rev.* **125**, 1203 (1962).

<sup>9</sup>C. Z. van Doorn and Y. Haven, *Phys. Rev.* **100**, 753 (1955).

<sup>10</sup>F. Okamoto, *Phys. Rev.* **124**, 1090 (1961).

<sup>11</sup>C. J. Delbecq, *Z. Physik* **171**, 560 (1963).