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Atomic Force Constants of Copper from Feynman's Theorem*

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In the Born-Oppenheimer approximation atomic force constants determine the elastic and vibrational behavior of crystals for small nuclear displacements. In this paper the first- through third-neighbor force constants in the copper crystal are found as the components of the change in force produced on the nuclei when in equilibrium positions by the infinitesimal unit displacements of one nucleus. By Feynman's theorem quantum-mechanical forces can be calculated directly from the electronic and nuclear charge distribution by Coulomb's law. The Slater-Koster formalism developed for localized perturbations in crystals is used to find the change in conduction electron charge density resulting from the infinitesimal unit displacement of a nucleus. Free-electron wave functions are used, and most of the perturbation energy matrix elements are neglected. Calculations are made for small crystals with up to 2048 atoms and two different shapes (Born-von Kármán boundary conditions): First-order perturbation theory gives exact results for atomic force constants. An approximate Thomas-Fermi calculation is also carried out for the perturbation in conduction electron density and simple approximations of this perturbation are discussed. The ion cores are assumed to move nearly rigidly, and their closed-shell repulsion is chosen so that the calculated atomic force constants lead to the values of the elastic constants found experimentally. The nine calculated atomic force constants are quite different from the values Jacobsen inferred from thermal diffuse x-ray scattering from a copper crystal.

1. INTRODUCTION

We wish to investigate the dynamical properties of metal crystals at the atomic level. From these microscopic properties we can not only predict macroscopic elastic and thermal vibration behavior and the interaction of the crystal with electromagnetic radiation but also obtain insight into various types of distortion of the perfect lattice.

In this paper, we develop a method of calculating the atomic force constants[1] of a simple metal independently of the elastic constants from the basic properties of the crystal. In most of the theoretical literature on thermal vibration spectra and specific heats of metals the atomic force constants (afc)[1] are chosen in a semi-empirical manner, usually to match the elastic constants.[2] Often somewhat arbitrary assumptions are made: e.g., central forces between atoms, or various limitations on the type and amount of electronic contribution to the afc. Since there are but a few elastic constants, in this approach the afc between higher order neighbors are assumed to be zero.

The core of our approach is to calculate forces between nuclei directly using Feynman's theorem.[3] Other papers in which afc in metals have been calculated directly[4] have evaluated them as second derivatives of the cohesive energy rather than as the ratio of the change in forces between nuclei to an infinitesimal nuclear displacement.

Post-war theoretical and experimental developments have made it possible both to measure the diffuse x-ray scattering from thermal motion in a crystal and to infer from the measurements the values of atomic force constants.[5] An x-ray investigation of copper by Jacobsen[6] was an important stimulus in undertaking the present calculation.

2. ADIABATIC APPROXIMATION AND FEYNMAN'S THEOREM

We assume the validity for copper of the Born-Oppenheimer approximation, according to which nuclear and electronic motions are separable for small deviations of the nuclei from an equilibrium configuration. Specifically, we consider the nuclei to be subject to an effective potential energy function which is the eigenvalue of the electrons for the nuclei fixed in each instantaneous configuration. The electrons are taken to remain during nuclear motion in the same quantum state, the characteristics of which adapt continuously to the shifting of the nuclei. Let us call this effective potential $U(X_1,\cdots,X_{3N})$ for the N nuclei at coordinates X_i. If we expand U about the equilibrium position, the first-order terms must vanish and we have[7]

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[1] Hereafter, "atomic force constants" will often be abbreviated as afc.

[2] E.g., J. de Launay, J. Chem. Phys. **21**, 1975 (1953); R. Leighton, Revs. Modern Phys. **20**, 166 (1948); H. B. Rosenstock, Phys. Rev. **97**, 290 (1955); G. K. Horton and H. Schiff, Phys. Rev. **104**, 32 (1956).

[3] R. P. Feynman, Phys. Rev. **56**, 340 (1939).

[4] E.g., A. B. Bhatia, Phys. Rev. **97**, 363 (1955); W. Brenig, Z. Naturforsch. **9A**, 560 (1954).

[5] H. Cole and B. E. Warren, J. Appl. Phys. **23**, 335 (1952); R. E. Joynson, Phys. Rev. **94**, 851 (1954); H. Curien, Acta Cryst. **5**, 392 (1952).

[6] E. H. Jacobsen, Jr., Phys. Rev. **97**, 654 (1955).

[7] M. Born and K. Huang [*Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), p. 172] show that fifth and higher order terms in this expansion are inconsistent with the assumption of separability of nuclear and electronic motion, as justified by a quantum mechanical perturbation theory expansion.

$$U(X_1,\cdots,X_{3N})=U_0+\sum_{i,j}\left.\frac{\partial^2 U(X_1,\cdots,X_{3N})}{\partial X_i\partial X_j}\right|_{X_k=X_k^0,\text{ for } k=1\text{ to }3N}(X_i-X_i^0)(X_j-X_j^0),$$

$$+\text{third- and fourth-order terms in nuclear displacements.}$$

The coefficients of the second-order terms we define as our interatomic force constants; they are seen to have the appropriate general characteristics.

We follow the usual treatment of thermal vibrations in crystals in which the higher order terms in the above expansion are neglected. Then the lattice of atoms resembles a large collection of simple harmonic oscillators. Its motion can be analyzed in terms of normal coordinates, leading to a representation of the vibration as a superposition of normal modes of oscillation whose frequencies depend on the values of the atomic force constants.[8] By a standard thermodynamical derivation the specific heat of the metal as a function of temperature can then be found. Such properties as thermal expansion cannot, however, be explained by this "harmonic" approximation.[9]

Born and Huang, and Peierls[10] in recent books have denied the legitimacy of the Born-Oppenheimer approximation for metals. In the usual derivation by perturbation theory the ratio of electronic to nuclear mass is used as the expansion parameter, and the approximation appears as valid for metals as for other solids. Born and Huang, however, have recast the derivation in such a way that the coupling terms between nuclear and electronic motion depend on the reciprocal of differences between ground- and excited-state energies of the electrons.[11] According to Born and Huang, the quasi-continuous nature of the energies of conduction electrons in a metal implies that this coupling is large; i.e., the electrons change states in adjusting to nuclear motion and hence one cannot clearly define an effective potential energy function for nuclear motion. Born and Huang have not actually evaluated for a metal their coupling terms, which contain critical factors other than the energy ones on which they base their conclusion. The theory of conductivity treats a somewhat similar problem in the exchange of energy between electrons and lattice vibrations. There it is found that little change in the energy of the nuclear vibrations results from the exchange.[9,12] Another way to express the Born and Huang objection partially is to say that the interaction of nuclear vibrations with the long-range collective oscillations of the plasma of electrons in a metal is neglected in the adiabatic approximation. The effect of such collective oscillations on vibrational behavior has not been found to be large away from absolute zero.[13] For example, there is not a large difference between static and ultrasonic values of the elastic constants.[14] Both in the theory of conductivity and the papers on thermal behavior of metals, the Born-Oppenheimer approximation has been used almost universally. The recent papers[5,6] obtaining afc from thermal diffuse x-ray scattering from Fe, Al, Zn, and Cu are the experimental sources with which we wish to compare our theoretical results: the dynamical theory on which they are based also uses the adiabatic approximation. The errors in using the adiabatic approximation are probably no worse than in making the further assumption of a quadratic form for the potential energy.

The first derivative of U with respect to a nuclear coordinate evaluated with all the nuclear coordinates held constant is a force of the type Feynman has considered.[3] Feynman shows that for any system of electrons and fixed nuclei, the derivative with respect to a nuclear coordinate of the expected value of the energy operator over the wave function of the electrons is identical with the expected value over the wave function of the derivative of the energy operator. The latter is shown to be simply the classical Coulomb force exerted by the nuclear charges and the sum of the one-electron charge densities given by integrating the many-electron probability density over the coordinates of all electrons but one.

An atomic force constant by definition is the limit of the ratio, to the displacement, of the difference between the force component exerted on another nucleus by a nucleus when displaced from equilibrium along a crystal axis and when at the equilibrium position. Hence by Feynman's theorem the afc are the force components on one nucleus exerted by the change in electron and nuclear charge distributions resulting from a small unit displacement of the other nucleus along an axis in a crystal in equilibrium.

Feynman's theorem is only applicable to systems for which the adiabatic approximation holds. The quadratic terms in the nuclear potential energy which we calculate by the use of it are not to be equated, however, with the quadratic terms in the usual perturbation theory expansion of the energy. The latter terms reflect only the zero-order electronic wave function, which represents the electronic state for the nuclei in

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[8] E. W. Montroll, Technical Report No. 6, Institute for Fluid Dynamics and Applied Mathematics, University of Maryland, April, 1954 (unpublished).

[9] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[10] R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1953), p. 6.

[11] Reference 7, Appendix VIII.

[12] J. Bardeen, Revs. Modern Phys. **23**, 261 (1951).

[13] D. Pines and D. Bohm, Phys. Rev. **85**, 338 (1952); D. Bohm, Phys. Rev. **84**, 836 (1951).

[14] E. Goess and J. Weerts, Physik. Z. **37**, 321 (1936); R. F. S. Hearmon, Revs. Modern Phys. **28**, 409 (1946); H. Jones, Physica **15**, 17 (1949); J. Gaffney and W. C. Overton, Phys. Rev. **95**, 602 (1954); D. Lazarus, Phys. Rev. **76**, 545 (1949).

TABLE I. Dynamical matrices[a] between origin nucleus and nuclei of first three neighbor rings[b] in fcc monatomic lattice.

$$\left.\begin{matrix}\mathfrak{D}^{1}\\ \mathfrak{D}^{7}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\alpha_1&0&0\\0&\beta_1&\gamma_1\\0&\gamma_1&\beta_1\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{2}\\ \mathfrak{D}^{8}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\alpha_1&0&0\\0&\beta_1&-\gamma_1\\0&-\gamma_1&\beta_1\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{3}\\ \mathfrak{D}^{9}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_1&0&\gamma_1\\0&\alpha_1&0\\\gamma_1&0&\beta_1\end{bmatrix},$$

$$\left.\begin{matrix}\mathfrak{D}^{4}\\ \mathfrak{D}^{10}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_1&0&-\gamma_1\\0&\alpha_1&0\\-\gamma_1&0&\beta_1\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{5}\\ \mathfrak{D}^{11}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_1&\gamma_1&0\\\gamma_1&\beta_1&0\\0&0&\alpha_1\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{6}\\ \mathfrak{D}^{12}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_1&-\gamma_1&0\\-\gamma_1&\beta_1&0\\0&0&\alpha_1\end{bmatrix},$$

$$\left.\begin{matrix}\mathfrak{D}^{13}\\ \mathfrak{D}^{14}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\alpha_2&0&0\\0&\beta_2&0\\0&0&\beta_2\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{15}\\ \mathfrak{D}^{16}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_2&0&0\\0&\alpha_2&0\\0&0&\beta_2\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{17}\\ \mathfrak{D}^{18}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_2&0&0\\0&\beta_2&0\\0&0&\alpha_2\end{bmatrix},$$

$$\left.\begin{matrix}\mathfrak{D}^{21}\\ \mathfrak{D}^{35}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_3&\gamma_3&\epsilon_3\\\gamma_3&\beta_3&\epsilon_3\\\epsilon_3&\epsilon_3&\alpha_3\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{30}\\ \mathfrak{D}^{37}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_3&-\gamma_3&\epsilon_3\\-\gamma_3&\beta_3&-\epsilon_3\\\epsilon_3&-\epsilon_3&\alpha_3\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{25}\\ \mathfrak{D}^{40}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_3&\gamma_3&-\epsilon_3\\\gamma_3&\beta_3&-\epsilon_3\\-\epsilon_3&-\epsilon_3&\alpha_3\end{bmatrix},$$

$$\left.\begin{matrix}\mathfrak{D}^{23}\\ \mathfrak{D}^{38}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_3&-\gamma_3&-\epsilon_3\\-\gamma_3&\beta_3&\epsilon_3\\-\epsilon_3&\epsilon_3&\alpha_3\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{28}\\ \mathfrak{D}^{31}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_3&-\epsilon_3&\gamma_3\\-\epsilon_3&\alpha_3&-\epsilon_3\\\gamma_3&-\epsilon_3&\beta_3\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{22}\\ \mathfrak{D}^{36}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_3&-\epsilon_3&-\gamma_3\\-\epsilon_3&\alpha_3&\epsilon_3\\-\gamma_3&\epsilon_3&\beta_3\end{bmatrix},$$

$$\left.\begin{matrix}\mathfrak{D}^{39}\\ \mathfrak{D}^{24}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\alpha_3&-\epsilon_3&-\epsilon_3\\-\epsilon_3&\beta_3&\gamma_3\\-\epsilon_3&\gamma_3&\beta_3\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{32}\\ \mathfrak{D}^{29}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\alpha_3&-\epsilon_3&\epsilon_3\\-\epsilon_3&\beta_3&-\gamma_3\\\epsilon_3&-\gamma_3&\beta_3\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{20}\\ \mathfrak{D}^{34}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_3&\epsilon_3&\gamma_3\\\epsilon_3&\alpha_3&\epsilon_3\\\gamma_3&\epsilon_3&\beta_3\end{bmatrix},$$

$$\left.\begin{matrix}\mathfrak{D}^{19}\\ \mathfrak{D}^{33}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\alpha_3&\epsilon_3&\epsilon_3\\\epsilon_3&\beta_3&\gamma_3\\\epsilon_3&\gamma_3&\beta_3\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{42}\\ \mathfrak{D}^{26}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\alpha_3&\epsilon_3&-\epsilon_3\\\epsilon_3&\beta_3&-\gamma_3\\-\epsilon_3&-\gamma_3&\beta_3\end{bmatrix},\qquad \left.\begin{matrix}\mathfrak{D}^{41}\\ \mathfrak{D}^{27}\end{matrix}\right\}=-m^{-1}\begin{bmatrix}\beta_3&\epsilon_3&-\gamma_3\\\epsilon_3&\alpha_3&-\epsilon_3\\-\gamma_3&-\epsilon_3&\beta_3\end{bmatrix}.$$

[a] The atomic force constant matrices times the negative reciprocal of the nuclear mass, m.
[b] Neighbor sites numbered as in Fig. 1.

equilibrium positions; whereas our calculation by Feynman's theorem of the coefficient of the quadratic terms includes the first-order perturbation of the electronic wave function by the nuclear displacement.

3. CRYSTAL SYMMETRY AND THE ELASTIC CONSTANTS

The low-frequency normal modes of thermal vibration in the crystal can be identified with the longitudinal and transverse modes of vibration in classical elasticity theory. Thus the elastic constants can be equated to certain sums of the atomic force constants. By a theorem of Born the stability of all the normal modes of vibration is assured if the elastic constant values correspond to stable acoustic modes.[15]

Fortunately symmetry considerations greatly reduce the number of distinct afc. Because of the translational symmetry of the crystal, the nine afc between a pair of nuclei do not depend on their absolute location but only on the difference between their equilibrium position vectors. Hence all the afc are given by three-by-three force constant matrices between one nucleus, which we shall take as the origin, and the other nuclei in the crystal. In applying Feynman's theorem, we shall take the virtual displacement of a nucleus used in calculating the afc as occurring for the origin nucleus.

The afc matrices between nuclei, from their definition, behave as tensors of the second rank with respect to coordinate transformations. Certain rotations of the coordinate axes lead to the new position vector of each nucleus being the same as the former position vector of another nucleus and will leave the over-all lattice position unchanged. When these transformations are applied to the afc matrices between the origin nucleus and the nuclei at a given distance away, it is readily seen that the nine elements in one matrix are merely permutations of those in one of the other matrices for members of the same ring of neighbors. Moreover, some of the rotations will leave the position vector of a given nucleus unchanged while leading to an apparent transformation of the afc matrix: then one finds symmetry restrictions on the internal structure of the force constant matrix by requiring the transformed matrix to be identical with the initial matrix.

The details of these derivations can be found in Begbie[16] and Jacobsen.[6] The results are given in Table I for the conventions of Fig. 1. There are nine independent afc from the first- through third-neighbor rings. Two different ϵ_3's, on opposite sides of the diagonal of the afc matrices, would in fact be consistent with lattice symmetry requirements. However, in order for the squares of the vibration frequencies of the normal modes to be real, the afc matrices must be Hermitian. The formulas connecting the afc and elastic constants for the face-centered cubic lattice are

$$ac_{11}=2\beta_1+2\alpha_2+8\alpha_3+4\beta_3+\text{further neighbor terms,}\tag{3.1}$$

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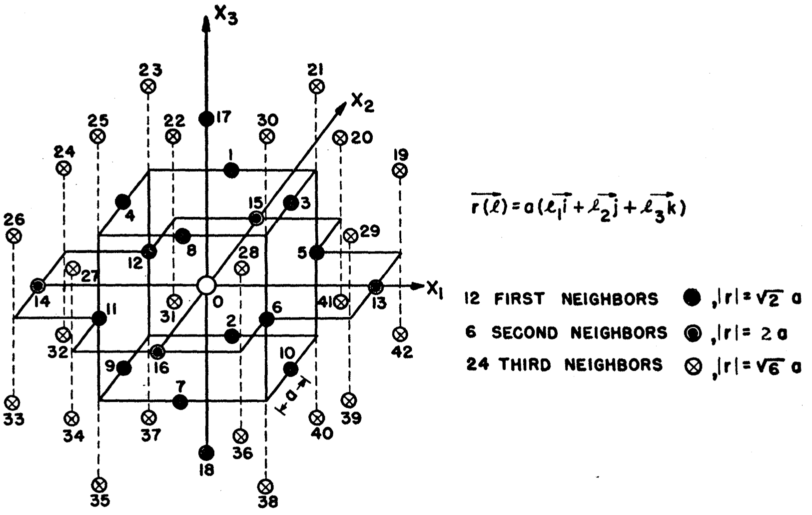
[15] M. Born, Proc. Cambridge Phil. Soc. **38**, 82 (1942); J. Chem. Phys. **7**, 591 (1939).

[16] M. Born and G. H. Begbie, Proc. Roy. Soc. (London) **188**, 179 (1946–7); G. H. Begbie, Proc. Roy. Soc. (London) **188**, 189 (1946–7).



		1st Neighbors												2nd					
ℓ	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ℓ_1	0	0	0	1	-1	1	1	0	0	-1	1	-1	-1	2	-2	0	0	0	0
ℓ_2	0	1	1	0	0	1	-1	-1	-1	0	0	-1	1	0	0	2	-2	0	0
ℓ_3	0	1	-1	1	1	0	0	-1	1	-1	-1	0	0	0	0	0	0	2	-2

	3rd Neighbors																							
ℓ	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42
ℓ_1	2	1	1	-1	-1	-2	-1	-2	-1	1	2	1	-1	-2	-2	-1	-1	1	-1	1	2	1	1	2
ℓ_2	1	2	1	2	1	1	-1	-1	-2	-2	-1	-1	2	1	-1	-2	-1	-2	1	-1	-1	1	2	1
ℓ_3	1	1	2	1	2	1	2	1	1	1	1	2	-1	-1	-1	-1	-2	-1	-2	-2	-1	-2	-1	-1

FIG. 1. Face-centered cubic structure.

$$ac_{44} = \alpha_1+\beta_1+2\beta_2+2\alpha_3+10\beta_3 + \text{further neighbor terms}, \quad (3.2)$$

$$a(c_{12}+c_{44}) = 2\gamma_1+4\gamma_3+16\epsilon_3 + \text{further neighbor terms}, \quad (3.3)$$

where a is the spacing of atomic planes, 1.80 A in the case of copper. We will see later than the fourth- and higher order neighbor afc are very small, but the number of nuclei in further neighbor rings is large and we have not proved that their contribution to the elastic constants is negligible. Since the elastic constants are known with accuracy, we shall use the foregoing equations as a guide in the calculation of the afc. However, these equations would not be exact even if all the afc were included and were correct, because the afc only represent the quadratic terms in the expansion of the effective nuclear potential energy about the equilibrium configuration. The values of the c_{ij} used should be those determined in ultrasonic not static experiments, since the latter imply macroscopic distortions of the crystal not consistent with the assumptions of our afc calculations.

4. ION CORE MODEL

We shall not attempt to calculate the exact one-electron wave function of the copper crystal called for in Feynman's theorem. The ion core electrons will be taken as localized about the various nuclei in tight closed shells which are spherically symmetric. We assume that the origin ion core moves nearly rigidly for the virtual displacement δ. Then the change in Coulomb field resulting from the shift of the origin ion core charge is to a first approximation that of a dipole with charges e and moment arm δ (located $\delta/2$ distant from the origin). Because of shielding by the ion core electrons, the effective nuclear charges exposed to the dipole field will be just $+e$. The resulting contributions to the force constants are given in column 1 of the Table of Results, multiplied by 1.06 for reasons explained later in this section.

The ion cores are not tiny, and the shift in the origin ion core will result in addition in changed penetration of its ion core into the ion cores of its twelve nearest neighbors. According to Feynman's theorem the effect of this changed penetration is given by the classical Coulomb force produced by the corresponding change in charge density. However, we shall treat this closed-shell repulsion effect phenomenologically. The interaction force is central, of short range, and two-body. The virtual displacement of the origin ion core along a crystal axis leads to a change in the magnitude and a change in the direction of this interaction force, say R and A, respectively. From the geometry it follows that

$$\beta_1 = R-A, \quad \gamma_1 = R+A, \quad \text{and} \quad \alpha_1 = -2A.$$

Fuchs in his calculation of the elastic constants of copper[17] used an approximate form of the closed-shell

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[17] K. Fuchs, Proc. Roy. Soc. (London) **153**, 622 (1936); **157**, 444 (1936); but see F. G. Fumi [Phil. Mag. **46**, 1007 (1955)] for a later calculation.

interaction developed by Lenz from a Thomas-Fermi approximation. If $2W(r)$ is the interaction energy of a pair of copper ions, in terms of the above notation we have

$$R=\left.\frac{\partial^2 W}{\partial r^2}\right|_{r_0},\quad A=-\left.\frac{1}{r_0}\frac{\partial W}{\partial r}\right|_{r_0}.$$

Here r_0 is the first-neighbor distance in copper, 2.54 A. Lenz' values are

$$A=0.085\times10^4 \text{ dynes/cm},\quad R=1.40\times10^4 \text{ dynes/cm}.$$

However, Seitz and Huntington distrust these values for a variety of reasons. They have suggested[18] both shifting his distance scale by 17% to smaller values or alternatively using a Born-Mayer type interaction energy: $W(r)=A\exp(-r/\rho_0)$. Subsequent articles by them and other authors on copper have generally followed the latter suggestion.[19] The A and ρ_0 parameters are chosen to give agreement with the experimental elastic constants using a variety of assumptions about what fraction of the c_{ij} result from the closed-shell interaction and what fraction from conduction-electron contributions. Our detailed calculation of the conduction-electron contribution to the afc and thence to the elastic constants is probably more reliable than any published previously and so we shall treat R and A as disposable parameters to be chosen to give the best match of our calculated totals to the experimental elastic constants. It is superfluous for this purpose to assume any particular functional form for the interaction energy between the closed shells.

The remaining problem, on which we have chosen to focus the major share of our attention in this paper, is to evaluate the change in conduction electron charge density produced by the virtual displacement of the origin nucleus plus ion core electrons. Exchange and correlation between the origin ion core and the conduction electrons have an effect, which we crudely approximate together with the self-consistent-field effect resulting from the size of the ion core as follows.

There is a partial exclusion of the conduction electrons from the ion core, as can be seen for example from Fuchs' self-consistent-field wave function for the 4s electron in copper.[17] We assume that the conduction electron is free and therefore uniformly distributed everywhere outside the copper ion core, from which it is entirely excluded. We take the ion core to have the effective radius 1.1 A suggested both by Fuchs' results and the semiempirical calculations on additivity of ion core radii in crystals.[9] The virtual displacement of the ion core will eliminate a crescent of conduction electrons from its path, and a similar crescent of volume formerly occupied by the ion core will be filled by conduction electrons. The net electrostatic effect of the change in conduction electron distribution is exactly the same as if a sphere of the size of the ion core and with a positive charge density equal in magnitude to that of the conduction electrons is shifted δ away from the origin. That is, the effect is that of a pure dipole. For the ion core radius we use, the dipole moment is about six percent of that of the ion core, and adds to it.

5. THOMAS-FERMI MODEL FOR THE CONDUCTION ELECTRONS

It is the electrostatic field of the dipole of moment $(+e\delta)$, representing the virtual displacement through a distance δ of the origin ion core, which produces the major perturbation of the conduction electron distribution in our model. In the treatment of this perturbation the following considerations should be borne in mind:

(1) A formulation should be used which is suitable for a localized perturbation, such as one of those developed for impurity problems.

(2) The calculated change in conduction electron density must give rise to complete screening of the ion core dipole within a few angstroms, from electrostatic principles.

(3) A self-consistent-field technique must be used, since the perturbing potential affecting a given electronic wave function will be in large part the effect of perturbations in all the other electronic wave functions. In a field with dipole symmetry, no bound state can emerge to effect most of the screening.

(4) The calculations must be accurate within the immediate vicinity of the origin. Within a radius of, say, 3 A is found the largest change in density and contribution to the afc.

(5) First-order perturbation theory is rigorous, because the virtual displacement δ is by definition infinitesimal.

We call the change in conduction electron density $\Delta\rho$, and we assume that the displacement of the ion core is along the x_1 axis without loss of generality.

First we develop an approximate Thomas-Fermi treatment, following Mott's approach for the screening of an impurity atom in a metal.[20] Assume that the conduction electrons form a plasma gas with initial Fermi level E_F through which the neutralizing ion core charge is uniformly spread. Let U be the electric potential acting on each electron as a result of the dipole perturbation at the origin. The density of the electrons ρ will be approximately proportional to $(E_F-eU)^{\frac{3}{2}}$ from the Pauli and Heisenberg principles. Then by Poisson's equation, the Laplacian of the total electric potential on the electron is proportional to $(E_F-eU)^{\frac{3}{2}}$. We expand the parenthesis by the binomial theorem and since U is infinitesimal, neglect all terms beyond the

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[18] F. Seitz and H. B. Huntington, Phys. Rev. **61**, 320 (1942).

[19] H. B. Huntington [Phys. Rev. **91**, 1092 (1953)] summarizes and evaluates the situation; but see K. Kambe, Phys. Rev. **99**, 419 (1955).

[20] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936); I. Isenberg, Phys. Rev. **79**, 736 (1950).

second. We cancel the terms not containing the perturbation potential U and find that

$$\nabla^2 U = q^2 U, \quad \text{where} \quad q^2 = 16\pi^2 me^2 (3n_0/\pi)^{\frac{1}{3}}(1/h^2);$$

n_0 is the density of atoms, and we use esu. U must vanish at infinity and reduce to a dipole potential at the origin. The latter boundary condition is equivalent to adding the inhomogeneous term $4\pi e\{\delta(\mathbf{r}-\delta\mathbf{i})-\delta(\mathbf{r})\}$ to the right side of the equation. Using the standard Green's function approach and neglecting higher order terms in the virtual displacement δ, we obtain

$$U(\mathbf{r}) = [(e\delta)\cos\theta/r^2](1+qr)e^{-qr},$$

which in fact exactly satisfies the scalar wave equation. The quantity in brackets is the potential of the ion core dipole; our screening factor differs from that of Mott by the $(1+qr)$ term.

The change in conduction electron density is proportional to $U(r)$. The total screening charge, the integral of the magnitude of $\Delta\rho$, is $(eq\delta)$ and it has a dipole moment of $(-e\delta)$. By direct calculation $q = 1.81$ A^{-1}. With this value of q all but a few percent of the $\Delta\rho$ lies within the first-neighbor ring.

The forces on the neighboring nuclei can be calculated directly by taking the gradient of U and include the effect of the ion-core dipole as well as of the change in conduction electron distribution. Dividing by δ we find the afc listed in the first column of Table II. Jacobsen's afc[6] are given in the Table of Results. The closed-shell repulsion is negligible beyond first neighbors; so the x-ray values should agree with those calculated from the Thomas-Fermi U for second and third neighbors. Instead the x-ray values are much larger. Moreover, the first-neighbor Thomas-Fermi afc are so small also that very large closed-shell repulsion contributions must be assumed to obtain elastic constants as big as the experimental ones.

If almost all the $\Delta\rho$ is within the first-neighbor ring, its electrostatic field at and beyond this ring is equivalent to that of a multipole expansion at the origin, according to a well-known theorem. It is easy to show that in the fcc lattice the forces due to (axial) quadrupoles and sixteen-poles have the wrong symmetry for afc. The dipole and octopole forces have the right general symmetry, but only for the dipole is there a single value for ϵ_3. In Table IV we exhibit the afc produced by a dipole in column 1: they do not have the same relative sizes as the Thomas-Fermi afc for an undifferentiated plasma with $q=1.81$ A^{-1}.

TABLE II. Atomic force constants[a] from Thomas-Fermi model.

afc	$q=1.81$ A^{-1}	$q=0.93$ A^{-1}
α_1	-0.08	-0.43
β_1	0.19	0.58
γ_1	0.26	1.01
α_2	0.04	0.34
β_2	···	-0.07
α_3	···	0.07
β_3	···	···
γ_3	···	0.02
ϵ_3	···	0.05

[a] In units of 10^4 dynes/cm.

Mott treated q as an undetermined parameter, which he chose to be 3 A^{-1} to give best agreement with the measurements on impurity resistivity. Trial and error led us to the value of $q=0.93$ A^{-1} as giving reasonable agreement with Jacobsen's second- and third-neighbor x-ray afc (see Table II). About 20% of the $\Delta\rho$ lies outside the first-neighbor ring for this value of q and we therefore do not expect the α_1, β_1, and γ_1 to be those of a dipole. The second- and third-neighbor afc for $q = 0.93$ A^{-1}, however, are in rough agreement with those caused by a dipole of positive moment at the origin.

Although the Thomas-Fermi treatment has the five characteristics called for at the beginning of this section, it is not satisfactory. It does not reflect the fcc structure of copper. We have no rationale for treating q as a disposable parameter. In any case it is not pleasing to choose q so as to reach the best agreement with the x-ray afc whose validity we wish to test.

A perturbation theory solution of the Schrödinger equations of the conduction electrons is called for. We assume that expansion of the perturbed wave functions in the unperturbed wave functions of the 4s band alone is sufficient, and we shall approximate the latter by free-electron plane waves for actual calculations. Most of the published formulations of localized perturbations in a periodic potential[21] are not appropriate to our problem, usually because they critically depend on the spherical symmetry of the perturbation and on the creation of bound states which account for most of the screening by conduction electrons. The Thomas-Fermi treatment above will serve as a zero-order approximation indicating what simplifications of the self-consistent perturbation potential can be made.

6. SLATER-KOSTER FORMULATION FOR LOCALIZED PERTURBATIONS IN A MICROSCOPIC CRYSTAL

In a macroscopic metal crystal the conduction electron eigenvalues are very closely spaced, but since they are discrete it is theoretically possible to formulate perturbation effects in terms of changes in eigenvalues. Such a formulation becomes feasible when restricted to crystals with dimensions of a few atomic planes, in which there are but a few, rather well-separated states in the conduction band. Koster and Slater have found for a monopole perturbation in an idealized simple cubic lattice that the curves of the energy of the state split off from the band *vs* perturbation magnitude are nearly identical for the infinite lattice and the lattice of twelve atomic planes on an edge.[22]

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[21] E.g., E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950); H. B. Huntington, Phys. Rev. **61**, 325 (1942); J. Friedel, Phil. Mag. **43**, 153 (1952), Phil. Mag. Suppl. **3**, 446 (1954).

[22] J. C. Slater, Technical Report No. 5, Solid State and Molecular Theory Group, Massachusetts Institute of Technology,

We shall find $\Delta\rho$, the perturbation in conduction electron density, by discrete eigenvalue perturbation theory applied to microscopic crystals. Since the dipole perturbation is by definition infinitesimal, even for a macroscopic crystal first-order perturbation theory is rigorous. We use Born-von Kármán periodic boundary conditions.[9] Ledermann[23] has shown they are equivalent to surface effects; so we justify their use when we convince ourselves that the smallness of the crystal does not appreciably affect the $\Delta\rho$ resulting from the localized dipole perturbation.

Expansion of the perturbed wave function in terms of localized and orthogonal orbitals such as the Wannier functions would seem appropriate. Substitution of the expansion in Schrödinger's equation leads in the standard way to a set of linear homogeneous equations in the coefficients and a corresponding secular determinant fixing the energy. However, the determinant has as many rows and columns as the crystal has atoms.

One way to simplify the determination of the expansion coefficients is to split them into a factor corresponding to the unperturbed wave function and a factor representing the effect of the perturbation. By suitable approximation Wannier's differential equation in the perturbation factor can be derived, in the free-electron approximation a second-order equation. Another way, developed by Slater and Koster,[22] retains the focus on the perturbation in eigenvalues and the advantages in using localized Wannier functions but uses an initial expansion in Bloch waves.

Expand χ, a perturbed wave function, in the unperturbed Bloch wave eigenfunctions, u_k: $\chi=\sum F_k u_k$, where the summation is over all the propagation vectors $\mathbf{k}$ in the 4s band Brillouin zone. Substitute this expansion in the Schrödinger equation

$$H_0\chi+V\chi=E\chi,$$

where V is the perturbation energy and $H_0u_k=E_ku_k$. Multiplying by $u_{k'}^*$ and integrating over the crystal volume, we obtain

$$F_{k'}E_{k'}+\sum(\mathbf{k})F_k(k'|V|k)=EF_{k'},\qquad(6.1)$$

where $(k'|V|k)=\int u_{k'}^*Vu_kd\tau$, and $\sum(\mathbf{k})$ means summation over $\mathbf{k}$. Let $a(\mathbf{r}-\mathbf{R}_j)$ be the Wannier function centered on the site R_j in the lattice; $u_k=(1/\sqrt{N})\sum(\mathbf{R}_j)\times\exp(i\mathbf{k}\cdot\mathbf{R}_j)a(\mathbf{r}-\mathbf{R}_j)$, with the summation over all the sites in the lattice and N the number of atoms in the crystal. Equation (6.1) can be rewritten

$$F_{k'}=(1/N)[1/(E-E_{k'})]\sum(\mathbf{k})F_k\sum(\mathbf{R}_i,\mathbf{R}_j)\times\exp(i\mathbf{k}\cdot\mathbf{R}_j)\exp(-i\mathbf{k}'\cdot\mathbf{R}_i)[R_i|V|R_j].\qquad(6.2)$$

Here $[R_i|V|R_j]$ is the average of the perturbation energy V over the Wannier functions localized about sites R_i and R_j:

$$[R_i|V|R_j]=\int a^*(\mathbf{r}-\mathbf{R}_i)Va(\mathbf{r}-\mathbf{R}_j)d\tau.$$

By expanding the F_k coefficients in the coefficients of the expansion of χ in Wannier functions, one can obtain from Eq. (6.2) a transformed determinant for the energy E of much smaller size than the usual secular determinant mentioned earlier. One finds the same transformed determinant by introducing displaced Bloch waves,[22] however, and we shall find this approach more efficient for calculating $\Delta\rho$.

Let us define

$$A(R_i)=(1/N)\sum(\mathbf{k},\mathbf{R}_j)[R_i|V|R_j]\exp(i\mathbf{k}\cdot\mathbf{R}_j)F_k.\qquad(6.3)$$

Substituting Eq. (6.3) in Eq. (6.2), we see

$$F_{k'}=1/(E-E_{k'})\sum(\mathbf{R}_i)A(R_i)\exp(-i\mathbf{k}'\cdot\mathbf{R}_i).\qquad(6.4)$$

In turn substituting Eq. (6.4) in Eq. (6.3), there results

$$A(R_i)=(1/\sqrt{N})\sum(\mathbf{R}_j,\mathbf{R}_p)\times[R_i|V|R_j]G_E(R_j,R_p)A(R_p).\qquad(6.5)$$

The quantity

$$G_E(R_j,R_p)=(1/\sqrt{N})\sum(\mathbf{k}')\times\exp[i\mathbf{k}'\cdot(\mathbf{R}_j-\mathbf{R}_p)]/(E-E_{k'})\qquad(6.6)$$

is the equivalent for finite difference equations of the Green's function; the sum in Eq. (6.6) is analogous to the expansion of a Green's function in the eigenfunctions of the corresponding homogeneous equation.[24] Equation (6.5) represents a set of N linear homogeneous equations in the N unknowns $A(R_i)$. For the set to be consistent the determinant of the coefficients must be zero. The Green's function contains E as a parameter; so the determinant is essentially a transformed secular determinant, although it is not Hermitian nor in general symmetric in other ways. The complex way in which the perturbed energy E appears in the transformed determinant is offset by the reduced effective size of the determinant. $[R_i|V|R_j]$ is negligible if either of the Wannier functions centers on a site appreciably removed from the localized perturbation at the origin. From Eq. (6.3) we see that $A(R_i)$ is also negligible if R_i is not near the origin.

In our calculation for $\Delta\rho$ first-order perturbation theory is rigorous, and this leads to important simplifications. If E is one of the perturbed energies closest to the unperturbed eigenvalue E_q, Eq. (6.6) reduces to

$$G_E(R_j,R_p)=(1/\sqrt{N})[1/(E-E_q)]\times\sum(\mathbf{k}'\text{ degenerate at }E_q)\exp[i\mathbf{k}'\cdot(\mathbf{R}_j-\mathbf{R}_p)],$$

where $q\sim|\mathbf{k}'|^2$. The determinant in the coefficients of the $A(R_j)$ then applies only to the perturbed states which reduce to the E_q state; but the determinantal

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Cambridge, 1953 (unpublished); G. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); **96**, 1208 (1954); G. Koster, Phys. Rev. **95**, 1436 (1954).

[23] W. Lederman, Proc. Roy. Soc. (London) **A182**, 362 (1944).

[24] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

equation can be put in a more familiar form:

$$0=\text{determinant}\{(E-E_q)\delta(R_i,R_p)-(1/N)\sum(R_j) \times[R_i|V|R_j]\sum(\mathbf{k}' \text{ degenerate at } E_q) \times\exp[i\mathbf{k}'\cdot(\mathbf{R}_j-\mathbf{R}_p]\}, \quad (6.7)$$

where the quantity in brackets is the general term in the determinant and $\delta(R_i,R_p)$ is 0 if $\mathbf{R}_i\neq\mathbf{R}_p$ and 1 if $\mathbf{R}_i=\mathbf{R}_p$. The determinant is still not Hermitian.

The perturbation energy V necessarily has dipole symmetry in the $x_1=0$ plane: i.e., $V(x_1,x_2,x_3)=-V(-x_1,x_2,x_3)$ when the origin nucleus displacement is along the x_1 axis. The Wannier functions $a(\mathbf{r}-\mathbf{R}_i)$ centered on the sites of the crystal lattice form an orthonormal set, but they have an identical functional form, which is symmetric. Hence the diagonal matrix element between Wannier functions centered on the origin site is zero: $[0|V|0]=0$. Also the matrix elements of V between the origin site and the four first-neighbor sites on the $x_1=0$ plane are zero. Moreover, on a given side of the $x_1=0$ plane $V(r)$ has the cubic symmetry of the unperturbed crystal. Therefore the matrix elements between the origin site and the four first-neighbor sites on one side of the $x_1=0$ plane are all equal and are the negative of those between the origin site and the opposite four first-neighbor sites; let us designate the four matrix elements for the first-neighbor sites with $x_1>0$ as $[1|V|0]$.

We assume that all other matrix elements in V are negligible. The Thomas-Fermi formula for the perturbation energy eU derived earlier is a reasonable first approximation in a self-consistent-field treatment. Approximations to the exact Wannier function have been given elsewhere. Rough calculations using these formulas indicate that matrix elements of V involving at least one second- or higher-neighbor site are very small, although there are of course very many such matrix elements. When R_i and R_j are different first-neighbor sites $[R_i|V|R_j]$ is less than 10% of $[1|V|0]$. The weakest assumption is that $[R_i|V|R_i]$ is negligible when R_i is a first-neighbor site, for the rough calculation indicates it is comparable to $[1|V|0]$.

The determinant in Eq. (6.7) can be reduced to size 9×9: with only $[1|V|0]$ retained, at most nine perturbed levels can be split off from each of the initially degenerate groups of eigenstates to which Eq. (6.7) refers for different E_q. Similarly the coefficients $A(R_j)$ of the displaced Bloch waves are zero save for the origin site and the eight first-neighbor sites not on the $x_1=0$ plane. The determinantal equation in fact is reducible from a ninth-order to a quadratic equation, one level being split off upward from the group of levels initially degenerate at E_q and another downward by the same magnitude. This magnitude of the splitoff is a maximum in the middle of the band and zero at the edges: no bound impurity levels are formed.

It is an enormous simplification to retain only one matrix element in V: instead of carrying out a self-consistent-field solution of many steps, assuming numerical values for the $[R_i|V|R_j]$ magnitudes retained, calculating the $\Delta\rho$ in terms of the $A(R_j)$, and then recalculating new $[R_i|V|R_j]$'s, we may factor out the single magnitude and guarantee self-consistency in one step at the end. If we had taken $[1|V|0]$ zero and retained instead only the diagonal matrix elements $[R_i|V|R_i]$ for the first-neighbor sites, there would have been no contribution from the origin site: $A(0)$ would have been zero, instead of dominant. Yet the pattern of the other eight $A(R_j)$ would not have been markedly different. In retaining but one matrix element we obtain only the main features of the $\Delta\rho$ that would result from the full self-consistent treatment. It is therefore important with a dipole perturbation to retain the $[1|V|0]$ elements which lead to the important contribution from the origin site displaced Bloch wave. For a monopole perturbation, such as that treated by Koster and Slater,[22] the $[R_i|V|R_i]$ for first-neighbor sites would be the matrix element which would by itself most nearly lead to the correct $\Delta\rho$. The Wannier differential equation mentioned earlier neglects elements such as $[1|V|0]$ in favor of the $[R_i|V|R_i]$ elements and so is inappropriate for our problem.

7. PERTURBATION IN CONDUCTION ELECTRON DENSITY

The qualitative results for the perturbation energy and coefficients indicated above are valid whatever the unperturbed energy spectrum of the microcrystal. We obtain specific results for the free-electron model.[25] Here the unperturbed energy is proportional to $|\mathbf{k}|^2$, and so each group of initially degenerate Bloch eigenstates contains all those and only those states with $\mathbf{k}$ vectors of the same magnitude.

We consider microcrystals of two shapes: (1) cubic; (2) parallelopiped—specifically, the same shape as the Bravais unit cell, which contains only one ion core. Only certain $\mathbf{k}$ vectors are consistent with Born-von Kármán boundary conditions applied to crystals of these two shapes.

For shape (1) $\mathbf{k}=(\pi/na)(k_1\mathbf{i}_1+k_2\mathbf{i}_2+k_3\mathbf{i}_3)$, with no restrictions on the integers k_1, k_2, k_3, where $\mathbf{i}_1$, $\mathbf{i}_2$, $\mathbf{i}_3$ are the unit vectors along the x_1, x_2, x_3 axes of Fig. 1, respectively. In this formula a is the spacing of atomic planes as shown in Fig. 1 ($a=1.8$ A for Cu), and $2n$ is the number of atomic planes along a crystal edge. For shape (2) $\mathbf{k}$ is given by the same formula, but the k_i integers must all be even or all odd: the allowed $\mathbf{k}$ vectors form a bcc mesh in reciprocal space. In this case n is the number of Bravais unit cells, of edge length a, along each edge of the parallelopiped microcrystal. The edges of the crystal run along the [110], [101], and [011] directions, for the conventions of Fig. 1.

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[25] For somewhat more general formulas reference should be made to the author's unpublished Ph.D. thesis on file at the Massachusetts Institute of Technology.

We use the correspondence scheme in which the central Brillouin zone corresponds to the $4s$ conduction band. Hence the mesh of allowed $\mathbf{k}$ vectors found above for either shape crystal is terminated at the planes $|k_1|\leq n$, $|k_2|\leq n$, $|k_3|\leq n$, and $|\pm k_1 \pm k_2 \pm k_3| \leq 3n/2$. The free-electron Bloch waves are $u_k=(1/\sqrt{v}) \times \exp(i\mathbf{k}\cdot\mathbf{r})$, where v is the volume of the microcrystal. The unperturbed energy is $E_q=(\hbar^2\pi^2 q/2m^* n^2 a^2)+$constant, where $q=k_1^2+k_2^2+k_3^2$, and m^* is the effective mass.

The free-electron solution of Eq. (6.7) is $E-E_q =\pm(C_3C_4)^{\frac{1}{2}}$. C_3 is $[1|V|0]/N$ times the number of $\mathbf{k}$ vectors with the same squared magnitude $\pi^2 q/n^2a^2$; while

$$\begin{aligned}C_4=32([0|V|1]/N)\sum \sin(\pi|k_1|/n)\\ \times[\cos(\pi|k_2|/n)+\cos(\pi|k_3|/n)]\\ \times \sin(\pi|k_1|/n)\cos(\pi|k_2|/n),\end{aligned}$$

where the sum is to be understood to extend over all sets of $|k_i|$ integers (positive) leading to the same squared magnitude $q\pi^2/n^2a^2$. The corresponding $A(R_j)$ coefficients are

$$\begin{aligned}A(3)/A(0),\quad A(5)/A(0),\quad A(6)/A(0),\quad \text{and}\\ A(10)/A(0)=+C_3/(E-E_q);\\ A(4)/A(0),\quad A(9)/A(0),\quad A(11)/A(0),\quad \text{and}\\ A(12)/A(0)=-C_3/(E-E_q),\end{aligned}$$

using the notation of Fig. 1 for the first-neighbor sites R_j. $A(0)$ is determined by normalizing the perturbed wave function χ_q:

$$\begin{aligned}1=|A(0)|^2\sum\{1/(E-E_q)^2\\ +[16C_3^2/(E-E_q)^4]\sin^2(\pi k_1/n)\\ \times[\cos(\pi k_2/n)+\cos(\pi k_3/n)]^2\},\end{aligned}$$

with the sum as above. The Wannier function derived from free-electron Bloch waves is real and so $[1|V|0]$, C_3, and C_4 are real. It can be shown by a little manipulation that

$$|A(0)|^2=4[1|V|0]C_4/N.$$

The perturbed wave function split off the top of the group of levels initially degenerate at E_q, call it χ_q^+, and that split off the bottom, call it χ_q^-, are as before the sum over all the $\mathbf{k}$ vectors in the $4s$ band of the Bloch functions u_k times F_k. F_k is given by Eq. (6.4). Let us designate as u_q^+ and u_q^- the linear combinations of the unperturbed Bloch wave eigenfunctions u_k with eigenvalue E_q to which the perturbed wave functions χ_q^+ and χ_q^- reduce as the perturbation goes to zero. The perturbation in conduction electron density caused by the displacement of the origin nucleus along the x_1 axis is

$$\Delta\rho=-2e\sum\{\chi_q^{+*}\chi_q^{+}-u_q^{+*}u_q^{+}+\chi_q^{-*}\chi_q^{-}-u_q^{-*}u_q^{-}\},$$

where the sum is over all q in the lower half of the $4s$ band except $q=0$. The factor of two in front represents the effect of spin degeneracy. Evaluating this sum is a straightforward though somewhat intricate matter. We, of course, neglect all terms proportional to the square of the ion core displacement δ. For convenience we define the subsidiary functions,

$$\begin{aligned}Q_q=v^{\frac{1}{2}}\sum u_k,\\ iR_q=v^{\frac{1}{2}}\sum \sin(\pi k_1/n)[\cos(\pi k_2/n)+\cos(\pi k_3/n)]u_k,\end{aligned}$$

where the sums are over all $\mathbf{k}$ degenerate at E_q (in contrast with the sums above). The crystal volume v equals $2Na^3$. Both Q_q and R_q are real. The formula becomes

$$\Delta\rho=-16R(n^2/N^2)\sum[Q_qR_{q'}+Q_{q'}R_q]/(q'-q); \tag{7.1}$$

here we sum over all q' in the upper half of the $4s$ band and $q'=0$, and also over all q in the lower half of the $4s$ band, provided $q\neq q'$. $R=-em^*[1|V|0]/a\pi^2\hbar^2$, and is positive since $[1|V|0]<0$. Q_q represents the effect of the $A(0)$ perturbation coefficient.

Equation (7.1) has the correct general properties. If we extend the sum of q and q' over all the $4s$ band, $\Delta\rho$ becomes zero, as we must require for a closed shell. Q_q is even in x_1 and R_q odd; so $\Delta\rho$ is odd in x_1, and it is of the right sign to tend to cancel the ion core dipole effect. Similarly, $\Delta\rho$ is even in x_2 and x_3 and symmetrical between them. Once we have calculated $\Delta\rho$ in the one-sixteenth of the crystal bounded by the planes $x_1=0$, $x_2=0$, and $x_3=x_2$ in the $(+++)$ octant, we know $\Delta\rho$ everywhere in the crystal. For small r, $\Delta\rho$ is linear in x_1, but not in the same way as it is in the Thomas-Fermi model. It is consistent to assume $[1|V|0]$ is independent of n for large n: the various powers of n to which separate terms in $\Delta\rho$ are proportional for large n cancel out on this assumption. Moreover, the sum of the magnitudes of the perturbation in energy levels in the band, twice the sum of $|E-E_q|$ where q runs over the lower half of the $4s$ band, is independent of n for large n. For large enough n, $\Delta\rho$ is independent of the shape of the crystal, since the ratio of surface sites to total sites goes to zero.

Our first task is to show that even with n small enough for calculations to be feasible, the $\Delta\rho$ from Eq. (7.1) does not depend strongly on the exact value of n and the shape of the microcrystal but rather is a good approximation to the $\Delta\rho$ for a macrocrystal. Satisfactory accuracy in the evaluation of $\Delta\rho$ by Eq. (7.1) for small n requires that care be taken with certain details. Some of the points in the mesh of $\mathbf{k}$ vectors allowed for a given microcrystal lie on the surface of the central Brillouin zone and thus only partly belong to the central zone. When we sum over such a set of $\mathbf{k}$'s to evaluate $Q_{q'}$ and $R_{q'}$ for maximum q' we must multiply the result by the reciprocal of the number of zones which share the set; in this way the symmetry of $\Delta\rho$ is not disturbed by totally excluding some of the $\mathbf{k}$'s on some arbitrary basis. The summation over q in

TABLE III. $Q_q(\mathbf{r})$ and $R_q(\mathbf{r})$ for various patterns of the wave-vector integer components, k_i, and for $\mathbf{r}$ along the [110] axis: $\mathbf{r}=(\alpha,\alpha,0)a$.

(k_1,k_2,k_3)	$Q_q(\mathbf{r})$
$(a,0,0)$	$2[2\cos(\pi a\alpha/n)+1]$
$(a,a,0)$	$4[\cos^2(\pi a\alpha/n)+2\cos(\pi a\alpha/n)]$
(a,a,a)	$8[\cos^2(\pi a\alpha/n)]$
$(a,b,0)$	$8[\cos(\pi a\alpha/n)\cos(\pi b\alpha/n)+\cos(\pi a\alpha/n)+\cos(\pi b\alpha/n)]$
(a,b,b)	$8[\cos^2(\pi b\alpha/n)+2\cos(\pi a\alpha/n)\cos(\pi b\alpha/n)]$
(a,b,c)	$16[\cos(\pi a\alpha/n)\cos(\pi b\alpha/n)+\cos(\pi a\alpha/n)\cos(\pi c\alpha/n)+\cos(\pi b\alpha/n)\cos(\pi c\alpha/n)]$
(k_1,k_2,k_3)	$R_q(\mathbf{r})$
$(a,0,0)$	$4[\sin(\pi a/n)\sin(\pi a\alpha/n)]$
$(a,a,0)$	$4\{\sin(\pi a/n)[1+\cos(\pi a/n)]\}\{\sin(\pi a\alpha/n)[1+\cos(\pi a\alpha/n)]\}$
(a,a,a)	$16[\sin(\pi a/n)\cos(\pi a/n)][\sin(\pi a\alpha/n)\cos(\pi a\alpha/n)]$
$(a,b,0)$	$4\{\sin(\pi a/n)[1+\cos(\pi b/n)]\}\{\sin(\pi a\alpha/n)[1+\cos(\pi b\alpha/n)]\}+\{4\sin(\pi b/n)[1+\cos(\pi a/n)]\}$ $\times\{\sin(\pi b\alpha/n)[1+\cos(\pi a\alpha/n)]\}$
(a,b,b)	$16[\sin(\pi a/n)\cos(\pi b/n)\sin(\pi a\alpha/n)\cos(\pi b\alpha/n)]+8\{\sin(\pi b/n)[\cos(\pi a/n)+\cos(\pi b/n)]$ $\times\sin(\pi b\alpha/n)[\cos(\pi a\alpha/n)+\cos(\pi b\alpha/n)]\}$
(a,b,c)	$8\{\sin(\pi a/n)[\cos(\pi b/n)+\cos(\pi c/n)]\sin(\pi a\alpha/n)[\cos(\pi b\alpha/n)+\cos(\pi c\alpha/n)]\}$ $+8\{\sin(\pi b/n)[\cos(\pi a/n)+\cos(\pi c/n)]\sin(\pi b\alpha/n)[\cos(\pi a\alpha/n)+\cos(\pi c\alpha/n)]\}$ $+8\{\sin(\pi c/n)[\cos(\pi a/n)+\cos(\pi b/n)]\sin(\pi c\alpha/n)[\cos(\pi a\alpha/n)+\cos(\pi b\alpha/n)]\}$

Eq. (7.1) should include only those states in the lower half of the band, since there is but one conduction electron per atom in our model. In general the half-way mark falls within a set of degenerate states. $A(0)$ has opposite signs for the two perturbed states, one split off upward and one downward from the degenerate set, so the contributions from the two states together to $\Delta\rho$ have dipole symmetry, but not the contribution from either by itself. On thermodynamic grounds it might appear that the electrons would only occupy the state perturbed downward, but the perturbation in our case is virtual. Therefore we can use in Eq. (7.1) the total contribution of the half-way set of states multiplied by the ratio of the number of electrons with that energy to the number of states of that energy.

Equation (7.1) resembles a Fourier expansion of $\Delta\rho$. However, the coefficient of a given trigonometric term in Eq. (7.1) is not the same for two different values of n. The Q_q and R_q formulas can be considerably simplified when the position vector $\mathbf{r}$ is taken to lie along the [100], [111], or [110] axes. Most of our calculations of $\Delta\rho$ were made for points along these three axes. In Table III there are listed as an example the specific formulas for $Q_q(r)$ and $R_q(r)$ when $\mathbf{r}=(\alpha,\alpha,0)a$; the six possible patterns of the k_i integer components of the wave vector give rise to distinct formulas.

Equation (7.1) and the subsidiary formulas and discussion are valid for both the cubic and parallelopiped microcrystals, but the meanings of n and the range of q in the sum are different in the two cases. N is the number of atoms in the crystal and therefore the number of allowed $\mathbf{k}$ values in the central Brillouin zone. For the cubic shape, $N=4n^3$, for the parallelopiped, $N=n^3$. In the latter case there are only about one-fourth as many q values in the band as for the former case; hence the double sum in Eq. (7.1) is about one-sixteenth as big for the latter as for the former shape. It follows that even for small n, $\Delta\rho$ will be approximately the same for microcrystals of the two shapes and the same n. By simply omitting terms in the sum over q and q' for the $\Delta\rho$ of a cubic crystal, we can at once find the $\Delta\rho$ for the parallelopiped crystal of one-fourth the size with much saving in calculation.

The computations for $\Delta\rho$ were performed on a Fridén desk calculator. Half an hour was sufficient to calculate $\Delta\rho$ at one location in the smallest crystal; two days were required to find each value of $\Delta\rho$ in the largest crystal considered. The variety of crystal sizes and shapes for which calculations were to be made were such that the use of a digital computer seemed inappropriate.

In Fig. 2 the values of $\Delta\rho$ at the point $\mathbf{r}=(a,0,0)$ are shown for crystals of different sizes and the two shapes. At several other points with $r<a$, almost exactly the same shape curves was found. It seems clear that in this region of the crystal the $\Delta\rho$ obtained for an 864-atom crystal of cubic shape ($n=6$) will be an accurate approximation to the $\Delta\rho$ for a macrocrystal. In the region $a<r<2a$ the behavior of $\Delta\rho$ as a function of

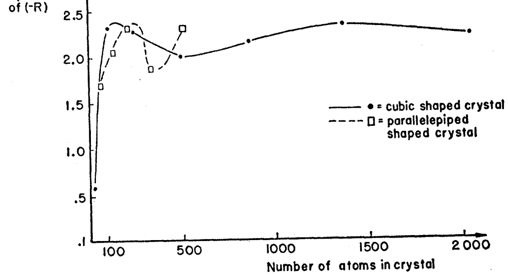

FIG. 2. $\Delta\rho$ *vs* size and shape of crystal at the representative point $\mathbf{r}=(a,0,0)$.

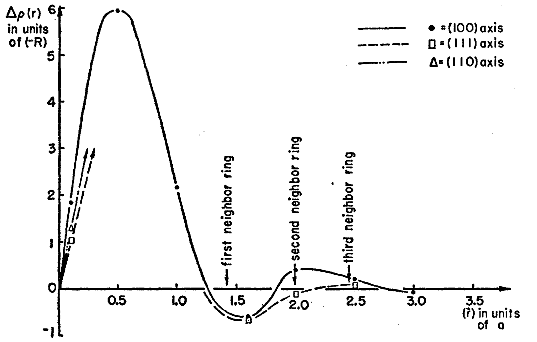

FIG. 3. Δρ along principal axes for face-centered cubic crystal with cubic shape and width of twelve atomic planes.

crystal size and shape is not as consistent, but here too the cubic crystal for $n=6$ yields satisfactory results. For $r>2a$ the behavior of Δρ as a function of crystal size varies from point to point. The value of Δρ is small in this region, and computational errors are significant. There is a general tendency at points in this outer region of the crystal, however, for Δρ to become steadily smaller for larger n. In view of the Thomas-Fermi results in Sec. 5, it is a reasonable approximation to set Δρ zero for $r>2a$. The sizes of crystals for which we have computed Δρ range from 108 to 2048 atoms.

In Fig. 3 the behavior of Δρ as a function of r along the positive [110], [111], and [100] axes is given, for the 864-atom crystal of cubic shape ($n=6$). These are the results we shall use in computing the contributions to the atomic force constants. For comparison, in Figs. 4 and 5 the Δρ for the 500-atom crystal of cubic shape ($n=5$) is given. From Fig. 5 we can see that Δρ is almost independent of the azimuthal angle at $r=0.5a$; the same independence is found for many other values of r. In particular Δρ is no larger at ion core sites than at other points with the same r and polar angle. It is reassuring that Δρ is not unusually large near the ion core sites, since we know that our formulas are not accurate within the ion cores. At any point on the $x_1=0$ plane, Δρ is zero.

All the graphs give Δρ in units of $(-R)$, [see Eq. (7.1)] and for x_1 positive. The negative hump in the Δρ curves near $r=1.5a$ represents a deficiency of conduction electrons as compared with the unperturbed situation. Instead of screening the ion core dipole, this hump enhances it. The Thomas-Fermi Δρ has no such feature. However, Huntington[21] has obtained an analogous result in studying the diffusion mechanism in copper; when an ion core is removed from the metal he finds in the free-electron model not only a large deficit in the conduction electron density adjacent to the site but a hump of added density distant from the site by about $1.2a$ in our units. Since a hump of about the size shown in Figs. 3 and 4 occurs in the Δρ curves along the [100], [110], and [111] axes for all sizes and the two shapes of microcrystals studied, this feature must be accepted to the extent the model as a whole is accepted.

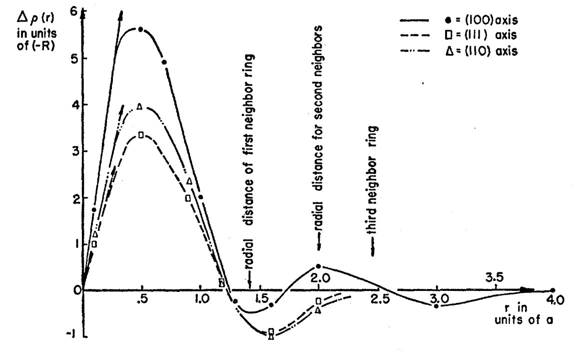

FIG. 4. Δρ along principal axes for face-centered cubic crystal with cubic shape and width of ten atomic planes.

It remains to fix $[1|V|0]$ and thus the unit R. This can be done by requiring the $[1|V|0]$ to be self-consistent. Let $\eta(\mathbf{r})[1|V|0]$, where $\eta(\mathbf{r})$ is necessarily independent of $[1|V|0]$, be the contribution of the distortion in conduction electron charge density to the total perturbation potential energy acting on a conduction electron. Even for a microcrystal there is negligible error in including the distortion in a given wave function in the perturbation affecting that wave function, since no one-electron state contributes a large fraction of the perturbation potential. We can calculate $\eta(\mathbf{r})$ by the usual Coulomb integration, using our results for Δρ, which is proportional to $[1|V|0]$. To insure self-consistency we require that

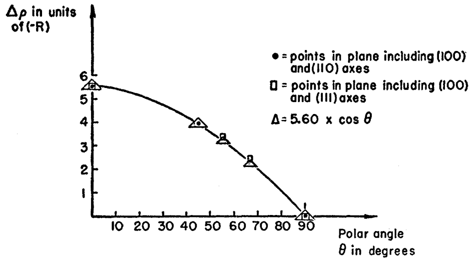

FIG. 5. Variation of Δρ with polar angle at $r=0.5a$ for 500-atom crystal with cubic shape.

$$[1|V|0]=[1|V(\text{ion core})|0]+[1|V|0][1|\eta(\mathbf{r})|0],$$

where V(ion core) is the potential energy of an electron in the field of the ion core dipole and we use the notation $[1|X|0]$ for the matrix element of X between the Wannier functions centered on the origin site and a first-neighbor site with $x_1>0$. Thus

$$[1|V|0]=[1|V(\text{ion core})|0]/\{1-[1|\eta(\mathbf{r})|0]\}.$$

A rough calculation indicates that $[1|\eta(\mathbf{r})|0]$ is about -0.5 and $[1|V(\text{ion core})|0]$ is about $-(3\delta/a)$ ev.

We establish self-consistency in only a narrow sense by the above procedure. The values of the matrix elements we neglected originally are certainly not zero for the Δρ and $\eta(\mathbf{r})$ we have found; in particular the matrix element of V between two Wannier functions centered on the same first-neighbor site is large. Therefore we will fix $[1|V|0]$ in the next section by the more general requirement that the total dipole moment of $\Delta\rho$ shall cancel that of the ion core dipole plus excluded electrons, $+1.06e\delta$. The $[1|V|0]$ we determine in this way is of the same order of magnitude as, although larger in absolute value than, that found in the previous paragraph

8. CALCULATED ATOMIC FORCE CONSTANTS

The ion core contributions to the afc described in Sec. 4 are given in the first two columns of Table IV. In the third column appears the part of the afc produced by $\Delta\rho$ for $r<a$; in the fourth column appears the contribution from $\Delta\rho$ for $a<r<2a$. We use a simplified model of the results of Fig. 3 in calculating the contribution to the afc produced by $\Delta\rho$.

For $r<a$ the following formula represents $\Delta\rho$ within an average accuracy of three percent: $\Delta\rho=-5.95R \times\cos\theta \sin(r\pi/1.1a)$, where θ is the polar angle measured from the positive x_1 axis to r. This density value applies within the differential volume element for the spherical coordinate system in r, θ, and φ integrated over φ, a volume $dv=2\pi r^2 \sin\theta d\theta dr$. Consider, on the other hand, the change in charge distribution produced by displacing a sphere of radius r and constant charge density ϵ centered at the origin a distance dr along the positive x_1 axis. This change occurs in the space entered and the space vacated by the sphere and is given by $\epsilon dv'$, where the differential volume element at r and θ is $dv'=2\pi r^2 \sin\theta d\theta(dr \cos\theta)$. We see that $\Delta\rho dv=\epsilon dv'$ if we set $\epsilon=-5.95R\sin(r\pi/1.1a)$. Since a sphere of constant charge density is equivalent when viewed from outside to a point charge at its center, the external electrostatic effect of the shift in the sphere of density ϵ is exactly that of a dipole of moment $\frac{4}{3}\pi r^3\epsilon dr$. Yet the effect of the shift of the sphere is also just that computed from the resulting change in charge distribution. Hence the effect of the $\Delta\rho$ in the volume element dv integrated over θ is equivalent to that of a dipole at the origin of moment $\frac{4}{3}\pi r^3(-5.95R)\sin(r\pi/1.1a)dr$. Integrating over r, we find that the electric field beyond $r=1.1a$ resulting from $\Delta\rho$ for $r<1.0a$ is that of a dipole of moment $(-4.57Ra^4)$ along the x_1 axis at the origin. Hence Column (3) in Table IV is proportional to Column (1). In order to satisfy symmetry requirements the field produced by the $\Delta\rho$ inside $r=a$ has to be that of a dipole (see Sec. 5); deriving this result directly from our calculated $\Delta\rho$ gives us confidence in our model.

TABLE IV. Calculated atomic force constant contributions.[a]

afc	(1) Ion core plus excluded electron dipole contribution	(2) Closed shell repulsion contribution	(3) Contribution from conduction electron $\Delta\rho$ for $r<a$	(4) Contribution from conduction electron $\Delta\rho$ for $a<r<2a$
α_1	-1.47	$-2A$	$+2.45$	-0.70
β_1	$+0.74$	$R-A$	-1.23	-0.52
γ_1	$+2.22$	$R+A$	-3.70	-0.10
α_2	$+1.04$		-1.74	$+0.56$
β_2	-0.52		$+0.87$	-0.42
α_3	$+0.28$		-0.47	$+0.17$
β_3	-0.14		$+0.23$	-0.09
γ_3	$+0.14$		-0.23	$+0.11$
ϵ_3	$+0.28$		-0.47	$+0.20$

[a] In units of 10^4 dynes/cm.

We represent $\Delta\rho$ in the region $1.45a<r<2a$ by a spherical cap of constant surface charge density $\sigma=+0.065Ra$, aperture $\theta=75°$, at a radius $1.7a$; and by a similar spherical cap with $\sigma=-(0.065Ra)$ for $x_1<0$. The electrostatic potential produced by such a cap can be represented as an expansion in Legendre polynomials.[24] We carry out the expansion to terms in the fifth degree $[P_5(\cos\theta)]$ both for $r<1.7a$ and for $r>1.7a$. The terms of even degree from the two caps cancel; the terms of odd degree reinforce each other. The dipole moment along the x_1 axis of the spherical caps viewed from outside $1.7a$ is $(+1.8Ra^4)$.

In the region $a<r<1.45a$, $\Delta\rho$ can also be approximated in terms of a pair of spherical caps, but with a surface density of dipole moment rather than charge. In view of the crudity of our model we neglect this contribution. For $r>2a$, $\Delta\rho$ is taken to be zero.

The electric field produced by the $\Delta\rho$ in each of the above ranges of r is easily found as the gradient of the electric potential formulas we have derived. Multiplying the field by the charge of the ion core, $+e$, and evaluating the components of the resulting force at the various lattice sites, we obtain the forces produced on the other nuclei by the displacement δ, of the origin ion core. If we divide these force components by δ, we have the contributions to the atomic force constants produced by the distortion in conduction electron distribution. By inspection of Table I we can observe that all nine distinct atomic force constants can be calculated from the virtual displacement of the origin ion core along the x_1 axis which we have specified throughout for convenience. As mentioned in Sec. 3, two different values of ϵ_3, on opposite sides of the diagonal in the afc matrices, are consistent with lattice symmetry. Two values were in fact found from the calculations from $\Delta\rho$ for $a<r<2a$; each of these two values is within ten percent of the average value we give for ϵ_3 in Column (4) of Table IV. The 10% discrepancy is a measure of the inadequacy of our model for $\Delta\rho$ in this region.

By the principles of electrostatics no net dipole moment should be observed from a distance as a result of the virtual displacement of the origin nucleus; clearly no net charge will be observed, because of the dipole symmetry of the total perturbation. The dipole moment corresponding to the shift in ion core dipole plus excluded conduction electrons is $+1.06e\delta$; that corresponding to the Coulomb perturbation of the conduction electrons, $\Delta\rho$, is $-2.74Ra^4$. Thence R/δ

TABLE V. Table of results.

Atomic force constants	Calculated values[a]	Jacobsen x-ray values[a]
α_1	-0.24	$+0.48$
β_1	$+1.71$	$+0.87$
γ_1	$+1.66$	$+1.25$
α_2	-0.13	$+0.35$
β_2	-0.07	-0.07
α_3	-0.01	$+0.09$
β_3	$+0.005$	-0.02
γ_3	$+0.02$	-0.02
ϵ_3	$+0.01$	$+0.06$

[a] In units of 10^4 dynes/cm.

$=+0.39e/a^4$; and $[1|V|0]$ is about $-(8\delta/a)$ ev. Thus is fixed the average size of $\Delta\rho$ and of its contribution to the atomic force constants. In the Thomas-Fermi model the total screening charge displaced is $qe\delta$ or about $1.7e\delta/a$; here the integral of the absolute value of $\Delta\rho$ is about $2.3e\delta/a$.

In the second column of Table IV are given only the form of the closed-shell repulsion contributions to the afc, as determined in Sec. 4. The numerical values were found by substitution of the total calculated afc from Table IV into Eqs. (3.1) and (3.3); fortunately Eq. (3.2) is consistent with the same R and A values. The room temperature elastic constants as measured by ultrasonic techniques[12] are $c_{11}=17.0\times10^{11}$ dynes/cm^2, $c_{44}=7.52\times10^{11}$ dynes/cm^2, $(c_{12}+c_{44})=19.82\times10^{11}$ dynes/cm^2. For the closed-shell repulsion parameters the values $R=2.98\times10^4$ dynes/cm and $A=0.26\times10^4$ dynes/cm are obtained. These values are close to those used by Seitz and Huntington,[19] and are considerably larger than the values Fuchs[17] took from the model of Lenz.

In the second column of Table V are listed the atomic force constants calculated by Jacobsen[6] from his x-ray data by application of the Born theory of thermal diffuse scattering from lattice vibrations. The first column contains the total atomic force constants we have calculated using Feynman's theorem. The two sets of results differ very considerably. Jacobsen calculated the elastic constants corresponding to his atomic force constants from Eqs. (3.1), (3.2), and (3.3). The calculated values agree well with the experimental ones, the worst discrepancy being in c_{44}, where his calculated value is about 15% too low.

9. DISCUSSION

In this paper the use of Feynman's theorem to find quantum mechanical forces directly has been shown to be practicable for crystal problems. It seems clear that considerable gain in insight as well as in ease of calculation results thereby. In the application of Feynman's theorem to the calculation of the contribution to the afc from the change in conduction electron density, the advantages of the Slater-Koster formulation for localized perturbations are brought out: in particular the relative simplicity of obtaining self-consistency is made clear. The solution of other crystal perturbation problems in terms of discrete eigenvalue perturbation theory applied to microcrystals is worth exploration in view of the convergence of our results for the conduction electron behavior in microcrystals of different sizes and shapes.

An adequate treatment of the closed-shell interaction of copper ions is badly needed; our whole calculation of the afc will remain unreliable until such a treatment is available. The semiempirical values we have obtained for the first and second derivatives of the closed-shell interaction energy with respect to ionic separation are in rather close agreement with those chosen largely on grounds of plausibility by Seitz and Huntington (and others) in various papers. It seems that the results obtained by Lenz through a Thomas-Fermi treatment are too small, but his is the only direct theoretical treatment available.

Numerous approximations have been made in our derivation of the contribution to the afc from the change in conduction electron density produced by the displacement of the origin ion core. As a result of our approximations the only specific attributes of copper reflected in our results for $\Delta\rho$ are the lattice parameter and effective mass; our formulas would be as applicable logically to silver and gold and indeed may not be too inaccurate for the alkali metals. From the definition of afc it follows that our exclusive use of first-order perturbation theory is entirely rigorous. Use of the free-electron approximation for unperturbed energies and wave functions probably does not introduce the most serious errors.[26] The chief error is in the neglect of most of the matrix elements of the perturbation energy averaged over Wannier functions centered on different lattice sites: this neglect leads to an unrealistically simple form for the change in electron density and to lack of self-consistency. The results we obtain for crystals with dimensions of only a few atomic planes converge as the dimensions increase and seem for this localized dipole perturbation to be a good approximation to those for a macrocrystal.

Our treatment of the Coulomb interaction of copper ion cores is crude.[27] In particular our assumption that the effective charge of the ion core is exactly e is unjustified. This assumption is particularly crucial in our microcrystal calculation, in which the change in electron density $\Delta\rho$ is very sensitive to the exact fraction to which the conduction band is filled. The exclusion of conduction electrons from the ion core is treated in Sec. 4 in a crude manner inconsistent with the free-electron model of the later sections. More serious is our neglect of the influence of exchange interaction

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[26] D. Howarth (private communication); also Proc. Roy. Soc. (London) **A220**, 513 (1953).

[27] See K. Ladanyi, Acta Phys. Acad. Sci. Hung. **5**, 361 (1956).

with the ion cores on the density of states in the conduction band.[28]

Our results for $\Delta\rho$ and the ion core interaction are reasonable qualitatively. The crucial difficulty is that many of the afc we calculate are the differences of several large terms, and hence are sensitive to the inaccuracies discussed above. We cannot give any useful estimate of the uncertainty in our calculated atomic force constants for copper.

It is also difficult to assess the reliability of the afc Jacobsen obtains by application of scattering theory to his data for thermal diffuse x-ray scattering from a copper single crystal.[29] Only rather crude approximations to the Compton scattering and the structure and Debye temperature factors for copper were available to him. Somewhat different values are obtained for the afc according to which particular points in the x-ray reciprocal space are used in the evaluation.

The three elastic constants for copper as calculated either from Jacobsen's afc or from those found in this paper are in good agreement with the experimental results. Only Jacobsen's afc were found in a way formally independent of knowledge of the experimental values of the elastic constants. Our two parameters R and A were chosen so that the closed shell repulsion contribution to the three c_{ij} would equal the experimental values less the Coulomb contributions. However, the signs and magnitudes of R and A found in this way are in the range we would expect on independent grounds.

As mentioned earlier, the values we choose for R and A and thus for the closed-shell contribution to the elastic constants do not agree with those used by Fuchs in his direct calculation of the elastic constants.[17] Moreover, Fuchs' calculations gave for the Coulomb contribution to $c_{11}-c_{12}$ the value $+0.57\times10^{11}$ dynes/cm^2 and to c_{44} the value $+2.57\times10^{11}$ dynes/cm^2; our results are for $c_{11}-c_{12}$ the value -1.8×10^{11} dynes/cm^2, and for c_{44} the value -4.75×10^{11} dynes/cm^2.

By arbitrarily setting q equal to 0.93 A^{-1} we showed in Sec. 5 that the Thomas-Fermi model for the Coulomb contribution could lead to second- and third-neighbor afc in good agreement with the x-ray results. But implausible values of the parameters for the closed-shell interaction would have to be introduced to then obtain even partial agreement between the two sets of first-neighbor afc. It is difficult to see how a definitely positive value for α_1, such as Jacobsen finds, can be reconciled with any model based on Feynman's theorem. In the case of α_1 the ion core and conduction electron Coulomb contributions will tend to cancel each other, and the closed-shell contribution is surely negative.

The discrepancy between our calculated and Jacobsen's x-ray values for the atomic force constants is so great that only a few conclusions can be drawn about the true values. Either set of results contradicts the familiar assumption of central forces between atoms, for α_1 is not zero and $\beta_1\neq\gamma_1$; also, second-neighbor afc are not negligible. Although the third-neighbor afc in either set are small individually, there are twenty-four sites in the third-neighbor ring and the total contribution to the elastic constants is sizable.

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[28] J. Bardeen, Phys. Rev. **52**, 688 (1937).

[29] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1948); M. Born, in *Reports on Progress in Physics* (The Physical Society, London, 1942–43), Vol. 9, p. 356.