

Axial Ratios in Hexagonal Crystals*

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A theoretical study has been made of the deviations of the axial ratios of hexagonal metal crystals from the ideal close-packing value, both for pure metals and alloys. The deviation is expressed in terms of the "effective stress" which would tend to change the axial ratio in the close-packed configuration, and the observed elastic constants. Using a change of scale procedure, a formula for the "effective stress" is derived in terms of integrals over the electronic wave function in the close-packed configuration. When the Hartree-Fock approximation is used to evaluate the expression for the "effective stress," three contributions are found: (1) a "kinetic stress," (2) an "electrostatic stress," and (3) an "exchange stress." Estimates of each term for pure beryllium indicate that (1), which resembles the effects estimated by Jones and Goodenough, is most important; (2) is negligible; and (3) may be appreciable. It is found that the change in axial ratio with alloying is due to a different mechanism than that proposed by Jones. However, an argument is presented which leads to qualitatively the same conclusions as his concerning the connection between the change in axial ratio and the band structure.

1. INTRODUCTION

IF the forces between atoms in a hexagonal close-packed lattice were central forces between nearest neighbors only, the configuration for minimum energy would be that in which all nearest neighbor distances are equal.¹ For this ideal close-packed configuration the axial ratio; i.e., the ratio of the distance (c) between identical hexagonal planes to the distance (a) between nearest neighbors in these planes; would have the value $(8/3)^{1/2} = 1.633$.

There are a number of metals with hexagonal crystal structures which have axial ratios that deviate from the ideal value by small amounts. A few of these metals are listed in Table I. The deviations from close-packing can be changed by changing the temperature and by alloying with another metal. Moreover, it is very interesting that the changes in axial ratio produced in a given metal by alloying with any other metal at constant temperature seem to depend chiefly upon the electron-to-atom ratio in the alloy.^{2,3}

H. Jones has treated the problem of the change in axial ratio with alloying.⁴ He made the hypothesis that the changes in axial ratio produced by alloying are due to changes in the Fermi energy arising from the distortion of the Brillouin zone. His theory makes use of the fact that the Brillouin zone for a hexagonal lattice is anisotropic and, as he considered cases in which the Fermi surface overlaps some of the zone faces, the Fermi

surface is anisotropic. A change in axial ratio distorts the zone, forcing a distortion of the Fermi surface that, in general, changes the energy of the conduction electrons. Thus, in a manner of speaking, there exists an "effective stress" due to the conduction electrons, tending to change the axial ratio. The equilibrium axial ratio depends on a balance between the "effective electron stress" and the stress due to changes in all the other contributions to the total energy.

Jones assumed that upon alloying, the valence electrons of the solute atom go into the conduction bands of the solvent and increase the "effective stress" due to the conduction electrons. Thus he reasoned that the "effective electron stress," and thereby the axial ratio, is a function of the number of valence electrons per atom. He estimated the change in energy of each one-electron state with change in axial ratio by assuming that the energy of the state changes with shear like a free electron state with the same wave number. Under the above assumption, the change in axial ratio with alloying depends upon the band structure in the vicinity of the Fermi surface, as the structure determines the assignment of the extra valence electrons to positions in the Brillouin zone, and the assignment determines the change in "effective stress."

TABLE I. Summary of experimental data.

Metal	Beryllium	Magnesium	Zinc	Cadmium
c/a	1.565 ^a	1.625 ^b	1.856 ^c	1.89 ^d
ϵ_{obs}	-0.028	-0.003 ₃	0.091	0.107
μ (ev/atom)	15.8 ^e	8.81 ^e	6.45 ^e	6.35 ^e
σ (ev/atom)	-0.44	-0.028	0.56	0.66
η/μ	0.625	-0.047	-1.54	-1.52
$\partial\epsilon_{\text{obs}}/\partial x^{\dagger}$		0.023 ^b	1.0 ^e	

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¹ F. R. N. Nabarro and J. H. O. Varley, Proc. Cambridge Phil. Soc. **48**, 316 (1952), Part 2.

² G. V. Raynor, Proc. Roy. Soc. (London) **A174**, 457 (1940).

³ W. Hume-Rothery and G. V. Raynor, Proc. Roy. Soc. (London) **A177**, 27 (1940); G. V. Raynor, Proc. Roy. Soc. (London) **A180**, 451 (1942); R. S. Busk, J. Metals **188**, Trans. 1460 (1950); R. S. Busk, J. Metals **4**, Trans. 207 (1952).

⁴ H. Jones, Proc. Roy. Soc. (London) **A147**, 400 (1934); Phil. Mag. **41**, 633 (1950).

^a P. Gordon, J. Appl. Phys. **20**, 908 (1949).

^b See reference 3.

^c E. A. Owen and L. Pickup, Proc. Roy. Soc. (London) **A140**, 179, 344 (1933); E. A. Owen and J. Iball, Phil. Mag. **17**, 433 (1934).

^d F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 6.

^e The elastic constants of beryllium are those of L. Gold, Phys. Rev. **77**, 390 (1950). The other elastic constants are from the measurements of Wright and Grüneisen and Goens, as quoted in Gold's paper.

[†] The quantity x is the number of valence electrons per atom in the alloys.

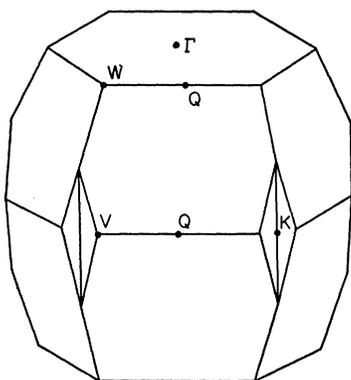


Fig. 1. The Brillouin zone for the hexagonal close-packed lattice which contains two electrons per atom.

In the 1950 work, Jones discussed the changes in axial ratio of magnesium induced by alloying. He attempted to establish the band structure of magnesium by constructing a simple model to fit the experimental data. In order to explain Jones's model, we refer to Fig. 1 which shows the second Brillouin zone for the hexagonal close-packed lattice. This zone contains exactly two electrons per atom. All of the valence electrons of pure magnesium would completely fill the zone; but magnesium is a metal and we know that in the ground state there is some overlapping into higher zones and some holes (unoccupied states) in the zone of Fig. 1. In analogy to the nearly free electron model, Jones assumed that the energy increases going away from the origin in reciprocal space. He took points K and Γ as possible overlap sites and points Q as possible hole sites.

Under the assumptions of the Jones theory, an electron added at point Γ tends to increase the axial ratio. (The energy of an electron at point Γ is decreased if the zone is distorted so that Γ moves nearer the origin. Such a distortion corresponds to an increase of the axial ratio of the direct lattice.) In like manner, an electron added at point K tends to decrease the axial ratio, and one added at point Q tends to increase the axial ratio. In order to fit the experimental data, Jones assumed that in pure magnesium there are overlaps at K and holes at Q , and that overlap takes place at Γ for valence electron to atom ratios slightly larger than two (2.0075).

The assumption that overlap occurs at Γ for a valence-electron-to-atom ratio of 2.0075 was made because there is experimental evidence that the derivative of the axial ratio with respect to the valence electron to atom ratio shows a sharp change at this point. The idea that the sharp change is due to the onset of overlap at the point Γ was proposed by Raynor.²

Such an onset of overlap should be noticeable in other properties of magnesium alloys. In particular, Schindler and Salkovitz⁵ have investigated the change in the Hall constant in magnesium alloys. They find evidence of a

⁵ A. I. Schindler and E. I. Salkovitz, Phys. Rev. **91**, 1320 (1953).

sharp change in the slope of the Hall constant *versus* the valence-electron-to-atom ratio curve in the neighborhood of 2.013 valence electrons per atom.

Goodenough⁶ has applied a similar theory to the case in which the Fermi surface is near to, but does not touch a set of Brillouin zone faces. Using the nearly-free electron model as a starting point, he argues that there is an effective attraction between the Fermi surface and the zone faces; i.e., due to the depression of energy beneath a zone face, the total energy of the electrons could be lowered by moving the zone face nearer to the origin in reciprocal space.

We illustrate Goodenough's ideas with the following example. Consider a pair of parallel zone faces (represented by P in Fig. 2) which are moved closer to the origin (P') as the result of a deformation. Figure 2 represents the variation of the electron energy as a function of wave number along a line perpendicular to the two planes and passing through the origin. The energy before deformation is represented by the solid curve and after deformation by the dashed curve. It is seen that the energies of the electrons in positions corresponding to F are lowered as a result of the deformation. Thus if the Fermi surface does not touch any of the zone faces, the total electronic energy is lowered.⁷ The change in energy with change in axial ratio given by the Goodenough mechanism gives rise to an "effective stress" which determines the axial ratio as in the theory of Jones.

The attractive feature of the above theories is that they seem to afford a way of utilizing the experimentally observed changes in axial ratio with alloying to obtain information about the band structure in the neighborhood of the Fermi surface. Such information, which is very interesting as it determines other properties of the metal, is difficult to obtain by fundamental calculation. Thus, any method which holds promise of easily obtainable information about the band structure deserves careful investigation. Both theories have a certain plausibility, but they both fail to take account of a number of contributions to the "effective stress" which one would expect to be important. For example, the assumption that the change in "effective stress" with alloying is due to the change in the stress arising from the "Fermi energy" alone, neglects contributions to the "effective stress" coming from changes in the energy of the bottom of the band, Coulomb, exchange, and correlation energies, and energy of lattice vibrations, all of which contribute to the total energy of the crystal. Further, the application of the nearly free electron model is equivalent to ignoring two important facts: the potential in which an electron inside a metal moves is very strong, and the valence electron wave functions

⁶ J. B. Goodenough, Phys. Rev. **89**, 282 (1953).

⁷ If the Fermi surface does touch some of the zone faces, some electrons must be displaced by the movement of the zone faces to other points on the Fermi surface, so that their energies are increased. Whether the total energy is increased or decreased will depend on the details of the band structure and the Fermi surface.

must be orthogonal to the closed-shell electron wave functions. Thus, since the behavior of electrons in real metals differs appreciably from their behavior in a free electron gas, it is not to be expected that results based on the nearly free electron model are valid.

In treating alloys, Jones assumed that the one-electron wave functions and energy spectrum of a dilute alloy are identical to those of the pure metal. Under such an assumption the effects due to alloying come from the increased (or decreased) number of valence electrons in the Fermi distribution. However, it is to be expected that there are other effects which are just as important; e.g., the interaction of the electrons already present with the impurity atoms.

In the present work, we develop a deductive theory of the deviations of the axial ratio from close-packing, which starts from fundamentals and applies to both pure metals and alloys. We display the factors important in determining the axial ratio in order to elucidate the basis of the theories of Jones and Goodenough. We carry the theory far enough to make numerical estimates of the divers factors in the case of pure beryllium, and to investigate the change in axial ratio with alloying.

In Sec. 2 the "effective stress" is defined, and its role in determining the axial ratio is discussed. A general expression for the "effective electron stress" is derived in Sec. 3. In Sec. 4 an expression for the "effective stress" for a pure metal is obtained using the Hartree-Fock approximation. Section 5 contains a discussion of the "effective stress" in the Wigner-Seitz-Slater approximation. In Sec. 6, the relation of the present work to that of Jones and Goodenough is discussed. A numerical application to pure beryllium is presented in Sec. 7. The change of lattice parameters with alloying is discussed in Sec. 8. Finally, in Sec. 9, the results of the paper are summarized and conclusions drawn.

2. ROLE OF THE EFFECTIVE STRESS

We now derive an expression for the value of the axial ratio at absolute zero of temperature, in terms of the observed elastic constants and the "effective stress" tending to shear the crystal. In this section we also briefly discuss the question of the temperature dependence of the axial ratio.

The equilibrium configuration of a crystal at absolute zero of temperature and under no external stress is that configuration for which the total energy is a minimum. We will expand the energy of the crystal in a Taylor's series about a configuration (hereafter called the ideal configuration) which has the observed atomic volume and the ideal axial ratio corresponding to perfect close-packing. We expand in terms of a parameter ϵ , defined by the equations

$$c = c_0(1 + \epsilon); \quad a = a_0(1 - \frac{1}{2}\epsilon), \quad (2.1)$$

where c_0 and a_0 are the values of c and a in the ideal configuration. It is seen that, to first order in ϵ , a change in ϵ represents a change in axial ratio at constant

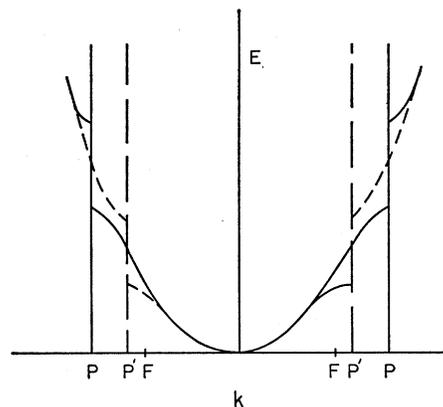


FIG. 2. Schematic representation of the variation of the electron energy with wave number for two configurations of the lattice.

volume. To first order we have

$$c/a = (8/3)^{1/2}(1 + \frac{3}{2}\epsilon). \quad (2.2)$$

Neglecting terms higher than second order, we write for the energy at absolute zero

$$E = E_0 - \sigma\epsilon + \frac{1}{2}\mu\epsilon^2, \quad (2.3)$$

where E_0 is the energy in the ideal configuration and σ and μ are constant coefficients. Minimizing expression (2.3) with respect to ϵ , we find

$$\epsilon_{\min} = \sigma/\mu. \quad (2.4)$$

A theoretical calculation of σ and μ would, of course, give a theoretical value of ϵ_{\min} and the axial ratio. However, we shall confine ourselves to a theoretical calculation of σ , the "effective stress," as this quantity is of most physical interest. We obtain an approximate value of μ using the observed elastic constants. The quantity μ is given by the second derivative (at constant volume) of E with respect to ϵ , evaluated in the ideal configuration. To the extent that the quadratic approximation is valid [Eq. (2.3)], the value of the derivative is the same in the ideal configuration as in the observed configuration. But the latter is a combination of the elastic constants observed at absolute zero. The expression for μ is given by Jones in the 1950 paper.

In Table I are listed the observed values of ϵ_{\min} and the values of σ necessary to produce the observed deviations from close-packing. Though the data in the table was not obtained at absolute zero, the differences of the values listed from the correct values at absolute zero are probably small. For example, the order of magnitude of thermal expansion coefficients is 10^{-5} , so that up to 1000°K the change in ϵ_{\min} is of the order of 0.01. Though the elastic constants used to compute μ were not measured as a function of temperature, the adiabatic compressibility and rigidity modulus of beryllium show very little dependence on temperature.⁸ The fact

⁸ W. C. Overton, J. Chem. Phys. 18, 113 (1950). The apparent discontinuity of the rigidity modulus in Table II is the result of a misprinted decimal point in the values for 140°K and below.

that the observed values of ϵ_{\min} are small justifies the approximation made in Eq. (2.3).

Thus, a calculation of σ , the "effective stress," serves to calculate the axial ratio. It follows from (2.3) that σ is the negative of the derivative (at constant volume) of the energy with respect to ϵ , evaluated in the ideal configuration. The total energy at absolute zero is equal to the total energy with the nuclei held fixed on the sites of a perfect lattice (which we shall call the electronic energy) plus the zero point energy of the nuclear vibrations. As the latter energy is much smaller than the former, we shall neglect it in this paper.⁹ Thus, in the present approximation, the axial ratio is determined by the negative of the derivative of the electronic energy, which we shall call the "effective electron stress."

We shall close this section with a few brief comments on the temperature dependence of the axial ratio. To determine the axial ratio at a finite temperature, one must minimize the Helmholtz free energy with respect to the axial ratio and atomic volume. The second order coefficients in the Taylor's expansion of the free energy can be approximated by combinations of the isothermal elastic constants. The "effective stress" tending to change the axial ratio or the volume is found by taking the appropriate first derivative of the free energy.

Considering first the contribution of the lattice vibrations to the free energy, we note that the derivative with respect to ϵ (or the volume) will depend on temperature in a manner resembling the total vibrational energy of the lattice. If the derivative is assumed to be proportional to the vibrational energy, the theory of Grüneisen is obtained.¹⁰

The derivative of the electronic energy with respect to ϵ (or the volume) likewise behaves qualitatively like the total electronic energy. Provided that there is no peculiarity in the density of states at the Fermi level, the "effective electron stress" is equal to the stress at absolute zero plus a term proportional to the square of the absolute temperature. The thermal expansion coefficients would then contain terms proportional to the absolute temperature. The possibility of the existence of such a linear term in the volume expansion coefficient was pointed out by Visvanathan.¹¹ The linear contribution to the thermal expansion coefficient of the axial ratio may be too small to measure, however.

3. GENERAL EXPRESSION FOR THE EFFECTIVE ELECTRON STRESS

In this section we derive an exact expression for the "effective electron stress" of a single state of the system

⁹ It is possible that the derivative of the zero-point energy with respect to ϵ could be of the order of magnitude of the zero-point energy itself. As the order of magnitude of the zero-point energy is 0.1 eV per atom, the resultant stress would not be negligible, though it still would be less important than the "electronic stress," with the possible exception of magnesium.

¹⁰ For a discussion of the Grüneisen theory, together with a review of the data on thermal expansion of anisotropic metals, see B. G. Childs, *Revs. Modern Phys.* **25**, 665 (1953).

¹¹ S. Visvanathan, *Phys. Rev.* **81**, 626 (1951).

in terms of integrals over the wave function of the ideal configuration. The expression derived is in the form of a generalized virial theorem. By generalizing the procedure still further, it would be possible to calculate the "effective stress" due to the lattice vibrations, though we have not so attempted in this paper.

We imagine that initially the nuclei are held rigid in the ideal configuration. We will compute the first-order change in energy in going to a slightly different configuration (hereafter called the strained configuration) derived from the ideal configuration by application of the infinitesimal strain tensor \mathbf{s} . We have

$$\mathbf{R}'_{\mu} = (\mathbf{1} + \mathbf{s}) \cdot \mathbf{R}_{\mu}, \quad (3.1)$$

where \mathbf{R}_{μ} and \mathbf{R}'_{μ} are the positions of the μ th nucleus in the ideal and strained configurations, respectively. In the special case of the change in axial ratio, the tensor \mathbf{s} is given in terms of the scalar ϵ defined in (2.1) by

$$s_{xx} = s_{yy} = -\frac{1}{2}\epsilon; \quad s_{zz} = \epsilon, \quad (3.2)$$

all other components being zero.

We write the Hamiltonian for the ideal configuration:

$$H_0 = \sum_j \mathbf{p}_j^2 / 2m + V(\mathbf{R}_{\mu}, \mathbf{r}_j), \quad (3.3)$$

where the sum j is over all electrons, \mathbf{r}_j and \mathbf{p}_j are the position and momentum vectors of the j th electron, m is the mass of the electron and the potential V is the electrostatic potential energy of all the electrons and nuclei. We have neglected all other contributions to the energy as, for example, spin-orbit coupling. The Hamiltonian for the strained configuration is then

$$H_1 = \sum_j \mathbf{p}_j^2 / 2m + V[(\mathbf{1} + \mathbf{s}) \cdot \mathbf{R}_{\mu}, \mathbf{r}_j]. \quad (3.4)$$

We now make a change of variables such that

$$\mathbf{r}_j = (\mathbf{1} + \mathbf{s}) \cdot \mathbf{r}'_j. \quad (3.5)$$

Inserting (3.5) into (3.4) and expanding to first order in \mathbf{s} yields

$$H_1(\mathbf{r}'_j) = H_0(\mathbf{R}_{\mu}, \mathbf{r}'_j) - \sum_j \mathbf{p}'_j \cdot \mathbf{s} \cdot \mathbf{p}'_j / m + \sum_j \mathbf{r}'_j \cdot \mathbf{s} \cdot \nabla'_j V + \sum_{\mu} \mathbf{R}_{\mu} \cdot \mathbf{s} \cdot \nabla_{\mu} V, \quad (3.6)$$

where \mathbf{p}'_j denotes the momentum conjugate to \mathbf{r}'_j .

The advantage of making the change in variables is that the eigenfunctions of (3.6), expressed as functions of the \mathbf{r}'_j , satisfy the same boundary conditions as the eigenfunctions of (3.3), since the \mathbf{r}_j run over a cell in the strained lattice as the \mathbf{r}'_j run over a cell in the ideal lattice. Thus we may find the eigenvalue of (3.6) by standard perturbation theory.

Because we are interested in the first-order change in energy, we need only use first-order perturbation theory; thus we find for the first-order change in energy:

$$\delta E(\mathbf{s}) = \langle - \sum_j \mathbf{p}_j \cdot \mathbf{s} \cdot \mathbf{p}_j / m + \sum_j \mathbf{r}_j \cdot \mathbf{s} \cdot \nabla_j V + \sum_{\mu} \mathbf{R}_{\mu} \cdot \mathbf{s} \cdot \nabla_{\mu} V \rangle, \quad (3.7)$$

where the angular brackets denote the expectation value taken with the wave function for the ideal configuration and the primes have been dropped from the variables of integration.

Equation (3.7) is exact in the case that the expectation value is taken with the exact wave function and is seen to provide a generalized virial theorem.¹²

An approximate value of the "effective stress" can be obtained by evaluating (3.7) with an approximate wave function. The approximate "effective stress" calculated in such a fashion is not necessarily equal to the derivative of the energy calculated in the same approximation. (I.e., the approximate derivative of the energy may not be equal to the derivative of the approximate energy.) However, the two ways of calculating the approximate stress do give the same answer in the important case of the Hartree-Fock approximation. The equivalent result to (3.7) in the Hartree-Fock approximation was derived by Fuchs and Peng.¹³

We now note that the expression (3.7) can be rewritten as

$$\delta E(\mathbf{s}) = C + B, \quad (3.8a)$$

$$C = - (i/\hbar) \sum_j \langle [H_0, \mathbf{r}_j \cdot \mathbf{s} \cdot \mathbf{p}_j] \rangle, \quad (3.8b)$$

$$B = \sum_\mu \mathbf{R}_\mu \cdot \mathbf{s} \cdot \langle \nabla_\mu V \rangle, \quad (3.8c)$$

where the square brackets in (3.8b) denote the commutator. In evaluating expressions (3.8) we have the choice of finding the total value for a finite sample, or the value per unit volume in a very large sample. We shall use the latter procedure in treating pure metals, and the former in discussing alloys. We now use the first procedure to discuss the physical meaning of the expressions (3.8).

If the sample is finite, the integrations in (3.8) may be taken over all space. We first consider (3.8b); carrying out a partial integration on the variable \mathbf{r}_j we obtain

$$\begin{aligned} C = & - (i/\hbar) \sum_j \int d^3r_1 \cdots \\ & \times \int d^3r_N [(H_0 \Psi)^* \mathbf{r}_j \cdot \mathbf{s} \cdot \mathbf{p}_j \Psi - \Psi^* \mathbf{r}_j \cdot \mathbf{s} \cdot \mathbf{p}_j H_0 \Psi] \\ & + (\hbar/2mi) \sum_j \int d^3r_1 \cdots \int d\mathbf{S}_j \cdots \\ & \times \int d^3r_N [(\nabla_j \Psi)^* \mathbf{r}_j \cdot \mathbf{s} \cdot \mathbf{p}_j \Psi - \Psi^* \nabla_j (\mathbf{r}_j \cdot \mathbf{s} \cdot \mathbf{p}_j) \Psi], \quad (3.9) \end{aligned}$$

¹² A tensor virial theorem has been discussed by E. N. Parker [Phys. Rev. **94**, 1441 (1954)] in another connection.

¹³ K. Fuchs and H. W. Peng, Proc. Roy. Soc. (London) **A180**, 451 (1942). These authors used the change of coordinates procedure and did a perturbation calculation on the one-electron Hartree-Fock wave functions. They also derived the surface integral form [Eq. (4.10) of the present paper], but expressed the remaining terms in a different form than in the present paper. Their derivation applies only to cases in which the wave functions are periodic, while our results can be applied to alloys.

where Ψ is (in this discussion) the exact many-electron wave function. The first term in (3.9) is zero as Ψ is an eigenfunction of H_0 and the second is zero as the wave function becomes vanishingly small at infinity.

Thus, in the case under discussion, the entire contribution to δE comes from B . By Feynman's theorem,¹⁴ the quantity $\langle \nabla_\mu V \rangle$ is equal to the negative of the force on the μ th nucleus due to all the other particles in the metal. As the total force on each nucleus must be zero in order to maintain the configuration, an outside force equal to $\langle \nabla_\mu V \rangle$ must be applied to the μ th nucleus. The quantity B is then seen to be equal to the work done by the outside forces during the deformation described by \mathbf{s} .

As deep in the crystal each atom is surrounded symmetrically by its neighbors, $\langle \nabla_\mu V \rangle$ is appreciable only for the atoms near the surface. In order to calculate δE by the present method it would be necessary to know the variation of the potential near the physical surface.¹⁵ Such a calculation would be quite difficult, though we shall see in Sec. 8 that the difficulty can be obviated if one is interested only in the change in δE with alloying.

4. EFFECTIVE ELECTRON STRESS FOR A PURE METAL IN HARTREE-FOCK APPROXIMATION

In this section an expression for the "effective stress" per unit volume is derived using the Hartree-Fock approximation. We imagine that the sample is infinitely large, and that the wave function is normalized inside a large volume Ω . We calculate δE inside a smaller volume ω , divide by ω and take the limit as both ω and Ω become infinite.

In carrying out the above limiting procedure, care must be taken to avoid divergences introduced by the fact that the coordinates appear linearly in the expression for δE [Eqs. (3.8)]. As the total potential is a function of differences of coordinates, we could have made the Taylor's expansion [Eq. (3.6)] in terms of differences of coordinates. Such an expansion in differences of coordinates would converge like the potential itself. We could obtain the expression (3.7) from the expression involving differences of coordinates by a change of variables, provided that the regions of integration (or summation) of all coordinates are the same. Thus, in calculating δE inside ω , we shall include only interactions between particles inside ω , which guarantees that the correct limiting value of δE will be obtained.

In order to facilitate the calculation outlined above, it is convenient to introduce a quantity $V_o(\mathbf{r}_j)$, which is the instantaneous potential of interaction between the j th electron and all the particles outside ω . With the use of $V_o(\mathbf{r}_j)$, the contribution of the volume ω to C can now

¹⁴ R. P. Feynman, Phys. Rev. **56**, 340 (1939).

¹⁵ A calculation by this method would be similar to the calculation of the work function. See, for example, J. Bardeen, Phys. Rev. **49**, 653 (1936) or R. Smoluchowski, Phys. Rev. **60**, 661 (1941).

be written

$$C(\omega) = - (i/\hbar) \sum_j \int_{\Omega} d^3r_1 \cdots \int_{\omega} d^3r_j \cdots \\ \times \int_{\Omega} d^3r_N \Psi^* [H_0 - V_o, \mathbf{r}_j \cdot \mathbf{s} \cdot \mathbf{p}_j] \Psi, \quad (4.1)$$

where Ψ is the many-electron wave function.

We now make use of the Hartree-Fock approximation and let the wave function Ψ be a normalized determinant of one-electron spin orbitals $\psi_{\alpha}(\mathbf{r}_j)$ which satisfy the Hartree-Fock equation $H_F \psi_{\alpha} = \mathcal{E}_{\alpha} \psi_{\alpha}$, where H_F is the one-electron Hartree-Fock Hamiltonian and \mathcal{E}_{α} is the one-electron Hartree-Fock eigenvalue. We make the convention that the quantum number α stands for both spatial and spin quantum numbers and that when \mathbf{r}_j appears as the argument of a ψ_{α} it stands for both spatial and spin variables, integration over \mathbf{r}_j being understood to include summation over spin variables. We normalize the ψ_{α} to unity in the large volume Ω .

Consider first the part of (4.1) which depends upon the full Hamiltonian. We perform a partial integration on the variable \mathbf{r}_j , obtaining an expression identical to (3.9) except that the regions of integration are different. When the determinantal wave function is substituted into the expression, the term analogous to the first term on the right in (3.9) vanishes, as integration over all coordinates except \mathbf{r}_j transforms the total Hamiltonian into the Hartree-Fock Hamiltonian. Because of the *ortho*-normality of the one-electron orbitals, the surface

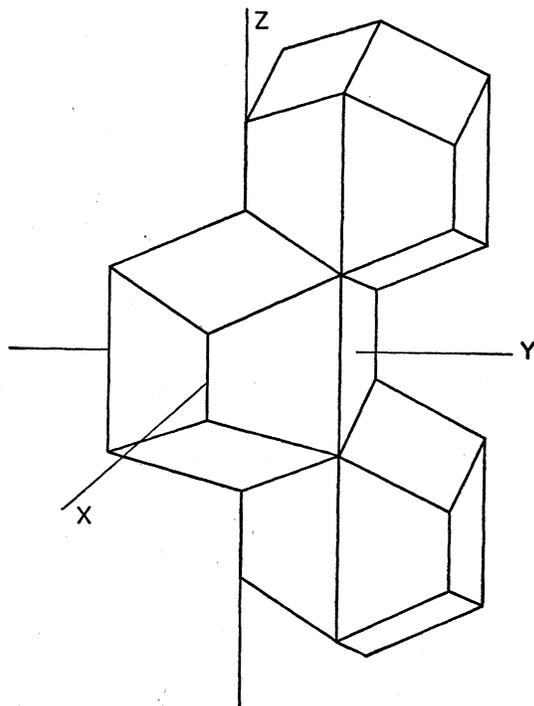


FIG. 3. The central atomic polyhedron and a few of its neighbors

integral reduces to a sum of integrals involving one ψ_{α} at a time. The part of (4.1) which depends upon the commutator of V_o gives rise to terms representing an electrostatic interaction of the electrons inside ω with all particles outside of ω , and an exchange interaction between the electrons inside ω and the electrons outside of ω . The expression for C in terms of the one-electron orbitals is

$$C(\omega) = D + G + X, \quad (4.2)$$

$$D = (-i\hbar/2m) \sum_{\alpha} \int_{\omega} d\mathbf{S} \\ \cdot [(\nabla\psi_{\alpha})^* \mathbf{r} \cdot \mathbf{s} \cdot \mathbf{p} \psi_{\alpha} - \psi_{\alpha}^* \nabla(\mathbf{r} \cdot \mathbf{s} \cdot \mathbf{p}) \psi_{\alpha}], \quad (4.2a)$$

$$G = - \int_{\omega} d^3r_1 \rho(\mathbf{r}_1) \mathbf{r}_1 \cdot \mathbf{s} \cdot \nabla_1 \\ \times \int_o d^3r_2 P(\mathbf{r}_2) / |\mathbf{r}_1 - \mathbf{r}_2|, \quad (4.2b)$$

$$X = \sum_{\alpha\beta} \int_{\omega} d^3r_1 \int_o d^3r_2 \psi_{\alpha}^*(\mathbf{r}_1) \\ \times \psi_{\beta}(\mathbf{r}_1) \psi_{\beta}^*(\mathbf{r}_2) \psi_{\alpha}(\mathbf{r}_2) \mathbf{r}_1 \cdot \mathbf{s} \cdot \nabla_1 e^2 / |\mathbf{r}_1 - \mathbf{r}_2|, \quad (4.2c)$$

where the sum α is over occupied states and the subscript o indicates that the integration is over the volume outside of ω . The quantity ρ is the average charge density due to the electrons, and P is the total average charge density. They are given by

$$\rho(\mathbf{r}) = -e \sum_{\alpha} |\psi_{\alpha}(\mathbf{r})|^2, \quad (4.3a)$$

$$P(\mathbf{r}) = \rho(\mathbf{r}) + \sum_{\mu} Ze \delta(\mathbf{r} - \mathbf{R}_{\mu}), \quad (4.3b)$$

where $-e$ is the charge on an electron, Ze is the charge on a nucleus, and $\delta(\mathbf{r})$ is the Dirac delta function.

We next make use of the periodicity of the wave functions to transform G into a lattice sum inside ω . We then shall combine it with B to obtain a simple result. We first express G as a sum of integrals over atomic polyhedra. These polyhedra are the same as the Wigner-Seitz cells, the polyhedron about a given atom being the smallest volume contained by the perpendicular bisecting planes of the lines joining the atom in question to all other atoms. A polyhedron and a few of its neighbors are shown in Fig. 3. These polyhedra have the same symmetry as the space lattice; in particular, for the hexagonal close-packed lattice, the total charge and the dipole moment within a polyhedron are zero.

Denoting the polyhedron about the μ th atom as $[\mu]$, we have for G ,

$$G = - \sum_{\mu} \int_{[\mu]} d^3r_1 \rho(\mathbf{r}_1) [\mathbf{R}_{\mu} + (\mathbf{r}_1 - \mathbf{R}_{\mu})] \cdot \mathbf{s} \cdot \nabla_{\mu} \\ \times \int_o d^3r_2 \frac{P(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (4.4)$$

where the superscript ω on the summation sign means that the summation is over those \mathbf{R}_μ inside ω . We specify that the surface of ω coincides with the bounding surfaces of atomic polyhedra. Thus, the field strength inside ω due to the charges outside ω will be appreciable only near the surface, there being no net charge outside ω or surface dipole moment on the surface of ω . Since, in (4.4), $\mathbf{r}_1 - \mathbf{R}_\mu$ is always of the order of magnitude of an interatomic distance, the part of G proportional to $\mathbf{r}_1 - \mathbf{R}_\mu$ will give a term proportional to the area of the surface, and may be neglected in the limit of infinite volume.

In the remaining part of (4.4), we write the integral over the region outside of ω as an integral over all space minus an integral over the volume ω ,

$$G = - \sum_{\mu}^{\omega} \mathbf{R}_{\mu} \cdot \mathbf{s} \cdot \int_{[\mu]} d^3 r_1 \rho(\mathbf{r}_1) \nabla_1 \times \left[\int_{\Omega} d^3 r_2 \frac{\mathbf{P}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \int_{\omega} d^3 r_2 \frac{\mathbf{P}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right]. \quad (4.5)$$

The contribution of the first term in the square brackets to the integral over the polyhedron represents the average force on the electrons in the polyhedron, and vanishes by symmetry. Expressing the remaining integral over ω as a sum over polyhedra, we have

$$G = \sum_{\mu\nu}^{\omega} \mathbf{R}_{\mu} \cdot \mathbf{s} \cdot \int_{[\mu]} d^3 r_1 \int_{[\nu]} d^3 r_2 \rho(\mathbf{r}_1) \mathbf{P}(\mathbf{r}_2) \nabla_1 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (4.6)$$

Remembering that we must count only interactions between particles inside ω , we express B [Eq. (3.8c)] as

$$B = \sum_{\mu\nu}^{\omega} Z e \mathbf{R}_{\mu} \cdot \mathbf{s} \cdot \nabla_{\mu} \int_{[\nu]} d^3 r_2 \frac{\mathbf{P}(\mathbf{r}_2) - Z e \delta(\mathbf{r}_2 - \mathbf{R}_{\mu})}{|\mathbf{r}_2 - \mathbf{R}_{\mu}|}, \quad (4.7)$$

where the delta function cancels the interaction of the μ th nucleus with itself. By summing these two expressions and averaging over an interchange of μ and ν , we find

$$S = B + G = \frac{1}{2} \sum_{\mu\nu}^{\omega} (\mathbf{R}_{\mu} - \mathbf{R}_{\nu}) \cdot \mathbf{s} \cdot \int_{[\mu]} d^3 r_1 \int_{[\nu]} d^3 r_2 \mathbf{P}(\mathbf{r}_1) \mathbf{P}(\mathbf{r}_2) \nabla_1 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (4.8)$$

We have finally expressed the "effective stress" due to a many-electron Hartree-Fock state as the sum of three terms,

$$\delta E(\mathbf{s}) = D + S + X, \quad (4.9)$$

where the expressions for the individual terms are given by Eqs. (4.2a), (4.8), and (4.2c), respectively. We next shall discuss the physical interpretations of each of the three terms.

We begin by discussing term D [Eq. (4.2a)]. We

make use of the periodicity of the wave functions to reduce D to an integral over the surface of a unit cell, obtaining

$$D(\omega) = \sum_{\alpha} D_{\alpha} = (\omega/\Delta) (-i\hbar/2m) \sum_{\alpha} \int_{\Delta} d\mathbf{S} \cdot [(\nabla\psi_{\alpha})^* \mathbf{r} \cdot \mathbf{s} \cdot \mathbf{p} \psi_{\alpha} - \psi_{\alpha}^* \nabla(\mathbf{r} \cdot \mathbf{s} \cdot \mathbf{p}) \psi_{\alpha}], \quad (4.10)$$

where D_{α} stands for the contribution to D from the one-electron state α . The symbol Δ stands for the unit cell so that the factor ω/Δ is the number of unit cells in ω . Due to the fact that in the evaluation of term S , the surface of ω was chosen to coincide with the surfaces of atomic polyhedra, the unit cell used in expression (4.10) must be composed of two neighboring atomic polyhedra, in adjacent planes (see Fig. 3). Because the contributions to D come from the region between atoms, the valence electrons will be most important in determining its value. In metals in which the interatomic distance is large compared to the ionic radius, the contribution from inner shell electrons should be negligible. In the other metals, however, the contributions from these electrons may have to be taken into account.

It is possible to construct a classical analog of term D . Consider a number of electrons per unit volume n having velocity \mathbf{v} and momentum \mathbf{p} . The flux of particles through the surface element $d\mathbf{S}$ is $n d\mathbf{S} \cdot \mathbf{v}$, and the force on the surface element due to the momentum transport is $n(d\mathbf{S} \cdot \mathbf{v})\mathbf{p}$. Now suppose that the cell is deformed by a strain \mathbf{s} . The work done by this force acting through the displacement $\mathbf{s} \cdot \mathbf{r}$ is given by

$$\delta E = -n \int_S (d\mathbf{S} \cdot \mathbf{v})(\mathbf{r} \cdot \mathbf{s} \cdot \mathbf{p}). \quad (4.11)$$

Equation (4.11) can be seen to be a classical analog to (4.10) with \mathbf{v} taking the place of the current operator. Thus we call term D the "kinetic stress" due to the electrons. We shall see in Sec. 6 that the term D corresponds to the stresses estimated by Jones and Goodenough.

Now we consider term S . Inspection of the structure of Eq. (4.8) shows that S represents the work done against the electrostatic forces between polyhedra in carrying out the deformation described by \mathbf{s} . As each polyhedron is electrically neutral, it is to be expected that S is small and that is what we find in Sec. 7.

The term X represents an exchange effect. It arises from the increased attraction of the medium outside of ω for an electron in ω , due to the fact that electrons of the same spin are kept apart by the determinantal wave function. A crude estimate of X in Sec. 7 indicates that it may be appreciable.

Finally, we note that the formalism developed in this section can be applied to find the linear change in energy of any solid under deformation. Note that it gives the change in energy of the total solid, not the change in one-electron energy parameters. To find the exact

change in Hartree-Fock energy parameters, a self-consistent calculation would be necessary. Such a calculation has been discussed by Bardeen.¹⁶ However, the self-consistent calculation can be avoided in cases in which Koopmans's theorem¹⁷ is valid. For example, the change in a certain one-electron energy parameter can be calculated by calculating the change in total energy for a state in which the one-electron state is occupied, and subtracting the change in energy of another state which differs from the first in that the particular one-electron state is empty, and one electron is removed from the crystal. The change with strain of the energy parameters is of interest in connection with the change with strain in the energy gap of a semiconductor,¹⁸ the explanation of the elastoresistance of germanium,¹⁹ and the deformation potential theory.²⁰

5. EFFECTIVE STRESS IN THE WIGNER-SEITZ-SLATER APPROXIMATION

In treating the cohesive energy of monovalent metals, Wigner and Seitz²¹ took the potential in which a valence electron moves to be the potential $v_i(\mathbf{r})$ due to the ion in the polyhedron in which the electron is instantaneously located. The one-electron Schrödinger equation

$$[\mathbf{p}^2/2m + v_i(\mathbf{r})]\psi_\alpha(\mathbf{r}) = \mathcal{E}_\alpha\psi_\alpha(\mathbf{r}) \quad (5.1)$$

was solved in the polyhedron subject to the Bloch boundary conditions at the surface of the polyhedron.²² The sum of the energy parameters \mathcal{E}_α so obtained was found to be a very good approximation to the total energy of the metal, relative to the state in which the ions and electrons are infinitely dispersed.²³

We now consider the effect of deforming the metal by a strain \mathbf{s} . The Schrödinger equation, (5.1), is unchanged, but the boundary conditions do change. We will repeat the device of changing coordinates, Eq. (3.5), so that the wave function expressed in the new coordinates satisfies the original boundary conditions. Expanding to first order in \mathbf{s} , we find

$$\delta\mathcal{E}_\alpha(\mathbf{s}) = \int_{[0]} \psi_\alpha^*[-\mathbf{p}\cdot\mathbf{s}\cdot\mathbf{p}/m + \mathbf{r}\cdot\mathbf{s}\cdot\nabla v_i(\mathbf{r})]\psi_\alpha. \quad (5.2)$$

¹⁶ J. Bardeen, Phys. Rev. **52**, 688 (1937).

¹⁷ T. Koopmans, Physica **1**, 104 (1934). See also the discussion in F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 313.

¹⁸ See, for example, R. W. Keyes, Phys. Rev. **92**, 580 (1953).

¹⁹ E. N. Adams, Phys. Rev. **96**, 803 (1954).

²⁰ J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950). See also W. P. Dumbke, Bull. Am. Phys. Soc. **29**, No. 7, 15 (1954).

²¹ E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

²² Actually, Wigner and Seitz simplified the boundary conditions by replacing the polyhedron by a sphere. J. C. Slater [Phys. Rev. **45**, 794 (1934)] made a calculation in which he satisfied the Bloch boundary conditions at a few points on the surface of the polyhedron. In this section we shall assume that the exact boundary conditions have been satisfied.

²³ Wigner and Seitz also made a more elaborate calculation than the one described above. However, we will confine our attention to the simpler case.

Transforming to a surface integral as before, we find

$$\delta\mathcal{E}_\alpha(\mathbf{s}) = -(i\hbar/2m) \int_{[0]} d\mathbf{S} \cdot [(\nabla\psi_\alpha)^*\mathbf{r}\cdot\mathbf{s}\cdot\mathbf{p}\psi_\alpha - \psi_\alpha^*\nabla(\mathbf{r}\cdot\mathbf{s}\cdot\mathbf{p})\psi_\alpha]. \quad (5.3)$$

Expression (5.3) is seen to be the same as D_α , Eq. (4.10), except that (5.3) is calculated with the Wigner-Seitz wave functions and (4.10) is calculated with the exact wave functions.²⁴

The result (5.3) is very interesting, considering that, in the simple Wigner-Seitz approximation, the sum of the \mathcal{E}_α is equal to the total energy of the metal. Unfortunately, the situation in a divalent metal is much more complicated so that no simple analogous statement can be made.

6. COMPARISON WITH THE WORK OF JONES AND GOODENOUGH

In this section we discuss the relationship of our work to that of Jones and Goodenough. We find, that with suitable assumptions, term D , Eq. (4.10), can be made to yield the estimates of Jones and Goodenough for the "effective stress."

Both authors base their estimates on the weak-potential model,²⁵ and neglect any changes in energy gaps with strain. Such a neglect in the weak-potential model is equivalent to assuming that the magnitudes of corresponding Fourier coefficients of the potential are unchanged by deformation. However, if the Fourier coefficients were actually constant, the potential would be "deformable;" that is, the potential after deformation is given in terms of the original potential by

$$v_s[(1+\mathbf{s})\cdot\mathbf{r}] = v_0(\mathbf{r}), \quad (6.1)$$

where v_0 and v_s are the potentials before and after deformation.

Using Eq. (6.1) for the transformation of the potential and the method used before of changing variables to calculate the change in the one-electron energy eigenvalue, we obtain

$$\delta\mathcal{E}_\alpha = D_\alpha' = - \int_{\Omega} d^3r \psi_\alpha^*(\mathbf{p}\cdot\mathbf{s}\cdot\mathbf{p}/m)\psi_\alpha. \quad (6.2)$$

We have called this expression D_α' as it is analogous to D_α . It is to be noted that there is no potential energy term in (6.2). If the wave functions are expressed as linear combinations of plane waves, D_α' becomes

$$D_\alpha' = - \sum_{\mathbf{k}} \kappa |a_\alpha(\mathbf{k}+\mathbf{K})|^2 (\hbar^2/m) (\mathbf{k}+\mathbf{K})\cdot\mathbf{s}\cdot(\mathbf{k}+\mathbf{K}), \quad (6.3)$$

²⁴ The fact that expression (5.3) gives the change in the Wigner-Seitz energy when the polyhedron is replaced by a sphere, was pointed out by Fuchs and Peng (reference 13). They used the expression to derive the formulas of H. Fröhlich [Proc. Roy. Soc. (London) **A158**, 97 (1937)] and J. Bardeen [J. Chem. Phys. **6**, 372 (1938)] for the dependence on volume of the Wigner-Seitz energy of the state of wave number zero.

²⁵ L. Brillouin, *Quantenstatistik* (Verlag Julius Springer, Berlin, 1931).

where $a_\alpha(\mathbf{k}+\mathbf{K})$ is the coefficient of the normalized plane wave of propagation vector $\mathbf{k}+\mathbf{K}$, and the \mathbf{K} are reciprocal lattice vectors multiplied by 2π .

In order to obtain the Jones and Goodenough estimates we assume that the wave functions are the nearly-free electron wave functions,²⁵ i.e., all a 's are zero except a few corresponding to the smallest magnitudes of $\mathbf{k}+\mathbf{K}$. When \mathbf{s} is given by (3.2), we distinguish three cases.

(1) If the end of the vector \mathbf{k} lies at certain points of high symmetry, all the factors $(\mathbf{k}+\mathbf{K}) \cdot \mathbf{s} \cdot (\mathbf{k}+\mathbf{K})$ have the same value. As the sum of the a 's is unity (due to the normalization condition), we find

$$D_\alpha' = -(\hbar^2/m)\mathbf{k} \cdot \mathbf{s} \cdot \mathbf{k}. \quad (6.4)$$

The expression (6.4) is the change with strain of a free electron state with propagation vector \mathbf{k} , and thus is equal to the Jones estimate.

(2) For other points on the zone faces, the present method is different from that of Jones, though the two methods yield the same result in the weak potential case. To find the average change in energy of holes near points such as the corners of the zone V and W , Jones takes the change of free electron energy at the corners. [The change in free electron energy at point V is equal to the change in free electron energy at point W for the deformation (3.2).] However, the quantity D_α' , evaluated for the state at W (or V), gives the change in energy of the state originally at W (or V). Under the deformation (3.2) the two states move away from points W and V , and, in fact, the values of D_α' associated with the two states are not equal. In order to find the average change in energy of holes originally near points V and W we must average the two values of D_α' , weighting each value with the appropriate density of states. If we use the free electron densities of states for points V and W , we obtain the same estimate as Jones.

(3) In the case that the end of the vector \mathbf{k} is near to but does not touch a zone face, Eq. (6.3) gives, besides the change in free electron energy, a contribution which depends on the variation of the a 's with \mathbf{k} . The value of D_α' in this case works out to be the estimate of Goodenough, plus a term $\mathbf{k} \cdot \mathbf{s} \cdot \nabla_{\mathbf{k}} \delta_\alpha$ which is zero when summed over the Fermi distribution as the tensor defined by (3.2) has no trace.

We are now able to state the assumptions which will lead to the theories of Jones and Goodenough. First of all, the effects considered by these authors are contained in term D . Further, they take only that part of D which would result if the self-consistent potential were "deformable." Finally, they evaluate the "deformable" part of D using nearly-free electron wave functions.

7. NUMERICAL APPLICATION TO BERYLLIUM

In this section we make numerical estimates of the various contributions to the "effective electron stress" in the case of pure beryllium. We chose beryllium as it is

TABLE II. Results of calculation of term D_α , the "kinetic stress."

α (State)	$\frac{D_\alpha \text{ (OPW)}}{D_\alpha \text{ (free)}}$	$D_\alpha \text{ (free)}/\epsilon$ (ev)	$^* a_F ^2$
Γ_4^-	0.714	-22.4	1.03
Γ_3^+	0.984	-22.4	0.985
K_6	0.865	13.2	0.91

^{*} $|a_F|^2$ is the absolute square of the coefficient of the nearly-free electron wave function in the orthogonalized plane wave function.

the only hexagonal close-packed metal for which one-electron wave functions have been calculated for states other than the central point in the Brillouin zone. The wave functions available are approximate Hartree wave functions calculated by Herring and Hill,²⁶ using the orthogonalized plane wave method.²⁷§

First, we discuss term D , Eq. (4.10). The individual contributions from each state, D_α , are fairly easily calculated with the orthogonalized plane waves. Each valence-electron wave function is expressed as a linear combination of plane waves and inner-shell wave functions, the coefficients chosen to minimize the valence-electron energy while keeping the valence-electron wave function orthogonal to the inner-shell wave functions. The inner-shell wave functions in the case of beryllium are very small (about 10^{-3} of the value at the atom) in the region between atoms where the surface of integration is located; therefore, we neglect the contributions of the inner-shell parts of the wave function to the "effective stress." Thus, we need only evaluate D_α with a combination of a few plane waves.

From the computational view, there are two reasons why the actual value of D_α will be different from the value predicted on the nearly-free electron model. We may think of the wave function as being made up of an inner shell part, a combination of plane waves which would be the wave function in the nearly-free electron approximation, and higher plane waves. The value of D_α is then different from that for free electrons both because of the contributions of the higher plane waves, and because the coefficient of the nearly-free electron wave function is different from unity.

We have evaluated D_α for several states in the Brillouin zone, the results being listed in Table II. The labeling of states is the same as in the Brillouin zone of Fig. 2. For simplicity, we express our results by giving the ratio of our value of D_α to the value obtained on the nearly-free electron model for the same point in the Brillouin zone. For each of the states investigated, the amplitude of the nearly-free electron part of the wave function is nearly unity (see Table II) and the amplitudes of the higher plane waves are small. As a result, the computed values of D_α resemble the free electron

²⁶ C. Herring and A. G. Hill, Phys. Rev. 58, 132 (1940).

²⁷ C. Herring, Phys. Rev. 57, 1169 (1940).

§ Note added in proof.—It has been brought to the author's attention that calculations have been performed for several points in the Brillouin zone for magnesium. See M. Trlifaj, Czech. J. Phys. 1, 110 (1952).

values rather more than might have been expected *a priori*.

It should be noted that though the contribution to D from each of the states listed in Table II is similar in magnitude to the free electron contribution, the sum over the Fermi distribution could be very much different from the sum calculated using the free electron approximation. This is true because the total sum is a small difference between large terms, so that a deviation from the free electron value which is different in different parts of the zone could cause a large error in the sum. Such an error would, of course, cause a large error in the calculated value of the axial ratio.

From the information given in Table II, we can get some idea about the effect of strain on the energy gap. As Γ_4^- is the state just above the top face of the zone, and Γ_3^+ is the state just below, the difference between $D(\Gamma_4^-)$ and $D(\Gamma_3^+)$ would be the change in energy gap if one could neglect the effects of terms S and X . Table II shows that this change is of the order of thirty percent of the change in free electron energy.

We now consider the contribution of term S to the "effective stress." In order to make an estimate of S , we approximate the total charge density as that given by positive charges of $2e$ on the atomic positions and a uniform negative charge of $-2e$ per polyhedron. It is then convenient to transform S to a somewhat different form. It can be shown that

$$S(\omega) = \delta W(\omega) + (2\omega/\Delta)(4e/\Delta) \int_{[0]} d^3r \mathbf{r} \cdot \boldsymbol{\epsilon} \cdot \nabla \phi(\mathbf{r}), \quad (7.1)$$

where δW is the change with shear of the electrostatic energy of the simple model assumed above, and ϕ is the electrostatic potential of such a charge density.

The first term in Eq. (7.1), δW , can be calculated using the method of Ewald,²⁸ as developed by Fuchs.²⁹ That the variation of W with c/a is a factor in determining the axial ratio was pointed out by Herring and Hill.²⁶ We find

$$\delta W = -(2\omega/\Delta)0.00155e^2\epsilon/a. \quad (7.2)$$

It can be shown that if $\phi(\mathbf{r})$ were spherically symmetrical, the second term in (7.1) would be zero. We imagine expanding ϕ as a sum of multipoles. The largest contribution should come from the quadrupole term as the operator $\mathbf{r} \cdot \boldsymbol{\epsilon} \cdot \nabla$ has quadrupole symmetry when operating on a spherically symmetric function. The coefficient of the quadrupole term in the expression for ϕ has been calculated by Campbell, Keller, and Koenigsberg.³⁰ Replacing the polyhedron by a sphere of

equal volume, we find for the second term in (7.1)

$$(4e/\Delta) \int_{[0]} d^3r \mathbf{r} \cdot \boldsymbol{\epsilon} \cdot \nabla \phi \cong 0.0025e^2\epsilon/a. \quad (7.3)$$

We then find for the approximate value of S in the case of beryllium 0.006ϵ electron volts per atom. Referring to Table I, we see that this value is small compared to the observed values of the "effective stress." Though our estimate of S is admittedly approximate, the small value obtained is an indication that the contribution of term S to the "effective stress" for a pure metal can be ignored.

Term X is very complicated and we have been able to make only a rough estimate of its value. If, in deriving the expression for the "effective stress," it is specified that the one-electron wave functions are solutions of the Hartree equations (instead of the Hartree-Fock equations), it is found that term X takes the somewhat different form,

$$X = -(e^2/2) \sum_{\alpha\beta} \int_{\Omega} d^3r_1 \int_{\Omega} d^3r_2 \psi_{\alpha}^*(\mathbf{r}_1) \psi_{\beta}(\mathbf{r}_1) \\ \times \psi_{\beta}^*(\mathbf{r}_2) \psi_{\alpha}(\mathbf{r}_2) (\mathbf{r}_1 - \mathbf{r}_2) \cdot \boldsymbol{\epsilon} \cdot \nabla (1/|\mathbf{r}_1 - \mathbf{r}_2|). \quad (7.4)$$

As the Herring and Hill wave functions are Hartree wave functions, expression (7.4) should be used in calculating X .

In evaluating (7.4), we neglect interaction between the valence electrons and closed shells³¹ and replace the valence electron wave functions by plane waves. In such an approximation, the value of X depends sensitively upon the occupation of states in reciprocal space, being zero for a spherical Fermi surface. We attempt to represent the effect of the full zone which contains two electrons per atom by assuming the electrons occupy an ellipsoid of revolution which has the same volume and quadrupole moment [integrated value of $\frac{1}{2}(3k_z^2 - k^2)$] as the zone. With the above assumption, we obtain an estimate of 0.1ϵ ev per atom for X for beryllium. Though the estimate is crude, it indicates that the exchange effect is important.

We are now in a position to try to make an estimate of the total "effective electron stress" in beryllium. Following Jones, we think of the total stress as that due to the full zone plus that due to overlap electrons minus that due to holes. We will approximate the term D for the full zone by summing the free electron value of D_{α} over the zone. Such a sum yields

$$\sum_{\alpha, z} D_{\alpha} \cong 0.8\epsilon \text{ ev per atom,}$$

²⁸ See, for example, M. Born and M. Goeppert-Mayer, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 710.

²⁹ K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).

³⁰ Campbell, Keller, and Koenigsberg, Phys. Rev. **84**, 1256 (1951).

³¹ In beryllium the exchange interaction between closed shells on different atoms is negligible, but can be important in other metals. [See K. Fuchs, reference 29; also, Proc. Roy. Soc. (London) **A153**, 622 (1936); **A157**, 444 (1936).] However, to the extent that such interactions are represented by central forces between nearest neighbors only, they will produce no "effective stress" tending to change the axial ratio.

where the subscript z means that the sum is over the complete zone. Adding this to the estimate of X for the full zone made above, we have for the "effective stress" due to the full zone

$$\sigma_z \cong -0.9 \text{ ev per atom.}$$

The observed "effective stress" in beryllium is minus 0.44 ev per atom (see Table I), about one-half our estimate. If there occurred overlap at point K and holes at points V and W as the results of Herring and Hill suggest, the correction for the difference from a filled band would increase the calculated "effective stress" even more.

The above estimate of the "effective stress" is in error due to the partial use of the free electron approximation in obtaining it. Even so, the approximation is sufficiently good to yield an estimate for the "effective stress" in beryllium of the right sign and order of magnitude. For metals of larger atomic number whose wave functions are more complicated, it is to be expected that the free electron approximation is less accurate. In zinc and cadmium, the "effective stress" actually has the opposite sign to that predicted with the free electron approximation.

8. EFFECTS OF ALLOYING

In this section we discuss the change in lattice parameters caused by alloying. We find that the method used by Jones to calculate the change in axial ratio with alloying is incorrect, though we show that the correct method may lead to conclusions similar to those of Jones.

Besides changing the axial ratio, alloying causes changes in the volume, and produces local distortions of the crystal structure. We shall describe each configuration by giving the average axial ratio and average volume. For a given configuration the equilibrium positions of the nuclei are determined by the condition that the energy is a minimum subject to the constraint on the average axial ratio and average volume. We use the parameter ϵ as defined before, and introduce a parameter δ which is equal to one-third of the fractional difference between the average volume of the configuration and the volume of the pure metal at absolute zero.

The equilibrium values of ϵ and δ are those which minimize the total energy. The expansion (to second order) of the total energy in terms of ϵ and δ is

$$E = E_0 - \sigma\epsilon - \pi\delta + \frac{1}{2}\mu\epsilon^2 + \frac{1}{2}\nu\delta^2 + \eta\epsilon\delta. \quad (8.1)$$

Minimizing (8.1) with respect to ϵ yields

$$\epsilon_{\min} = (\sigma - \eta\delta) / \mu. \quad (8.2)$$

We could, of course, minimize the energy with respect to δ , and make a theoretical calculation of both ϵ and δ . However, we shall instead take δ from experiment, approximate μ and η by the appropriate combinations of elastic constants, and confine ourselves to the calculation of σ .

It is seen that the axial ratio changes with alloying because of three effects: the change in elastic constants, the change in atomic volume, and the change in the "effective stress."

We cannot say how large the effect due to the change of elastic constants is, since measurements of the relevant elastic constants for alloys of hexagonal metals have not been made. However, measurements on other systems indicate that the percentage change in elastic constants per atomic percent of solute varies from 0.5 to 5.³² From Table I we see that the percentage change in ϵ_{obs} per atomic percent of solute is of the order of 10, so that the change in elastic constants may well have an important effect.

The change in axial ratio due to the change in atomic volume, given by the last term in (8.6), is the same as that derived by Jones using a somewhat different argument.

The change in the "effective stress" with alloying is due to the changes in the "effective phonon stress" and the "effective electron stress." We shall treat here only the change in the "effective electron stress" and neglect the change in the "effective phonon stress."

The "effective stress" is, as before, the negative of the derivative of the energy with respect to ϵ . A change in ϵ not only changes the average axial ratio but also affects the local distortions. We could express the actual deformation as a homogeneous deformation which changes the axial ratio, plus local deformations. The local deformations do not cause a first-order change in energy as the energy of the ideal configuration is a minimum with respect to local deformations. Thus we may obtain σ by calculating the linear change in energy caused by a homogeneous deformation.

We shall calculate the change in "effective electron stress" with alloying using the formulation discussed in Sec. 3, so that the total "effective stress" comes from the contributions of the surface atoms to B [Eq. (3.8c)].³³ We limit the discussion to the case of infinite dilution, so that there is a negligible number of impurity atoms near the surface. At first thought it might seem that the impurity atoms could not contribute to the surface stress due to the fact that the forces between atoms are short-ranged. However, the *stress field* due to the presence of the impurity atoms is long-ranged. In fact, the field at large distances from the impurity can be treated by classical elasticity theory, and falls off as the inverse cube of the distance from the impurity atom.

In calculating the excess in term B due to the presence of the impurities, we may replace the summation over μ by an integration over the surface of the sample, as the excess surface stress is a slowly varying

³² R. A. Artman and D. O. Thompson, J. Appl. Phys. **22**, 358 (1951); A. D. N. Smith, J. Inst. Metals **80**, 477 (1952).

³³ The quantity $\langle \nabla_{\mu} V \rangle$ is zero for nuclei in the interior of the sample. If this were not so, the energy could be lowered by displacing interior atoms, but the energy of the ideal configuration is a minimum with respect to such displacements.

function. We find

$$\delta E = \delta E_0 + \int_s (d\mathbf{S} \cdot \boldsymbol{\tau}) \cdot \mathbf{s} \cdot \mathbf{r}, \quad (8.3)$$

where δE_0 is the linear change in energy for the pure metal and $\boldsymbol{\tau}$ is the stress tensor due to the presence of impurities. As the leading term in the stress varies as the inverse cube of the distance from the impurity, the second term in (8.3) will be proportional to the total number of impurities in the sample.³⁴ Thus the change in lattice parameters will be proportional to the concentration of impurities (for small concentrations). The stress field itself is determined by the atomic displacements near the impurity atoms. A complete theoretical calculation of the change in lattice parameters with alloying then involves a calculation of the local displacements.³⁵

The results of the above discussion support the simple view of a metal as being made up of atoms which interact through short-range forces. That classical elasticity theory can be applied to the problem of change of lattice parameters has been recognized for a long time.³⁶ The importance of the present results is that they show that the simple "Brillouin zone effects" on the change of lattice parameters with alloying as hitherto calculated, do not exist. Note that there would be no change in average lattice parameters if there were not local distortions of the lattice, a fact in direct contradiction with the theory of Jones.

The reason for the failure of the Jones model can be elucidated by the following discussion. Let us calculate by our method the change with alloying of the contribution of term D [Eq. (4.2a)] to the "effective stress," remembering that such a contribution is analogous to the stress calculated by Jones. We shall further assume that there are no local distortions of the lattice. We choose the surface of ω to be far from impurity atoms. We then find that D is unchanged by the addition of the impurities. The reason is roughly this: the perturbation of the charge distribution due to an impurity atom dies off exponentially with distance from the impurity, so that the charge density at the surface of ω is the same as for the pure metal.³⁷ Thus, though there may be a contribution to the stress from the extra electrons introduced by alloying, it is exactly cancelled by the change in the stress due to the electrons already present.

In order to explain the experimental regularities in the

³⁴ Actually, there is also a constant term in the stress tensor due to impurities. In the method of this section the magnitude of the constant term is determined by the condition upon the average axial ratio and average volume. A more straightforward procedure would be to apply originally the boundary condition that there are no surface stresses and determine the change in lattice parameters from the surface displacements.

³⁵ For a discussion of the calculation of local atomic displacements in several cases, see D. L. Dexter, *Phys. Rev.* **87**, 768 (1952).

³⁶ B. Ya. Pines, *J. Phys. (U.S.S.R.)* **3**, 309 (1940).

³⁷ Actually, it is necessary that the contribution to the charge density at the surface of ω from each group of states with the same energy is unchanged by alloying. See J. Friedel, *Advances in Physics* **3**, 446 (1954).

change in lattice parameters it is now necessary to explain why there are regularities in the local displacements caused by alloying.³⁸ We present here a rough argument which indicates that such a program is possible. We assume that the behavior of the electrons near the impurity can be described in the effective mass approximation.³⁹ For the sake of argument, let us assume that the energy band structure is that proposed by Jones and discussed in Sec. 1 of this paper. There will be several types of states with energy near the energy of the Fermi level, corresponding to the different regions K , V , and Γ . Let us consider the region Γ . In analogy to the weak potential case, we may expect that the effective mass parallel to the c axis is smaller than that perpendicular to the c axis. Thus the orbit of an electron of effective mass corresponding to region Γ and which is bound to the impurity would extend further away from the impurity in the direction of the c axis than perpendicular to the c axis. Thus the contribution to the excess charge density from such electrons would extend farther up the c axis than perpendicular to it, causing a greater repulsive force on nuclei which lie in the direction of the c axis away from the impurity atom. Thus, electrons in states such as Γ tend to increase the axial ratio, the same conclusion as that drawn by Jones. Naturally, a sudden onset of overlap at Γ would cause a change in the excess charge density, which in turn would effect the lattice parameters. The same reasoning gives a conclusion qualitatively the same as Jones's concerning the region K , though the effect of the holes at points V will depend on details of the band structure which are not as easily ascertained.

9. SUMMARY AND CONCLUSIONS

The main purpose of this paper was to investigate the bases of the theories of Jones and Goodenough concerning the change in axial ratios of hexagonal crystals with alloying. As explained in the introduction, the theories are interesting as they seem to afford easy ways of getting information about the band structure. In order to elucidate these theories we carried out two separate investigations which, surprisingly enough, turned out to be rather unrelated.

The first investigation (Secs. 3 through 7) consisted of examining the factors responsible for the deviation of the axial ratios of pure metals from the ideal close-packing value. The major factor found was the "kinetic stress," which resembles the stresses estimated by Jones and Goodenough. In fact, in beryllium the contributions of each one-electron state to the "kinetic stress" are

³⁸ Another kind of argument to show that the "effective sizes" of solute atoms (and thus local displacements) depend upon the relative valency of the solvent and solute has been made by J. H. O. Varley, *Phil. Mag.* **45**, 887 (1954).

³⁹ For a discussion of the validity of the effective-mass approximation as applied to impurity states, as well as a discussion of the character of the exact solutions, see G. F. Koster and J. C. Slater, *Phys. Rev.* **95**, 1167 (1954).

numerically very much like those given by the Jones theory. It is pointed out, however, that the sum of the contributions from all states could be very much different. Two other factors tending to change the axial ratio were found, one of which, the exchange stress, could be appreciable. A rough estimate made of the "effective stress" in beryllium was of the right order of magnitude.

The second investigation concerned the change of the lattice parameters with alloying. It was found that the change in axial ratio with alloying is due to a different mechanism from that proposed by Jones. However, use of the effective-mass theory allowed us to establish a connection between the band structure and the change in axial ratio when the correct mechanism is taken into account. It is remarkable that using the correct method, we draw the same qualitative conclusions concerning

band structure as does Jones! It may be necessary to use a more sophisticated method in order to obtain numerical agreement with experiment, but the effective-mass treatment doubtlessly contains the essential physics. Thus, the most attractive feature of the Jones theory remains, i.e., the possibility of getting information about the band structure from the alloying data.

In the course of the first investigation a formalism was developed which is capable of giving the first-order effect of a homogeneous deformation on the energy band structure. Several possible applications of such a formalism were mentioned in Sec. 4.

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Properties of Germanium Doped with Nickel

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The temperature dependence of electrical resistivity in *p*- and *n*-type nickel-doped germanium crystals indicates that nickel introduces two acceptor levels in germanium at 0.22 ± 0.01 eV from the valence band and 0.30 ± 0.02 eV from the conduction band. Ionization energies deduced from infrared photoconductivity studies at 77°K are in agreement with the values obtained from resistivity measurements. *N*-type samples show higher photosensitivity than *p*-type samples and demonstrate quenching effects. The distribution coefficient for nickel in germanium is about 2.3×10^{-6} .

I. INTRODUCTION

THIS paper presents measurements of electrical and optical properties of germanium crystals containing nickel as the major impurity. Results are similar in most respects to those reported previously for Fe-doped^{1,2} and Co-doped³ germanium crystals. In a paper primarily concerned with the effects of Ni and Cu on carrier lifetime in germanium, Burton *et al.*⁴ have reported low-temperature conductivity and Hall coefficient data which indicated that Ni introduces an acceptor level at about 0.23 eV from the valence band of germanium. This conclusion is confirmed. In addition, evidence is presented indicating that Ni introduces another acceptor level at about 0.30 eV from the conduction band. A summary is given comparing the properties of Fe-, Co-, and Ni-doped germanium crystals.

¹ W. W. Tyler and H. H. Woodbury, *Phys. Rev.* **96**, 874 (1954).

² R. Newman and W. W. Tyler, *Phys. Rev.* **96**, 882 (1954).

³ Tyler, Newman, and Woodbury, *Phys. Rev.* **97**, 669 (1955).

⁴ Burton, Hull, Morin, and Severiens, *J. Phys. Chem.* **57**, 853 (1953).

II. EXPERIMENTAL RESULTS

A. Crystal Preparation

The methods of crystal growth and sample preparation used with Ni-doping experiments were similar to those used in previous work with Fe- and Co-doping.^{1,3} Experimental techniques used in studying the Ni-doped samples have also been described.^{1,2}

Johnson Matthey Company (JM) "spectroscopically pure" Ni and Sigmund Cohn (SC) "chemically pure" Ni were used for doping. Initial experiments using the JM Ni indicated that about 10 percent of the carriers introduced into the Ge crystals as a result of doping were probably due to low ionization energy acceptor impurities in the Ni. The SC Ni proved somewhat more satisfactory either because of a lower concentration of specific low ionization energy acceptor impurities or because acceptor impurities were compensated by donor impurities. Spectroscopic analyses of both sources of Ni indicated "barely detectable" amounts of *B* and "traces" of Al. The SC Ni analysis also indicated a