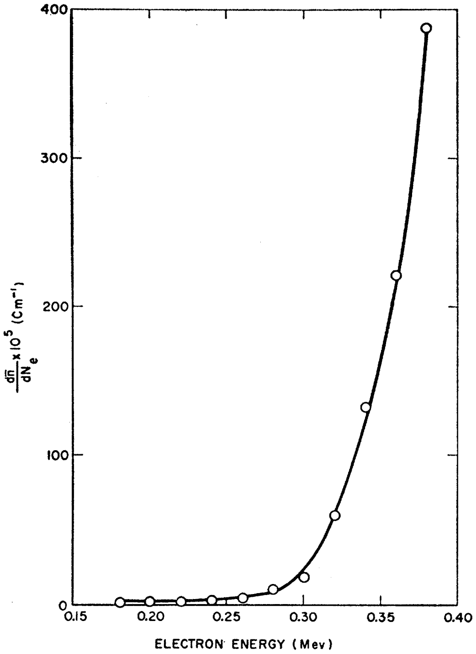

FIG. 1. (Carriers removed per cm^3)/(bombarding electrons per cm^3), $d\bar{n}/dN_e$, as a function of the energy of the bombarding electrons.

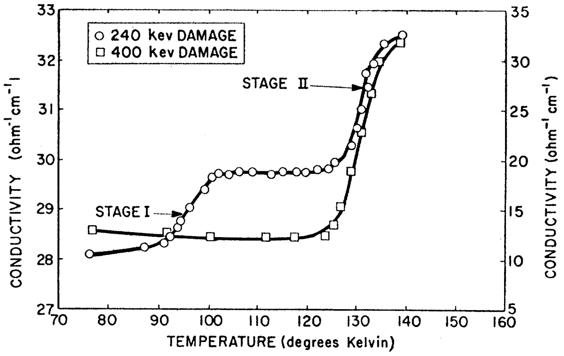

FIG. 2. Isochronal recovery of electron damage produced at 240 kev and 400 kev. The scale on the left is for the 240-kev damage.

isochronal data to obtain activation energies for the recovery of damage,[1] yielding 0.23 ev for Stage I and 0.56 ev for Stage II. The conductivity recovery in Stage I obeyed first-order kinetics and may be due to the recombination of close vacancy-interstitial pairs. Satisfactory interpretation of the isothermal data for Stage II and the unexpectedly large relative difference in the two activation energies has not yet been achieved. Further work is in progress to clarify these points.

ACKNOWLEDGMENTS

We wish to thank Dr. H. P. R. Frederikse of the National Bureau of Standards for supplying the InSb and R. C. Dahleen for preparation of the samples and assistance in making the measurements.

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[1] For a discussion of the method, see C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

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d Bands in the Body-Centered Cubic Lattice

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A model of a crystal, consisting of positive point charges neutralized by a uniform distribution of negative charge, is employed to study the form of the d bands in a body-centered cubic lattice as a function of the lattice spacing. The wave functions are expressed as linear combinations of plane waves and the potential treated as a perturbation. It is shown that the perturbation series for the energy is a power series in Za, where Z is the atomic number and a is the lattice parameter. The leading term in the series is of the order $(1/a)^2$, and the coefficients of successive terms in the series decrease rapidly. The first three terms are evaluated for the states of predominantly d symmetry at the center of the Brillouin zone, and the corner H.

INTRODUCTION

ALTHOUGH there have been many calculations of energy bands in the transition elements,[1] the band structures of these elements are not well understood. Recently it has been proposed that the d-band structure of the body-centered cubic transition elements, iron and chromium, is radically different from that of the face-centered cubic elements, nickel and copper.[2] Experimental information adequate to resolve the problem does not exist. In view of the complexities of careful theoretical computation for these elements, it remains interesting to study a model whose simplicity permits more exact calculation.

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[1] A review of band calculation has been given by J. Callaway, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 99.

[2] N. F. Mott and K. W. H. Stevens, Phil. Mag. **2**, 1364 (1957).

A simple model of crystal, which is not so unreal as to be uninteresting, is that of a body-centered cubic lattice of point charges (atomic number Z), neutralized by a uniform distribution of electrons. The simplicity of this model comes from the fact that the Fourier coefficients of the crystal potential can be calculated exactly, and have a simple analytic form.[3] The choice of body-centered cubic symmetry is made for two reasons: (1) the principal controversy concerns the form of the d bands in crystals of this symmetry, and (2) there are two points in the Brillouin zone where the wave function possesses full cubic symmetry. (There is only one such point for face-centered cubic crystals.)

If $\mathbf{k}$ is a reciprocal vector and Ω_0 is the volume of the unit cell ($\Omega_0=a^3/2$, where a is the lattice parameter), then the Fourier coefficients of potential are (in atomic units)

$$V(\mathbf{k})=-8\pi Z/\Omega_0\mathbf{k}^2 \quad \text{for } \mathbf{k} \text{ not zero,} \tag{1}$$

$$V(0)=-(1.245)Z/a. \tag{2}$$

The potential represented by these Fourier coefficients has cubic rather than spherical symmetry. We have that $k^2=4\pi^2\mathbf{n}^2/a^2$, where $\mathbf{n}^2$ is an even integer. Then

$$V(\mathbf{k})=-4Z/\pi a\mathbf{n}^2. \tag{3}$$

The crystal potential will be treated by perturbation theory. Provided that the unperturbed wave functions are symmetrical linear combinations of plane waves, solution of a secular equation is unnecessary, and ordinary perturbation theory for a nondegenerate state can be employed. The requirement that the perturbation expansion converge towards a state in the d band is, however, a severe one, and restricts greatly the number of states that can be effectively treated in this way. At a general point of the Brillouin zone, the wave function has no symmetry other than that required to satisfy Bloch's theorem. Not only d functions, but s, p, f, $\cdots$ as well are included. The perturbation expansion will converge toward the state of lowest energy of that $\mathbf{k}$ and this will not be a d-band state unless an orthogonality condition is imposed. However, for certain states at symmetry points of the zone, the perturbation expansion will converge toward d-band levels.

The only points of the zone where all of the levels in the d band at those points can be found in this way are the center of the zone, Γ, and the corner H (see Fig. 1). At both of these points, there are two states to be considered: one, triply degenerate, formed from states of xy, yz, or zx symmetries ($\Gamma_{25'}$, $H_{25'}$), and one, doubly degenerate, involving x^2-y^2 or $3z^2-r^2$(Γ_{12},H_{12}).[4] It is likely that a fair idea of the general form of the d band can be obtained by studying the behavior of these states. For instance, at least for reasonably small values of the lattice parameter, the separation between H_{12} and $H_{25'}$ gives a fair estimate of the width of the band.

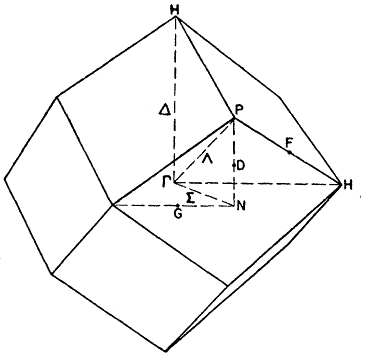

FIG. 1. Brillouin zone for the body-centered cubic lattice. Points and lines of symmetry are indicated.

At the other principal symmetry points of the zone, P and N, there are some states for which the perturbation expansion will yield d-band levels (P_3, N_2, N_3, N_4). But other states at these points mix s and d or p and d functions, so our attention will be restricted to Γ and H.

Considering these points, the results of band calculations[1] indicate that H_{12} is the lowest level, $\Gamma_{25'}$ and Γ_{12} are in the middle, and $H_{25'}$ is the highest level. The separation between $\Gamma_{25'}$ and Γ_{12} is much less than that between H_{12} and $H_{25'}$. The order of the d functions at the center of the zone ($\Gamma_{25'}$ below Γ_{12}) is the opposite of what it is at the corner H. On the other hand, the ideas of Mott and Stevens, and also of Pauling[5] require that the d band should be split into two parts, one band based on functions of $\Gamma_{25'}$ symmetry (presumably the lowest) and the other on functions of Γ_{12} symmetry. Thus a distinction between these types of band structures can be made from a study of these four levels. It was with this object in mind that this investigation was begun.

THEORETICAL FOUNDATION

Perturbation theory is to be employed to calculate the energy levels of an electron in a periodic potential defined through its Fourier coefficients (1) and (2). The unperturbed functions are symmetrized linear combinations of plane waves transforming according to Γ_{12}, $\Gamma_{25'}$, H_{12}, $H_{25'}$. The symmetrized functions were constructed as described in reference 6. The use of symmetrized plane wave combinations removes the necessity to employ degenerate perturbation theory since there are no matrix elements of the crystal potential between combinations of plane waves of different symmetry. The four states enumerated above will be denoted by an index i; and the linear combinations of plane waves possessing a given symmetry are denoted by an index j. The latter are the eigenfunctions of the unperturbed Hamiltonian. The plane wave combination of lowest kinetic energy has $j=0$. The kinetic energy of the plane wave combination j for state i is denoted by E_{ij}. Similarly $V_{i,jk}$ denotes a matrix element of the potential between the plane wave combinations j and

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[3] J. Callaway and M. L. G. Glasser, Phys. Rev. **112**, 73 (1958).

[4] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).

[5] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947); L. Pauling, Proc. Natl. Acad. Sci. U. S. **39**, 551 (1953).

k belonging to symmetry type i. The $V_{i,jk}$ are linear combinations of Fourier coefficients of potential. Then if E_i denotes the perturbed energy of the lowest level of symmetry i, we have to second order in the potential

$$E_i=E_{i0}+V_{i,00}+\sum_j{}' \frac{|V_{i,0j}|^2}{E_{i0}-E_{ij}}. \tag{4}$$

As examples of the combinations of the Fourier coefficients occurring in Eq. (4), the $V_{i,00}$ are given below. In these formulas, $V(\mathbf{n}^2)$ denotes a Fourier coefficient given by Eqs. (2) or (3).

$$\begin{aligned} H_{12}&: \; V(0)-2V(2)+V(4), \\ \Gamma_{25'}&: \; V(0)-2V(4)+V(8), \\ \Gamma_{12}&: \; V(0)-2V(2)+2V(4)-2V(6)+V(8), \\ H_{25'}&: \; V(0)-V(4)-V(8)+V(12). \end{aligned} \tag{5}$$

The orders of magnitude of the successive terms in the perturbation series may easily be determined. The kinetic energy E_{i0} is of the order $1/a^2$. We have seen that the Fourier coefficients of potential are proportional to Z/a. Thus $V_{i,00}$ is of order Z/a, and the second order perturbation is of order Z^2. Each additional term in the expansion introduces a matrix element and another energy denominator in each order. Consequently an additional factor Za is contributed by each order beyond the second. The perturbation series is a power series whose nth term is proportional to $(1/a^2)(Za)^n$. (We count the kinetic energy as the zeroth term.) The quantity $\lambda_i=aE_i/Z$ is then a function of the single variable Za.

RESULTS AND DISCUSSION

The terms of Eq. (4) have been evaluated numerically for the four states considered. In calculating these energies, eight groups of plane waves were included in each case except $\Gamma_{25'}$, for which nine were used. The numbers of plane waves involved are 128, 126, 104, and 108 for $\Gamma_{25'}$, Γ_{12}, $H_{25'}$, and H_{12}, respectively. The second order perturbation is believed to be correct within about one or two percent in each case. The results are, in atomic units:

$$\begin{aligned} H_{12}&: \; E=39.478/a^2-0.2905(Z/a)-0.00267Z^2, \\ \Gamma_{25'}&: \; E=78.957/a^2-0.7679(Z/a)-0.00509Z^2, \\ \Gamma_{12'}&: \; E=78.957/a^2-0.3435(Z/a)-0.00499Z^2, \\ H_{25'}&: \; E=118.43/a^2-0.8740(Z/a)-0.01065Z^2. \end{aligned}$$

The results are shown in Fig. 2, where the dimensionless parameter $\lambda=aE/Z$ is plotted as a function of Za.

In considering these results, we observe first of all that the coefficients of the various terms decrease quite rapidly. This feature can be expected to continue in higher orders of perturbation theory. The size of the matrix element is indicated by the second term in the equations, and no energy denominators smaller than $8\pi^2/a^2$ appear. Thus, the perturbation expansion should be quite well convergent for small Za.

For small values of Za, the series are dominated by the kinetic energy. Band calculations suggest this ordering also obtains for the transition metals at the actual lattice spacing.[1] Thus the much larger separation of the d-band levels at the corner H than at the zone center Γ appears as a consequence of the degeneracy of the latter in the free electron limit.

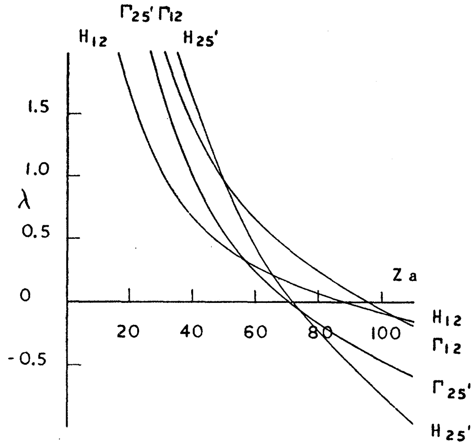

FIG. 2. The dimensionless parameter $\lambda=aE/Z$ is given as a function of Za for the four states considered.

For large Za, the energies of the states must approach the same limit, depending only on Z. Although the perturbation series is certainly numerically unreliable in this limit, the results presented above suggest that the order of the d-band levels, might be quite different for large Za. In order of increasing energy, we might have $H_{25'}$, $\Gamma_{25'}$, Γ_{12}, H_{12}; the order of the levels at the zone corner being reversed. Such a situation, which would correspond to the idea of a d band split into two parts, has been suggested.[2,6] The splitting, in this model, would be a consequence of the nonspherical character of the potential. A numerical calculation, not employing perburbation theory, indicates that the separation does not occur for $Za<50$. Considering this, it seems unlikely that the d band is split in the transition metals at the observed atomic spacing, unless the splitting is brought about by exchange and correlation interactions in some fashion as yet unclear.

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[6] J. Callaway, Phys. Rev. **99**, 500 (1955).