

## *d* Bands in Cubic Lattices. III

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A simple model of an ionic crystal is considered, consisting of a lattice of point charges ( $Z_1e$ ) and ( $Z_2e$ ) arranged in the rocksalt structure, and screened by a uniform distribution of negative charge. This lattice defines a periodic potential in which electron energy levels are calculated. The energies of five states pertaining to the *d* band are calculated, by expansion in symmetrized combinations of plane waves, as functions of the average binding and relative ionicity.

### INTRODUCTION

THIS work is a continuation of studies of energy levels of *d* electrons in the periodic potential of a model crystal.<sup>1,2</sup> The previous work has been concerned with monatomic structures only, with particular attention to the body-centered cubic lattice. A lattice of point charges (atomic number  $Z$ , lattice parameter  $a$ ), screened by a uniform distribution of negative charge has been considered. The energy of an electron state  $E_i$  in this potential may be expressed in atomic units as a function of a single variable, the binding parameter  $Za$ :

$$aE_i/Z = f_i(Za). \quad (1)$$

The object of the calculations has been to determine, for a few states at symmetry points of the Brillouin zone, the function  $f(Za)$ .

The work reported here was suggested by the following considerations: Compounds of the type  $RX$ , where  $R$  is a transition metal and  $X$  is a nonmetal are of considerable interest, both practically and theoretically, with respect to their electric and magnetic properties. The most common crystal structures are of the rocksalt and nickel arsenide types. On the basis of simple band theory, such materials should have unfilled *d* shells, and thus should exhibit metallic conductivity. In fact, many of them do appear to behave as poor metals, a few apparently have a transition between metallic and semiconducting states at the Néel temperature,<sup>3</sup> but some are good insulators, particularly if  $X$  represents oxygen and  $R$  lies beyond chromium in the periodic table. The behavior of materials of the latter sort, such as  $MnO$  and  $NiO$  has not been adequately explained, but probably indicates a failure of the band approximation. It is, however, of considerable interest to examine the predictions of conventional band theory for the entire class of materials. A self-consistent calculation for any one would be extremely laborious with present techniques, but it would seem to be possible to study some very general features of the band structure on the basis of a simple model.

In this calculation, a model crystal consisting of two

kinds of point charges, with atomic numbers  $Z_1$  and  $Z_2$  (we shall always take  $Z_1 \geq Z_2$ ), arranged in the rocksalt lattice, and screened by a uniform distribution of negative charge is considered. In the Wigner-Seitz cell containing a charge  $Z_1$ , there is a net negative charge  $(Z_1+Z_2)/2$ : so that this cell is positively charged. The cell containing  $Z_2$  is negatively charged. We thus have a very simple, although quite unrealistic, model of an ionic crystal. If for fixed  $Z_1$ , we imagine  $Z_2$  to vary between 0 and  $Z_1$ , we pass from the ordinary monatomic face-centered cubic lattice through a range of ionic structures to the simple cubic lattice. The lattice parameter,  $a$ , employed is the shortest distance between two like atoms. In the limit  $Z_1=Z_2$  this parameter has twice the usual value.

The simplicity of this model with respect to the energy band calculation comes from the Fourier coefficients of potential. Note that in a face-centered cubic structure, if we write a reciprocal lattice vector  $\mathbf{K}_n$  as  $(2\pi/a)(n_1, n_2, n_3)$  where  $n_1, n_2, n_3$  are integers (positive or negative); either the  $n_1, n_2, n_3$  are all odd or all even. The Fourier coefficients have the following values:

$$V(K_n) = \frac{-8\pi}{\Omega_0 \mathbf{K}_n^2} (Z_1 + Z_2) = \frac{-8}{\pi a \mathbf{n}^2} (Z_1 + Z_2) \quad \text{if } n_1, n_2, n_3 \text{ are even,} \quad (2)$$

$$V(K_n) = \frac{-8\pi}{\Omega_0 \mathbf{K}_n^2} (Z_1 - Z_2) = \frac{-8}{\pi a \mathbf{n}^2} (Z_1 - Z_2) \quad \text{if } n_1, n_2, n_3 \text{ are odd.}$$

Here  $\mathbf{n}^2 = n_1^2 + n_2^2 + n_3^2$ , and we do not include  $\mathbf{n}=0$ .  $\Omega_0$  is the volume of the (fcc) unit cell.

This ionic crystal model may be described in terms of two parameters: a generalized binding parameter  $(Z_1+Z_2)a$ , and the relative ionicity  $(Z_1-Z_2)/(Z_1+Z_2)$ . The energies of the states,  $E_j$ , in this model may be expressed as functions of these two variables:

$$\frac{aE_j}{(Z_1+Z_2)} = g_j \left[ (Z_1+Z_2)a; \frac{Z_1-Z_2}{Z_1+Z_2} \right]. \quad (3)$$

<sup>1</sup> J. Callaway, Phys. Rev. **115**, 346 (1959).

<sup>2</sup> J. Callaway, Phys. Rev. **120**, 731 (1960).

<sup>3</sup> F. J. Morin, Phys. Rev. Letters **3**, 34 (1959).

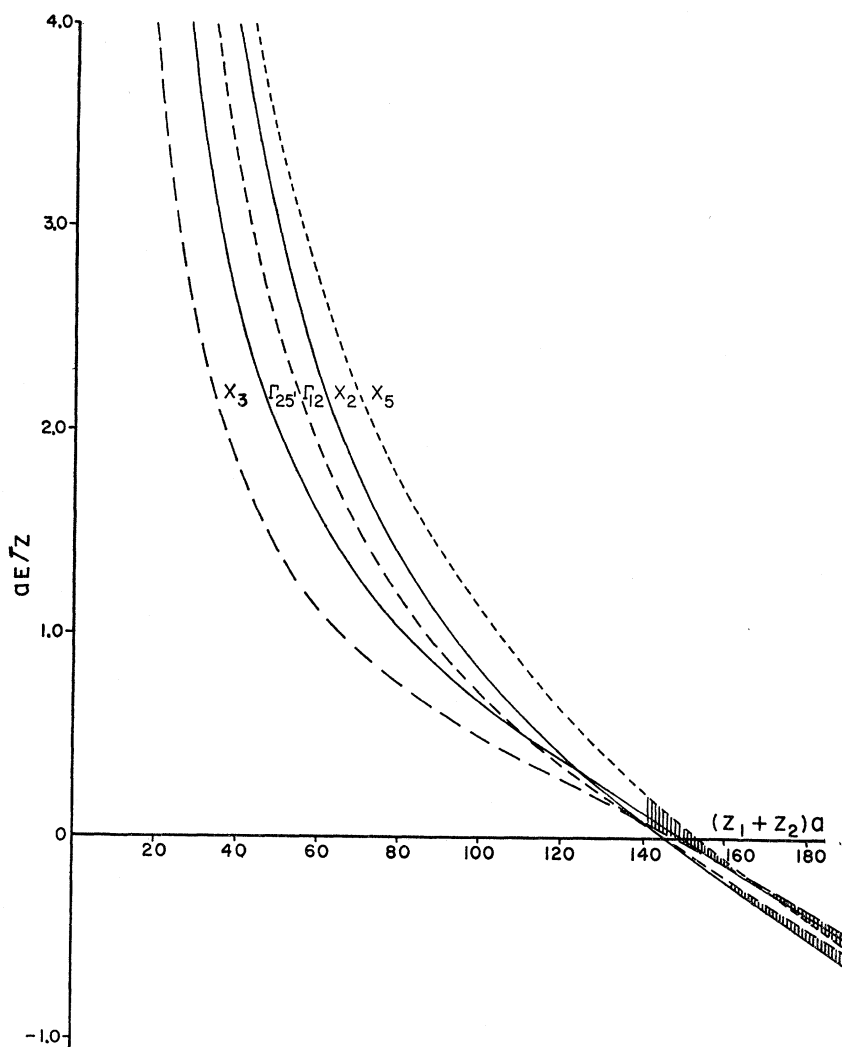


FIG. 1. The energies of five states at  $\Gamma$  and  $X$  are shown as functions of the binding parameter  $(Z_1 + Z_2)a$  for the case  $Z_2/Z_1 = \frac{1}{2}$ .

The objective of the present work is to investigate the general dependence of the energies of  $d$ -like states of high symmetry on the binding and the ionicity, with the hope that some of the qualitative features observed may apply to real systems.

A calculation somewhat similar to this was previously performed by Behringer, who attempted to calculate the dependence on lattice parameter of the energy gap between the last filled and the first empty energy band in  $\text{LiH}$ .<sup>4</sup>

#### PROCEDURE

Since it is the Fourier coefficients of the crystal potential, rather than the potential itself, which have a simple form, the natural approach to the energy band problem is in terms of expansion in plane waves. This method can be usefully applied, however, only to states at points of high symmetry in the Brillouin zone. Since our interest in this work is in  $d$ -band levels, in order to

obtain results valid for reasonably large values of the binding parameter it is necessary to choose states which are orthogonal by reasons of symmetry to all  $s$ - and  $p$ -like "core" states.

The rocksalt lattice is face-centered cubic. The points of highest symmetry in the Brillouin zone are  $\Gamma$ , the zone center, and  $X$ , the center of a square face. A typical point  $X$  has coordinates  $(2\pi/a)(1,0,0)$ . A complication in band calculation typical of crystals with more than one atom per unit cell is that the wave function may have different symmetries about the different atoms. For instance, a wave function  $d$ -like about an atom of type 1 may be  $p$ -like about an atom of type 2.<sup>5</sup> Fortunately, this complication is not present for states at the two symmetry points considered here.

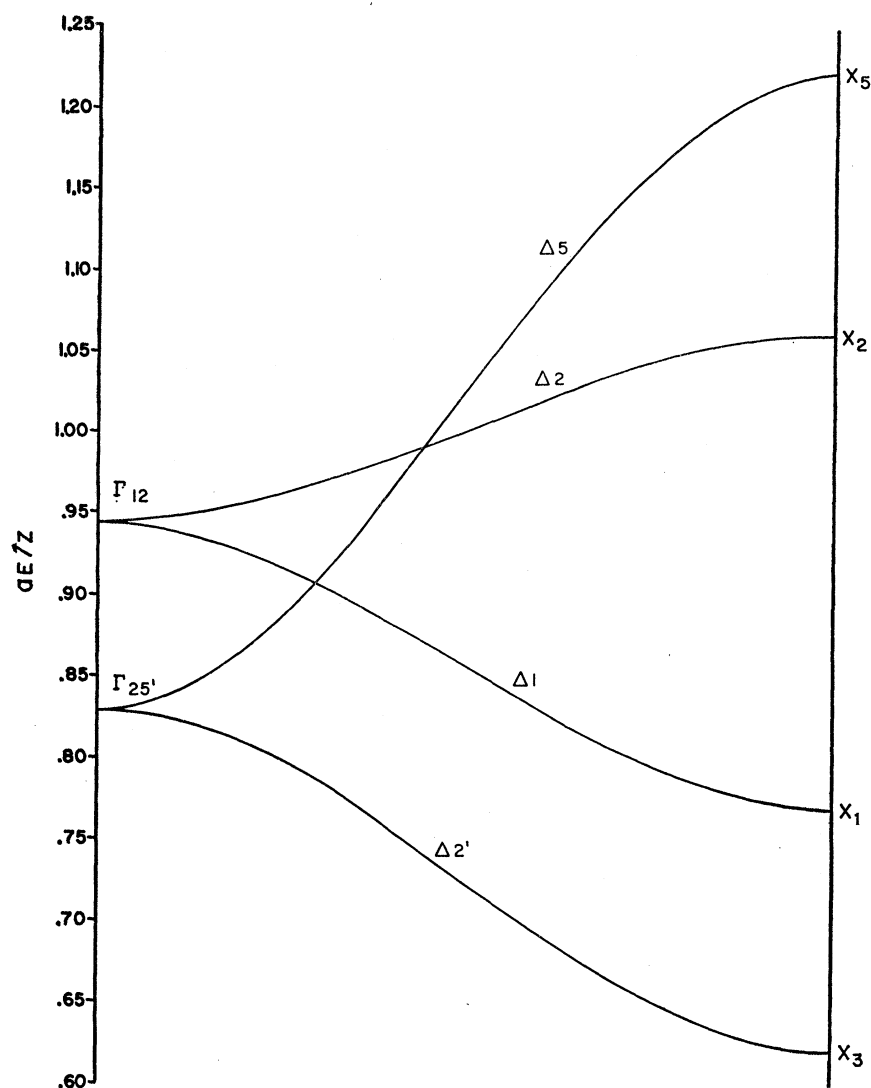
At the center of the zone, the states considered are  $\Gamma_{25}'$  and  $\Gamma_{12}$ , which are triply degenerate and doubly degenerate, respectively.<sup>6</sup> At the point  $X$ , the important

<sup>5</sup> D. H. Ewing and F. Seitz, Phys. Rev. **50**, 760 (1936).

<sup>6</sup> Notation according to L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

<sup>4</sup> R. H. Behringer, Phys. Rev. **113**, 787 (1959).

FIG. 2. Energy bands along the  $[100]$  axis are shown for the case  $(Z_1+Z_2)a=80$ ,  $Z_2/Z_1=\frac{2}{3}$ . The energies of the states  $\Gamma_{25'}$ ,  $\Gamma_{12}$ ,  $X_5$ ,  $X_2$ , and  $X_3$  were determined from the numerical calculation described in the text. The energies of states at intermediate points along the axis, and of the state  $X_1$  were inferred from a tight-binding interpolation scheme.



levels are  $X_5$  (doubly degenerate);  $X_3$ , and  $X_2$  (non-degenerate). The symmetries of the levels are:  $\Gamma_{25'}$  ( $xy, yz, zx$ );  $\Gamma_{12}$  ( $x^2-y^2, 3z^2-r^2$ );  $X_3$  ( $yz$ );  $X_5$  ( $xz, xy$ ); and  $X_2$  ( $y^2-z^2$ ). The state  $X_1$  also belongs to the  $d$  band; but also contains an  $s$ -like part. The energy of this state cannot be obtained by the present technique. Although knowledge of the energy of these five states is, of course, insufficient to characterize the  $d$  band in detail, it is possible to make reasonable estimates of bandwidth and band splittings. For example, for not too large values of the binding parameter, the  $d$  bandwidth is approximately the difference of the energies of the states  $X_5$  and  $X_3$ . For large values of the binding parameter, crystal field effects may be expected to split the  $d$  band into sub-bands based on functions of  $t_{2g}$  and  $e_g$  symmetries. The sub-band widths may, in principle, be roughly estimated from the energies of these states.

Symmetrized plane wave combinations were con-

structed for the states of interest, including all plane waves with  $[(a/2\pi)k]^2 \leq 32$  for the states at the zone center and waves with  $[(a/2\pi)k]^2 \leq 30$  for states at  $X$ . The matrix elements of the Hamiltonian on the basis of these functions were constructed as described in reference 1. If, in accord with Eq. (3) we consider  $[a/(Z_1+Z_2)]H$ , where  $H$  is the Hamiltonian for one electron in the periodic potential, the matrix elements have a very simple dependence on the binding parameter and relative ionicity. For states at  $\Gamma$  and  $X$ , the diagonal terms are of the form  $A/(Z_1+Z_2)a+B$ . The first term represents the kinetic energy.  $B$  (which is independent of the variables) comes from the expectation value of the potential obtained with a symmetrized combination of plane waves.  $A$  is of order of magnitude 100, while  $B$  is of order of magnitude 1. There are two types of off-diagonal matrix elements according as they are formed as linear combinations of Fourier coefficients of the potential with even or odd wave vectors. Those

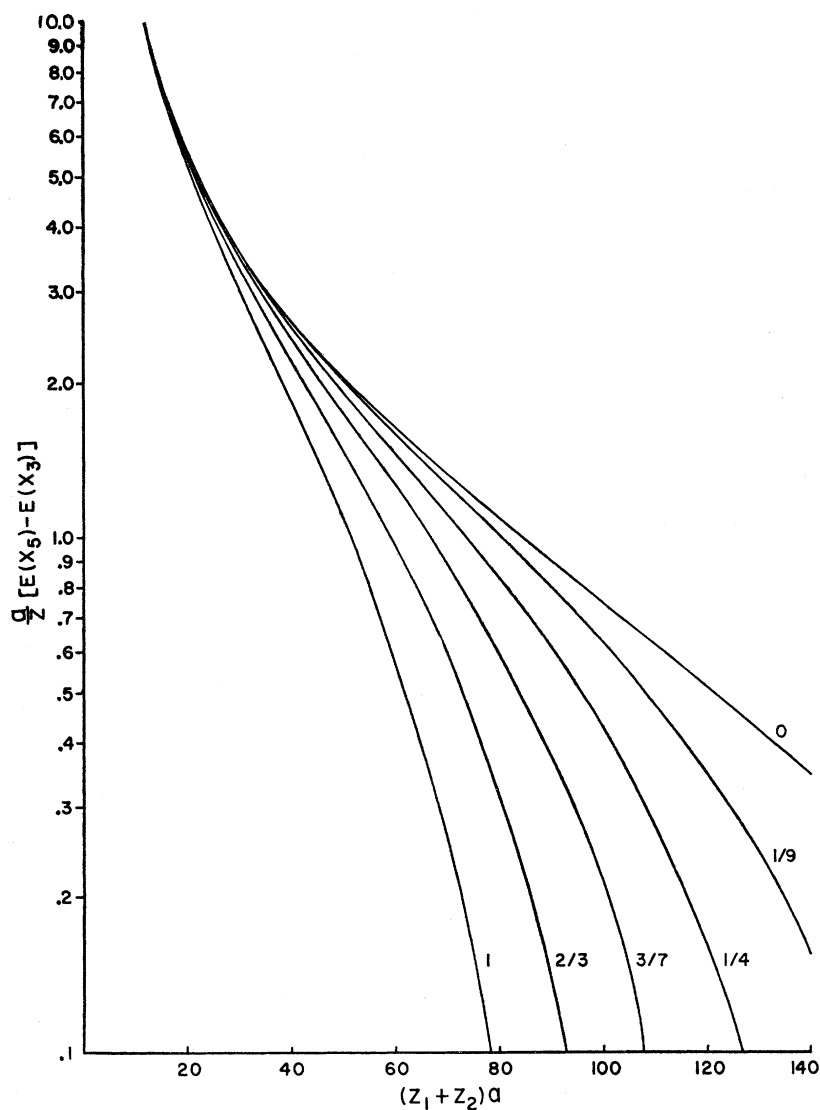


FIG. 3. Variation of  $d$ -band width with binding parameter. Each curve is labeled according to the appropriate value of the relative ionicity  $(Z_1 - Z_2)/(Z_1 + Z_2)$ .

based on even wave vectors do not depend on either basic parameter; those based on odd wave vectors are of the form  $C (Z_1 - Z_2)/(Z_1 + Z_2)$ .

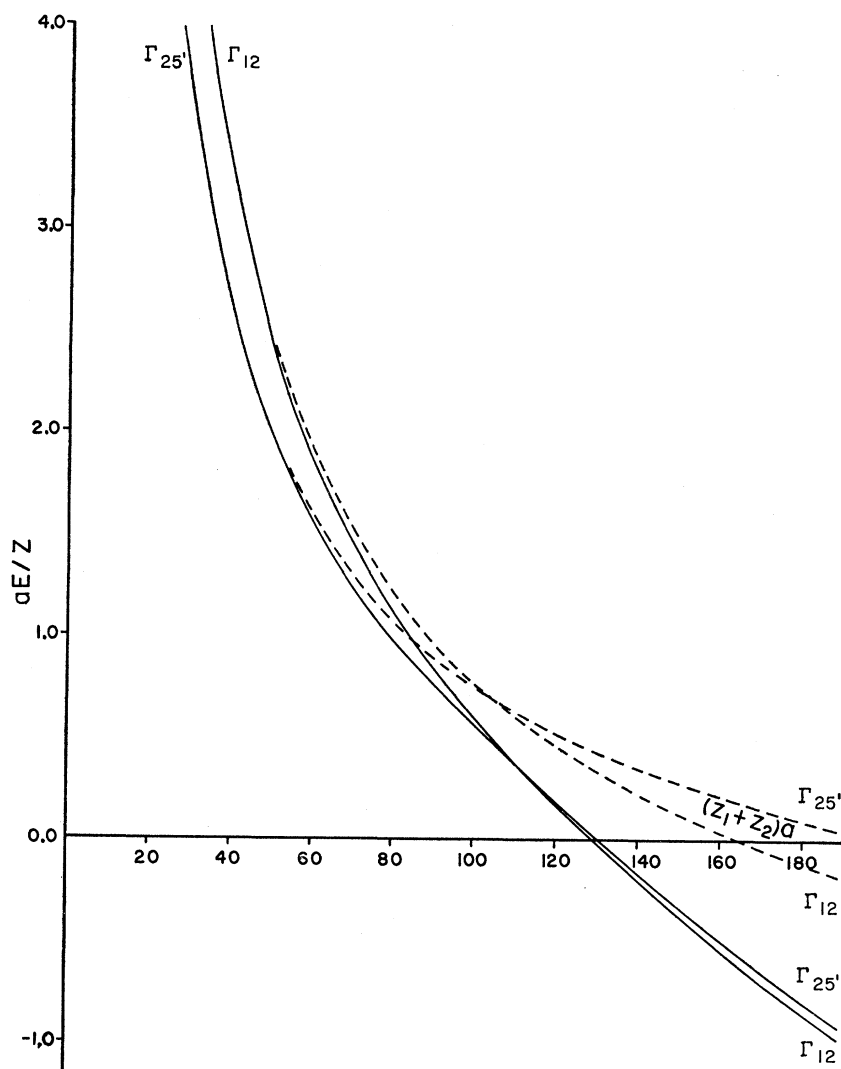
It is possible to obtain perturbation series solutions for the energy of the states, treating the crystal potential as a perturbation, in analogy with the results of references 1 and 2. These will be discussed in the next section. Since it was desired to have results valid beyond the region of relatively small binding parameters for which the perturbation series applies, the lowest eigenvalue of the appropriate Hamiltonian matrix was determined numerically for each of the states considered. Calculations were made for fifteen different values of the binding parameter lying between ten and two hundred:  $(Z_1 + Z_2)a = 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180, 200$ . For each value of the binding parameter, six values of the relative ionicity  $(Z_1 - Z_2)/(Z_1 + Z_2) = 0, 1/9, 1/4, 3/7, 2/3, 1$  were considered. These values were chosen to correspond to

values of the ratio of the charge on the different atoms  $Z_2/Z_1 = 1, 4/5, 3/5, 2/5, 1/5, 0$ . In all, the energy of each of the five basic states was determined for ninety different values of the parameters.

The calculation was performed on an IBM-704 computing machine at the Westinghouse Laboratories in East Pittsburgh. The expressions for the matrix elements as functions of the binding parameter and relative ionicity were given to the machine, which evaluated the matrix elements as required and calculated the lowest eigenvalue and eigenvector by a standard process. The computation required about twenty minutes of machine time in all.

In the limit  $Z_2 = Z_1$  for which the lattice becomes simple cubic, the solutions may still be obtained from the same expansions. However, the labelling of some of the states changes: The level previously referred to as  $\Gamma_{25}'$  becomes  $R_{25}'$  and  $X_3$  becomes  $M_3$ . The other states retain their original designation.

FIG. 4. Comparison of the perturbation series and numerical solutions for the case  $Z_2/Z_1 = \frac{3}{5}$ . The perturbation solutions are represented as dashed lines.



### RESULTS

The results of the perturbation series are presented for the states  $\Gamma_{25'}$  and  $\Gamma_{12}$ , including the second-order perturbation. The computation was carried out in the manner described in reference 1.<sup>7</sup> The results for the other states are similar to those given here. The relative

$$\frac{aE(\Gamma_{25'})}{(Z_1+Z_2)} = \frac{118.43}{(Z_1+Z_2)a} - 0.3045 - 0.00113(Z_1+Z_2)a \times \left[ 1 + 3.28 \left( \frac{Z_1-Z_2}{Z_1+Z_2} \right)^2 \right] + \dots, \quad (4)$$

<sup>7</sup> An average crystal potential was computed for a simple cubic lattice of charge  $\frac{1}{2}(Z_1+Z_2)$  per cubic unit cell. The result,  $V(0) = (-0.5236/a_e)(Z_1+Z_2)$ , where  $a_e$  is the lattice parameter of the cubic lattice, was employed in this calculation. There is, however, some ambiguity in the determination of  $V(0)$ : See J. L. Birman, J. Phys. Chem. Solids **6**, 65 (1958). The assumed  $V(0)$  does not affect, in any way, the relative position of the bands.

$$\frac{aE(\Gamma_{12})}{Z_1+Z_2} = \frac{157.91}{(Z_1+Z_2)a} - 0.5697 - 0.00205(Z_1+Z_2)a \times \left[ 1 + 5.66 \left( \frac{Z_1-Z_2}{Z_1+Z_2} \right)^2 \right] + \dots \quad (5)$$

ionicity appears in the second-order term<sup>8</sup> and there enters quadratically and in conjunction with the binding parameter. The bandwidth decreases with increasing ionicity: this decrease becomes more important as the binding parameter increases. These results, suggested by perturbation theory, are confirmed by the more accurate calculation.

In Fig. 1, the dependence of the energies of the five states considered on the binding parameter  $(Z_1+Z_2)a$  is shown for the case  $Z_2/Z_1 = 4/5$ . The general form of

<sup>8</sup> This result is in agreement with a suggestion made by Herman in a different connection: F. Herman, J. Electronics **1**, 103 (1955).

the curves is typical also of the other ionicities considered. It will be observed that the band structure must be qualitatively quite different in the limit of tight binding from what it is for small binding parameters. In the latter case, the ordering of levels conforms to that of  $d$  levels in an empty face-centered cubic lattice. This structure is believed to be characteristic of face-centered cubic metals (see, for instance, the tight-binding calculation of energy bands in nickel by Fletcher<sup>9</sup> and the cellular-method calculation of energy bands in copper by Howarth<sup>10</sup>).

The qualitative similarity between these results and those of Fletcher in the limit of small binding parameters suggests that the tight-binding interpolation scheme of Slater and Koster<sup>11</sup> could be used to sketch the form of the bands. The energies of five states give just enough information to determine the five parameters required for the tight-binding approximation including first neighbor interactions between like atoms (crystal field effects are included by allowing different  $k$  independent terms for the  $\epsilon_g$  and  $t_{2g}$  states in the diagonal matrix elements of the effective Hamiltonian). As an illustration of this procedure, the energy bands along the  $[100]$  axis are shown in Fig. 2 for the case  $Z_2/Z_1=2/5$ ,  $(Z_1+Z_2)a=80$ .

For fixed binding parameter, the bandwidth decreases with increasing values of the relative ionicity. In Fig. 3, the bandwidth is shown as a function of binding parameter for each of the values of the relative ionicity considered in this calculation, in the region in which the bandwidth may be approximately defined as the difference between the energies of the states  $X_5$  and  $X_3$ .

In the limit of large binding parameter, it will be observed from Fig. 1 that the band is split into sub-bands, with  $\epsilon_g$  states lying below the  $t_{2g}$  ones. This effect is presumably due to the cubic components of the crystal field. Following the calculation of Callaway and Edwards,<sup>12</sup> the crystal field splitting can be estimated for this model: Define

$$\Delta E = E(t_{2g}) - E(\epsilon_g) = -10D_q, \quad (6)$$

where  $D_q$  is the conventional crystal field parameter, and assume that the  $d$  electrons have hydrogenic radial wave functions (centered on an atom of type 1).

$$R_d = (\alpha^7/6!)^{1/2} r^2 e^{-\alpha r}. \quad (7)$$

It is found in the limit of large  $\alpha a$  that

$$\frac{\alpha \Delta E}{(Z_1+Z_2)} = \frac{2.39 \times 10^5}{(\alpha a)^4} \left[ 1 - 1.152 \frac{Z_1 - Z_2}{Z_1 + Z_2} \right]. \quad (8)$$

The crystal field splitting is positive; the  $t_{2g}$  states lie above the  $\epsilon_g$  ones for  $(Z_1 - Z_2)/(Z_1 + Z_2) < 0.87$ . It

should be observed that the splitting here is opposite in sign here to that usually observed in real crystals and also opposite to the more usual point-charge model, which has  $Z_2 = -Z_1$ . [That case may, however, be studied as a limiting case of Eq. (8).] The convergence of the band calculations does not seem to be good enough in this region to make reasonable estimates of the sub-band widths.

In Fig. 4, the perturbation expansions for the states  $\Gamma_{12}$ ,  $\Gamma_{25}'$  are compared with the numerical solutions for the case  $Z_2/Z_1=3/5$ . The perturbation series is quite accurate for small binding parameters, and holds reasonably well out to about  $(Z_1+Z_2)a=90$  according to the criterion of 20% difference between the energies as determined by the different methods. The point of crossover of the  $\Gamma_{12}$  and  $\Gamma_{25}'$  levels is given reasonably well from the perturbation theory. Comparison of the series and the numerical solutions as functions of the relative ionicity yields curves of qualitatively similar form, except that for fixed binding parameter, the relative accuracy of the perturbation expressions decreases with increasing values of the relative ionicity. For instance, for  $Z_2/Z_1=1/5$ , the point of 20% difference between the perturbation and the numerical results occurs for  $(Z_1+Z_2)a=60$ . This result seems quite reasonable qualitatively since increasing the charge on one atom hastens the formation of a "bound state." It is quite likely that a similar result holds for the convergence of the truncated plane wave expansions: that the convergence becomes poorer as  $Z_2/Z_1$  decreases. It does not, however, appear to be possible to make precise statements about the convergence of the expansions.

## CONCLUSIONS

The model crystal considered here is so simple in comparison with actuality that quantitative predictions about the band structure of real materials cannot be made on this basis. Qualitative features which may be valid in the more complicated cases of the sort discussed briefly in the introduction are the following:

- (1) The  $d$ -band structure in the limit of fairly weak binding should be similar to that of a face-centered cubic metal.
- (2) Effects of the relative ionicity enter quadratically for small ionicities.
- (3) The bandwidth decreases with increasing difference between the atomic numbers, other parameters being fixed.
- (4) In the tight-binding limit, the  $d$  band is split into separate sub-bands by the crystal field.

## ACKNOWLEDGMENTS

The author is greatly indebted to Dr. A. E. Fein of the Westinghouse Research Laboratories, who prepared the computer program for this calculation.

<sup>9</sup> G. C. Fletcher, Proc. Phys. Soc. (London) **A65**, 192 (1952).

<sup>10</sup> D. J. Howarth, Proc. Roy. Soc. (London) **A220**, 513 (1953).

<sup>11</sup> J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

<sup>12</sup> J. Callaway and D. M. Edwards, Phys. Rev. **118**, 923 (1960).