

### III. SOLID STATE PHYSICS

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#### A. EXTENSION OF THE ENERGY BAND THEORY

1. The application of energy band theory to antiferromagnetism is being considered, with particular application to MnO and related oxides which have been studied by neutron diffraction by Shull at Oak Ridge. At least some of these antiferromagnetic oxides, NiO in particular, are semiconductors or insulators, and Mott (1) has assumed that this means that the energy band method is inapplicable to them, on the assumption that the energy band theory would lead to a single band for the 3d electrons, capable of holding ten such electrons, whereas NiO has only eight 3d electrons per Ni atom. Hence he considers that the band would be only partly filled, and NiO should be a conductor. To investigate this situation, the writer is looking into possible sources of splitting the 3d band into sub-bands, such that the available electrons in NiO would just fill certain sub-bands, leaving an energy gap below the next empty bands, and being an insulator. Two sources of splitting into sub-bands are being considered. First, in a ferromagnetic or antiferromagnetic material, different Hartree-Fock potentials should be used for the electrons of the two spins. The exchange correction to the potential for an electron of given spin depends on the density of electrons of that spin; and if there is an unbalanced magnetic moment in an atom, the Hartree-Fock potential for electrons of the spin pointing in the direction of this magnetic moment is lower than for electrons with opposite spin. This correction is usually considered only as a perturbation energy, in connection with multiplet calculations, but should properly come into the potential and hence the Schrödinger equation. In an antiferromagnetic, then, in which the spins show a unit cell twice as great in each direction as is shown by the ordinary crystal structure, the Hartree-Fock potential for electrons of a given spin will likewise show this double unit cell. This in turn will split the energy bands in two, the lower sub-band accommodating five d electrons per atom of one spin, the other one accommodating five of the other spin. MnO is a particularly simple case, since it contains just five 3d electrons per atom, which presumably fill the lower sub-band. Self-consistent field calculations are being made for MnO, and have been carried far enough to see that this splitting of the band will have a magnitude of the order of a number of volts. The calculations also have been carried far enough to show that the 3d electrons of Mn have wave functions which overlap the oxygen atoms so much that it is not hard to see why an Mn atom can have antiferromagnetic interactions with neighbors at a considerable distance.

A second source of splitting of the 3d band into sub-bands, which presumably is operative in NiO, is that arising from the cubic field in the crystal (which has the NaCl

structure). This would split the band into one sub-band holding three electrons, another holding two. It seems not inconceivable that in NiO the latter lies highest and is empty, leaving a gap between it and the lower filled levels, and hence explaining the insulating property. Detailed calculations have not yet been made.

2. The splitting of the d band in a cubic field is being looked into by Mr. W. H. Kleiner, in connection with the problem of paramagnetic resonance in the potassium and ammonium chrome alums, under investigation by Prof. Kip and students. The theory of this splitting has so far been investigated **only from the standpoint** of the group theory, by Bethe, and by Van Vleck and his school. To get a better physical insight into the problem, we are starting with the one-electron 3d functions, with their splitting in a cubic field (such as one approximately has in the alums on account of the six water molecules surrounding the  $\text{Cr}^{+++}$  ion) into a three-fold and a two-fold level, as mentioned in the preceding section. Starting with these one-electron functions, we are building up the whole multiplet theory, as in ordinary spectrum theory, with the addition of the cubic perturbation and eventually of other perturbations as well. It is hoped in this way that it may be possible to throw light on certain complications which Prof. Kip is finding in the experiments. At the same time, we hope to make a close connection between the paramagnetic theory and the antiferromagnetic case, in each of which the iron group ion is surrounded by six neighboring oxygen ions, in about the same arrangement. It is hoped that the perturbed multiplet structure derived from this theory may be applied to the study of the absorption spectra of the iron group salts. They, of course, are known to show bright colors.

3. Considerable attention is being given to the problem of the solution of the Schrödinger equation in a crystal. As a first step, to make the problem spherically symmetrical, we can imagine averaging the potential acting on an electron in the neighborhood of an atom or ion in the crystal over spheres with the atom as a center, and solving Schrödinger's equation in the resulting spherically symmetrical field. This is presumably the best starting point for a calculation of wave functions in the periodic potential by the cellular method introduced by the writer in 1934; it also is the best starting point for wave functions for studying the effect of a cubic field, as in the preceding paragraph.

This method can also be used for an atom in a liquid, where the averaging over orientations is practically necessary, and the method is being applied by Miss Hilda Hsieh, under the direction of Prof. P. M. Morse, to the problem of a very dense gas of a light element, so dense that the electrons are forced out of quantized levels into an energy band. A self-consistent problem is being solved, using a spherically averaged potential, so that the electrons reduce to a free electron gas at a distance from the atom in question. A solution then is found for the potential and charge density in the atom, independent of its neighbors.

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It seems not impossible that this method may have some application to the electronic structure of an atom of one metal immersed in another metal, in an alloy. X-ray evidence, particularly from Miss Cauchois, has recently shown that the emission spectrum of such an atom in an alloy is almost identical with that of the same atom in a pure metal, as if it carried its electronic structure around with it when it was alloyed. A method like that being used by Miss Hsieh gives information about the behavior of a single atom immersed in a sea of others, without regard to the precise arrangement of the others, and this may be what is wanted for this problem.

4. Löwdin (2) has recently suggested the use of orthogonal atomic orbitals for molecular calculations. These orbitals are similar to those introduced by Wannier in 1936 for the study of crystal problems. Since most of the difficulty associated with the Heitler-London method for molecules arises on account of the nonorthogonality of atomic orbitals, it is an attractive possibility, suggested by Löwdin, that if we set up a Heitler-London method starting with the orthogonal atomic orbitals instead of the usual functions, we might avoid these difficulties. The writer has looked into this possibility, and finds that unfortunately it does not work out. By using the simple case of the hydrogen molecule as an example, we show that one can, it is true, set up a formal analogy to the Heitler-London theory, but the state which in that theory is the ground state of the molecule proves in this revised theory to show no molecular binding at all. The reasons for this, together with various interesting relations between the molecular orbital method and the Heitler-London method, are discussed by the writer in a note submitted to the Journal of Chemical Physics.

#### References

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J. C. Slater

### B. SELF-CONSISTENT CALCULATIONS FOR $\text{Cu}^+$

The calculation of the self-consistent field for  $\text{Cu}^+$  has been completed. The results obtained are based upon the atomic wave functions furnished by the differential analyzer. These wave functions can be improved considerably by supplementing the work of the analyzer by a method to be mentioned later. The object of the self-consistent method is to achieve an agreement between the assumed potential field of the atom and the potential field calculated on the basis of this assumption. The following table indicates the results obtained.

Log r	Initial $2Z_p$	Calculated $2Z_p$
-4.20	54.10	53.79
-3.20	48.80	48.78
-2.80	45.28	44.04
-2.00	35.46	33.51
-1.20	22.95	22.05
-0.60	12.47	12.54
0.00	4.72	5.02

A great deal of work has been done in examining methods by which the results given by the differential analyzer might be improved. One can, of course, write Schrödinger's equation in the form of a set of simultaneous difference equations. This method has been studied and some valuable conclusions drawn as to the effect of the interval between successive points on the final result. On the whole, however, this method did not prove satisfactory. One can solve Schrödinger's equation as an integral equation and refine the results by iteration. This method has been closely examined and shows considerable promise. The main advantage of this scheme from the computing point of view is the ease of hand computation and the rapidity of convergence of the iterated wave functions. Further work is being done on this method.

An inquiry has been conducted in an effort to find the most efficient combination of methods and high-speed computing machines for the purpose of self-consistent field calculations. One must, in such an investigation, break down the solution of the differential equation involved into a series of mechanical steps which can be duplicated by digital or analog machines. These so-called algebraised procedures must be tested by hand calculation before one attempts to program them for a particular machine.

Four methods for solving Schrödinger's equation have been examined. They are the simultaneous difference equations method, the direct numerical integration of Schrödinger's equation, the method of iterated integral equations, and the Runge-Kutta method. The evaluation of these methods is nearing completion and it is hoped that the results obtained will make possible self-consistent calculations for a large number of complex atoms.

G. W. Pratt, Jr.

### C. ENERGY BANDS IN SOLIDS

The determinantal equation given in the Quarterly Progress Report, October 15, 1950, has been found to be incorrect. As was pointed out by the writer then, this equation is the solution of the boundary-value problem involved in Slater's method (i. e. the electronic wave functions and their radial derivatives are made continuous at the boundaries of the spheres surrounding the atoms of the crystal). On the other hand, this equation gives no assurance that the wave functions will satisfy Schrödinger's equation in the regions outside the spheres, and therefore must be considered wrong.

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Slater's solution (see Phys. Rev. 51, 846, 1937) does not suffer from this defect and is quite correct. It can be shown that it gives the correct free-electron energy dependence in the case of the empty lattice (i. e. constant potential).

The practical value of Slater's method in numerical calculation will be dependent upon the rapidity with which the roots of his determinantal equation converge (as the order of the determinant is increased). For energies where the wave vector has some of the symmetries of the reciprocal lattice, this convergence can be greatly facilitated by a suitable transformation of the determinant. In general, however, it appears that the question of convergence must be settled by testing each particular case numerically. At present calculations are beginning on the lithium crystal. R. H. Parmenter

#### D. THEORY OF MOLECULAR OXYGEN

As is usual in problems of multiplet structure, we are concerned with the solution of a secular equation obtained from the condition that a linear combination of certain many-electron determinantal wave functions be an eigenfunction of our molecular Hamiltonian. The elements of these determinants are single-electron wave functions; out of the set of 2p atomic wave functions we form what we consider suitable molecular wave functions with which we perform the perturbation calculation.

The use of a Heitler-London method means that we take as our molecular functions the atomic functions themselves; we assign each electron to a hydrogenic orbital centered about one of the ion cores. Using the notation

$$\begin{aligned} p_0 &\sim r_A \cos \theta_A e^{-\frac{\kappa r_A}{2}} & p'_0 &\sim r_B \cos \theta_B e^{-\frac{\kappa r_B}{2}} \\ p_+ &\sim r_A \sin \theta_A e^{-\frac{\kappa r_A}{2}} e^{i\phi} & p'_+ &\sim r_B \sin \theta_B e^{-\frac{\kappa r_B}{2}} e^{i\phi} \\ p_- &\sim r_A \sin \theta_A e^{-\frac{\kappa r_A}{2}} e^{-i\phi} & p'_- &\sim r_B \sin \theta_B e^{-\frac{\kappa r_B}{2}} e^{-i\phi} \end{aligned}$$

where A and B denote the ion cores, the elements of our antisymmetrical many-electron wave functions are simply a selection of eight of these atomic orbitals multiplied by spin functions. The trouble with this approach is that we have to use nonorthogonal functions; keeping track of overlap integrals becomes a bewildering job in the attempt to formulate the secular determinant completely.

It is always possible to construct orthogonal functions from a set of nonorthogonal functions by taking appropriate linear combinations. Replacement of the atomic orbitals by orthogonal functions constructed in this way must give the same answers to the

complete solution of the secular equation. We are only performing an identity operation on any determinantal wave function by adding multiples of rows or columns. We shall discuss two ways of getting orthogonal functions from the nonorthogonal atomic function; the Bloch-Mulliken method of linear combinations of atomic orbitals (l. c. a. o. 's) and the introduction of orthogonalized atomic orbitals (o. a. o. 's).

Consider  $p_o$  and  $p_o'$ . We want two linear combinations of these which shall be orthogonal to one another.

$$\begin{aligned} a p_o + b p_o' \\ c p_o + d p_o' \end{aligned}$$

Each of these functions is already an eigenfunction of  $L_z$ , the z-component of total orbital angular momentum. The demands for orthogonality and normalization give three equations for the four coefficients. The fourth equation will be that one which tells how these functions behave under the interchange of nuclei. We derive the l. c. a. o. 's by stipulating that one function be symmetrical, the other antisymmetrical under this operation:

$$\begin{aligned} \phi_o &= e(p_o + p_o') \\ \chi_o &= f(p_o - p_o') \end{aligned}$$

The o. a. o. 's are derived by the requirement that the interchange of nuclei sends one function into the other.

$$\begin{aligned} a_o &= c_{11} p_o + c_{12} p_o' \\ a_o' &= c_{12} p_o + c_{11} p_o' \end{aligned} .$$

The o. a. o. 's bear the same relation to the l. c. a. o. 's as do the spin eigenfunctions of  $\sigma_x$  to those of  $\sigma_z$ . Physically, an l. c. a. o. represents charge distributed equally between the two ion cores. As for the o. a. o. 's, we choose the roots of an ensuing quadratic equation such that  $c_{11} \rightarrow 1$  and  $c_{12} \rightarrow 0$  as the internuclear distance becomes infinite. In this way we retain the Heitler-London character of our set-up; the charge distribution favors one ion core, and correspondence with the separated atom state can be seen by inspection. Moreover, the writing down of matrix elements using o. a. o. 's appears to be simpler. In any case the perturbation problem has been set up using them.

Work has progressed to the point where calculation of integrals is called for. The difficult integrals are those in which the integrand is a product of wave functions centered about different nuclei. The use of ellipsoidal coordinates for certain integrals and the technique of expansion about one core of the wave function centered about the other core for the others should get them all evaluated.

A. Meckler

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E. ON THE FERROELECTRICITY OF THE  $\text{TiO}_6$  COMPLEX

It has been suggested that in  $\text{BaTiO}_3$  the spontaneous polarization arises from a combination of the high polarizability of the  $\text{TiO}_6$  octahedra with the (rather high) polarizability of the BaO (see reference 1 and 2). Moreover, it is evident that the BaO is relatively unimportant in its effect on the dielectric constant, for the isomorphous replacement of barium by strontium has little effect on the critical temperature, after correction is made for the change of volume with substitution (3). This result is confirmed by the detailed calculations of Slater (4), which showed that, at the critical temperature, the polarization resulting from the barium ions was about five percent of the total polarization in magnitude, but opposite in direction. It was thought to be of interest, therefore, to compute the dielectric constant of a fluid of (hypothetical)  $\text{TiO}_6$  complexes, to see whether this complex alone can give rise to ferroelectric behavior. In this computation Slater's method is used to obtain exactly the Lorentz correction for the interaction of the atoms of a given complex with one another, but the usual isotropic Lorentz correction is used for the interaction of different complexes. The complexes are practically spherical in shape, and so the isotropic Lorentz correction can be expected to apply to this situation.

In applying Slater's method to this problem, we start by writing the effective or local field acting on each atom of the complex in the form

$$\text{Field on atom } i = E + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \frac{3p_j \cdot r_{ij} \frac{r_{ij} - r_{ij}^2}{r_{ij}^5} p_j}{r_{ij}^5} \quad i, j = 1, \dots, 7 \quad (1)$$

where the electric dipole moment  $p_j$  of atom  $j$  is given by

$$p_j = (\text{polarizability of atom } j)(\text{field on atom } j) \quad (2)$$

and mks units are used throughout. (To transform to Gaussian units we simply replace  $1/\epsilon_0$  by  $4\pi$ .) The polarizability of the titanium atom is the sum of the electronic polarizability  $a_{\text{Ti}}$  and the ionic polarizability  $a'_{\text{Ti}}$ , whereas that of the oxygen atoms is taken to be just the electronic polarizability  $a_0$ . In the numerical work which follows, the electronic polarizabilities were assumed, following Slater, to be

$$\frac{a_{\text{Ti}}}{\epsilon_0} = 2.34 \times 10^{-24} \text{ cm}^3, \quad \frac{a_0}{\epsilon_0} = 30.0 \times 10^{-24} \text{ cm}^3 \quad (3)$$

and the ratio of ionic to electronic polarizability of titanium was introduced as a parameter,  $a'_{\text{Ti}}/a_{\text{Ti}} = \lambda$ . (For  $\text{BaTiO}_3$ , Slater found that  $\lambda = 5.09$ .)

The  $\text{TiO}_6$  complex has such symmetry (octahedral) that the polarizability ellipsoid reduces to a sphere, and so it suffices to solve Eqs. 1 and 2 for the special case in

which the applied field is along a Ti-O bond direction. We introduce a cartesian coordinate system with origin at the titanium atom and Z-axis in the field direction; then we must distinguish between the two oxygen atoms at  $(0, 0, \pm \ell)$ , which we call oxygen atoms of type a, and the other four, which we call oxygen atoms of type b. Under these conditions Eqs. 1 and 2 reduce to the following:

$$\begin{aligned}
 p_{\text{Ti}} &= (1 + \lambda) a_{\text{Ti}} E + \frac{(1 + \lambda) a_{\text{Ti}}}{4\pi \epsilon_0} \frac{4}{\ell^3} (p_{\text{Oa}} - p_{\text{Ob}}) \\
 p_{\text{Oa}} &= a_o E + \frac{a_o}{4\pi \epsilon_0} \frac{1}{\ell^3} (2p_{\text{Ti}} + \frac{1}{4} p_{\text{Oa}} + \frac{1}{\sqrt{2}} p_{\text{Ob}}) \\
 p_{\text{Ob}} &= a_o E + \frac{a_o}{4\pi \epsilon_0} \frac{1}{\ell^3} (-p_{\text{Ti}} + \frac{1}{2\sqrt{2}} p_{\text{Oa}} - \frac{4\sqrt{2} + 1}{8} p_{\text{Ob}}) \quad (4)
 \end{aligned}$$

with all dipole moments in the field direction.

The solution of this last set of equations is

$$\begin{aligned}
 Q_{\text{Ti}} &= \frac{p_{\text{Ti}}}{(4\pi \ell^3 \epsilon_0 E)} = (1 + \lambda) \left( \frac{X_{\text{Ti}}}{\Delta} \right) \left( 1 + \frac{4\sqrt{2} - 1}{8} X_o + \frac{39 + 92\sqrt{2}}{32} X_o^2 \right) \\
 Q_{\text{Oa}} &= \frac{p_{\text{Oa}}}{(4\pi \ell^3 \epsilon_0 E)} = \left( \frac{X_o}{\Delta} \right) \left( 1 + \frac{8\sqrt{2} + 1}{8} X_o + 2(1 + \lambda) X_{\text{Ti}} - \frac{47 - 2\sqrt{2}}{4} (1 + \lambda) X_{\text{Ti}} X_o \right) \\
 Q_{\text{Ob}} &= \frac{p_{\text{Ob}}}{(4\pi \ell^3 \epsilon_0 E)} = \left( \frac{X_o}{\Delta} \right) \left( 1 + \frac{\sqrt{2} - 1}{4} X_o - (1 + \lambda) X_{\text{Ti}} - \frac{47 - 2\sqrt{2}}{4} (1 + \lambda) X_{\text{Ti}} X_o \right) \quad (5)
 \end{aligned}$$

where

$$X_{\text{Ti}} = \frac{a_{\text{Ti}}}{(4\pi \epsilon_0 \ell^3)}, \quad X_o = \frac{a_o}{(4\pi \epsilon_0 \ell^3)},$$

and

$$\Delta = 1 + \frac{4\sqrt{2} - 1}{8} X_o - \frac{4\sqrt{2} + 9}{32} X_o^2 - 12(1 + \lambda) X_{\text{Ti}} X_o \quad (6)$$



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For later numerical work we take  $\ell = 2.00 \text{ \AA}$ , the spacing in barium titanate; hence  $X_{\text{Ti}} = 0.0233$ ,  $X_{\text{O}} = 0.298$ . The field  $E$  in Eqs. 5 is of course the local field acting on the complex. As discussed above, it is related to the external field  $E_{\text{ext}}$  by the usual isotropic Lorentz correction  $E = E_{\text{ext}} + P/(3\epsilon_0)$ , where  $P = n(p_{\text{Ti}} + 2p_{\text{Oa}} + 4p_{\text{Ob}})$  and  $n$  is the number of complexes per unit volume. Eliminating  $E$ , we find

$$\frac{P}{\epsilon_0 E_{\text{ext}}} = \kappa - 1 = \frac{n(4\pi\ell^3)(Q_{\text{Ti}} + 2Q_{\text{Oa}} + 4Q_{\text{Ob}})}{1 - \frac{1}{3}n(4\pi\ell^3)(Q_{\text{Ti}} + 2Q_{\text{Oa}} + 4Q_{\text{Ob}})} \quad (7)$$

The vanishing of the denominator of Eq. 7 is of course the condition for ferroelectricity, and provides a relationship between the number of complexes per unit volume,  $n$ , and the ratio of ionic to electronic polarizability of titanium,  $\lambda$ . Expressing  $n$  in terms of the equivalent radius  $R$  of the complex ( $1/n = 4\pi R^3/3$ ), we obtain the values of  $\lambda$  given in Table I. The other columns of this table are the relative contributions to the polarization  $P$  from the titanium ionic polarizability ( $P'_{\text{Ti}}$ ), the titanium electronic polarizability ( $P_{\text{Ti}}$ ), and the electronic polarizability of the two type a oxygen atoms ( $2P_{\text{Oa}}$ ) and the four type b oxygen atoms ( $4P_{\text{Ob}}$ ), respectively.

Table 1

$R(\text{\AA})$	$\lambda$	$P'_{\text{Ti}}$	$P_{\text{Ti}}$	$2P_{\text{Oa}}$	$4P_{\text{Ob}}$
2.6	3.57	0.083	0.023	0.478	0.416
2.68	5.09	0.129	0.025	0.507	0.338
2.8	6.73	0.192	0.029	0.546	0.232
3.0	8.42	0.271	0.032	0.602	0.093
3.2	9.45	0.337	0.036	0.638	-0.011
3.4	10.14	0.384	0.038	0.663	-0.083

Slater's analysis of barium titanate showed that  $\lambda = 5.09$ , so we should expect  $\lambda$  to be close to that value here. The value  $R = 2.6 \text{ \AA}$  corresponds to no voids in the fluid (based on conventional ionic radii (ref. 5)  $R_{\text{Ti}} = 0.68 \text{ \AA}$ ,  $R_{\text{O}} = 1.40 \text{ \AA}$ ), and the value  $R = 3.4 \text{ \AA}$  corresponds to the smallest sphere which will circumscribe the entire structure and hence represents a situation in which a considerable part of the space is taken up by voids. For  $\lambda = 5.09$  the former case corresponds to ferroelectric behavior, the latter does not. We might imagine that the complex would have an equivalent radius of 2.9 to 3.0  $\text{\AA}$ , for which Eq. 7 gives a dielectric constant of ten to twelve. This calculation therefore makes it appear that a fluid of  $\text{TiO}_6$  complexes would have an abnormally high dielectric constant but would probably not be ferroelectric.

## References

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H. C. Schweinler

## F. FERROELECTRICITY IN THE ILMENITE STRUCTURE.

Single crystals of  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  were found to be ferroelectric by Matthias and Remeika (1). These crystals belong to the trigonal system, and have the following lattice parameters:  $\text{LiNbO}_3$ ,  $a_0 = 5.47 \text{ kx}$ ,  $\alpha = 55^\circ 43'$ ;  $\text{LiTaO}_3$ ,  $a_0 = 5.49 \text{ kx}$ ,  $\alpha = 56.5^\circ$ . Their structure is the ilmenite structure, space group  $C_{3i}^2$ , with Li at  $\pm(uuu)$ , Nb or Ta at  $\pm(vvv)$ , and O at  $\pm(xyz)$ ,  $\pm(yzx)$ ,  $\pm(zxy)$ . The parameters  $u, v, x, y, z$ , are not known for either of these crystals; but the ilmenite structure is closely related to the corundum structure, and so the parameters for the "ideal" case of the corundum-type structure will be used in the following:  $u = 1/3$ ,  $v = 1/6$ ,  $x = 7/12$ ,  $y = -1/12$ ,  $z = 1/4$ . In addition the intermediate angle  $\alpha = 56^\circ$  is used for the computations which follow.

The Slater method for evaluating the Lorentz correction (2) is being applied. In this method the field of a lattice of dipoles is first obtained at the positions of the atoms, and then the dipole moment of each atom is put equal to the product of the polarizability and the total field at the position of the atom. The set of equations thus obtained can be solved for the polarization of each kind of atom. These equations are

$$\frac{P_i}{X_i} = \epsilon_0 E + \sum D_{ij} \cdot P_j$$

where  $P_i$  is the polarization of the  $i^{\text{th}}$  lattice of atoms,  $X_i = \alpha_i / \epsilon_0 v$  with  $\alpha_i$  the polarizability of atom  $i$  and  $v$  the volume of the unit cell, and  $D_{ij} = D(r_{ij})$  is a dyadic:

$$D_{ij} = \frac{v}{4\pi} \sum \frac{(3RR - R^2 I)}{R^5}$$

with  $R = r_{ij} - r_1$ ,  $r_1$  a direct lattice vector.

The  $D_{ij}$  have been evaluated by the method of Ewald and partially checked; those given below have been checked for two values of the arbitrary parameter introduced by Ewald and so are almost certainly correct. They are:

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$$D_{ii}(000) = 0.354650(ii + jj) + 0.290699kk$$

$$D_{ij}\left(\frac{1}{6}\frac{1}{6}\frac{1}{6}\right) = -0.335106(ii + jj) + 1.670211kk$$

$$D_{ij}\left(\frac{1}{3}\frac{1}{3}\frac{1}{3}\right) = 0.706082(ii + jj) - 0.412163kk$$

$$D_{ij}\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right) = 0.291328(ii + jj) + 0.417345kk$$

Here  $k$  is a unit vector in the direction of  $a_1 + a_2 + a_3$ ,  $i$  is a perpendicular unit vector in the plane of  $k$  and  $a_1$  such that  $i \cdot a_1 > 0$ , and  $j = k \times i$ . The remaining  $D_{ij}$  have been computed but not yet checked; they will be reported later. It is interesting to note from  $D_{ij}\left(\frac{1}{6}\frac{1}{6}\frac{1}{6}\right)$  that the interaction of Li and Nb or Ta is enhanced by a factor of more than five compared with the isotropic value, for polarizations along the three-fold ( $k$ ) axis.

#### References

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H. C. Schweinler

### G. IONS IN A CUBIC ELECTRIC FIELD

An investigation is being made of the effect of a cubically symmetrical electrostatic potential of the form  $A(x^4 + y^4 + z^4 - 3/5 r^4)$  on the energy levels of ions of the iron group. The wave functions used are linear combinations of antisymmetrized, one-particle wave functions, including spin, which are diagonal with respect to the total spin and total orbital angular momenta. The  $d^2$  configuration is now being examined. The  $d^3$  configuration is of particular interest in that Prof. A. F. Kip and Mr. C. F. Davis have made an intensive investigation of  $Cr^{+++}$  in single chrome alum crystals using microwave techniques. This configuration will be examined presently.

W. H. Kleiner

### H. SOFT X-RAY VACUUM SPECTROGRAPH

We have succeeded in obtaining the emission band of aluminum corresponding to the valence band-2p transition. The curve of Fig. III-1 is a direct recording on an Esterline-Angus recording milliammeter of the photon counting rate as a function of the position of the photomultiplier along the Rowland circle. The driving mechanism of the recording meter is mechanically coupled to the lead screw which moves the photomultiplier. The bombardment potential and current were 560 volts and 2.5 ma, respectively. The aluminum was prepared by evaporation of high-purity wire from a tantalum cup; the surface of the target was maintained at approximately 100°C by water cooling. The

image and object slits were adjusted to give a resolution of approximately 1.0 Å or 0.4 eV in terms of transition energies. While runs taken at five-minute intervals after evaporation indicate a gradual contamination of the surface, probably a result of oxidation, the similarity of the first two or three curves indicates that the initial run represents a sufficiently clean surface. The results are in excellent agreement with previous work on aluminum in this wavelength range (1, 2, 3).

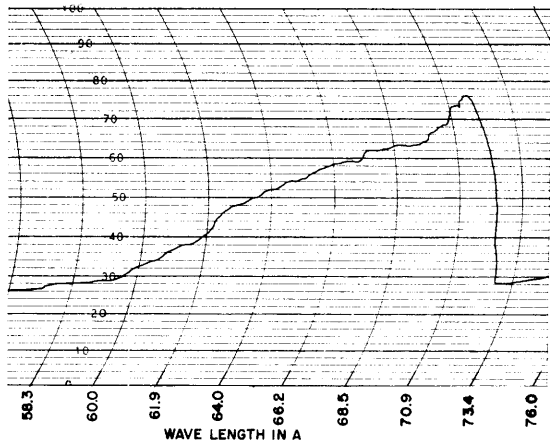


Fig. III-1 Photon counting-rate as a function of wavelength for aluminum. Full scale deflection is 500 counts per second.

The curve of Fig. III-2 shows the number of s electrons in aluminum as a function of the energy. This curve is obtained by plotting the original curve of Fig. III-1 against photon energy in electron volts, having altered the height by division by a factor proportional to  $E^4$ . This alteration is necessary since the spectrograph sees equal increments of wavelength as it records, rather than equal increments of energy, and the transition probability of any electron is also a function of the energy. The over-all correction thus becomes  $E^4$ . (See reference 2 for a thorough discussion of this conversion.) The small irregularities in the original curve are a result of the randomness of the counting rate and have therefore been smoothed.

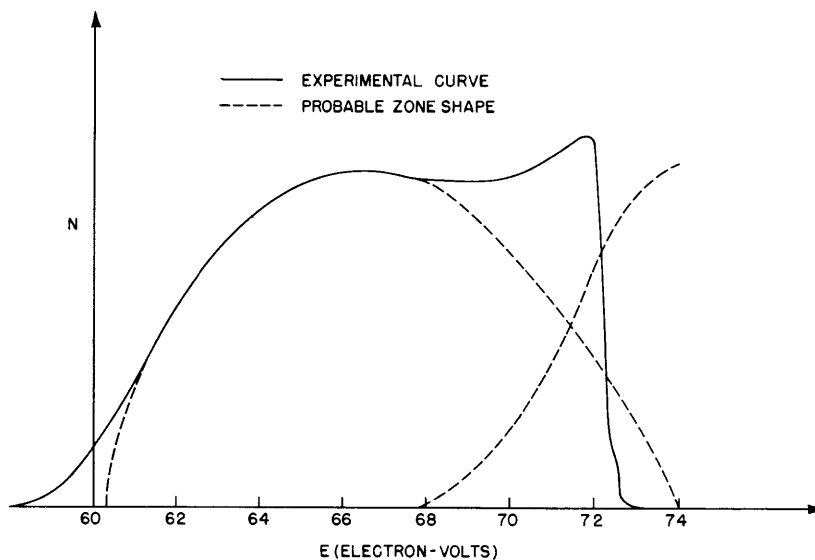


Fig. III-2 Number of s electrons per unit energy range in aluminum.

### (III. SOLID STATE PHYSICS)

The dashed lines in Fig. III-2 are the probable Brillouin zone shapes, as deduced from the work of Matyas (4) on the electronic structure of aluminum, and Jones, Mott, Skinner (5) on the relative densities of s and p electrons in electronic energy bands.

We now have some tentative data on magnesium and plan to study several other metals of the light elements. Future work will include a study of the complete iron transition group.

As an alternative to preparation of samples by evaporation we have under construction a mechanical device with which we hope to clean the surface of the metal by scraping.

#### References

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#### I. PARAMAGNETIC RESONANCE EXPERIMENTS

We have continued our investigations on single crystals of paramagnetic salts. Our recent work has been concentrated on investigations of ammonium chrome alum below the transition which occurs at about 80°K. The simple theory worked out originally by P. Weiss (1) gives good agreement above the transition temperature for all of the chrome alums investigated. This theory involves the perturbation of the lowest energy levels of the Cr<sup>+++</sup> ion by the surrounding crystalline electric field. Agreement with experimental results is given by assuming an electric field of cubic symmetry plus a small axial field of trigonal symmetry. Below the transition in ammonium chrome alum, this theory no longer can be fitted to experimental results. In an effort to understand the nature of the crystalline field below the transition we are extending our measurements.

We have added to our earlier measurements at 3-cm microwave frequencies, measurements in the region of 1 cm. The first measurements at this frequency were made with the use of a large electromagnet kindly loaned to us by Prof. F. Bitter. On the basis of results with this magnet, in which the field could be carried up to 15,000 gauss, we have modified our own magnet so that we can reach 10,000 gauss, which turns out to be as high a field as we need.

We are now measuring the ammonium chrome alum spectrum at 1, 3 and 5 cm, using various angles of orientation of the crystal. It is hoped that careful study of the individual lines will allow a more complete understanding of the nature of the crystalline

fields below the transition.

Description of other work in progress will be postponed until the next report, since no significant new results have yet been obtained.

A. F. Kip, C. F. Davis, Jr., W. Kleiner, R. Weinstein

Reference

1. P. R. Weiss: Phys. Rev. 73, 470 (1948).