

Co²⁺ sites has, to first approximation, cubic symmetry. It was not observed in a salt where the crystal field had tetrahedral symmetry. The absorption is interpreted as resulting from transitions between energy levels of the **L·S** fine structure multiplet. These levels do not appear to be completely explicable in terms of a proposed crystal field theory.² The introduction of various solid state interaction mechanisms such as phonons or exchange may be required for quantitative understanding of both the basic absorption process, and of the finer details that are observed such as optical polarization and antiferromagnetic effects.

It should be pointed out that the fine structure absorption in Co salts offers the possibility of application in an infrared quantum detector of the type described by Bloembergen.¹⁶

ACKNOWLEDGMENTS

We are indebted to P. P. Friguiletto who prepared many of the crystals used in this work. We should also like to express our thanks to E. O. Kane for both his general interest in this work and for his help in performing some of the calculations cited in the paper.

¹⁶ N. Bloembergen, Phys. Rev. Letters 2, 84 (1958).

Variational Approach to Deviations from Ohm's Law*

I. ADAWI

RCA Laboratories, Princeton, New Jersey

(Received December 15, 1958; revised manuscript received April 23, 1959)

In a perturbation framework, Kohler's variational method has been extended to obtain deviations from Ohm's law for a nondegenerate electron gas. Solution for the distribution function reduces to solving sets of linear algebraic equations. It is shown that, to second order in the field strength, the "popular" Maxwellian distribution (with a new temperature) is only a first-order variational solution. The method becomes extremely simple if the diffusion approximation is introduced and a relaxation time can be defined. Under these conditions, the second-order term in the mobility is expressed as the ratio of two infinite determinants using the usual representation, in which the unknown function is expressed as an energy polynomial. This ratio can be expressed by an infinite series.

1. INTRODUCTION

FOR the past decade, Kohler's variational method¹⁻³ has been very useful in treating otherwise formidable problems in the theory of *linear* conductivity in solids. There is at the present considerable theoretical and experimental interest in the *nonlinear* part of the conductivity in semiconductors and insulators. One is usually interested in two regions of field strength. The first is the weak-field region in which the system does not deviate substantially from thermal equilibrium. The second is the high-field region in which the system departs considerably from its thermal behavior. It is with the weak-field region that this paper is concerned.⁴

We shall limit this treatment to a nondegenerate electron gas obeying classical statistics. For small

departures from equilibrium, perturbation theory is valid and the distribution function is expanded in powers of the field. The Boltzmann equation is reduced to a set of linear equations in which the collision operator is symmetric and positive definite. Consequently, Kohler's variational method can be applied to solving these equations and thus obtaining deviations from Ohm's law. Although this method does not reduce the number of equations one has to solve to obtain corrections to Ohm's law, to a certain order in the field, yet for a given set of trial functions this method offers the best solution.

To obtain approximate solutions, the variational method offers a powerful practical tool. Its application leads to solving sets of linear algebraic equations whose number is not large in practice. This is a more general method than a numerical solution for the distribution function which is quite tedious. Needless to say, exact solutions are out of the question except in a limited number of cases.

In Sec. 3, two important applications of this variational method are discussed. The first application concerns the Maxwellian distribution (with a new temperature) which has become popular in discussing hot electron problems. To second order in the field, we shall show that under broad general conditions, a

* This part covers the theoretical aspects of a paper presented at the 1959 Cambridge meeting of the American Physical Society. Part II of this work will deal with deviations from Ohm's law in nonpolar crystals. See I. Adawi, Bull. Am. Phys. Soc. 4, 129 (1959).

¹ M. Kohler, Z. Physik 124, 772 (1948); 125, 679 (1949).

² E. H. Sondheimer, Proc. Roy. Soc. (London) A203, 75 (1950).

³ See A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1954), Chap. X, second edition. Other references will be found there.

⁴ Preliminary calculations for germanium at room temperature, for example, indicate that the theory is valid for fields below, say, 10⁹ volts/cm.

Maxwellian is a one-parameter variational solution. In the second application the diffusion approximation⁵ is used. A large class of problems, for which a relaxation time can be defined, is then discussed and a formal solution is given to second order in the field. The variational solution is carried out using the usual useful representation in which the unknown function is expressed as an energy polynomial. The second-order correction to the mobility is expressed as the ratio of two infinite determinants which can be evaluated by much the same methods that are used in the theory of linear conductivity.

A geometrical interpretation of the variational method is given in the Appendix.

2. THEORY

Let the electrostatic field \mathbf{E} point in the z direction, then the transport equation reads

$$\frac{qE}{\hbar} \frac{\partial f}{\partial k_z} = \int [W(\mathbf{k}', \mathbf{k})f(\mathbf{k}') - W(\mathbf{k}, \mathbf{k}')f(\mathbf{k})] d^3k', \quad (1)$$

where q is the charge, \mathbf{k} is the wave vector, f is the distribution function and $W(\mathbf{k}', \mathbf{k})$ is the transition probability from state \mathbf{k}' to \mathbf{k} . With no loss of generality, we set

$$f = CM\Phi, \quad (2)$$

where C is a normalization constant and M is the Maxwellian distribution, namely,

$$M(\mathbf{k}) = \exp[-\epsilon(\mathbf{k})/KT], \quad (3)$$

where ϵ and KT are the electron and thermal energies, respectively. We shall discuss only the cases where $\epsilon(\mathbf{k}) = \epsilon(|\mathbf{k}|)$ and W is cylindrically symmetric with \mathbf{k} as an axis of symmetry. We can then expand Φ in a series of Legendre's polynomials,

$$\Phi(\mathbf{k}) = \sum_{l=0}^{\infty} \phi_l(k) P_l(\cos\alpha), \quad (4)$$

where α is the angle between \mathbf{k} and \mathbf{E} . Substituting (2), (3), and (4) into (1) and using the properties of Legendre's polynomials, we obtain

$$\begin{aligned} & -\frac{qE}{\hbar} \left\{ \frac{lk^{l-1}}{(2l-1)dk} \frac{d}{dk} (k^{l-1}M\phi_{l-1}) \right. \\ & \quad \left. + \frac{(l+1)}{(2l+3)} \frac{1}{k^{l+2}} \frac{d}{dk} (k^{l+2}M\phi_{l+1}) \right\} \\ & = \int V(\mathbf{k}', \mathbf{k}) \{ \phi_l(k) - P_l(\cos\theta)\phi_l(k') \} d^3k', \\ & \quad \quad \quad l=0, 1, 2, 3, \dots, \quad (5) \end{aligned}$$

where

$$V(\mathbf{k}', \mathbf{k}) \equiv M(\mathbf{k}')W(\mathbf{k}', \mathbf{k}) = M(\mathbf{k})W(\mathbf{k}, \mathbf{k}'), \quad (6)$$

⁵ By the diffusion approximation we mean that only the first two Legendre coefficients are retained in the distribution function.

and θ is the angle between \mathbf{k} and \mathbf{k}' . The last equality in (6) follows from thermal equilibrium, when $E=0$, and shows that V is symmetric in \mathbf{k} and \mathbf{k}' . We shall for convenience introduce an abbreviated notation. Treat Φ as a column matrix with elements ϕ_l . Define the diagonal matrix Λ whose elements are Λ_l such that $\Lambda_l\phi_l$ stands for the integral on the right of (5). Introduce the matrix S with $S_{l,l\pm 1}$ as the only nonvanishing elements. Define these elements such that $ES_{l,l-1}$ and $ES_{l,l+1}$ are the differential operators in (5) operating on ϕ_{l-1} and ϕ_{l+1} , respectively. Thus (5) can be replaced by the matrix equation,

$$ES\Phi = \Lambda\Phi, \quad (7)$$

which is satisfied by the solution,

$$\phi_r = E^r \sum_{n=0}^{\infty} a_{r,r+n}(k) E^{2n}, \quad (8)$$

found by inspection.⁶ Substitute (8) in (7) and equate the coefficients of equal powers of E on both sides and an infinite system of equations connecting the a 's is obtained. The first few are

$$0 = \Lambda_0 a_{00}, \quad (9.1)$$

$$S_{10} a_{00} = \Lambda_1 a_{11}, \quad (9.2)$$

$$S_{01} a_{11} = \Lambda_0 a_{01}, \quad (9.3)$$

$$S_{21} a_{11} = \Lambda_2 a_{22}, \quad (9.4)$$

$$S_{10} a_{01} + S_{12} a_{22} = \Lambda_1 a_{12}, \quad (9.5)$$

$$S_{01} a_{12} = \Lambda_0 a_{02}, \text{ etc.} \quad (9.6)$$

Now, Λ_l , which is in general an integral operator, can be shown from (5) and (6) to satisfy the two relations,

$$\begin{aligned} (u, \Lambda_l v) &= (v, \Lambda_l u) \equiv \int u \Lambda_l v d^3k, \\ (u, \Lambda_l u) &\geq 0, \end{aligned} \quad (10)$$

where u and v are any two functions of k for which the above scalar products exist. Λ_0 has a constant c as an eigenfunction with zero eigenvalue. At the same time $(c, S_{01}\phi_1) = 0$ which shows that if ϕ_1 were known, then the equation

$$S_{01}\phi_1 = \Lambda_0\phi_0 \quad (11)$$

would determine ϕ_0 within an additive constant. Variational methods can be used for solving (11) and these are well discussed in the literature.^{3,7} All other Λ_l 's do not have a zero eigenvalue. This can be seen by showing that for $u \neq 0$, $(u, \Lambda_l u) > 0$, for $l > 0$. Consequently, the equation $\Lambda_l u = \text{known function}$ determines u uniquely if $l > 0$.

With this information at hand, we proceed to solve

⁶ It is only at this point that perturbation theory is introduced in Eq. (8).

⁷ See also Appendix.

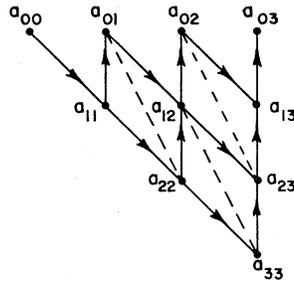


FIG. 1. A diagram showing the order in which the coefficients a are evaluated. The dotted line connecting two coefficients indicate that both of these coefficients are used to obtain the coefficient immediately to the right of the dotted line, for example, a_{01} and a_{22} are needed to determine a_{12} . If the system is truncated (all ϕ_l 's are set equal to zero for l greater than a certain value), then the lowest two rows will be connected by a sawtooth solid line similar to that connecting the upper two rows.

the system (9). Equation (9.1) does not determine the constant a_{00} uniquely. We shall arbitrarily set $a_{00}=1$, and (9.2) can then be solved for $a_{11}(k)$. Once a_{11} is known, (9.3) can be solved for a_{01} , and (9.4) for a_{22} . In the solution of a_{01} , however, we have an additive constant at our disposal. We adjust this constant so as to normalize Ma_{01} to zero.⁸ In general we normalize Ma_{0n} , $n>0$, to zero and this will determine $a_{0n}(k)$ uniquely. The scheme for solving the system (9) has become clear and can be continued to any order. It should be pointed out that (9.2) is Kohler's equation and the system (9) defines the generalization, which is the core of this development.

Figure 1 shows the sequence in which the a 's are evaluated. It is seen that if we calculate the coefficients up to a_{nn} then ϕ_0 is determined to order E^{2n} and ϕ_1 to order E^{2n-1} , and consequently the electrical conductivity will be determined to order $E^{2(n-1)}$.

This method is valid if the series (8) converges. For strong fields, the series might converge slowly (and a large number of terms might be needed), or not at all. In the latter case a solution can be obtained by different means (such as expanding the collision term in a Taylor's series) and the two solutions can be joined by some interpolation scheme.⁹

3. APPLICATIONS

For purposes of illustration we shall consider two applications of special interest:

(a) Maxwellian Distribution

Several authors have assumed a Maxwellian (with a new temperature) for the spherically symmetric part

⁸ This choice is unique. For when we normalize $CM\phi_0$ to 1, we obtain $1=C[\langle a_{00} \rangle_{Av} + \langle a_{01} \rangle_{Av}E + \langle a_{02} \rangle_{Av}E^2 + \dots]$, where the brackets are used for averages. This equality will hold for all E in a neighborhood of $E=0$ if and only if all $\langle a_{0n} \rangle_{Av}=0$ for $n>0$.

⁹ The standard method of expanding the collision term in a Taylor series is, in general, a high-field approximation and does not necessarily hold in the domain where perturbation theory, as discussed here, is applicable. There are, in certain situations, field

of the distribution function $M\phi_0$. The justification is that electron-electron collision dominates other energy exchange mechanisms.^{10,11} In this treatment we ignore electron-electron collision altogether. It is therefore instructive to show that the Maxwellian distribution occurs in a *natural way* in the variational solution. To prove this, consider Eq. (9.3) in which a_{11} is assumed to be known from solving Eq. (9.2). The proof does not depend, however, on how (9.2) has been solved. Let us represent a_{01} as a polynomial in energy:

$$a_{01} = \sum_{r=1}^n c_r \epsilon^r. \quad (12)$$

It follows from the variational principle³ that the coefficients c_r in (12) satisfy the set of linear algebraic equations,

$$(\epsilon^r, S_{01}a_{11}) = \sum_{s=1}^n (\epsilon^r, \Lambda_0 \epsilon^s) c_s, \quad r=1, 2, \dots, n. \quad (13)$$

If we set $n=1$, we obtain from (12) and (8) that

$$M\phi_0 \approx M(1 + c_1 E^2 \epsilon). \quad (14)$$

We get from (13), after multiplying both sides by the normalization constant⁸ C and E^2 , that

$$(\epsilon, S_{01}a_{11})CE^2 = (\epsilon, \Lambda_0 \epsilon) c_1 CE^2. \quad (15)$$

Equation (15) can then be identified as an energy balance equation to order E^2 . The left-hand side is the energy supplied by the field per unit time, namely, $q\mu E^2$ (μ is the mobility to zeroth order), and the right-hand side is the energy loss by collisions per unit time. But, this energy balancing is the method used to determine the new temperature of the Maxwellian solution.¹⁰ Furthermore, the form of $M\phi_0$ given by (14) is identical to that of a Maxwellian with a temperature $T^*=T+\Delta T$, where $\Delta T \ll T$. For to first order in ΔT ,

$$M(T+\Delta T) \approx M(T)[1 + (\Delta T/KT^2)\epsilon]. \quad (16)$$

Comparing (16) and (14), we identify $c_1 E^2$ with $\Delta T/KT^2$. This completes the proof that a Maxwellian, to order E^2 , is a first-order variational solution ($n=1$). It cannot be reliable in general, as we have shown recently in a specific case.¹² The solution is improved by taking $n>1$. (The normalization of Ma_{01} to zero is performed as the final step, and does not enter into the above discussion.)

(b) Problems with a Relaxation Time in the Diffusion Approximation

Many problems in semiconductors are treated using the following model. All ϕ_l 's=0 for $l>1$, (the diffusion

ranges for which neither theory is valid. Interpolation schemes become then essential. See. I. Adawi, Bull. Am. Phys. Soc. 4, 244 (1959).

¹⁰ H. Fröhlich and B. V. Paranjape, Proc. Phys. Soc. (London) B69, 21 (1956).

¹¹ R. Stratton, Proc. Roy. Soc. (London) A242, 355 (1957).

¹² I. Adawi, Phys. Rev. 112, 1567 (1958).

approximation). The energy ϵ is parabolic in k and m is an effective mass. Finally, a relaxation time exists. A relaxation time can be defined for scattering by impurities, acoustical phonons when equipartition is valid, and optical phonons in nonpolar crystals when the cross section is isotropic, to mention only a few examples.

For this model the system (5) reduces to two equations in ϕ_0 and ϕ_1 . $\Lambda_1\phi_1$ reduces to $M\phi_1/\tau$, where τ is the relaxation time and ϕ_1 is expressed in terms of ϕ_0 . Introduce the dimensionless variable $x=\epsilon/KT$ and $d^3k \rightarrow x^3dx$. The mobility μ is given by

$$\mu = \frac{4q}{3m\pi^{3/2}} \int_0^\infty \tau x^3 e^{-x} \left(\phi_0 - \frac{d\phi_0}{dx} \right) dx. \tag{17}$$

The normalization is such that $C=2\pi^{-3/2}$, $a_{00}=1$, and

$$2\pi^{-3/2} \int_0^\infty e^{-x} \phi_0 x^3 dx = 1.$$

To obtain μ to second order in E , we have to solve (9.3). After substituting for a_{11} from the preceding equation (9.2), we obtain the equation

$$-\frac{2q^2 x^{-3/2}}{3mKT} \frac{d}{dx} (\tau x^3 e^{-x}) = \Lambda_0 a_{01}, \tag{18}$$

which will now be solved by variational methods, no matter how complex Λ_0 might be. Represent a_{01} by a power series in x plus a constant so that $M a_{01}$ is normalized to zero as was discussed in Sec. 2. This is most conveniently written as

$$a_{01} = \frac{q}{KT} \sum_{r=1}^\infty c_r \left(x^r - \frac{3}{2} \frac{5}{2} \dots \frac{2r+1}{2} \right). \tag{19}$$

The coefficients c_r are then determined by solving the infinite set of equations:

$$b_r = \sum_{s=1}^\infty d_{rs} c_s,$$

where

$$b_r = -\frac{2q}{3m} \int_0^\infty x^{r+3/2} \tau e^{-x} dx, \tag{20}$$

$$d_{rs} = d_{sr} = \int_0^\infty x^{r+3/2} \Lambda_0 x^s dx.$$

From (19), (17), and (20) we obtain that

$$\mu = 2\pi^{-3/2} \left\{ b_1 + \frac{qE^2}{KT} \sum_{r=1}^\infty c_r b_r' + \dots \right\},$$

where

$$b_r' = (r+1)^{-1} b_{r+1} - b_r - \frac{3}{2} \frac{5}{2} \dots \frac{2r+1}{2} b_1. \tag{21}$$

The sum in (21) can be expressed as the ratio of two infinite determinants. Denote this sum by β , and we have

$$\beta \equiv \sum_{r=1}^\infty c_r b_r' = - \begin{vmatrix} 0 & b_1' & b_2' & \dots \\ b_1 & d_{11} & d_{12} & \dots \\ b_2 & d_{21} & d_{22} & \dots \\ \vdots & \vdots & \vdots & \dots \end{vmatrix} \div \begin{vmatrix} d_{11} & d_{12} & \dots \\ d_{21} & d_{22} & \dots \\ d_{31} & d_{32} & \dots \\ \vdots & \vdots & \dots \end{vmatrix}. \tag{22}$$

This result can be simplified further by the method discussed by Wilson.^{3,13} Let $D^{(n)}$ be the determinant obtained by taking only the first n rows and columns of $|d_{rs}|$. Let $D_b^{(n-1)}$ be the determinant formed from $D^{(n)}$ by replacing the last row (or column) by b_1, b_2, \dots, b_n . $D_{b'}^{(n-1)}$ is similarly defined. Then,

$$\beta = \frac{b_1 b_1'}{d_{11}} + \sum_{n=2}^\infty \frac{D_b^{(n-1)} D_{b'}^{(n-1)}}{D^{(n)} D^{(n-1)}}. \tag{23}$$

The series on the right of (23) can be evaluated to any desired accuracy. In practice a few terms will do,¹⁴ and this is why the variational method is quite simple and useful.¹⁵

The last example is simple when treated by this method. It is quite important¹⁶ and has been discussed in some detail to illustrate how this method can be used to handle more difficult problems to any accuracy. In concluding, we remark that this method might be extended in two directions. The first is to include more complex energy surfaces which would require the expansion of f in the surface harmonics Y_m^l . The second is to use Fermi-Dirac statistics. It should be borne in mind that Kohler's collision operator is linear only to the first order in E when we use Fermi-Dirac statistics.

¹³ This is a special case of Jacobi's theorem. See C. V. Durell and A. Robson, *Advanced Algebra* (G. Bell and Sons, London, 1952), Vol. III, p. 411.

¹⁴ It is interesting to observe that (23) gives $\beta=0$ to a first approximation when $b_1'=0$. From (21), $b_1'=0$ when $b_2=5b_1$. This can happen for a proper combination of scattering mechanisms, such as for example, ionized impurities and lattice vibrations. Since b_1' depends only on integrals involving τ , it follows that the details of Λ_0 do not enter, to a first approximation, in determining when the E^2 -term correction to the mobility (which is proportional to β) should vanish. To higher approximations, the details of Λ_0 enter through the elements d_{rs} in determining when $\beta=0$ as can be seen from (23). The first approximation is equivalent to the use of a Maxwellian as we discussed before. In the problem we worked out earlier,¹² there was hardly any difference between the exact and the Maxwellian solutions regarding the condition for $\beta=0$.

¹⁵ See D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953), for calculations of this type.

¹⁶ A problem of this type has been treated approximately by J. Yamashita, Phys. Rev. **111**, 1529 (1958). See also, J. B. Gunn, J. Phys. Chem. Solids **8**, 239 (1959); and T. N. Morgan, J. Phys. Chem. Solids **8**, 245 (1959). From a rigorous point of view, the slope of the distribution function at the origin, namely, $\xi'(0)$ in Yamashita's notation, is determined by the behavior of ξ at ∞ . This slope is finite, in general, and not zero, as Yamashita apparently assumes. Only the proper slope leads to a distribution which can be normalized.

ACKNOWLEDGMENTS

The author is grateful to F. Herman and R. H. Parmenter for a critical review of the manuscript.

APPENDIX. GEOMETRICAL MEANING OF THE VARIATIONAL METHOD

The task is to solve the equation,

$$g = \Lambda\psi, \quad (\text{A1})$$

for ψ , where g is a known function (orthogonal to all the eigenfunctions of Λ with zero eigenvalue) and Λ is a symmetric and positive-definite operator. To obtain a variational solution, express ψ in terms of a complete set of functions u_r :

$$\psi = \sum_{r=1}^n c_r u_r; \quad (\text{A2})$$

it follows that the coefficients c_r are determined by maximizing $(\psi\Lambda\psi)$ subject to the condition

$$(\psi, g) = (\psi\Lambda\psi). \quad (\text{A3})$$

From here on, we depart from the standard method of introducing Lagrange's multipliers. Instead, we shall determine the c_r 's from geometrical considerations. Introduce the column matrix \mathbf{B} with elements b_r and the symmetric matrix \mathbf{D} with elements d_{rs} , where

$$b_r = (u_r, g), \quad d_{rs} = (u_r \Lambda u_s) = d_{sr}. \quad (\text{A4})$$

Let \mathbf{C} be any column vector in the n -dimensional c space with components c_r . The problem then reduces to finding the maximum value of z for which the plane $\mathbf{C}^T \mathbf{B} = z$ cuts for real \mathbf{C} the quadratic $\mathbf{C}^T \mathbf{D} \mathbf{C} = z$. The superscript T denotes the transpose. Since \mathbf{D} is symmetric and positive-definite, then $\mathbf{C}^T \mathbf{D} \mathbf{C} = z$ is an ellipse in n dimensions and $z \geq 0$. If we write down *formally* the equations for all the tangent planes which touch the ellipse, $\mathbf{C}^T \mathbf{D} \mathbf{C} = z$, at its points of intersection with the plane $\mathbf{C}^T \mathbf{B} = z$, regardless whether these points are real or complex, then we easily see that all these tangent planes pass through the common point P whose position vector \mathbf{P} is determined by $\mathbf{D}\mathbf{P} = \mathbf{B}$. Thus, P is invariant and does not depend on the parameter z . Clearly, if P lies inside the ellipse, the plane does not intersect the ellipse in real points, and this happens when $\mathbf{P}^T \mathbf{B} < z$. On the other hand, for all $\mathbf{P}^T \mathbf{B} > z$, P lies outside the ellipse and the plane intersects the ellipse in real points. Hence, the maximum value of z is $\mathbf{P}^T \mathbf{B} = \mathbf{B}^T \mathbf{D}^{-1} \mathbf{B}$. This happens when the plane touches the ellipse at P and $\mathbf{P} = \mathbf{C}$ which gives

$$\mathbf{D}\mathbf{C} = \mathbf{B}, \quad (\text{A5})$$

which is the equation determining the c_r 's.

Physically, the system of equations (A5) represents a set of transfer equations, or balance equations, for the set of functions u_r .

Suggestion Concerning Magnetic Interactions in Spinels*

D. G. WICKHAM AND J. B. GOODENOUGH

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts

(Received April 6, 1959)

The indirect-exchange mechanisms which produce spontaneous magnetization in metal oxides are an optimum if two interacting cations are located on opposite sides of an anion. The coupling rules which have been developed for this case are not applicable to spinels in which the cation-anion-cation angles differ appreciably from 180° . An examination of the d -orbital symmetry of various cations in respect to the crystal lattice leads to several suggestions concerning the magnetic interactions in spinels. Of particular interest are those spinels containing cations with three or fewer d electrons in the octahedral sites, or four if the symmetry is tetragonal. The properties of several spinels of this kind are considered in the light of the suggestions offered. Direct interactions between octahedral-site cations appear to be possible.

IN metal oxides, the cations are separated by relatively large distances, and the magnetic interactions of principal previous interest have been indirect interactions in which an anion is an intermediary. Such indirect-exchange mechanisms are an optimum if the two cations are located on opposite sides of an anion.¹ An indirect-exchange mechanism and consequent cou-

pling rules have been proposed²⁻⁴ for this case which are at once consistent with recent detailed calculations⁵ and with experimental data on perovskite-type and rock salt-type structures. In the spinel lattice the situation is complicated by the fact that the cations are not located on opposite sides of the anion. The tetrahedral (A) cation-anion-octahedral (B) cation angle is $\sim 125^\circ$,

* The work reported in this paper was performed by Lincoln Laboratory, a center for research, operated by Massachusetts Institute of Technology with the joint support of the U. S. Army, Navy, and Air Force.

¹ P. W. Anderson, Phys. Rev. **79**, 350 (1950).

² J. B. Goodenough, Phys. Rev. **100**, 564 (1955).

³ J. B. Goodenough, J. Phys. Chem. Solids **6**, 287 (1958).

⁴ J. B. Goodenough, J. phys. radium (to be published).

⁵ P. W. Anderson, Phys. Rev. (to be published).