value calculated from molecular field theory with $J_1 = 0$ and $J_2 = -1.76k$ is 82°K, whereas with $J_1 = -1.3k$ and $J_2 = -1.76k$ a θ value of 97°K is obtained. From paramagnetic resonance measurements on dilute solid solutions of MnF_2 in ZnF_2, Owen, Brown, Coles, and Stevenson[23] have concluded that J_1 is ferromagnetic and equal to $(0.2 \pm 0.1)k$ which within experimental error is consistent with our limiting Weiss θ but not with the value of $J_1 = -1.3k$ inferred from the low-temperature values of $\chi_{\parallel}$. The reason for this discrepancy is not clear.

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[1] See T. Nagamiya, K. Yosida, and R. Kubo, Suppl. Phil. Mag. 4, 1 (1955) for a review of antiferromagnetism.

[2] P. W. Anderson, Phys. Rev. 86, 694 (1952).

[3] R. Kubo, Phys. Rev. 87, 568 (1952); Rev. Modern Phys. 25, 344 (1953).

[4] J. M. Ziman, Proc. Phys. Soc. (London) A65, 540, 548 (1952).

[5] J. R. Tessman, Phys. Rev. 88, 1132 (1952).

[6] J. A. Eisele and F. Keffer, Phys. Rev. 96, 929 (1954).

[7] J. Kanamori and K. Yosida, Progr. Theoret. Phys. (Kyoto) 14, 423 (1955).

[8] T. Oguchi, Phys. Rev. 111, 1063 (1958); 117, 117 (1960).

[9] F. Keffer and R. Loudon, Suppl. J. Appl. Phys. 32, 2S (1961).

[10] J. Kanamori and M. Tachiki, J. Phys. Soc. Japan 17, 1384 (1962).

[11] F. H. Johnson and A. H. Nethercot, Jr., Phys. Rev. 114, 705 (1959).

[12] S. Foner, Phys. Rev. 107, 683 (1957).

[13] V. Jaccarino and R. G. Shulman, Phys. Rev. 107, 1196 (1957).

[14] V. Jaccarino and L. R. Walker, J. Phys. Radium 20, 341 (1959).

[15] H. Bizette and B. Tsai, Compt. Rend. 209, 205 (1939); 238, 1575 (1954).

[16] W. J. de Haas, B. H. Schultz, and J. Koolhaas, Physica 7, 57 (1940).

[17] M. Griffel and J. W. Stout, J. Chem. Phys. 18, 1455 (1950).

[18] S. Foner, J. Phys. Radium 20, 336 (1959).

[19] P. Pincus and J. Winter, Phys. Rev. Letters 7, 269 (1961).

[20] A. Arrott and J. E. Goldman, Rev. Sci. Instr. 28, 99 (1957).

[21] C. L. Brandt, Ph.D. thesis, University of Chicago, 1959 (unpublished).

[22] J. W. Stout and E. Catalano, J. Chem. Phys. 23, 2013 (1955).

[23] J. Owen, M. R. Brown, B. A. Coles, and R. W. H. Stevenson, Suppl. J. Phys. Soc. Japan 17, 428 (1961).

EFFECT OF CORRELATION ON THE FERROMAGNETISM OF TRANSITION METALS

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The purpose of this Letter is to present a new approach to the problem of ferromagnetism in a metal. A correlated wave function for the electrons in the $3d$ band is proposed as approximation to the ground state. The expectation value of the energy is evaluated by diagram techniques. The simplest example of a face-centered cubic structure (whose density-of-states curve is parabolic at the bottom and has a peak at the top) is discussed. Under these assumptions the arguments show that the ferromagnetic state is lower if the band is nearly full, whereas the nonmagnetic state has the lower energy if the band is nearly empty.

The main attempt so far to explain ferromagnetism in metals is based on the collective electron theory of ferromagnetism,[1] in which both the magnetic and the nonmagnetic ground states are assumed to be antisymmetrized products of Bloch functions. The expectation value of the energy in the nonmagnetic state contains a large term which is due to the repulsion of two electrons of opposite spin at the same lattice site. Slater,[2] in particular, pointed out that this term should be reduced by considering correlated wave functions before the effects of exchange are discussed. The collective electron theory fails especially in the limit of large spacing between the lattice sites, a situation comparable to that of the relatively tight $3d$ levels in the transition metals.

The present model is an attempt to deal with this particular difficulty. The correlated wave function Ψ is obtained from the antisymmetrized product Φ of Bloch functions by simply eliminating those parts in Ψ in which two electrons of opposite spin happen to be at the same lattice site.

Consider a lattice of L sites which are numbered by an index g. To each site belongs, for a given spin, only one orbital $\varphi(x-g)$ of the Wannier type

$$\int\varphi^*(x-g_1)\varphi(x-g_2)dx=\delta_{g_1g_2}. \tag{1}$$

The restriction to Wannier functions is made in this Letter in order to bring out more clearly the way in which the correlation between electrons of opposite spin is achieved. The generalization to nonorthogonal orbits is feasible, and the present theory is viewed as an approximation which is valid for small overlap between two orbits $\varphi(x-g_1)$ and $\varphi(x-g_2)$ belonging to different sites in the lattice. Bloch waves $\psi_k(x)$ are constructed by forming

$$\psi_k(x)=L^{-1/2}\sum_g\exp(ikg)\varphi(x-g). \tag{2}$$

Each of these wave functions is to be multiplied with a spin function, indicated by an arrow, $\uparrow$ or $\downarrow$, as index. Corresponding to $\varphi(x-g)$, there is a Fermion creation operator a_g^+, in the usual manner; and corresponding to $\psi_k(x)$, there is a Fermion creation operator a_k^+, with the relation (2) now becoming

$$a_k^+=L^{-1/2}\sum_g\exp(ikg)a_g^+. \tag{3}$$

The wave function Φ is represented by

$$\Phi=\prod_{\{k\}}a_{k\uparrow}^+\prod_{\{\kappa\}}a_{\kappa\downarrow}^+\Phi_0, \tag{4}$$

where Φ_0 is the vacuum. The sets $\{k\}$ and $\{\kappa\}$ extend over the appropriate regions in reciprocal space. These regions are, in general, the inside of some Fermi surface, and it may well be that the Fermi surface S for the set $\{k\}$ with spin up does not coincide with the Fermi surface Σ for the set $\{\kappa\}$ with spin down. The total number N of electrons described by Φ does not have to be in any simple relation to the number L of lattice sites. Indeed, if one takes the liberty of grouping the 4s electrons in Ni with the effective periodic potential, one is left with a fractional value of N/L for the 3d band. If there are more electrons than lattice sites, the whole formalism can be written in terms of holes instead of electrons, so that one may always assume $N\leq L$.

The correlated wave function Ψ is defined by

$$\Psi=\prod_g[1-(1-\eta)N_{g\uparrow}N_{g\downarrow}]\Phi, \tag{5}$$

where $N_g=a_g^+a_g$. As $L\to\infty$, the function Ψ becomes an eigenfunction of the operator $W=\sum_g N_{g\uparrow}N_{g\downarrow}$. For a given antisymmetrized product Φ, the value of η is to be considered as a function of $\langle W\rangle$.

By a straightforward computation, the norm of Ψ is shown to be

$$(\Psi|\Psi)=1+\sum_{m=1}^{L}\frac{(\eta^2-1)^m}{m!}\sum_{g_1\cdots g_m}\begin{vmatrix}W(g_1-g_1)\cdots W(g_1-g_m)\\ \vdots\qquad\vdots\\ W(g_m-g_1)\cdots W(g_m-g_m)\end{vmatrix}\cdot\begin{vmatrix}\omega(g_1-g_1)\cdots\omega(g_1-g_m)\\ \vdots\qquad\vdots\\ \omega(g_m-g_1)\cdots\omega(g_m-g_m)\end{vmatrix}, \tag{6}$$

where the kernels $W(g)$ and $\omega(g)$ are given by

$$W(g)=\frac{1}{L}\sum_{k\subset S}\exp(ikg),\quad \omega(g)=\frac{1}{L}\sum_{\kappa\subset\Sigma}\exp(i\kappa g). \tag{7}$$

Similar but somewhat more complicated expressions can be obtained for $(\Psi|a_f^+a_h|\Psi)$, etc. Of particular interest is the expectation value

$$\langle W\rangle=\tfrac{1}{2}\eta\cdot\partial\ln(\Psi|\Psi)/\partial\eta. \tag{8}$$

Expressions such as (6) cannot be evaluated directly. However, a fairly simple diagrammatic analysis can be used. Each of the m! permutations which occur in expanding the determinants of (6) can be viewed as the result of performing the appropriate cycle permutations. Each cycle is represented by an oriented polygon whose vertices are labeled by the numbers of the cycle in their correct order. There are two kinds of polygons, one for spin-up particles and one for spin-down particles. Corresponding vertices, i.e., vertices which are labeled by the same number, are connected by a dashed line to complete the diagram. The contribution of each diagram to $(\Psi|\Psi)$ is easily found.

The subdivision of a diagram into linked clusters, the assignment of a symmetry number to each linked cluster, and the counting of equivalent diagrams is done in the usual manner. The result is

$$(\Psi|\Psi) = \exp\left[\sum_{\nu=1}^{L} \frac{(\eta^2-1)^{\nu}}{\nu!}\sum\Lambda_{\nu}\right], \qquad (9)$$

where Λ_ν stands for the contribution of a particular linked cluster of order ν. The contribution Λ_ν of each linked cluster is proportional to L. Moreover, Λ_ν is proportional to $(N/L)^{\nu+1}$. For instance, $\langle W\rangle = \eta^2 N_\uparrow N_\downarrow/L$ from the term $\nu = 1$ in (9). All expectation values of interest can, therefore, be computed with good accuracy for $N \ll L$. (In the 50-50 alloy of Ni and Cu, which is still ferromagnetic, one has $N/L \lesssim 1/10$.)

The occupation probability $N_{k\uparrow} = \langle a_{k\uparrow}{}^{+}a_{k\uparrow}\rangle$ is given to second order in N/L by

$$N_{k\uparrow} = \begin{cases} 1-(1-\eta)^2 n_\downarrow & \text{for } k \subset S, \\ (1-\eta)^2 n_\uparrow n_\downarrow & \text{for } k \not\subset S, \end{cases} \qquad (10)$$

where $n_\uparrow = N_\uparrow/L$ and $n_\downarrow = N_\downarrow/L$. The average number of particles inside the Fermi surface is reduced by a factor $[1-(1-\eta)^2 n_\downarrow]$. In the special case $\eta = 0$, it turns out that $N_{k\uparrow} = 1 - n_\downarrow$ for $k \subset S$ quite independently of the magnitude of $n_\uparrow$ and $n_\downarrow$. For $N = L$ and $\eta = 0$ one has, therefore, $N_{k\uparrow} = N_{k\downarrow} = \frac{1}{2}$ over the whole Brillouin zone, independently of the choice of Φ, in agreement with the Heisenberg model of ferromagnetism.

It is instructive to apply these results to the following example. The Hamiltonian is given by

$$H = \sum_k E_k (N_{k\uparrow} + N_{k\downarrow}) + C\sum_g N_{g\uparrow} N_{g\downarrow}. \qquad (11)$$

The first part of H arises from solving Schrödinger's equation for a single electron in the effective periodic potential of the lattice. The second part describes the repulsion between two electrons of opposite spin which happen to be in the same orbit around a particular lattice site. All those interactions whose matrix elements involve integrals over orbits at different sites, and this includes the interaction which is associated with the exchange integral, are grouped with the effective periodic potential.

If the crystal potential has a nonvanishing matrix element ϵ only between nearest neighbors, the function E_k is given for an fcc lattice by

$$E_k = -4\epsilon(\cos ak_1 \cos ak_2 + \cos ak_2 \cos ak_3 + \cos ak_3 \cos ak_1), \qquad (12)$$

with respect to cubic axes. For $\epsilon > 0$ the bottom of the band is at $E = -12\epsilon$, where the density of states dn/dE as a function of energy E vanishes like $(E + 12\epsilon)^{1/2}$. Near the top of the band at $E = 4\epsilon$ the density of states has a peak like $-\log(4\epsilon - E)^{1/2}$. The expectation value $\langle H\rangle_u$ can be obtained for Ψ in the nonmagnetic state by minimizing $\langle H\rangle$ with respect to η which is then found to be $(1 + C/8\epsilon)^{-1}$ for small values of $n = N/L$. The resulting value of $\bar{H}_u = \langle H\rangle_u/N$ is compared to $\bar{H}_f = \langle H\rangle_f/N$ for the magnetic state. The calculations are easily worked out if n is only a few percent.

The following results and typical figures are obtained. If the band contains only few electrons, then the nonmagnetic state Ψ has the lower $\langle H\rangle$, e.g., for $n = 0.01$ and $\eta = 0$, one has $\bar{H}_f = 1.07$ above the bottom of the band, and $\Delta E = \bar{H}_f - \bar{H}_u = 0.26\,\epsilon$. However, if the band is nearly full, then the magnetic state has a lower $\langle H\rangle$ than Ψ, provided C is sufficiently larger than the bandwidth $16\,\epsilon$. For instance, for $n = 0.01$ and $\eta = 0$, one has $\bar{H}_f = -0.022\,\epsilon$ below the top of the band, and $\Delta E = -0.007\,\epsilon$, whereas for $n = 0.01$ and $\eta = 0.2$ (corresponding to C equals twice the bandwidth) one still has $\bar{H}_f = -0.022\,\epsilon$, but $\Delta E = -0.0004\,\epsilon$.

The wave function (5) is only an approximation for the ground state, and, therefore, it is not certain that for a nearly full band the Hamiltonian (11) with the band structure (12) leads to ferromagnetism, while it does not for a nearly empty band. It seems rather that the exact ground state of the Hamiltonian (11) is never ferromagnetic. But it may be conjectured on the basis of the above figures that the exact nonmagnetic ground state of the Hamiltonian (11) lies much closer to the ferromagnetic ground state of the same Hamiltonian if the band is nearly full than if it is nearly empty. Also, this difference in behavior is certainly due to the different behavior of the density-of-states curve at the top and at the bottom of the band. The occurrence of ferromagnetism would then depend on the interaction of the electrons which is associated with the two-center Coulomb integrals, in particular, the exchange integral. But in view of the above correlation through the one-center Coulomb integral, the top of the band structure (12) has gained a decisive advantage for achieving ferromagnetism over the bottom. Indeed, the expectation value for the terms associated with the two-center Coulomb integrals is the same for the nearly empty and the nearly full bands, positive for the nonmagnetic state, zero for the ferromagnetic state.

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[1] See E. P. Wohlfahrt, Rev. Modern Phys. 25, 211 (1953).

[2] J. C. Slater, Rev. Modern Phys. 25, 199 (1953).

PAIR SPECTRA IN GaP

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Recent reports of the fluorescence in GaP have described amazingly complicated spectra with at least 100 sharp lines near the band gap energy.[1-3] The present Letter reports three quite distinct types of spectra in which a total of about 300 lines have been counted, and shows that the vast majority of these lines arise from the recombination of electrons and holes which are trapped on distant donor-acceptor pairs. By the use of the intensity patterns of the spectra, particular lines may be identified with known donor-acceptor separations, and from their energy positions the sum of the isolated donor and acceptor binding energies is obtained. The observation of such lines should be useful in the chemical analysis of crystals and in the study of donor and acceptor wave functions.

The sharp lines considered here fall in the green, between 2.317 eV and about 2.2 eV at 1.6°K, and appear to be independent of other broad emission bands, one of which lies at 2.22 eV.[2,3] The lines have a half-width of about 3×10^{-4} eV and occur without phonon cooperation. All the crystals which display the spectra have been grown from Ga solutions. Type I spectra were obtained from "undoped" crystals, type II from crystals grown from a solution containing Zn (an acceptor), and type O from a run in which air entered the system. Type II spectra often include weak type I lines. The spectra do not depend strongly on the thermal history of the sample. The spectra were recorded photographically using a grating spectrograph giving a dispersion of 2 Å/mm.

Donor-acceptor pairs have been suggested as an explanation of different fluorescent effects in SiC- and ZnS-type phosphors.[4,5] It has been difficult to identify conclusively pair effects, chiefly because it has been believed that the important pairs are only very closely spaced pairs, or excited states of pairs with larger internuclear separations, and the precise conclusions which can be drawn from the experimentally observed broad bands are few.

Distant donor-acceptor pairs are, in comparison, simple. By considering a Born cycle the energy of an electron and a hole (i.e., the energy of fluorescence) on an isolated distant donor and acceptor separated by a distance r is

$$E(r)=E_{\text{gap}}-E_D-E_A+e^2/\epsilon r-(e^2/\epsilon)(a/r)^6\cdots, \quad (1)$$

where E_D and E_A are the isolated donor and acceptor binding energies, ϵ the static dielectric constant, and a the effective van der Waals coefficient for the interaction between a neutral donor and a neutral acceptor. For an isolated pair [typically a pair separated by a distance less than r_0, where $r_0=(\text{donor or acceptor concentration})^{-1/3}$] and a given type of donor and acceptor, the possible values of r are discretely distributed. A spectrum of discrete lines will result. [When the distance between donor and acceptor becomes small, there will also be angular dependencies of $E(r)$ for fixed $|r|$ which will be related to the donor and acceptor wave functions, and the spectrum will become more complex, but remain discrete.]

It is expected that the fluorescent intensity from isolated pairs at large separation r will be proportional to the number of pairs, N_r, at that distance multiplied by a smooth and fairly slowly varying function of r. This function is controlled by the