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Exchange and Superexchange Coupling between Conduction Electrons and *d* Electrons in Magnetic Materials*

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An analysis is made of the magnetization of the conduction electrons in a ferromagnetic material induced by their exchange interaction with the *d* electrons. The problem is set up by using the density matrix, some special properties of which are proved in the Appendix. When this formalism is used, the exchange interaction between a conduction electron and the inner as well as the *d* electrons associated with a given atom are found as a function of the relative spin orientation of the atom and the conduction electron. The problem is treated for $T \ll T_C$ and for $T \sim T_C$. Results for Fe have been calculated by using the nearly free electron method and the cellular methods. The effect of correlation is taken into account by the Bohm and Pines technique. A magnetization of about $0.20\mu_0$ per atom is found. An antiferromagnetic coupling is found to be possible between magnetic ions in dilute alloys such as has been found experimentally in Cu-Mn. The mechanism is a superexchange coupling of the magnetic ions through the conduction electrons. A molecular field theory has been worked out for this case on the basis of an antiferromagnetic coupling between the magnetic ions and a ferromagnetic coupling between these ions and the conduction electrons. This theory is found to admit the possibility of an antiferromagnetic-ferromagnetic transition. Application of this theory to the Cu-Mn alloys shows that it is unnecessary to assume that the *s-d* exchange interaction is as weak as previously believed. It is, furthermore, suggested that the combination of direct and superexchange interactions between the 4*f* and conduction electrons in the rare earths is responsible for their magnetic properties and in particular is the source of the observed antiferromagnetic-ferromagnetic transitions in erbium and dysprosium.

I. INTRODUCTION

IN the last ten years the exchange interaction between the conduction electrons and *d* electrons in magnetic materials has been the subject of a number of investigations. One of the first to examine this interaction was Vonsovskii[1] who treated it as a perturbation acting on the conduction electrons. Due to the net spin of the *d* electrons in a ferromagnetic there is a stronger exchange interaction between a conduction electron with spin parallel to the net *d*-electron spin than for a conduction electron with opposite spin. Vonsovskii concluded that this would lead to a different $E(k)$ dependence for conduction electrons of different spin and would furthermore, give rise to a net magnetization of these electrons. In other words there is an exchange polarization[2] of the conduction electrons. He suggested that the fractional magnetic moments observed in ferromagnetics is a manifestation of this effect. The conduction electrons were treated by a nearest-neighbor-only, tight-binding method which puts many of his results on a phenomenological basis. More recently he and others have applied this approach to a number of other problems.[3] Zener[4] has proposed a theory in which the *d*-electron conduction electron exchange interaction is the basic source of ferromagnetism. Kasuya[5] has recently examined Zener's model and points out that since the $4f$ orbitals in the rare earths probably have no direct overlap, their magnetic properties are very likely derived from the $4f$ electron-conduction electron exchange interaction. The role of the exchange interaction between conduction and *d* electrons in the relaxation process in ferromagnetic resonance has also been examined.[6,7]

In this paper the exchange polarization of the conduction electrons is investigated with particular reference to Fe. The model used for Fe is that of the conduction electrons moving in a periodic lattice of Fe^+ cores, an isolated core having a $3d^7$ configuration. In the crystal a given *d* orbital is assumed to have a form such that it can be identified with a particular core and such that it is orthogonal to all other orbitals associated with that core and orthogonal to orbitals on all other cores. Therefore, the *d* orbitals behave much like Wannier functions. Each core is assumed to be in a state of maximum multiplicity ($S=\frac{3}{2}$ for Fe^+). Well below the Curie point each core is taken to have its maximum M_s value ($M_s=\frac{3}{2}$ for Fe^+) while above the Curie point the average of M_s over all cores is zero. The conduction electrons are assumed to occupy orbitals spread out over the entire crystal and when the core spins are perfectly ordered at 0°K, to satisfy the Bloch condition. The total wave function is set up in terms of the individual core states and the conduction electrons. By finding the expectation value of the total energy and varying this with respect to the conduction electron orbitals, regarding those functions associated with different spin but the same k as being independent in accord with the unrestricted Hartree-Fock method, the variational equations for these orbitals are found. These equations involve the exchange interaction be-

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[1] S. Vonsovskii, J. Phys. (U.S.S.R.) **10**, 468 (1946).

[2] G. W. Pratt, Jr., Phys. Rev. **102**, 1303 (1956).

[3] S. Vonsovskii and K. Vlasov, J. Exptl. Theoret. Phys. (U.S.S.R.) **28**, 327 (1953); E. A. Turov, J. Exptl. Theoret. Phys. (U.S.S.R.) **25**, 352 (1953); A. V. Sokolov and S. M. Tsips, Soviet Physics JETP **1**, 218 (1955); A. V. Sokolov, Soviet Physics JETP **1**, 333 (1955).

[4] C. Zener, Phys. Rev. **81**, 440 (1951).

[5] T. Kasuya, Prog. Theoret. Phys. Japan **16**, 45 (1956).

[6] T. Kasuya, Progr. Theoret. Phys. Japan **12**, 803 (1954).

[7] C. Kittel and A. H. Mitchell, Phys. Rev. **101**, 1611 (1956).

tween the conduction electrons and the cores. This is found to be a function of the spin of the conduction electron orbital and the M_s value of each core. The variational equations are written down for $T \ll T_C$ and $T \sim T_C$. Use is made in this paper of the density matrix and a number of properties of this matrix are stated with proofs given in the Appendix.

By using the results of a self-consistent field calculation on Fe based on the unrestricted Hartree-Fock method in which there are separate exchange potentials for electrons of different spin,[8] an estimate is made here of the magnetization of the conduction electrons. This was done by using both a nearly free electron description and a cellular description of the conduction electrons. Correlation effects between conduction electrons of opposite spin tend to decrease the magnetization. This was taken into account by a method used by Pines[9] in discussing spin paramagnetism. Including correlation the nearly free electron method gives a magnetization of 0.20μ per atom and the cellular method 0.16μ per atom. Callaway[10] was the first to estimate the magnetization of the conduction electrons in Fe and he arrived at a value of 0.07μ per atom. He also gives a discussion of the exchange splitting of the *d* band and conduction band in the magnetized state of Fe.

In order to investigate the *s-d* exchange interaction Owen, Browne, Knight, and Kittel[11] examined the properties of dilute alloys of Mn in Cu. It was expected that the *s-d* interaction would at low temperatures couple the spins of the Mn ions, which they thought would be in the Mn^{++} state with $S=5/2$, ferromagnetically. Their experiments showed that the coupling was antiferromagnetic instead. A possible mechanism for antiferromagnetic coupling in dilute alloys is given in this paper. It is based on a superexchange interaction in which the conduction electrons play a role similar to the electrons associated with the $\text{O}^{=}$ ions in MnO. This model leads to a prediction of the dependence of the Néel temperature as a function of alloy composition which is in agreement with that found by Owen *et al.*

A molecular field theory is worked out in the last section of the paper based on an antiferromagnetic interaction between the magnetic atoms or ions and a ferromagnetic coupling between the magnetic atoms and the conduction electrons. Two transition temperatures result from the molecular field equations, one being $\tau_C - \tau_N - C\Gamma$ and the other τ_N. Here τ_C is the ferromagnetic Curie point that would arise if the antiferromagnetic coupling between magnetic centers were absent. τ_N is the Néel temperature which would arise if the ferromagnetic coupling were zero. Γ is a molecular field coupling parameter and C a constant. If $\tau_C > \tau_N + \frac{1}{2}C\Gamma$, one can show that at 0°K the ordering must be ferromagnetic. However, τ_N may be greater than $\tau_C - \tau_N - C\Gamma$. In that case a remarkable thing occurs. As the material is cooled from high temperatures the temperature τ_N is reached first. Just below this point the magnetization of the conduction electrons is zero and the magnetic ions are antiferromagnetically ordered. Somewhere below the temperature $\tau_C - \tau_N - C\Gamma$ the ordering becomes ferromagnetic with a net magnetization of the conduction electrons appearing. It seems that some of the experimental results of Owen *et al.*[11] can be explained by the molecular field theory given here making it unnecessary to assume that the *s-d* exchange coupling is as weak as the theory given there implies.

It is to be noted that the rare earth metals erbium[12] and dysprosium[13] do show the magnetic transitions paramagnetic to antiferromagnetic to ferromagnetic with decreasing temperature. It seems very likely that a combination of direct exchange interaction between the $4f$ and conduction electrons acting ferromagnetically and a superexchange interaction between the $4f$ and conduction electrons acting antiferromagnetically will explain these properties. The writer is presently engaged in a complete molecular field analysis of this problem.

II. EXCHANGE INTERACTION BETWEEN THE CONDUCTION ELECTRONS AND *d* ELECTRONS

This section contains a formal analysis of the exchange interaction between the conduction and the *d* electrons. This is based on setting up the variational equations for the conduction electron wave functions, where functions associated with α spin are varied independently of those associated with β spin as in the unrestricted Hartree-Fock method.[2] Although the discussion deals primarily with the case of Fe, the results can be readily generalized to other ferromagnetics. The situation of perfect ferromagnetic alignment at low temperature is considered first. The equations for conduction electron wave functions are simplified by using the density matrix notation and an averaged exchange interaction. The case of $T \sim T_C$ is discussed next. More complicated equations are arrived at due to the disorder in the spin orientations of the ferromagnetic atoms. By invoking some special properties of the density matrix and an averaged exchange interaction these equations may be put in a very convenient form.

In setting out to examine the exchange interaction between electrons in the conduction band and electrons associated with the *d* band as well as the very tightly bound electrons there is an underlying assumption that it is indeed possible to distinguish a single conduction band. In Fe this band is commonly called the 4*s* band. At those places in *k* space where the conduction band crosses the *d* band, a mixing of levels takes place and

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[8] J. H. Wood and G. W. Pratt, Jr. (to be published).

[9] D. Pines, *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.

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

[11] Owen, Browne, Knight, and Kittel, Phys. Rev. **102**, 1501 (1956).

[12] Elliott, Legvold, and Spedding, Phys. Rev. **100**, 1595 (1955).

[13] Elliott, Legvold, and Spedding, Phys. Rev. **94**, 1143 (1954).

the assumption breaks down. However, if the s band varies rapidly in energy with k, these intersections will be sharp and the over-all approximation should not be too bad.[10,14] There is evidence that this is the case.

The model on which this discussion is based has been described in the Introduction. Because of strong intra-atomic exchange forces each Fe core is assumed to be in a state of maximum multiplicity at all temperatures. Well below the Curie point, the conduction electrons are viewed as moving through the crystal with the spins of all of the cores being aligned. There is an exchange interaction between the conduction electrons and the cores which in this case will be the same for all cores and will only depend on the spin of the conduction electron. As the temperature approaches the Curie temperature, the spins of the cores are rotated in a random fashion with respect to the direction of net magnetization. Therefore, the exchange interaction of a conduction electron with a core will depend on the direction of the core spin as well as that of the conduction electron and it will vary from core to core. Above the Curie point, the average exchange interaction over the cores will be independent of the conduction electron spin. These cases will be treated separately below.

A. $T\ll T_C$

Let $\psi_P\{S=\frac{3}{2}, M_s(P)\}$ represent a product core function constructed from the orbitals regarded as being tightly bound to the pth core. The total wave function corresponding to our model for $T\ll T_C$ is

$$\psi_T=A\{\psi_1(\tfrac{3}{2},\tfrac{3}{2})\psi_2(\tfrac{3}{2},\tfrac{3}{2})\cdots\psi_N(\tfrac{3}{2},\tfrac{3}{2})\phi_1\sigma_1\cdots\phi_N\sigma_N\}. \quad (1)$$

Here A is the antisymmetrizing operator, N is the number of Fe atoms in the repeating volume, and ϕ_i represents the ith conduction band orbital which has the spin σ_i associated with it.

ψ_T as it stands is not a state of definite multiplicity; however, the total core spin is diagonal. This can be seen as follows. Let S^2 operate on (1). Since S^2 and A commute, S^2 can operate on the product function with A operating on the result. In the product form the electrons are distinguishable so that the first $25N$ electrons are associated with the N cores, and the remaining N electrons with the conduction electrons. Let $\mathbf{S}$ be

$$\mathbf{S}=\sum_{i=1}^{25N}\mathbf{S}_i+\sum_{j=25N+1}^{26N}\mathbf{S}_j=\mathbf{S}_{\text{core}}+\mathbf{S}_{\text{cond}}. \quad (2)$$

Then

$$S^2=S_{\text{core}}^2+S_{\text{cond}}^2+2\mathbf{S}_{\text{core}}\cdot\mathbf{S}_{\text{cond}}. \quad (3)$$

Application of S_{core}^2 to the operand of A in (1) yields $N(\frac{3}{2})(\frac{3}{2}+1)\hbar^2$ times the original product while operating with S_{cond}^2 or $\mathbf{S}_{\text{core}}\cdot\mathbf{S}_{\text{cond}}$ generates a linear combination of products. Therefore, ψ_T takes into account the spin degeneracy problem for the cores but not that between the cores and conduction electrons nor among the conduction electrons themselves. This is equivalent to saying that the exchange interactions within and between the cores is strong while all other exchange forces are much weaker and may be treated as perturbations.

When one assumes the form (1) for the total wave function, the best ϕ's are found by the usual variational procedure. The expectation value of the total Hamiltonian

$$H=\sum_i\left\{-\frac{\hbar^2}{2m}\nabla_i^2-e^2Z\sum_g\frac{1}{|r_i-R_g|}+\sum_{j>i}\frac{e^2}{r_{ij}}\right\} \quad (4)$$

is taken with respect to (1) and this varied with respect to the ϕ's assuming that the core orbitals are known. Since we are interested in how the conduction electrons will behave if those associated with α spin are regarded independently of those with β spin, ϕ functions with α spin are varied independently of those with β spin. The resulting equation for a ϕ with α spin is

$$H_1\phi_i(r_1)+\left[\sum_k e^2\int\frac{u_k^*(r_2)u_k(r_2)}{r_{12}}d\tau\right]\phi_i(r_1)$$
$$-\left[\sum_j{}^\alpha e^2\int\frac{u_j^*(r_2)\phi_i(r_2)}{r_{12}}d\tau_2\right]u_j(r_1)=E_i\phi_i(r_1), \quad (5)$$

where H_1 is given by

$$H_1=-\frac{\hbar^2}{2m}\nabla^2-e^2\sum_g\frac{1}{|r-R_g|}. \quad (6)$$

The one electron function $u_k(r_2)$ stands for any orbital in the problem and the sum over k in the second term of (5) is over all functions including $u_k=\phi_i$. The sum $\sum_j{}^\alpha$ in the third term is over all orbitals associated with α spin including ϕ_i. The variational equation for a ϕ associated with β spin is exactly the same as (5) except that the sum $\sum_j{}^\alpha$ is changed to $\sum_j{}^\beta$.

A great simplification of these equations is brought about by averaging the exchange interaction according to Slater's method.[15] In the case where there is an unequal number of electrons of each spin, the averaged exchanged charge density for spin σ is[16]

$$\bar{\rho}_\sigma(r_1,r_2)=\frac{\sum_m{}^\sigma\sum_k{}^\sigma u_m^*(r_1)u_m(r_2)u_k^*(r_2)u_k(r_1)}{\sum_m{}^\sigma u_m^*(r_1)u_m(r_1)}. \quad (7)$$

The $\sum_m{}^\sigma$ stands for a sum over all orbitals m having spin σ associated with them.

The averaged exchange interaction reduces the variational equations to eigenvalue type of the form

$$H^\sigma\phi_i{}^\sigma=E_i{}^\sigma\phi_i{}^\sigma, \quad (8)$$

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[14] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[15] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[16] G. W. Pratt, Jr., Phys. Rev. **88**, 1217 (1952).

where

$$H^{\alpha}=H_1+e^2\int\left\{\frac{\sum_k u_k^*(r_2)u_k(r_2)-\bar{\rho}_{\alpha}(r_1,r_2)}{r_{12}}\right\}d\tau_2 \quad (9)$$

and

$$H^{\beta}=H_1+e^2\int\left\{\frac{\sum_k u_k^*(r_2)u_k(r_2)-\bar{\rho}_{\beta}(r_1,r_2)}{r_{12}}\right\}d\tau_2. \quad (10)$$

H^{α} operates only on ϕ's with α spin and H^{β} only on those with β spin.

The solutions to (5) and the corresponding equation for a ϕ with β spin or the solutions of the averaged equations (9) and (10) define the two conduction bands and the energies thereof.

B. T Comparable to T_C

In this case the intercore exchange energy is of the same order as the thermal energy and the alignment of the core spins begins to break down. Let the total wave function now be written as

$$\psi_T=A[\psi_1\{\tfrac{3}{2},M_s(1)\}\psi_2\{\tfrac{3}{2},M_s(2)\}\cdots \times\psi_N\{\tfrac{3}{2},M_s(N)\}\phi_1\sigma_1\cdots\phi_N\sigma_N]. \quad (11)$$

Each core is in a state of maximum multiplicity with $S=\frac{3}{2}$, but with the z component of the core spin left free. Thus each $\psi_i\{\frac{3}{2},M_s(i)\}$ now is a linear combination of products. The total core spin is no longer diagonal whereas the spin of each separate core is diagonal.

The result to which we will be led in the following analysis is that the exchange charge densities become functions of the M_s values for the individual cores. This is just what one would expect since a conduction electron will have an ever decreasing exchange interaction with a given core as the spin of that core rotates away from the direction parallel to the spin of the conduction electron.

The exchange energy of an electron in the orbital ϕ_i and with α spin for the new state (11) will be derived below. We need not consider anew the average of H_1 given by (6) with respect to ϕ_i nor the Coulomb interactions between an electron in ϕ_i and the other electrons since these two energies are completely independent of the spin orientations. The total exchange energy for the system is given by

$$E_{\text{ex}}=-\sum_{i>j}\int\chi^*H_{ij}P_{ij}\chi d\tau, \quad (12)$$

where χ is the operand of A in (11) and P_{ij} is the permutation which interchanges the space and spin coordinates of the ith and jth electrons.

χ is a linear combination of products and in each product a definite association may be made between the electron index and orbital index. That is, it may be said that the jth electron occupies the qth orbital. Let us define the set of electrons i, $i+1$, $\cdots i+K$ to be associated with the orbitals about the Rth core. Let electron j be taken to occupy a particular ϕ function say ϕ_j with α spin. By considering only those permutations where i ranges over the set i, $i+1$, $\cdots i+K$ and keeping j fixed, we limit ourselves to the exchange between ϕ_j and the core R. Keeping j fixed and taking all i gives the total exchange interaction for an electron in ϕ_j.

We first consider the exchange between ϕ_j and core R as a function of the M_s of that core. The exchange interaction of $\phi_j\alpha$ with the core state $\psi_R\{S,M_s(R)\}$ is the same for the doubly filled orbitals of the core for all M_s values. Therefore, it must be found how the exchange interaction changes as a function of the spin orientations of the unpaired orbitals. When $M_s=S$, ψ_R is a single product and the exchange interaction with $\phi_j\alpha$ is

$$-\sum\nolimits_i^0\{\phi_j^*(1)u_i^*(2)|u_i(1)\phi_j(2)\} -\sum\nolimits_i'\{\phi_j^*(1)u_i^*(2)|u_i(1)\phi_j(2)\}, \quad (13)$$

where $\sum_i^0$ runs only over doubly filled orbitals and $\sum_i'$ only over singly occupied orbitals. Therefore, we consider how the $\sum_i'$ term changes with M_s.

In the $\sum_i'$ term of (13) we recognize a density matrix formed from the unpaired orbitals

$$\rho'(2,1)=\sum\nolimits_i' u_i^*(r_2)u_i(r_1)=\rho_S'(\alpha,\ M_s=S,\ r_2,\ r_1). \quad (14)$$

The exchange interaction with the unpaired orbitals is

$$-e^2\int\int\frac{\phi^*(r_1)\phi(r_2)\rho_S'(\alpha,S,r_2,r_1)}{r_{12}}d\tau_{12}. \quad (15)$$

The subscript S on ρ' specifies the spin of the core. The parameter α in the argument of ρ' is used to indicate that this is the charge density which interacts with a ϕ function associated with α spin. Since this charge density will be found to be a function of M_s of the core, it is so indicated. Obviously, for the core where all unpaired orbitals have α spin, we have

$$\rho_S'(\beta,S,r_1,r_2)=0. \quad (16)$$

To proceed further we need to use some properties of the density matrix formed from the singly occupied orbitals. These properties will be stated below as a set of theorems the proofs of which are given in the Appendix.

Theorem 1.—The density matrix of any order for a state $\psi(S,M_s,\gamma)$ is independent of the M_s value of the state.

Theorem 2.—For any many-electron state of definite M_s the first order density matrix $\rho(r_1,r_2)$ can always be separated into two terms; one a sum over orbitals associated with α spin and the other a sum over orbitals associated with β spin. We define that sum only over α spin orbitals as

$$\rho_S(\alpha,M_s,r_1,r_2), \quad (17)$$

and that over β spin orbitals as

$$\rho_S(\beta,M_s,r_1,r_2). \tag{18}$$

Therefore,

$$\rho_S(r_1,r_2)=\rho_S(\alpha,M_s,r_1,r_2)+\rho_S(\beta,M_s,r_1,r_2). \tag{19}$$

Theorem 3.—For the state of maximum multiplicity S and arbitrary M_s,

$$\rho_S'(\alpha,M_s,r_1,r_2)=\{(S+M_s)/2S\}\rho_S'(r_1,r_2) \tag{20}$$

and

$$\rho_S'(\beta,M_s,r_1,r_2)=\{(S-M_s)/2S\}\rho_S'(r_1,r_2), \tag{21}$$

where the prime denotes the restriction that we only sum over the singly occupied functions. If $\rho_0(\alpha,r_1,r_2)$ denotes the contribution from the electrons in doubly filled orbitals with α spin and $\rho_0(\beta,r_1,r_2)$ that coming from the electrons in doubly filled orbitals with β spin, then

$$\begin{aligned}\rho_S(\alpha,M_s,r_1,r_2)&\\ &=\rho_0(\alpha,r_1,r_2)+\rho_S'(\alpha,M_s,r_1,r_2)\\ &=\rho_0(\alpha,r_1,r_2)+\{(S+M_s)/2S\}\rho_S'(r_1,r_2)\end{aligned} \tag{22}$$

and

$$\begin{aligned}\rho_S(\beta,M_s,r_1,r_2)=\rho_0(\beta,r_1,r_2)&\\ +\{(S-M_s)/2S\}\rho_S'(r_1,r_2).&\end{aligned} \tag{23}$$

The exchange interaction between $\phi_j\alpha$ and the core state $\psi_R\{S,M_s(R)\}$ can be written

$$-e^2\sum_i{}^R\int\psi_R\{S,M_s(R)\}\phi_j^*(j)\frac{P_{ij}}{r_{ij}}\times\psi_R\{S,M_s(R)\}\phi_j(j)d\tau_{ij}, \tag{24}$$

where the $\sum_i{}^R$ is over the set of orbitals i, $i+1$, $\cdots i+K$ associated with the Rth core. The only permutations which yield a nonvanishing result are those for which $\sigma(i)=\sigma(j)=\alpha$. Every allowable permutation gives rise to a term of the form

$$-e^2\int\frac{u_i^*(i)u_i(j)\phi_j^*(j)\phi_j(i)}{r_{ij}}d\tau_{ij}. \tag{25}$$

In general $\psi_R\{S,M_s(R)\}$ will be a linear combination of products each distinguished by a different spin assignment to the singly occupied core orbitals. It is readily seen that there will be no contributions to (24) from cross products. The sum over i of the terms (25) gives just

$$-e^2\int\frac{\rho_S(\alpha,M_s,r_1,r_2)\phi_j^*(r_2)\phi_j(r_1)}{r_{12}}d\tau_{12}. \tag{26}$$

Writing this as an explicit function of the M_s state of the core, we have

$$-e^2\int\frac{\{\rho_0(\alpha,r_1,r_2)+[(S+M_s)/2S]\rho_S'(r_1,r_2)\}\phi_j^*(r_2)\phi_j(r_1)}{r_{12}}d\tau_{12}. \tag{27}$$

The total exchange interaction between $\phi_j\alpha$ and all of the cores is given by the sum of (27) over the cores:

$$-e^2\sum_R\int\frac{\{\rho_0(\alpha,r_1r_2)+[(S+M_s(R))/2S]\rho_S'(r_1,r_2)\}_R\phi_j^*(r_2)\phi_j(r_1)}{r_{12}}d\tau_{12}. \tag{28}$$

Similarly the total exchange interaction between $\phi_k\beta$ and the cores is

$$-e^2\sum_R\int\frac{\{\rho_0(\beta,r_1,r_2)+[(S-M_s(R))/2S]\rho_S'(r_1,r_2)\}_R\phi_k^*(r_2)\phi_k(r_1)}{r_{12}}. \tag{29}$$

In addition to the exchange interaction between the conduction electrons and the cores, there is the exchange interaction between the conduction electrons themselves. For $\phi_j\alpha$, this can be written as

$$-e^2\int\frac{\rho_c(\alpha,r_1,r_2)\phi_j^*(r_2)\phi_j(r_1)}{r_{12}}d\tau_{12}, \tag{30}$$

where

$$\rho_c(\alpha,r_1,r_2)=\sum_j{}^\alpha\phi_j^*(r_1)\phi_j(r_2). \tag{31}$$

The situation for β spin is exactly the same.

A Slater averaging procedure can be carried out for this more general case. The exchange charge density which interacts with $\phi_j\alpha$ is

$$\left\{\frac{\sum_R[\rho_0(\alpha,r_2,r_1)+[(S+M_s)/2S]\rho_S'(r_2,r_1)]_R+\rho_c(\alpha,r_2,r_1)}{\phi_j^*(r_1)\phi_j(r_1)}\right\}\phi_j^*(r_1)\phi_j(r_2). \tag{32}$$

The probability that the conduction electron associated with α spin at r_1 be in ϕ_j is

$$\phi_j^*(r_1)\phi_j(r_1)/\rho_c(\alpha,r_1,r_1). \tag{33}$$

Therefore, the average exchange charge density for a conduction electron with α spin is

$$\xi(\alpha,r_2,r_1)=\left\{\frac{\sum_R[\rho_0'(\alpha,r_2,r_1)+[(S+M_s)/2S]\rho_S'(r_2,r_1)]_R+\rho_c(\alpha,r_2,r_1)}{\rho_c(\alpha,r_1,r_1)}\right\}\rho_c(\alpha,r_1,r_2). \quad (34)$$

A similar expression can be written for the β spin case where in (34) α is everywhere replaced by β and M_s by $-M_s$. If $\rho(r_2,r_1)$ denotes the total second-order density matrix made up from all cores, all conduction electrons, and both spins, we can write the equations for the conduction electrons as

$$\left[H_1+e^2\int\frac{\rho(r_2,r_1)-\xi(\sigma,r_2,r_1)}{r_{12}}d\tau_2\right]\phi_P{}^\sigma(r_1)$$
$$=E_P{}^\sigma\phi_P{}^\sigma(r_1). \quad (35)$$

Equation (35) is to be used to find the two sets of conduction band wave functions, one for $\sigma=\alpha$ and the other for $\sigma=\beta$, when the exchange polarization by the cores is included.

III. EFFECT OF EXCHANGE POLARIZATION ON THE BAND STRUCTURE

Since we are treating the conduction electrons associated with α spin independently of those with β spin, two conduction bands will be obtained, one for electrons of each spin. In the case of Fe where the cores have a net spin, there will be unequal exchange interaction with the conduction electrons. As a result the bottom of the α spin conduction band will occur at a lower energy than that of the β spin band, if one assumes that the M_s of the cores is positive. This separation of the conduction band has been pointed out by Callaway.[10] Aside from being shifted in energy, the bands will have slightly different shapes and effective masses.

Although the emphasis here has been on the conduction band, the d band can be similarly treated, the fivefold d band for α spin lying lower than that of β spin. Callaway estimates this splitting to be of the order of the band width for the unmagnetized state. He is led to a picture of the magnetized state of Fe in which the d band is split into two halves with a gap in between.

A. Nearly Free Electron Treatment

In this section an estimate of the exchange splitting of the conduction band in Fe will be made using first-order perturbation theory and by representing the Bloch functions of the conduction band as plane waves. If we regard the conduction electrons as forming a degenerate electron gas, the net magnetization of the conduction electrons by the core exchange interaction may be simply carried out.

The energy as a function of k to the first order is given in the nearly free electron approximation as

$$E(k)=V_{000}+(\hbar^2/2m^*)k^2. \quad (36)$$

The Fourier coefficients of the crystal potential $V(r)$ are given by

$$V(\mathbf{K}_j)=(1/\Delta)\int V(r)e^{-i\mathbf{K}_j\cdot\mathbf{r}}dv, \quad (37)$$

where the integration is over the unit cell whose volume is Δ. If we represent $V(r)$ as the sum of cellular potentials, i.e., $V(r)=\sum_n V(r-R_n)$, such that the potential $V(r-R_n)$ is zero outside the nth cell, then the $V(r)$ function in (37) is the cellular potential about the origin. Let $V(r)$ now be split into a Coulomb part and an exchange part. The exchange potential which a conduction electron sees depends of course on the spin of that electron. Therefore, the energy of an α spin conduction electron will be given by

$$E(\alpha,k)=V_{000}(\text{Coulomb})$$
$$+V_{000}(\alpha,\text{exchange})+(\hbar^2/2m_\alpha)k^2 \quad (38)$$

and for β spin

$$E(\beta,k)=V_{000}(\text{Coulomb})$$
$$+V_{000}(\beta,\text{exchange})+(\hbar^2/2m_\beta)k^2. \quad (39)$$

Regarding the exchange potential as a perturbation, we see that the first-order theory displaces the two bands by a constant amount equal to

$$E(\alpha,k)-E(\beta,k)=V_{000}(\alpha,\text{exchange})$$
$$-V_{000}(\beta,\text{exchange}). \quad (40)$$

Second-order perturbation theory introduces k-dependent terms in $E(\alpha,k)-E(\beta,k)$. Callaway[17] has made a Fourier analysis of the exchange potential used in his Fe calculation. It turns out that while the Fourier coefficients of the Coulomb part of the crystal potential do not fall off rapidly with increasing K, the coefficients of the exchange potential do fall off rather fast. Therefore, in this case the major effect of the exchange interaction with the cores is just to displace the bands. This effect is shown in Fig. 1.

The number of conduction electrons with α spin is given by

$$n_\alpha=\frac{1}{2\pi^2}\int_0^{K_0(\alpha)}k^2dk \quad (41)$$

and the number with β spin is

$$n_\beta=\frac{1}{2\pi^2}\int_0^{K_0(\beta)}k^2dk, \quad (42)$$

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[17] J. Callaway, Ph.D. thesis, Princeton University, 1953 (unpublished).

where $K_0(\alpha)$ is the k value of the highest occupied level in the α spin conduction band and $K_0(\beta)$ is the k value of the highest occupied level in the β spin conduction band. For Fig. 1 we see that[18]

$$(\hbar^2/2m_\alpha)[K_0(\alpha)]^2=(\hbar^2/2m_\beta)[K_0(\beta)]^2 + V_{000}(\beta)-V_{000}(\alpha). \quad (43)$$

Therefore,

$$[K_0(\beta)]^3=[K_0(\alpha)]^3\left\{\left(\frac{m_\beta}{m_\alpha}\right)^{\frac{3}{2}} -\frac{3}{2}\left(\frac{m_\beta}{m_\alpha}\right)^{\frac{1}{2}}\left(\frac{V_{000}(\beta)-V_{000}(\alpha)}{(\hbar^2/2m_\beta)K_0(\alpha)^2}\right)+\cdots\right\}. \quad (44)$$

Setting $m_\alpha=m_\beta=m$ and using the relation that

$$n_\alpha-n_\beta=(1/6\pi^2)\{[K_0(\alpha)]^3-[K_0(\beta)]^3\}, \quad (45)$$

we find that

$$n_\alpha-n_\beta=\{K_0(\alpha)/4\pi^2\}(2m/\hbar^2)\{V_{000}(\beta)-V_{000}(\alpha)\}. \quad (46)$$

The exchange potential can be conveniently treated using the $\xi(\sigma,r_2,r_1)$ function defined in (34). If the density matrices $\rho_c(\alpha,r_1,r_2)$ and $\rho_c(\beta,r_1,r_2)$ due to the conduction electrons are constructed from an unperturbed set of plane waves with $n_\alpha=n_\beta$, then $\rho_c(\alpha,r_1,r_1)=\rho_c(\beta,r_1,r_1)=n/2$, where n is the total conduction electron density. One finds then that

$$\xi(\beta,r_2,r_1)-\xi(\alpha,r_2,r_1) = (e/n)\textstyle\sum_R\{[M_s(R)/S]\rho_S'(r_2,r_1)\}_R\rho_c(r_1,r_2). \quad (47)$$

Here $\rho_c(r_1,r_2)=\sum_j\phi_j^*(r_1)\phi_j(r_2)$, where j runs over all occupied conduction band levels of both spin. The difference in exchange potentials is

$$V(\beta)-V(\alpha)=-e\int\frac{\xi(\beta,r_2,r_1)-\xi(\alpha,r_2,r_1)}{r_{12}}d\tau_2. \quad (48)$$

This shows the expected result that if the net M_s of all the cores vanishes, $V(\beta)-V(\alpha)$ is zero and the two conduction bands are coincident. The (0,0,0) Fourier coefficient of (48) is to be used in (46).

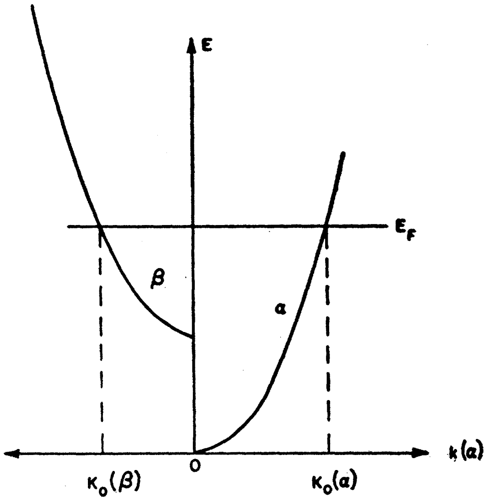

FIG. 1. Schematic representation of the splitting of the conduction band due to exchange interactions with the cores. The abscissa to the right of zero represents the α spin conduction band, and that to the left of zero the β spin conduction band.

In order to obtain a qualitative numerical estimate of the extent of the exchange polarization in Fe the results of a self-consistent field calculation on the Fe atom by Wood and the author[8] were used. In this work two potentials were constructed for the atom, one for all electrons of α spin and another for those of β spin. The exchange terms were averaged according to Slater's free electron method.[15] The atomic calculation was based on a $3d^6$, $4s^2$ configuration. In order to apply this work to the present problem two new exchange potentials were calculated. One was for a $3d^7$, $4s\alpha$ configuration and the other for a $3d^7$, $4s\beta$ configuration. The exchange potential for the crystal was represented as

$$W(\alpha,r)=\textstyle\sum_n V(\alpha,r-R_n),$$

and a similar expression for the β spin exchange potential. $V(\sigma,r-R_n)$ was taken to be the exchange potential for the atom with the modified configuration. The quantities $V_{000}(\sigma,\text{exchange})$ in (40) were taken as

$$V_{000}(\sigma,\text{exchange})=(4\pi/\Delta)\int_0^R V(\sigma,r)r^2dr. \quad (49)$$

The radius R of the S sphere replacing the Wigner-Seitz polyhedron is given by Callaway[17] as $2.667a_h$. The result of the calculation was

$$V_{000}(\beta)-V_{000}(\alpha)=0.36\times10^{-11}\text{ erg},$$

resulting in a value of $n_\alpha-n_\beta$ from (46) of

$$n_\alpha-n_\beta=0.22\times10^{23}/\text{cm}^3.$$

The total conduction electron density $n_\alpha+n_\beta$ is $0.85\times10^{23}/\text{cm}^3$ assuming one $4s$ electron per atom.

This treatment of the magnetization of the conduction electrons has so far neglected the effects of correlation. Such a neglect always tends to favor the case in which there is a net spin alignment due to the correlation introduced between electrons of parallel spin by the exclusion principle. If one could take into account the correlation which must exist between electrons of antiparallel spin, the tendency for electrons to align their spins would be reduced. An estimate of the reduction by correlation of the exchange polarization can be obtained in the following way. Let the exchange interaction with the cores be represented by a fictitious

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[18] For brevity $V_{000}(\beta,\text{exchange})$ and $V_{000}(\alpha,\text{exchange})$ are written in the following equations as $V_{000}(\beta)$ and $V_{000}(\alpha)$, respectively.

internal magnetic field H whose strength is given by

$$\begin{aligned} 2\mu_0 H &= E(\beta,k)-E(\alpha,k) \\ &= V_{000}(\beta)-V_{000}(\alpha). \end{aligned} \tag{50}$$

This suggests treating the problem as one of spin paramagnetism and using the collective electron treatment of correlation as applied to spin paramagnetism by Pines.[9] In this theory $n_\alpha - n_\beta$ is given by

$$n_\alpha - n_\beta = (2n\mu_0 H)/\alpha. \tag{51}$$

The value of α as given by Pines is

$$\alpha = (20/9)E_f + (8/9)E_{\text{exch}} + \alpha_{\text{l.r.}} + \alpha_{\text{s.r.}}, \tag{52}$$

where E_f is the Fermi energy of the conduction electrons, E_{exch} their exchange energy, $\alpha_{\text{l.r.}}$ accounts for their long-range correlation, and $\alpha_{\text{s.r.}}$ for their short-range correlation. The ratio of $n_\alpha - n_\beta$ as calculated with correlation to that found with no correlation is

$$(n_\alpha - n_\beta)_{\text{w.c.}}/(n_\alpha - n_\beta)_{\text{n.c.}} = \alpha_{\text{n.c.}}/\alpha_{\text{w.c.}}. \tag{53}$$

This turns out to be

$$(n_\alpha - n_\beta)_{\text{w.c.}} = \tfrac{3}{4}(n_\alpha - n_\beta)_{\text{n.c.}} = 0.17\times 10^{23}/\text{cm}^3.$$

This amounts to a magnetization of the conduction electrons of $0.20\mu_0$ per atom.

The magnetization of the conduction electrons is proportional to $V_{000}(\beta)-V_{000}(\alpha)$. Equations (28) and (29) show that this is in turn proportional to $\bar{M}_s/S$ where $\bar{M}_s$ is the average M_s over all the cores. Thus at $T>0$°K the magnetization of the conduction electrons is directly proportional to the net core magnetization.

B. Cellular Method

A second estimate of the separation of the two conduction bands at $k=0$ was obtained by taking the expectation value of

$$V(\beta,r)-V(\alpha,r)$$

with respect to the cellular function found by Callaway[19] for the Γ_1 state in his investigation of the band structure of Fe. The resulting separation was found to be 0.29×10^{-11} erg. Using this separation to define a fictitious magnetic field, Pines' treatment leads to a value of $n_\alpha - n_\beta$ including correlation of $0.14\times 10^{23}/\text{cm}^3$ or $0.16\mu_0$ per atom.

The values obtained here are in every case larger than the values obtained by Callaway[10] who found that the two conduction bands would be separated by 0.14×10^{-11} erg for two excess d electrons per atom of α spin which he calculated would produce an excess conduction electron spin per atom of $0.07\mu_0$.

IV. SUPEREXCHANGE COUPLING BETWEEN THE CONDUCTION ELECTRONS AND *d* ELECTRONS IN DILUTE ALLOYS

Owen, Browne, Knight, and Kittel[11] investigated the magnetic properties of dilute alloys of Mn in Cu. In these alloys it was felt that the Mn would go in as Mn^{++} which has a spin of 5/2. If these Mn^{++} ions were to partially line up their spins, one could picture the conduction electrons as moving in an internal magnetic field due to this partial alignment. This is not a true magnetic field but is the electrostatic exchange coupling which is often equated to a fictitious internal magnetic field. The theory of spin paramagnetism of conduction electrons shows that the total energy of the conduction electrons decreases as the square of the field.[20] Therefore, at 0°K the Mn^{++} ions, which are assumed to be coupled only to the conduction electrons through the Coulomb and exchange interactions, would be aligned ferromagnetically to produce the maximum internal magnetic field. Owen *et al.* discuss the *s-d* exchange coupling in the Cu-Mn case in terms of molecular fields using a single ferromagnetic coupling between the Mn ions and the conduction electrons. They find that the Mn^{++} ions should be ferromagnetically coupled with a Curie temperature of $3.5f$°K, where f is the atomic percent of Mn in Cu.

The experimental results indicated that the *s-d* exchange coupling was apparently much weaker than it would be for a free Mn^{+} ion and furthermore that at low temperatures the alloys were antiferromagnetic instead of ferromagnetic. Even the 1.4% Mn alloy was antiferromagnetic with a Néel temperature of about 12°K.

These results lead one to question the molecular field treatment given for the dilute alloy problem and further suggest that the source of the antiferromagnetic coupling is through the interaction of the Mn ions with the conduction electrons. It is true that Owen *et al.* were unable to determine the state of the Mn in the alloys, for example whether it was Mn^{++} or neutral Mn. As they point out, if it were neutral Mn, it would completely alter the interaction with the conduction electrons tending to decrease the exchange interaction. Let us simply assume that the Mn does go in as Mn^{++} and ask the question, can the interaction of these ions with the conduction electrons lead to an antiferromagnetic coupling of the Mn^{++} ions?

The answer to this question will be sought by introducing the superexchange mechanism. In MnO the antiferromagnetic interaction has been discussed on the basis of a very simplified model. Two Mn^{++} ions whose charge densities are assumed not to overlap are separated by an $\text{O}^{=}$ ion. One takes into consideration those configurations in which an electron from the $\text{O}^{=}$ is transferred to one of the Mn^{++} ions and also in which two electrons are transferred from the $\text{O}^{=}$, one

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[19] J. Callaway (private communication). The writer is indebted to Professor Callaway for the use of this function.

[20] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 601.

to each of the Mn^{++} ions. It is supposed that the solution of this configuration interaction problem will result in the situation in which the two Mn^{++} ions prefer not to align their spins. One can say that the theory can lead to this case but no one has actually carried out the calculation because the number of possible configurations is very large. Instead an even more simplified model is treated in which the Mn^{++} ions are replaced by centers with only one electron about them and the $O^{=}$ is replaced by a center with a doubly filled orbital. Such a system has been discussed by the writer,[21] and it was found that the theory does admit the possibility that the lowest state is that in which the spins about the centers which replace the Mn^{++} ions prefer not to align. A numerical example was worked out there in which this was found to be the case.

A superexchange mechanism which can lead to the observed antiferromagnetism in the Cu-Mn alloys is simply that in which the conduction electrons play the role of the $O^{=}$ electrons in MnO or those of the nonmagnetic center in the very simple four electron problem described above. Consider then the simplified model of two centers A and B, each with one electron about them in a crystal and so far apart that there is no direct interaction between them. They represent a very simplified picture of two Mn^{++} ions in Cu. The point to be examined is whether, as a result of their interaction with the conduction electrons, the electrons on these centers will or will not align their spins. Let these electrons be in localized orbitals $v(r-R_A)$ and $v(r-R_B)$ and consider their interaction with a particular Bloch function $b(k,r)$. The configurations which must be taken into account are

$$\phi_1=v(r_1-R_A)\alpha(1)b(k,r_2)\alpha(2)b(k,r_3) \times\beta(3)v(r_4-R_B)\beta(4), \quad (54)$$

$$\phi_2=v(r_1-R_A)\beta(1)b(k,r_2)\alpha(2)b(k,r_3) \times\beta(3)v(r_4-R_B)\alpha(4), \quad (55)$$

$$\eta_1=v(r_1-R_A)\alpha(1)v(r_2-R_A)\beta(2)b(k,r_3) \times\alpha(3)v(r_4-R_B)\beta(4), \quad (56)$$

$$\eta_2=v(r_1-R_A)\alpha(1)v(r_2-R_A)\beta(2)b(k,r_3) \times\beta(3)v(r_4-R_B)\alpha(4), \quad (57)$$

$$\eta_3=v(r_1-R_A)\alpha(1)b(k,r_2)\beta(2)v(r_3-R_B) \times\alpha(3)v(r_4-R_B)\beta(4), \quad (58)$$

$$\eta_4=v(r_1-R_A)\beta(1)b(k,r_2)\alpha(2)v(r_3-R_B) \times\alpha(3)v(r_4-R_B)\beta(4), \quad (59)$$

$$\eta_5=v(r_1-R_A)\alpha(1)v(r_2-R_A)\beta(2)v(r_3-R_B) \times\alpha(3)v(r_4-R_B)\beta(4). \quad (60)$$

ϕ_1 and ϕ_2 represent the two ground configurations. η_1 through η_5 represent the excited configurations in which various charge transfers are made and all possible spin orientations taken for each configuration of charges with the restriction that the total M_s be zero.

The configuration interaction may be very conveniently discussed by using Kramers' method.[22] The unperturbed states of the problem (54) through (60) are separated into two classes, the ground states and the excited states. The excited states are incorporated into an effective Hamiltonian matrix U_{km}, where k and m refer only to the ground set. Thus the effect of the excited states is that of a perturbation on the ground states. The matrix U_{km} is given by[23]

$$U_{km}=H_{km}+\sum_\alpha H_{k\alpha}H_{\alpha m}/(E-H_{\alpha\alpha}) +\sum_{\alpha\neq\beta} H_{k\alpha}H_{\alpha\beta}H_{\beta m}/(E-H_{\alpha\alpha})(E-H_{\beta\beta})+\cdots, \quad (61)$$

where H is the actual Hamiltonian for the four electron system and the Greek indices refer only to excited states, i.e., η_1 to η_5. Since $U_{11}=U_{22}$, this can be set as the zero of energy. If U_{12} is negative, the spins of the electrons localized about the centers A and B will be aligned in the lowest state, that is this state will have $S=1$. If U_{12} is positive, these spins will not be aligned and the lowest state will have $S=0$. The matrix element U_{12} turns out to be

$$U_{12}=+g^2/(E_2-E)-2d^2(J+g)/(E_1-E)^2 -4hdg/(E_1-E)(E_2-E), \quad (62)$$

where

$$g=e^2\int\int\frac{b(k,r_1)b^*(k,r_2)v^*(r_1-R_A)v(r_2-R_B)}{r_{12}}d\tau_{12}, \quad (63)$$

$$J=e^2\int\int\frac{b^*(k,r_1)b(k,r_2)v(r_1-R_A)v^*(r_2-R_A)}{r_{12}}d\tau_{12}, \quad (64)$$

$$\begin{aligned}d=&\int v^*(r_1-R_A)H_1b(k,r_1)d\tau_1\\&+e^2\int\int\frac{v^*(r_1-R_A)b^*(k,r_2)v(r_1-R_A)v(r_2-R_A)}{r_{12}}d\tau_{12}\\&+e^2\int\int\frac{b^*(k,r_1)b^*(k,r_2)b(k,r_1)v(r_2-R_A)}{r_{12}}d\tau_{12}\\&+e^2\int\int\frac{v^*(r_1-R_A)v(r_1-R_A)\times v^*(r_2-R_B)v(r_2-R_B)}{r_{12}}d\tau_{12}, \quad (65)\end{aligned}$$

and

$$\begin{aligned}h=&\int v^*(r_1-R_A)H_1b(k,r_1)d\tau_1\\&+2e^2\int\int\frac{v^*(r_1-R_A)b^*(k,r_2)v(r_1-R_A)v(r_2-R_B)}{r_{12}}d\tau_{12}\\&+e^2\int\int\frac{b^*(k,r_1)v^*(r_2-R_A)v(r_1-R_A)v(r_2-R_A)}{r_{12}}d\tau_{12}. \quad (66)\end{aligned}$$

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[21] G. W. Pratt, Jr., Phys. Rev. **97**, 926 (1955).

[22] H. A. Kramers, Physica **1**, 182 (1934).

[23] P. O. Löwdin, J. Chem. Phys. **19**, 1396 (1951).

E_1 is the diagonal energy of the excited states η_1 to η_4 corresponding to the case where one of the conduction electrons is captured by a magnetic center. E_2 is the diagonal energy of η_5 where both conduction electrons are trapped. The configuration η_5 must be included otherwise it can be proved that U_{12} can only be negative.[24] The first term in (62) comes entirely from η_5 the contributions from η_1 to η_4 cancelling out completely. Since $E_2 > E$, the first term[25] in (62) is positive definite. Therefore, if the higher order terms in U_{12} do not reverse the sign, the magnetic centers A and B do not align their spins in the lowest state. Under these circumstances the superexchange coupling of these centers via the Bloch function $b(k,r)$ is antiferromagnetic in character.

Suppose the term $+g^2/(E_2-E)$ is taken to represent the source of the antiferromagnetic interaction in a dilute alloy. Then it is possible to estimate the dependence of the Néel temperature on composition. The separation between the $S=0$ and $S=1$ states due to U_{12} is $2g^2/E_2$. Therefore, let the Néel temperature be taken proportional to g^2/E_2. It remains to determine the dependence of g and E_2 on composition.

The integral g defined in (63) is the electrostatic energy of two charge distributions,

$$\sigma(r_1)=b^*(k,r_1)v(r_1-R_A) \tag{67}$$

and

$$\sigma'(r_2)=b^*(k,r_2)v(r_2-R_B). \tag{68}$$

Since $v(r_1-R_A)$ is localized about R_A, so must be $\sigma(r_1)$. Similarly $\sigma'(r_2)$ is concentrated about R_B. If these charge distributions are non-overlapping, as we assume for a dilute alloy, g is essentially

$$g=\frac{e^2}{R_{AB}}\int\sigma(r_1)d\tau_1\int\sigma'(r_2)d\tau_2. \tag{69}$$

Let N_a represent the number of magnetic atoms per cm^3 in the alloy and N be the total number of atoms per cm^3. The assuming a uniform alloy R_{AB} is $(N/N_a)R_0$, where R_0 is the average nearest neighbor distance. Thus g^2 is proportional to $(N_a/N)^2$. In any actual case there will be many different g integrals. However, they will all have the same dependence on R_{AB}.

The quantity E_2 depends on R_{AB}, or composition, only through an integral of the form

$$e^2\int\int\frac{v^*(r_1-R_A)v(r_1-R_A)v^*(r_2-R_B)v(r_2-R_B)}{r_{12}}d\tau_{12}, \tag{70}$$

which is essentially a constant over R_{AB} by the same arguments used with the g integral. Therefore, E_2 may be written

$$E_2=C_1+C_2/R_{AB}. \tag{71}$$

Using the relation between R_{AB} and N_a the Néel temperature is

$$T_N\sim\left(\frac{N_a}{N}\right)\left(\frac{1}{C+D(N_a/N)}\right). \tag{72}$$

For a sufficiently dilute alloy $T_N\sim(N_a/N)$. This is shown to be true in the Cu-Mn case.[11] Although this result cannot be regarded as a very stringent test of the theory it does indicate that a model for Cu-Mn in which the Mn ions are uniformly dispersed can be consistent with the concentration dependence of the Neél temperature. Furthermore uniform dispersion with an antiferromagnetic coupling going as $1/R_{AB}$ would result in an ordered, probably two sublattice, structure in that nearest neighbor spins are antiparallel on the average.

V. MOLECULAR FIELD THEORY FOR A DIRECT EXCHANGE AND SUPEREXCHANGE COUPLED SYSTEM

In this section a molecular field description is given of a magnetic material which has an antiferromagnetic superexchange coupling between the magnetic ions (cores) and a ferromagnetic direct exchange between the cores and conduction electrons. The results obtained here will be applied to the experimental results of Owen *et al.*[11] on Cu-Mn alloys.

Let the magnetic atoms be assigned to two sublattices A and B. In the dilute alloy this corresponds to the idealized situation where the magnetic atoms are uniformly dispersed in the host crystal. The phenomenological Hamiltonian is taken to have the form

$$\mathcal{H}=\sum_{ij}{}'[-I_1\mathbf{S}_{Ai}\cdot\mathbf{S}_{Bj}-I_2(\mathbf{S}_{Ai}\cdot\mathbf{S}_e+\mathbf{S}_{Bj}\mathbf{S}_e) -I_3(\mathbf{S}_{Ai}\mathbf{S}_{Aj}+\mathbf{S}_{Bi}\mathbf{S}_{Bj})]. \tag{73}$$

Here $\mathbf{S}_e$ stands for the net spin of the conduction electrons. I_1 may be called the interaction integral coupling the spins of atoms on sublattices A and B. In the very simple four electron problem discussed above, I_1 is g^2/E_2; and in a more realistic problem, I_1 is derived from (61). For an antiferromagnetic coupling between sublattices A and B, I_1 is negative. There will be a coupling of the atoms on sublattice A with each other and of B atoms with each other. This is given in the last term of (73). The factor I_2 represents the direct exchange interaction between the conduction electrons and magnetic atoms. It is positive, indicating a ferromagnetic coupling. Equation (73) may be rewritten in terms of the total magnetizations of the

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[24] The proof is given in reference 19.

[25] Unfortunately this term was omitted in Eq. (29) of reference 19. The inequality given in (34) there should read

$$g^2/(E_2-E)-4hdg/(E_1-E)(E_2-E)>2d^2(J+g)/(E_1-E)^2.$$

In the numerical example considered, the omitted term must be taken as zero owing to the very small value of g. Therefore, Eqs. (40) and (41) and their consequences apply for the example as stated.

sublattices A and B and of the conduction electrons as

$$\mathcal{H}=-\frac{I_1 Z_{AB}\mathbf{M}_A\cdot\mathbf{M}_B}{\frac{1}{2}N(g\mu_B)^2}-\frac{I_2(\mathbf{M}_A+\mathbf{M}_B)\cdot\mathbf{M}_e}{2g\mu_B{}^2}-\frac{I_3}{\frac{1}{2}N(g\mu_B)^2}(Z_{AA}\mathbf{M}_A\cdot\mathbf{M}_A+Z_{BB}\mathbf{M}_B\cdot\mathbf{M}_B). \tag{74}$$

Where Z_{AB} is the number of nearest neighbor B sites to a given A site and vice versa and Z_{AA} is the number of nearest neighbor A sites to a given A site with Z_{BB} similarly defined in the B sublattice.

From (74) the fictitious internal magnetic field acting on an atom in sublattice A is

$$\mathbf{H}_A=\frac{I_1 Z_{AB}}{\frac{1}{2}N(g\mu_B)^2}\mathbf{M}_B+\frac{I_2}{2g\mu_B{}^2}\mathbf{M}_e+\frac{2I_3 Z_{AA}}{\frac{1}{2}N(g\mu_B)^2}\mathbf{M}_A. \tag{75}$$

The internal field acting on a B atom is

$$\mathbf{H}_B=\frac{I_1 Z_{AB}}{\frac{1}{2}N(g\mu_B)^2}\mathbf{M}_A+\frac{I_2\mathbf{M}_e}{2g\mu_B{}^2}+\frac{2I_3 Z_{AA}}{\frac{1}{2}N(g\mu_B)^2}\mathbf{M}_B. \tag{76}$$

The internal field acting on the conduction electrons is

$$\mathbf{H}_e=\frac{I_2}{2g\mu_B{}^2}(\mathbf{M}_A+\mathbf{M}_B). \tag{77}$$

Let $I_1 Z_{AB}/\frac{1}{2}N(g\mu_B)^2=-A$, where A is positive; $I_3 Z_{AA}/\frac{1}{2}N(g\mu_B)^2=-\Gamma/2$, which can be positive or negative; and $I_2/2g\mu_B{}^2=\eta$, with η positive. Then above all transition temperatures the magnetizations of the sublattices and conduction electrons in an applied field H_0 are given by

$$M_A=(C/2T)(H_0-AM_B+\eta M_e-\Gamma M_A), \tag{78}$$

$$M_B=(C/2T)(H_0-AM_A+\eta M_e-\Gamma M_B), \tag{79}$$

$$M_e=(M_A+M_B)\eta\chi_C+H_0\chi_C, \tag{80}$$

where $C=Ng^2\mu_B{}^2S(S+1)/3k$ and χ_C is the paramagnetic susceptibility of the conduction electrons. Setting H_0 equal to zero the possible transition temperatures are found by setting the determinant of the coefficients of M_A, M_B, and M_e in (78), (79), and (80) equal to zero. There are two possible transition temperatures

$$T_1=\tfrac{1}{2}C(A-\Gamma)=\tau_N, \tag{81}$$

$$T_2=C\eta^2\chi_C-\tfrac{1}{2}C(A+\Gamma)=\tau_C-\tau_N-C\Gamma. \tag{82}$$

Here τ_N is the Néel temperature which would be found if the ferromagnetic coupling were absent, i.e., $\eta=0$ and τ_C is the Curie temperature which would be found if both A and Γ were zero.

The susceptibility above the highest transition temperature is readily found to be

$$\chi=\chi_C+\frac{C(1+\eta\chi_C)^2}{T-\{C\eta^2\chi_C-\frac{1}{2}C(A+\Gamma)\}}. \tag{83}$$

The ordering at 0°K may be found by writing (74) as

$$\mathcal{H}=A\mathbf{M}_A\cdot\mathbf{M}_B+\Gamma/2(\mathbf{M}_A\cdot\mathbf{M}_A+\mathbf{M}_B\cdot\mathbf{M}_B)-\eta(\mathbf{M}_A+\mathbf{M}_B)\cdot\mathbf{M}_e \tag{84}$$

and comparing the energies of the ferromagnetic case, where $\mathbf{M}_A=\mathbf{M}_B$ both of which are in the direction of $\mathbf{M}_e$, and the antiferromagnetic case, where $\mathbf{M}_A=-\mathbf{M}_B$. The condition for antiferromagnetic ordering at 0°K is

$$A>2\eta^2\chi_C. \tag{85}$$

Therefore, if Γ is positive, a high temperature susceptibility of the form

$$\chi=\text{const}/(T-\theta), \tag{86}$$

with $\theta>0$ means that unless η, A, and Γ are temperature-dependent, the material must be ferromagnetically ordered at 0°K.

This molecular field treatment admits the interesting possibility of an antiferromagnetic-ferromagnetic transition. If

$$2C\eta^2\chi_C>CA, \tag{87}$$

the material is ferromagnetic at 0°C. However, the temperature τ_N in (81) corresponds to a spontaneous antiferromagnetic ordering, i.e., $\mathbf{M}_A=-\mathbf{M}_B$ and $M_e=0$. It is possible for (87) to be satisfied and at the same time to have $\tau_N>\tau_C-\tau_N-C\Gamma$ if

$$2C\eta^2\chi_C>CA>C\eta^2\chi_C. \tag{88}$$

Under these circumstances, as the material is cooled from high temperatures it reaches τ_N first, at which point it orders antiferromagnetically. This must change to ferromagnetic ordering at some lower temperature.

The equations for the magnetizations in the ferromagnetic case below the transition temperature are, for zero applied field,

$$M_A=\frac{N}{2}\mu_0 gSB_S\left[\left(\frac{\eta M_e-AM_B-\Gamma M_A}{kT}\right)Sg\mu_0\right], \tag{89}$$

$$M_B=\frac{N}{2}\mu_0 gSB_S\left[\left(\frac{\eta M_e-AM_A-\Gamma M_B}{kT}\right)Sg\mu_0\right], \tag{90}$$

$$M_e=(M_A+M_B)\eta\chi_C. \tag{91}$$

If M_e is eliminated in (89) and (90) by (91) and the argument of the Brillouin functions is taken to be small, the temperature at which the ferromagnetic ordering disappears can be solved for and turns out to be $\tau_C-\tau_N-C\Gamma$, i.e., the same as (82). Therefore, the antiferromagnetic-ferromagnetic transition must occur between 0°K and $T=\tau_C-\tau_N-C\Gamma$.

There is also the possibility that θ be positive in

(86) and that the material never order ferromagnetically. This comes about if

$$\theta = C\eta^2\chi_C - \tfrac{1}{2}C(A+)\Gamma > 0 \qquad (92)$$

and the antiferromagnetic conduction (85) is also satisfied. For this to obtain

$$-C\Gamma > CA - 2C\eta^2\chi_C, \qquad (93)$$

which can be satisfied for negative Γ. As such a material is cooled from high temperature, it reaches τ_N first, at which point $\mathbf{M}_A = -\mathbf{M}_B$ which persists to 0°K.

No choice of constants will allow the possibility of a change in ordering from ferromagnetic to antiferromagnetic as the temperature is decreased. That is, the conditions $\tau_C - \tau_N - C\Gamma > \tau_N$ and (85) cannot both be satisfied.

It is of interest to see how this molecular field treatment might serve to explain some of the experimental results of Owen *et al.*[11] on the dilute alloys of Mn in Cu. This theory can lead to the observed high-temperature susceptibility given in (86) with positive θ as is shown in (83). Furthermore, for a positive θ it can lead to the observed antiferromagnetic ordering below τ_N. The results of Owen, Browne, Knight, and Kittel indicate an *s-d* exchange interaction in the alloys somewhat stronger than that of the free ion on the basis of the predicted and observed Curie points while all of their other results pointed to a considerably weaker exchange interaction. In particular, their analysis of the Knight shift of the Cu nuclear resonance of a 0.03% alloy at 1.2°K was interpreted on the basis of their theory to mean that the actual *s-d* exchange interaction was very weak, perhaps one-fiftieth that of the free ion. They reasoned that if the alloy were in the paramagnetic state at that temperature, a Knight shift four times that in pure Cu should be observed as the result of the exchange coupling between the conduction electrons and the Mn ions. As shown in Sec. III a magnetization of the conduction electrons proportional to that of the magnetic cores due to direct *s-d* exchange comes about by the lowering of the energy of the conduction band of one spin with respect to the band of opposite spin. The superexchange effect described in Sec. IV is based on the capture by the core of a conduction electron of spin opposite to that of the core due to the Exclusion Principle. Consider the case of Cu-Mn where a net magnetization of the Mn^{++} ions has been induced by an external magnetic field. The conduction band with spin parallel to the net Mn^{++} spin will have its energy lowered by direct *s-d* exchange while the conduction band of opposite spin will have its energy lowered by the exclusive ability of these electrons to spend part of the time in a bound 3*d* orbital which partly screens the extra positive charge of the Mn^{++}. Thus the net lowering of one conduction band with respect to the other may be very small resulting in a very small net conduction electron magnetization.

The screening charge about an Mn^{++} has a contribution from conduction electrons of the same spin as the core. This is described by excited states where the conduction electrons have normally unoccupied k values. These states lead only to a ferromagnetic coupling, i.e., U_{km} of (61) negative to second order. It would be interesting to investigate a dilute alloy where the core has less than a half-full d shell so that the Exclusion Principle would not operate as in Cu-Mn.

Unfortunately there do not appear to be enough data in reference 11 to estimate the coupling constants η, A, and Γ. It would be particularly interesting to see whether neutron diffraction experiments show an antiferromagnetic-ferromagnetic transition. It seems that one can conclude that an *s-d* exchange coupling whose strength is comparable to that for the free ion is not inconsistent with the experimental results obtained on the Cu-Mn alloys if the more general molecular field treatment given here is used.

As pointed out earlier, the existence of an antiferromagnetic-ferromagnetic transition has been observed in the rare earths erbium and dysprosium. Since the 4*f* or magnetic electrons do not overlap between neighbors, the usual exchange mechanism of ferromagnetism in the transition elements does not apply here. It is the opinion of the writer that the direct and superexchange interactions between the 4*f* electrons and the conduction electrons is the basis of the magnetic properties of these metals. A complete molecular field treatment of this situation is being carried out and will be reported in a subsequent publication.

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APPENDIX

Theorem 1.—The density matrix of any order for a state $\psi(S,M_s)$ is independent of the M_s value of the state.

Proof.—Consider the first-order density matrix formed from the state $\psi(S,S)$. This is

$$\rho_S(r_1,r_1') = \int \psi^*(S,S;r_1\cdots r_n)\psi(S,S;r_1'\cdots r_n)d\tau_1'.$$

The first-order density matrix for the state $\psi(S,S-1)$ is

$$\rho_{S-1}(r_1r_1') = \int \frac{S^-}{\hbar(2S)^{\frac{1}{2}}}\psi^*(S,S,r_1\cdots r_n)\frac{S^-}{\hbar(2S)^{\frac{1}{2}}} \times\psi(S,S;r_1'\cdots r_n)d\tau_1',$$

which equals

$$\frac{1}{2S\hbar^2}\int S^+S^-\psi^*(S,S;r_1\cdots r_n)\psi(S,S,r_1'\cdots r_n)d\tau_1'.$$

But $S^+S^-/2S\hbar^2$ operating on $\psi(S,S)$ is equal to $\psi(S,S)$, so we have shown that

$$\rho_{S-1}(r_1,r_1')=\rho_S(r_1,r_1').$$

Let us assume that $\rho_{S-n}(r_1,r_1')=\rho_S(r_1,r_1')$. If we can establish that the same is true for $S-n-1$, then the theorem is proved by induction. We have

$$\int\psi^*(S,\,S-n-1\,;r_1\cdots r_n)\psi(S,\,S-n-1\,;r_1'\cdots r_n)d\tau_1'$$

$$=\frac{1}{\hbar^2(2S-n)(n+1)}\int S^+S^-\psi(S,\,S-n\,;r_1\cdots r_n)$$

$$\times\psi(S,\,S-n\,;r_1\cdots r_n)d\tau_1'.$$

But

$$S^+S^-\psi(S,\,S-n\,;r_1\cdots r_n)$$
$$=\hbar^2(2S-n)(n+1)\psi(S,\,S-n\,;r_1-r_n),$$

and so

$$\rho_{S-n-1}(r_1,r_1')=\rho_{S-n}(r_1,r_1').$$

Since the above proof is independent of the order of the density matrix, the theorem is proved.

Theorem 2.—For any many electron state of a definite M_s the first-order density matrix can always be separated into two terms; one a sum over orbitals associated with α spin and the other a sum over orbitals associated with β spin. We define that sum over only orbitals of α spin as $\rho_S(\alpha,M_s,r_1,r_1')$ and that only over β spins as $\rho_S(\beta,M_s,r_1,r_1')$.

Proof.—First consider a single determinant of one electron space and spin functions whose spatial parts are orthonormal. For this determinant,

$$\rho(r_1,r_1')=\sum_{\sigma k}\sum_k u_k^*(r_1)u_k(r_1')\sigma_k(1)\sigma_k(1').$$

Obviously one can separate $\sum_{\sigma k}$ into one part in which all $\sigma_k=\alpha$ and another in which all $\sigma_k=\beta$.

Any many-electron state of definite M_s can be expanded as a linear combination of determinants composed of orthonormal one-electron functions. Since in finding the first-order density matrix one integrates over all spatial coordinates but one, because of the orthogonality of the orbitals the only nonzero cross products will be between determinants differing only in the replacement of one spatial orbital by another. If u_p is replaced by u_q, the contribution of the cross product to $\rho(r_1,r_1')$ will be

$$u_p(r_1)u_q(r_1')\sigma_p(1)\sigma_q(1').$$

The total M_s can be preserved in two ways: first, $\sigma_p=\sigma_q$, in which case the cross product contributions can always be classified according to $\sigma_p=\sigma_q=\alpha$ or $\sigma_p=\sigma_q=\beta$; second, if $\sigma_p\neq\sigma_q$ with other spin differences arising to compensate this difference preserving the total M_s. But this must result in terms in the summation over all spins of the form

$$\sigma_{p=\alpha}(x)\sigma_{q=\beta}(x),$$

which is zero. Therefore, the only contributions to the first order density matrix are for $\sigma_p=\sigma_q$. Since we have shown that the direct products between determinants as well as the cross products can be classified according to spin direction, the theorem is established.

Corollary.—According to Theorems 1 and 2, the first-order density matrix for a state $\psi(S,M_s)$ may always be written as

$$\rho_S(r_1,r_1')=\rho_S(\alpha,M_s,r_1,r_1')+\rho_S(\beta,M_s,r_1,r_1').$$

Here $\rho_S(\alpha,M_s,r_1,r_1')$ is the total contribution to $\rho_S(r_1,r_1')$ coming from the orbitals associated with α spin and the second term is the total contribution coming from orbitals associated with β spin.

Theorem 3.—For the state of maximum multiplicity,

$$\rho_S(\alpha,M_s,r_1,r_1')=[(S+M_s)/2S]\rho_S(r_1,r_1')$$

and

$$\rho_S(\beta,M_s,r_1,r_1')=[(S-M_s)/2S]\rho_S(r_1,r_1').$$

Proof.—A state of multiplicity S and arbitrary M_s is given by

$$\psi(S,M_s)=\prod_{M=S}^{M=M_s+1}\left(\frac{1}{\hbar[(S+M)(S-M+1)]^{\frac{1}{2}}}\right)$$
$$\times(S^-)^{S-M_s}\psi(S,S).$$

For the state of maximum multiplicity, $\psi(S,M_s)$ is symmetric under any permutation of spin coordinates. Such a state is a linear combination of determinants, each with $S-M_s$ spins reversed and each appearing with a coefficient

$$(S-M_s)!\prod_{M=S}^{M=M_s+1}\left(\frac{1}{[(S+M)(S-M+1)]^{\frac{1}{2}}}\right).$$

No determinant appears twice, and with the above coefficients the state is normalized. If the one-electron function u_i has α spin associated with it in a given determinant, it will make a contribution to $\rho_S(\alpha,M_s,r_1,r_1')$ due to that determinant of

$$(S-M_s)!^2\prod_{M=S}^{M=M_s+1}\left\{\frac{1}{(S+M)(S-M+1)}\right\}u_i^*(r_1)u_i(r_1').$$

There will be no cross products, as proved in Theorem 2. The number of determinants in $\psi(S,M_s)$ in which u_i has α spin is

$$(2S-1)!/[(S-M_s)!(S+M_s-1)!].$$

The total contribution of u_i with α spin to $\rho_S(\alpha,M_s,r_1,r_1')$

is

$$\frac{(2S-1)!}{(S-M_s)!(S+M_s-1)!}(S-M_s)!^2 \times \prod_{M=S}^{M=M_s+1}\left\{\frac{1}{(S+M)(S-M+1)}\right\}u_i^*(r_1)u_i(r_1').$$

The sum over all u_i gives just $\rho_S(\alpha,M_s,r_1,r_1')$. Therefore,

$$\rho(\alpha,M_s,r_1,r_1')=\frac{(2S-1)!(S-M_s)!}{(S+M_s-1)!} \times \prod_{M=S}^{M=M_s+1}\left(\frac{1}{(S+M)(S-M+1)}\right)\rho_S(r_1,r_1').$$

The product π in the above equation is equal to

$$\prod_{M=S}^{M=M_s+1}\left(\frac{1}{(S+M)(S-M+1)}\right)=\frac{(S+M_s)!}{(2S)!(S-M_s)!}.$$

Therefore, $\rho_S(\alpha,M_s,r_1,r_1')$ is

$$\rho_S(\alpha,M_s,r_1,r_1')=\frac{(2S-1)!(S-M_s)!(S+M_s)!}{(S+M_s-1)!(2S)!(S-M_s)!}\rho_S(r_1,r_1')$$

$$=\frac{S+M_s}{2S}\rho_S(r_1,r_1').$$

From the Corollary, we have

$$\rho_S(\beta,M_s,r_1,r_1')=\rho_S(r_1,r_1')-\rho_S(\alpha,M_s,r_1,r_1').$$

Hence

$$\rho_S(\beta,M_s,r_1,r_1')=\left(\frac{S-M_s}{2S}\right)\rho_S(r_1,r_1').$$

Therefore, the theorem is proved.

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Energy of Formation of Vacancies in Copper and Gold

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From the anomalous rise of the thermal expansion near the melting point, a value of about 0.7 ev for the energy of formation of vacancies in copper and gold is found.

INTRODUCTION

FROM theoretical calculations it is known that the energy of formation of vacancies in copper and gold is of the order of 1 ev,[1] which is a value sufficiently low to expect appreciable concentrations of vacancies in thermal equilibrium at temperatures near the melting point. An anomalous rise of the electrical resistivity, which was attributed to the vacancies mentioned, was observed by Meechan and Eggleston[2] in copper and gold above 500°C. The extra resistivity closely followed an $\exp(E_f/kT)$ law, and values of the expected order of magnitude for the formation energy E_f of vacancies were obtained.

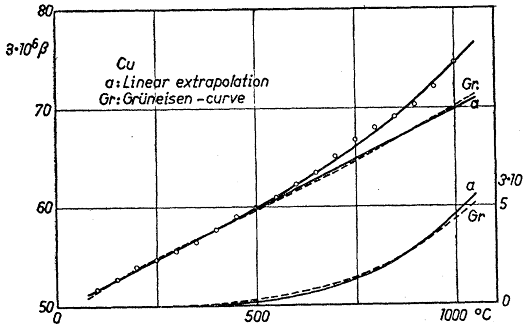

FIG. 1. Upper curves: Temperature dependence of coefficient of thermal expansion β of copper. Circles refer to actual measurements.[5] The dashed curve *Gr* represents the Grüneisen curve obtained by Nix and MacNair[4] from the data below 500°C; the straight line *a* is the linear extrapolation of the temperature dependence of β below 500°C. Lower curves: Smoothed differences between observed and extrapolated values of β, obtained from the upper part of the figure, as a function of temperature. *Gr*: differences with regard to the Grüneisen curve; *a*: differences with regard to the linearly extrapolated curve.

When vacancies are formed the metal must expand, so an anomalous rise of the thermal expansion will occur at sufficiently high temperatures. As far as we know, Gertsriken[3] was the first to deduce a value for the formation energy of vacancies in copper from this phenomenon; however, the data he used were not very accurate.

In the present paper we apply the same method, using more accurate data and a way of extrapolating the low-temperature values of the thermal expansion coefficient to higher temperatures which has a somewhat better theoretical justification.

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[1] H. B. Huntington and F. Seitz, Phys. Rev. 61, 315 (1942); H. B. Huntington, Phys. Rev. 61, 325 (1942); A. D. Le Claire, Acta Metallurgica 1, 438 (1953); F. G. Fumi, Phil. Mag. 46, 1007 (1955).

[2] C. J. Meechan and R. R. Eggleston, Acta Metallurgica 2, 680 (1954).

[3] G. D. Gertsriken, Compt. rend. 98, 211 (1954).