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Considerations on Double Exchange

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Zener has suggested a type of interaction between the spins of magnetic ions which he named "double exchange." This occurs indirectly by means of spin coupling to mobile electrons which travel from one ion to the next. We have calculated this interaction for a pair of ions with general spin S and with general transfer integral, b, and internal exchange integral J.

One result is that while the states of large total spin have both the highest and lowest energies, their average energy is the same as for the states of low total spin. This should be applicable in the high-temperature expansion of the susceptibility, and if it is, indicates that the high-temperature Curie-Weiss constant θ should be zero, and $1/\chi$ *vs* T a curved line. This is surprising in view of the fact that the manganites, in which double exchange has been presumed to be the interaction mechanism, obey a fairly good Curie-Weiss law.

The results can be approximated rather well by a simple semiclassical model in which the spins of the ion cores are treated classically. This model is capable of rather easy extension to the problem of the whole crystal, but the resulting mathematical problem is not easily solved except in special circumstances, e.g., periodic disturbances (spin waves).

I. INTRODUCTION

ZENER[1] has proposed a mechanism of electron spin interaction which he calls "double exchange." He suggested that this mechanism is responsible for ferromagnetism in the mixed-valency manganites of perovskite structure, such as $(La_xCa_{1-x})(Mn_x^{III}Mn_{1-x}^{IV})O_3$.[2] Zener points out that the extra electron on the Mn^{III} can travel back and forth between the two Mn ions, and that its spin will couple with those of both ion cores. This obviously leads to a spin coupling of some kind, which he shows is probably ferromagnetic. As Zener points out, if the transfer does not change the electron's spin, and if exchange between it and the ion is so large that it cannot be on an ion of the wrong spin, then the electron can move if the ions are parallel, and cannot move if they are not parallel. One expects therefore a parallel coupling of the order of magnitude of the transfer integral which causes the electron's motion.

We have investigated this mechanism in greater detail and with considerably more general assumptions than reference 1. We were interested in seeing whether it differed in any observable aspects from ordinary exchange. The result is indeed qualitatively different, as we could have anticipated from the fact that there is an extra degree of freedom, namely the motion of the electron, to be considered.

The results can be understood rather easily on a simple semiclassical model, which we shall give in the main body of the paper. The rigorous calculation will be given in an Appendix. Further, this simple model can be extended far enough so that we can see some of the characteristics of the problem which must be solved for an entire solid, although mathematical solution of this problem is practically impossible.

One of the major differences from ordinary exchange is that there are two levels for every spin arrangement of the ion cores, one as high in energy as the other is low. If exchange is small one of these corresponds to a spin-up traveling electron, the other to spin-down; while if exchange is large one is the symmetric, one the antisymmetric orbital state. Thus the *average* energy is not a function of total spin, and the series calculation of susceptibility[3] fails to give a second term, so that θ vanishes in the high-temperature Curie-Weiss law. This effect is not observed.[4]

II. THE MODEL; CONSIDERATION OF THE TRANSFER PROCESS

The model we use is shown in Fig. 1. We denote the magnetic atoms by Mn and some neutral intermediary atom by O (thinking of course of the case of the manganites). It is assumed that the O atom has a closed shell, the two magnetic atoms a number of d-electrons appropriate to give them each a spin S as well as one extra electron which may, of course, equally well be

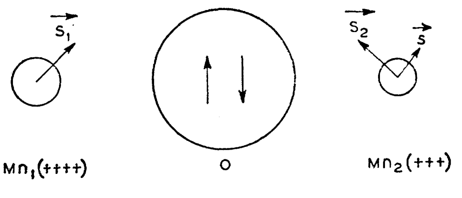

FIG. 1. Model for double exchange.

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* Part of this work was done while this author was a Fulbright Lecturer at the University of Tokyo. I should like to express my gratitude for the hospitality and support of the University and the Fulbright Commission.

[1] C. Zener, Phys. Rev. **82**, 403 (1951).

[2] G. H. Jonker and J. H. Van Santen, Physica **16**, 337, 599 (1950).

[3] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

[4] G. H. Jonker and J. H. Van Santen (private communication).

TABLE I. Labeling of wave functions in double exchange.

	Mn_1	O	Mn_2
A. Orbitals			
Mobile d-electron	d_1		d_2
Closed O shell		p	
Fixed d-electrons	d_1' etc.		d_2' etc.
B. Configurations			
I	$d_1' d_1$	p^2	d_2'
II	d_1'	p^2	$d_2' d_2$
III	$d_1' d_1$	p	$d_2' d_2$

on one or the other. The wave functions and configurations considered are labeled in Table I. We assume from the first that there is a unique orbital d_1 or d_2 into which the extra electron wishes to go; our results are valid under more general conditions[5] but this will give the qualitative picture of the process which we wish to convey. We then have a problem of configuration interaction between the two degenerate configurations I and II with the electron on the one atom or the other. Zener assumed that the intra-atomic exchange integral coupling the electron's spin to S, i.e., $J_{dd'}$, was infinitely large, so that he excluded states with $S_{\mathrm{tot}}=S-\frac{1}{2}$ from his configurations; we shall not make this assumption at first, although we believe this to be the most probable case. However, for the sake of simplicity we assume that the Mn atom core always has spin S; thus its internal exchange integrals are assumed infinitely large.

In order for there to be any coupling between the two Mn atoms, the extra electron must be able to get from one to the other. The transfer process must occur through the intermediary of the O atom for our picture. (Of course, there is nothing in our calculations requiring this, but most cases to which it is reasonable to apply these concepts do have a magnetically neutral atom present.) The transfer is most likely to occur in one of two ways. The first is that suggested by Zener: via the exchange type integral

$$J^*=\int d\tau\psi_{d1}(1)\psi_p(1)H\psi_p(2)\psi_{d2}(2), \tag{1}$$

which is however negligibly small (since the Mn atoms do not overlap) unless the p and d wave functions used are not orthogonal, in which case it is equal to

$$\begin{aligned} J^* &= S_{p-d}\int \psi_p V\psi_d d\tau \\ &= S_{p-d}H_{p-d}, \end{aligned} \tag{2}$$

where S is the overlap integral, V the averaged potential. This will then be of roughly the same magnitude as the ordinary $p-d$ exchange integral for nonorthogonal wave functions. J^* has simply the effect of moving the electron from atom 1 to atom 2, i.e., configuration I to II, without change of spin, as can be seen by Serber's method[6] (see Appendix I). If orthogonal wave functions are used we must as usual go to higher order configuration interactions to find a mechanism, but when we do can rely somewhat more on our results. The configuration which must be introduced is that in which a single p electron has been transferred from the O to the "other" Mn, i.e., configuration III. This is connected to the initial configuration I by the ordinary transfer integral H_{p-d} of (2); then this same transfer integral can connect it with II, since I and II are symmetrical relative to III. The details of this process are worked out also in Appendix I, where we prove that this too is a simple transfer, the electron ending on the second ion with the same spin direction from which it started on the first. Both processes give transfer integrals of the rough order of magnitude 0.1 v, while J, the intra-atomic exchange integral, is of order 1 v.

III. SEMICLASSICAL CALCULATION OF DOUBLE EXCHANGE

The preceding section showed that the primary transfer mechanisms which may occur in double exchange are both of a type which tend simply to transfer a single electron without change of spin from atom 1 to atom 2. We now proceed to calculate the energies of the states which follow from configurations I and II when we take into account this transfer integral (which for simplicity we shall call simply b) and also the fact that the electron's spin is coupled to the spin of the ion on which it finds itself by an intra-atomic exchange integral J. In the case of ions with less than half-filled shells, J tends to make the spins parallel; for more than half-filled shells, and if the odd electron falls into the d shell and not into an s function, we have an "effective" exchange integral J which is infinite and causes antiparallelism. However, for the present problem the sign of J itself is irrelevant.

Our procedure from here on will be to treat the problem semiclassically, that is, as if the two ions had very large spins S so that one could assign them definite directions in space and a definite angle relative to each other. Two nearly trivial modifications of this procedure lead to the exact answer as derived in Appendix II.

When the electron is on the first atom, it has two states, of energies

$$E_1=\pm JS,$$

lined up parallel and antiparallel to the spin $\mathbf{S}_1$. On atom 2 it also has these two states, but lined up in the direction of $\mathbf{S}_2$. We know, however, that the electron, when transferred, goes only into the parallel state. There are two possible ways of correcting for the difference in direction: either to transform the energies

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[5] These are either (a) the orbits are sufficiently quenched that S, $S+\frac{1}{2}$ and $S-\frac{1}{2}$ are unique states, and any other orbital states are of high energy, in which case our treatment in Appendix II is obviously valid; or else (b) J is large compared to the transfer integral and states S and $S+\frac{1}{2}$ are adequately quenched. We then ignore all $S-\frac{1}{2}$ states.

[6] R. Serber, Phys. Rev. **45**, 461 (1934).

on atom (2) into a coordinate system parallel to $\mathbf{S}_1$, or to transform the transfer matrix elements so that they refer correctly to the different directions. The latter procedure is somewhat simpler.

Let us label the two electronic spin functions referred to the direction of $\mathbf{S}_1$ by α and β, and those referred to $\mathbf{S}_2$ by α', β'. The eigenstates on atom 1 are $d_1\alpha$ and $d_1\beta$. These have the energies (if we make the first quantum-mechanical modification of using correct exchange energies)

$$\begin{aligned} E(d_1\alpha)&=-JS,\\ E(d_1\beta)&=J(S+1), \end{aligned} \tag{3}$$

for J ferromagnetic in sign. The eigenstates on (2) are

$$\begin{aligned} d_2\alpha'&:E=-JS,\\ d_2\beta'&:E=+J(S+1), \end{aligned} \tag{4}$$

while the transfer matrix elements are

$$\begin{aligned} (d_1\alpha|H|d_2\alpha)&=b,\\ (d_1\alpha|H|d_2\beta)&=0, \text{ etc.} \end{aligned} \tag{5}$$

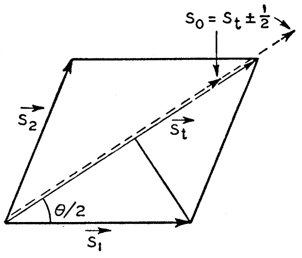

FIG. 2. Addition of spins in double exchange.

What we must do is to express α and β in terms of α' and β'. This transformation is well known,

$$\begin{aligned} \alpha&=\cos(\theta/2)\alpha'+\sin(\theta/2)\beta',\\ \beta&=-\sin(\theta/2)\alpha'+\cos(\theta/2)\beta', \end{aligned} \tag{6}$$

where θ is the angle between $\mathbf{S}_1$ and $\mathbf{S}_2$.

We can now immediately write down the secular equation:

$$|H-E|=0$$

$$H=\begin{array}{c|cccc} & d_1\alpha & d_1\beta & d_2\alpha' & d_2\beta' \\ \hline d_1\alpha & -JS & 0 & b\cos\theta/2 & b\sin\theta/2 \\ d_2\beta & 0 & J(S+1) & -b\sin\theta/2 & b\cos\theta/2 \\ d_2\alpha' & b\cos\theta/2 & -b\sin\theta/2 & -JS & 0 \\ d_2\beta' & b\sin\theta/2 & b\cos\theta/2 & 0 & J(S+1) \end{array}. \tag{7}$$

The secular equation reduces to

$$\{(\tfrac{1}{2}J-E)^2-[J(S+\tfrac{1}{2})+b\cos\theta/2]^2-b\sin^2\theta/2\}$$
$$\times\{(\tfrac{1}{2}J-E)^2-[J(S+\tfrac{1}{2})-b\cos\theta/2]^2-b^2\sin^2\theta/2\}=0,$$

which has the solutions

$$\begin{aligned} E&=\tfrac{1}{2}J\pm\{[J(S+\tfrac{1}{2})\pm b\cos\theta/2]^2+b^2\sin^2\theta/2\}^{\frac{1}{2}}\\ &=\tfrac{1}{2}J\pm[J^2(S+\tfrac{1}{2})^2+b^2\pm 2Jb(S+\tfrac{1}{2})\cos\theta/2]^{\frac{1}{2}}. \end{aligned} \tag{8}$$

This is the complete solution except that we must evaluate $\cos\theta/2$. In the semiclassical case this can be evaluated by noting that (see Fig. 2)

$$\frac{|\mathbf{S}_1+\mathbf{S}_2|}{2S}=\frac{S_t}{2S}=\cos\theta/2\cong\frac{S_0}{2S}, \tag{9}$$

where this equation defines S_t. Now in the semiclassical case we cannot meaningfully distinguish between S_t and S_0, the total spin including the odd electron (equal to $S_t\pm\frac{1}{2}$), so this is the complete answer in terms of this theory, as noted in the last equality of (9).

In Appendix II, we shall show that the only modification introduced by exact calculation is to replace (9) by the result, equivalent to terms of order $1/S$,

$$(\cos\theta/2)_{\text{exact}}=(S_0+\tfrac{1}{2})/(2S+1). \tag{10}$$

The result for the intermediate case $J\cong b$ is not of very great interest. It will suffice to discuss the two limiting cases, (A) $J\gg b$, and (B) $J\ll b$.

A. *$J\gg b$.*—This is the case considered by Zener. Here we can ignore the eigenvalues having a + sign on the square root as having very high energies (i.e., ignore $d_1\beta$ and $d_2\beta'$). We then neglect $b^2\sin^2\theta/2$ in the square root and

$$\begin{aligned} E&\cong-JS\pm b\cos\theta/2\\ &=-JS\pm b[(S_0+\tfrac{1}{2})/(2S+1)]. \end{aligned} \tag{11}$$

In case J has antiferromagnetic sign the result is unchanged except for a constant. S_0 can take on every value from $\frac{1}{2}$ to $2S+\frac{1}{2}$, so that $\cos\theta/2$ runs from $1/(2S+1)$ to 1. For each of these values there is one high-energy solution corresponding to each low-energy solution. Physically, what happens is that the effective transfer integral between the only two possible states for the electron is reduced by the ratio $(S_0+\frac{1}{2})/(2S+1)$, and the eigenstates are essentially the symmetrical and antisymmetrical combinations of the localized orbitals with the electron's spin parallel to $\mathbf{S}_1$ or $\mathbf{S}_2$, respectively.

B. *$J\ll b$.*—Here we again must neglect + values of the square root, and, adding a negligible term inside the square root to complete the square, we get

$$
\begin{aligned}
E &\cong \frac{J}{2} - \left[b \pm J(S+\tfrac{1}{2})\right] \cos\theta/2 \\
&= -b + \frac{J}{2} \pm \frac{J(S+\frac{1}{2})(S_0+\frac{1}{2})}{2S+1} \\
&= -b + \frac{J}{2} \pm \frac{J}{2}(S_0+\tfrac{1}{2}).
\end{aligned}
\tag{12}
$$

Again, for every value of S_0 there are two states, one high and one low. These correspond to spin up or down for the traveling electron, relative to the total spin $\mathbf{S}_1+\mathbf{S}_2$. Again the sign of J is immaterial.

IV. DISCUSSION OF RESULTS

The results (8), (11), and (12) of the last section are quite different from the usual form of exchange interaction. They are of interest not only because they refer to a mechanism which may be occurring in certain substances but also because this is one of the simplest problems of spin interaction in which orbital degeneracy enters in an essential way. It is, in fact, only because of the extra degree of freedom allowed by the electron's motion that we can obtain anything other than an $\mathbf{S}_1 \cdot \mathbf{S}_2$ interaction in this simple case.

Two differences are apparent: first, the linear variation with total spin S_0 in both (11) and (12), whereas $\mathbf{S}_1 \cdot \mathbf{S}_2$ varies quadratically; and second, the fact that for every S_0 there are two states, not one, which in both (11) and (12) are symmetrically disposed about the average energy.

The first difference does not seem to be very essential physically. However, the second has at least a very probable significance. The susceptibility of a paramagnetic substance can always be written[7]

$$\chi = \langle \mu^2 \rangle_{\mathrm{Av}} / 3kT, \tag{13}$$

where μ is the magnetic moment, which for a system with orbital quenching is

$$\boldsymbol{\mu} = g\beta \mathbf{S}, \tag{14}$$

g being the g-factor and β the Bohr magneton. Thus χ is proportional to $\langle S^2 \rangle_{\mathrm{Av}}/kT$. We may then take the average with a Boltzmann distribution

$$\langle S^2 \rangle_{\mathrm{Av}} = \frac{\sum_{S_0, n} S_0(S_0+1) e^{-E_n(S_0)/kT}}{\sum e^{-E_n(S_0)/kT}}, \tag{15}$$

which at high temperatures may be expanded into

$$\langle S^2 \rangle_{\mathrm{Av}} = \frac{\sum_{S_0} S_0(S_0+1) \sum_{n} \left(1 - \frac{E_n(S_0)}{kT} + \frac{E_n^2(S_0)}{2k^2T^2} \cdots \right)}{\sum_{S_0, n} \left(1 - \frac{E_n(S_0)}{kT} + \frac{E_n^2(S_0)}{2k^2T^2} \cdots \right)}.$$

If we wish only the first two terms we note that $\sum_n E_n(S_0)$ is independent of S_0, since the average energy for all S_0 is the same. Then up to terms in $1/T^2$

$$\langle S^2(T) \rangle_{\mathrm{Av}} = \langle S^2(\infty) \rangle_{\mathrm{Av}}.$$

and we may write

$$\chi = C/T + (\text{terms in } 1/T^3). \tag{16}$$

The corresponding expansion for ordinary exchange gives

$$\chi_{\text{ordinary}} = C/T + C\theta/T^2 + \cdots \cong C/(T-\theta), \tag{17}$$

where θ is a temperature of the order of magnitude of the Curie temperature, i.e., such that $k\theta$ is comparable to the total interaction. Thus we suspect that a double-exchange ferromagnet will have a $1/\chi - T$ plot as shown in Fig. 3, as compared to a ferromagnet, and also to a typical ferrimagnet.

Of course, all these conclusions are based on the simplest case of only two ions with one electron travelling between them. In the real solid there are a very large number both of ions and of electrons, and there are $(2S+1)^N$ states for the ions and N for an electron for every one of these. We can for the sake of simplicity assume that the number of electrons is relatively small and ignore their interactions, but even the calculation of the states of a single electron plus the ion system is very complex.

With the confidence gained from Sec. III in the semi-classical treatment of the ions, however, we can at least draw some qualitative conclusions in our two cases A and B.

In case A, $J \gg b$, the transfer integral between any

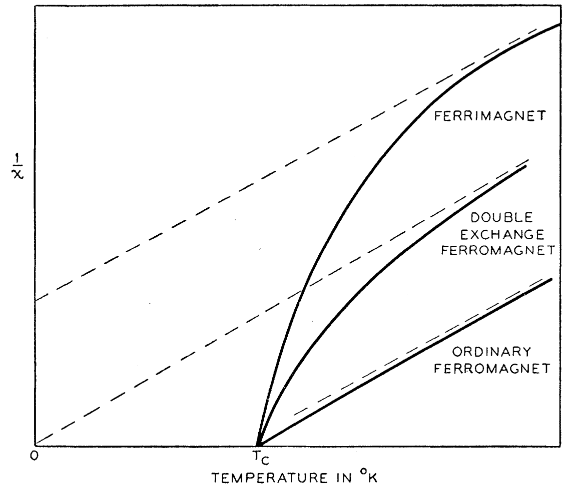

FIG. 3. Qualitative susceptibility curves for ferrimagnet, ferromagnet, and double exchange ferromagnet.

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[7] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 40.

two ions depends on $\cos\theta/2$ for the angle θ between their two spins. For a random, paramagnetic type of spin arrangement we have then a problem of electron motion in a random alloy, which has been the subject of much attention but has not been solved in the way needed here. This case of variable transfer integral is also not the usual one. However, it is still to be expected that for each arrangement there is created a band of electronic states, as many above as below the average arrangements. As the number of parallel pairs increases the width of this band increases.

A set of states of the lattice of spins in case A which are susceptible to exact treatment on this model consists of the states derived from the all-parallel state by a uniform twisting of the ion spins through an angle φ per atom layer (i.e., a "spin wave" of wave vector $2N\varphi/a$). Each of these states will produce a band of electronic states the width of which is decreased relative to the aligned state by a factor $\cos\varphi/2$ due to the reduced transfer integral. Thus our model obeys Herring's theorem[8] that the energy of a spin wave is proportional to k^2 for small k. The directions of the electron spins will follow accurately those of the ions.

Case B, $J \ll b$, is essentially that envisaged by Zener[9] in his model of ferromagnetism in metals. In this case the free electrons will travel some distance while maintaining their spins without regard to the directions of the ion core spins. Here the spin up and spin down electrons will have opposite energies. Ferromagnetism, if it occurs, will do so by the mutual polarization by the ions of the free electrons, which in turn polarize the ions. The fact that this is a two-stage process again makes very reasonable the idea that χ *vs* T at high temperatures will not contain the θ term.[10]

Thus in both cases A and B what little we can say of the probable state of affairs tends to indicate that the double exchange mechanism of spin interaction is quite different qualitatively from ordinary exchange, and in particular leads to a very different form (16) for the high-temperature susceptibility, which cannot be expected to extrapolate linearly to an intercept near the Curie point. As mentioned in the abstract, this result does not fit the experimental data on the manganites.[3]

ACKNOWLEDGMENTS

We should like to acknowledge helpful discussions with M. Shimizu, K. Yosida, D. Kleinman, and H. B. Callen.

APPENDIX I. TRANSFER PROCESSES

Throughout these appendices we shall use Serber's method[6,11] of treating configuration interactions. This method, based on Dirac's method for treating spin interactions within configurations, gives us the following rules for writing down the Hamiltonian matrix:

(1) Assign orbitals to the electrons in each configuration in some fixed, convenient order. Two orbitals, treated as if distinct, are to be assigned to electron pairs which are in the same orbital.

(2) Matrix elements of the Hamiltonian within configurations are to be computed as in Dirac's method, multiplying ordinary integrals by unity and exchange integrals by the spin permutation operator $-P_{12}$ of the spins in the appropriate orbitals.

(3) Matrix elements connecting different configurations are written down by exactly the same rules in the sense that the choice between "direct" and "exchange-type" integrals is made on the basis of the order number. That is, if the two configurations are, say, $\varphi(1)\chi(2)$ and $\varphi(1)\psi(2)$ the integral $\int\chi(1)H\psi(1)d\tau$ is a "direct" type, $\int\varphi(1)\chi(2)H\varphi(2)\psi(1)d\tau$ is "exchange" and is to be multiplied by the permutation operator $-P_{12}$ in the off-diagonal block.

(4) Where one configuration has a pair of electrons in the same orbital, the other not, the transition matrix elements leading to forbidden spin arrangements are to be eliminated by appropriate projection operators, while certain factors of $\sqrt{2}$ are to be multiplied into the remaining off-diagonal blocks.

The numbering of wave functions which we shall use is shown in the following table for the three configurations of Table I. We leave out any electrons in the core states d_1' and d_2' because these are irrelevant to the transfer mechanism, and will appear only in the final problem of Appendix II.

Configuration	d_1	p	p	d_2
I	1	2	3	
II		1	3	2
III	1	3		2

The two transfer mechanisms we consider are, first, the exchange-type integral:

$$J^* = \int d_1(1)p(2)Hd_2(2)p(1)d\tau;$$

and second, the second-order effect of configuration III on configurations I and II, which will be proportional to

$$|H_{p-d}|^2/(E_{\mathrm{III}}-E_{\mathrm{I}}).$$

These seem to be the only effects of sufficiently low order to be appreciable. We wish to show that each of these effects connects only the following wave functions in configurations I and II:

$$\alpha(1)[\alpha(2)\beta(3)-\alpha(3)\beta(2)] \leftrightarrow [\alpha(1)\beta(3)-\alpha(3)\beta(1)]\alpha(2), \quad \text{(A1)}$$

and similarly for the β's.

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[8] C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951).

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

[10] Unless the electron gas is degenerate. For a degenerate electron gas ($kT \ll b$) we can draw no conclusions for many reasons (electron interactions, second-order effects); thus the present considerations do not affect Zener's theory of ferromagnetism in metals.[9]

[11] P. W. Anderson, Phys. Rev. **79**, 350 (1950).

In the transfer "block" of the Hamiltonian connecting I and II, according to rule 3 J^* will be multiplied by P_{12}, the permutation operator connecting 1 and 2. It must also be multiplied by appropriate projection operators in order to "communicate" with configurations I and II, according to rule 4.

Transfer operator=

$$J^* O_{23} P_{12} O_{13}, \tag{A2}$$

where O_{13} and O_{23} are the projection operators eliminating triplet states for the pairs 13 or 23. First, since O_{23}, O_{13}, and P_{12} are all scalars, we know that indeed (A2) can only connect $S_z=+\frac{1}{2}$ with $+\frac{1}{2}$ and $-\frac{1}{2}$ with $-\frac{1}{2}$, so that our requirement is satisfied since (A1) are the only pair of wave functions of I and II with the right S_z's to be connected together. To get the correct numerical factor, we apply (A2) to

$$\frac{(\alpha_1\beta_3-\alpha_3\beta_1)\alpha_2}{\sqrt{2}}$$

$$\begin{aligned} J^* O_{23} P_{12} O_{13}\left(\frac{(\alpha_1\beta_3-\alpha_3\beta_1)\alpha_2}{\sqrt{2}}\right) &= J^* O_{23} P_{12}\left(\frac{(\alpha_1\beta_3-\alpha_3\beta_1)\alpha_2}{\sqrt{2}}\right) \\ &= \frac{J^*}{\sqrt{2}} O_{23}(\alpha_1\alpha_2\beta_3-\alpha_3\alpha_1\beta_2) \\ &= J^* \frac{\alpha_1(\alpha_2\beta_3-\alpha_3\beta_2)}{\sqrt{2}}. \end{aligned}$$

Thus we have the expected result, that the effect of J^* is just to replace an up spin in d_1 by an up spin in d_2 and vice versa.

The problem for $|H_{pd}|^2/(E_{\mathrm{III}}-E_{\mathrm{I}})$ is only slightly more complicated. In the perturbation procedure we go once from I to III, requiring an operator O_{23} and a factor $\sqrt{2}$, do nothing in III and go down to II with $\sqrt{2}\,O_{13}$. Thus

$$\text{Transfer operator}=-2|H_{pd}|^2 O_{23} O_{13}/(E_{\mathrm{III}}-E_{\mathrm{I}}). \tag{A3}$$

Again we note that the scalarity of O_{23} and O_{13} proves that we have a simple transfer operator, and calculate its magnitude:

$$\begin{aligned} O_{23} O_{13} \frac{(\alpha_1\beta_3-\alpha_3\beta_1)\alpha_2}{\sqrt{2}} &= O_{23} \frac{(\alpha_1\beta_3-\alpha_3\beta_1)\alpha_2}{\sqrt{2}} \\ &= \frac{1-P_{23}}{2}\left(\frac{\alpha_1\beta_3-\alpha_3\beta_1}{\sqrt{2}}\right)\alpha_2 \\ &= \frac{1}{2\sqrt{2}}(\alpha_1\alpha_2\beta_3-\beta_1\alpha_2\alpha_3-\alpha_1\beta_2\alpha_3+\beta_1\alpha_2\alpha_3) \\ &= -\tfrac{1}{2}(\alpha_1)\left(\frac{\alpha_2\beta_3-\alpha_3\beta_2}{\sqrt{2}}\right), \end{aligned}$$

so that again the factor multiplying the simple transfer integral is just unity.

APPENDIX II. QUANTUM CALCULATION OF DOUBLE EXCHANGE

With the assumptions stated in the text we can write down the following Hamiltonian matrix for our problem. We take the odd electron's spin as $\mathbf{s}$, the spins of the ion cores as $\mathbf{S}_1$ and $\mathbf{S}_2$. b is the transfer integral, either J^* for nonorthogonal wave functions or $|H_{pd}|^2/(E_{\mathrm{III}}-E_{\mathrm{I}})$ if we consider the transfer to go through configuration III.

$$H=\begin{array}{c|cc} & \mathrm{I} & \mathrm{II} \\ \hline \mathrm{I} & -2J\mathbf{S}_1\cdot\mathbf{s} & b\mathbf{1} \\ \mathrm{II} & b\mathbf{1} & -2J\mathbf{S}_2\cdot\mathbf{s} \end{array}. \tag{A4}$$

$\mathbf{1}$ is the unit operator. As in the text, we can diagonalize the blocks I—I and II—II by choice of the appropriate representation, but only of a different one in each block: namely, in I we combine

$$\mathbf{S}_1+\mathbf{s}=\mathbf{S}_1', \quad \mathbf{S}_1'+\mathbf{S}_2=\mathbf{S}_0, \tag{A5}$$

and use the representation in which S_0, M_{S_0}, and $S_1'=S\pm\frac{1}{2}$ are diagonal. Then $-2J(s\cdot S_1)=-JS$ or $J(S+1)$ for $S_1'=S+\frac{1}{2}$ or $S-\frac{1}{2}$. Similarly, we can diagonalize II but only by setting $S_2'=S\pm\frac{1}{2}$ diagonal, in which case S_1' is not.

One of two possible ways to proceed is to use the correct coordinates to diagonalize each diagonal block and transform $b\mathbf{1}$ to connect the blocks properly. This is easily done by replacing $\mathbf{1}$ by the unitary matrix which effects the transformation between the two representations. This matrix can be obtained by the use of Racah's methods.[12,13] In the notation of reference 13, the matrix element connecting the wave function for a particular value of S_1' with that for a value of S_2' is

$$\begin{aligned} &\langle S_1, sS_2(S_2'), S_0 | S_1 s(S_1'), S_2, S_0\rangle \\ &\qquad = [(2S_1'+1)(2S_2'+1)]^{\frac{1}{2}} W(S_1 s S_0 S_2; S_1' S_2'), \end{aligned}$$

which can be easily evaluated by the tables in reference

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[12] G. Racah, Phys. Rev. **62**, 438 (1943).

[13] Biedenharn, Blatt, and Rose, Revs. Modern Phys. **24**, 249 (1952).

13, using $S_1=S_2=S$; $s=\frac{1}{2}$. The resulting Hamiltonian matrix is

$$H=\begin{array}{rr|cccc|} & & S_1'-S+\frac12 & S_1'=S-\frac12 & S_2'=S+\frac12 & S_2'=S-\frac12 \\ \text{I:} & S_1'=S+\frac12 & -JS & 0 & (-1)^{1-2S_0}\dfrac{S_0+\frac12}{2S+1} & \left[1-\left(\dfrac{S_0+\frac12}{2S+1}\right)^2\right]^{\frac12} \\ & S-\frac12 & 0 & J(S+1) & -\left[1-\left(\dfrac{S_0+\frac12}{2S+1}\right)^2\right]^{\frac12} & (-1)^{1-2S_0}\dfrac{S_0+\frac12}{2S+1} \\ \text{II:} & S_2'=S+\frac12 & (-1)^{1-2S_0}\dfrac{S_0+\frac12}{2S+1} & -\left[1-\left(\dfrac{S_0+\frac12}{2S+1}\right)^2\right]^{\frac12} & -JS & 0 \\ & S-\frac12 & \left[1-\left(\dfrac{S_0+\frac12}{2S+1}\right)^2\right]^{\frac12} & (-1)^{1-2S_0}\dfrac{S_0+\frac12}{2S+1} & 0 & J(S+1) \end{array}. \qquad \text{(A6)}$$

This is identical with the Hamiltonian for the simple model, Eq. (7), if we set $\cos\theta/2=(S_0+\frac12)/(2S+1)$ as in Eq. (10).

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Effect of Pressure on the Electrical Resistance of Metals at Liquid Helium Temperatures

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The effect of pressures up to 5000 kg/cm² on the electrical resistance of polycrystalline copper, silver, gold, and platinum and on single crystals of arsenic, antimony, and bismuth has been measured at liquid helium temperatures. The pressures were generated by a piston and cylinder arrangement using solid hydrogen as the pressure transmitting medium.

INTRODUCTION

It is generally accepted that the electron-lattice interaction in a metal at low temperatures is an important factor in determining whether the metal will have a superconducting phase. An obvious method of seeking information about this interaction is to investigate how the electrical conductivity of metals at low temperatures is influenced when the lattice spacings are changed by application of pressure. In the case of nonsuperconductors, such measurements should be of intrinsic interest in the theory of metallic conduction, since at liquid helium temperatures the contribution to resistance from thermal scattering is small and the change with pressure from this cause may be expected to be negligible.

EXPERIMENTAL

A major technical problem to be faced is the method of applying hydrostatic pressure to the metallic specimen. Since even helium solidifies at quite low pressure in this temperature region, one is compelled to use a solid for transmission of the pressure, and if the stress transmitted to the specimen is to approximate a hydrostatic pressure, then a transmitting medium which will not support any appreciable shear stress is required. Presumably, helium would be the most satisfactory substance from this standpoint, and it might be practicable to use helium in a bomb type of apparatus similar to that which has been used in studying the thermodynamic properties of helium under pressure.[1] However,

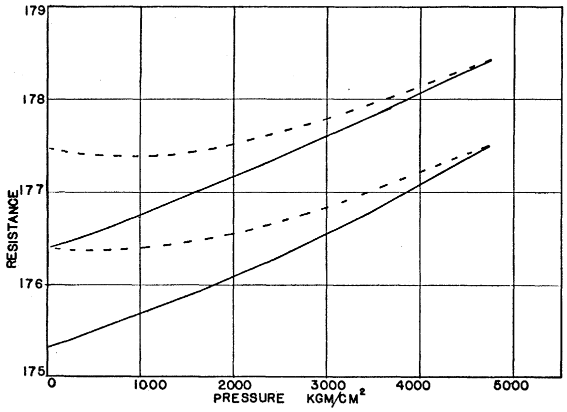

FIG. 1. Electrical resistance of copper *vs* pressure at 4.2°K.

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[1] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).