

# Symposium on Exchange—Introduction

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THIS symposium consisted of a round-table discussion on exchange forces in ferromagnetics, and began with the presentation of invited papers by C. Zener, J. C. Slater, E. P. Wohlfarth (read by E. C. Stoner), and J. H. Van Vleck. A lengthy but lively discussion period, partly with the audience participating,

followed the invited papers. It is unfortunately not possible to reproduce here the discussions, but R. Smoluchowski has been kind enough to prepare a brief summary and reconciliation of the invited papers: his discussion follows here after the papers.

# Exchange Interactions

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## I. INTRODUCTION

EXCHANGE interaction represents a characteristic quantum effect having no analog in classical mechanics. Before defining exchange interaction, we shall give a simple example of a two-electron system. Let  $A$  and  $B$  represent two quantum states, and let suffixes  $\alpha$  and  $\beta$  represent electron spins pointing parallel and antiparallel, respectively, to some preferred direction. Then the two states  $A_\alpha B_\beta$  and  $A_\beta B_\alpha$  are degenerate, i.e., have the same energy. Since these two states combine, more appropriate wave functions are

$$\begin{aligned}\psi_S &= A_\alpha B_\beta + A_\beta B_\alpha, \\ \psi_A &= A_\alpha B_\beta - A_\beta B_\alpha.\end{aligned}$$

These states are no longer degenerate. The energy values will be denoted by  $E_S$  and  $E_A$ , respectively. The energy difference  $E_S - E_A$  is called the exchange energy. The quantity  $(E_S - E_A)/\hbar$  is called the exchange frequency, and may be given the following vivid interpretation. Suppose that, through the appropriate linear combination of  $\psi_S \exp(-iE_S t/\hbar)$  and of  $\psi_A \exp(-iE_A t/\hbar)$ , we construct an approximate solution to the time dependent wave equation which reduces to  $A_\alpha B_\beta$  at  $t=0$ . We then have a wave function which oscillates between  $A_\alpha B_\beta$  and  $A_\beta B_\alpha$  with the exchange frequency.

Exchange energy is of particular importance to magnetism since the two states  $\psi_S$  and  $\psi_A$  represent different spin configurations. In the first state the two electron spins are parallel, in the second state they are antiparallel. This difference in relative spin orientation is necessarily associated with a difference in electron configuration. Thus, in the first state  $\psi_S$ , the two

electrons have a tendency to avoid one another, while in the second state  $\psi_A$ , the contrary is the case. It is, in fact, just this difference in electron configuration which gives rise to the exchange energy. In general, we define as the exchange energy that part of the total energy of a system which is dependent upon relative spin orientation, this energy excluding the pure magnetic energy arising from dipole-dipole interaction.

Since an exchange interaction has a meaning only in reference to the approximate wave functions with which we choose to describe our system, it is necessary in discussing such interactions to clearly describe the approximate wave functions from which one starts. A considerable difference of opinion exists as to the most appropriate type of approximate wave functions for solids. The most appropriate approximate wave functions for a particular investigation will depend to some extent upon the objective of the investigation. If this objective is to understand the basis for the various types of crystal structure, it is conceivable that the most appropriate starting wave functions for all the electrons will be the localized atomic wave functions. If this objective is to make a precise calculation of the binding energy, it is probable that the most appropriate approximate wave function for all electrons will be the band functions, i.e., solutions of a periodic potential. If, as in the present case, the objective is to understand the magnetic properties, the authors believe that for the inner incomplete  $d$  shell electrons the localized atomic wave functions are the most appropriate, while for the outer  $s$  electrons the band wave functions are the most appropriate. The last type of description will therefore be used in the present paper.

## II. DOMINANT EXCHANGE INTERACTIONS

Once having decided on our initial approximation to describe  $d$  electrons by localized atomic wave functions, outer  $s$  electrons by band wave functions, we find the following types of exchange interactions to be of dominant importance for magnetic properties.

### A. Arising from an Exchange of Electrons within the $d$ Shell of the Same Atom

This exchange interaction has been found by Slater<sup>1</sup> to provide the physical basis for Hund's rule<sup>2</sup> of highest multiplicity. Applied to the transition metal atoms or ions, this rule states that when a  $d$  shell first begins to be filled, all the electron spins point in the same direction. When the  $d$  shell is half-filled, five electrons have spins pointing in the same direction. Thereafter, further added electrons have spins pointing in the opposite direction. Hund's rule may be unambiguously tested for those transition metal ions in which the orbital angular momentum is completely quenched, as manifested by  $g$  being equal to 2. Such quenching appears to be complete in cubic lattices, examples of which are the ferrites<sup>3</sup> and the manganese perovskites.<sup>4,5</sup> In all these examples the saturation magnetic moment is just that which is predicted by application of Hund's rule. Since the consequences of the exchange interaction between electrons within the  $d$  shell of the same atom have been known for many years, and since there appears to be no difference of opinion regarding this exchange interaction, it will not be further discussed in this paper.

### B. Arising from an Exchange of Electrons between the $d$ Shells of Adjacent Atoms

This interaction, which we shall henceforth call *direct-exchange*, has been, and still is, the subject of considerable controversy. The controversy is over the sign of the exchange integral  $J$ . A positive  $J$  corresponds to a ferromagnetic coupling, a negative  $J$  to an anti-ferromagnetic coupling. Now the usual sign of  $J$  is negative, as is necessary in order that a chemical bond may be formed. In his classic paper on ferromagnetism Heisenberg<sup>6</sup> assumed that the direct exchange furnished the ferromagnetic coupling in Fe, Co, and Ni. In explaining the positive sign of  $J$  which such a coupling demanded, he pointed out that for a sufficiently large value of principal quantum number one would indeed anticipate a change in  $J$  from a negative to a positive sign. Heisenberg's explanation was rather unsatisfactory in that it left uninterpreted the absence of ferromagnet-

ism in the second and third transition periods, which according to his reasoning should be stronger than in the first transition period.

A way out of this dilemma was found by Slater,<sup>7</sup> who emphasized the importance of the degree of overlap of the  $d$  shells. He postulated that as the degree of overlap decreased from a large to a small value,  $J$  changed from a negative to a positive quantity. Since the degree of overlap is a continuously decreasing function of the ratio (internuclear distance)/(radius of  $d$  shell), Slater assumed that  $J$  varied in the general manner as indicated in Fig. 1. This single postulate explained not only why the ferromagnetism does not occur in the second- and third-row transition period, where the ratio (internuclear distance)/(radius of  $d$  shell) is smaller than in the first period, but also why only the last elements in the first transition row are ferromagnetic.

Slater's postulate was sufficiently satisfying so that it was accepted until 1951 by all those workers in the field who used the localized atomic model for the  $d$  electrons. In 1951 one of the present authors<sup>8</sup> pointed out that an important exchange interaction (see Sec. D) had heretofore been neglected, and that, when it was taken into account, the necessity for a positive  $J$  disappeared. It therefore appeared more logical to assume that the magnitude of  $J$  decreases as the ratio (internuclear distance)/(radius of  $d$  shell) increases. In view of the current interest in this subject, detailed arguments, of both theoretical and empirical character, are now presented in support of the thesis that  $J$  varies as represented in Fig. 2 rather than as in Fig. 1.

The exchange integral corresponding to the exchange of a single pair of electrons between two atoms contains two dominant terms,

$$J = A + B.$$

Here  $A$  is the mutual energy of the two exchange charge distributions, while  $B$  is the sum of the energies of the

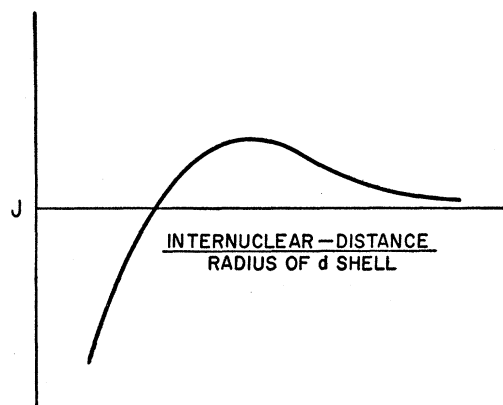


FIG. 1. Variation of exchange integral postulated by Slater (see reference 7).

<sup>1</sup> J. C. Slater, Phys. Rev. 34, 1243 (1929).

<sup>2</sup> F. Hund, *Linienpektren und Periodisches System der Elemente* (Verlag Julius Springer, Berlin, 1927) p. 124.

<sup>3</sup> L. Neel, Ann. phys. 3, 137 (1948).

<sup>4</sup> G. H. Jonker and J. H. Van Santen, Physica 16, 337 (1950).

<sup>5</sup> J. Volger, *Semi-Conducting Materials* (Butterworths Scientific Publications, Ltd., London, 1951), p. 162.

<sup>6</sup> W. Heisenberg, Z. Physik 49, 619 (1928).

<sup>7</sup> J. C. Slater, Phys. Rev. 36, 57 (1930).

<sup>8</sup> C. Zener, Phys. Rev. 81, 440 (1951); 83, 299 (1951).

two exchange charges in the "reduced" potential of the two atoms. In obtaining the reduced potential, we first take the actual potential of the two atoms, the two electrons which are exchanging being considered as absent. This potential is then multiplied by the total exchange charge of one of the exchanging electrons. The first term  $A$  is always positive, while the second term  $B$  is always negative. The sign of  $J$  therefore depends upon which of the two terms dominates.

Under certain conditions  $A$  dominates. This occurs when the pertinent wave function on the two atoms are orthogonal to one another, thereby leading to a zero total exchange charge, and hence to a zero  $B$ . This condition is satisfied in a diatomic molecule when the exchanging electrons are in two states having angular momental with different projections on the axis of the molecule. Under this condition,  $J$  is positive for all distances of separation.

Another set of conditions favors the dominance of  $B$ . This condition is that the atoms between which the two electrons are exchanging have several electrons in the same shell as the exchanging electrons. Since these additional electrons shield the nuclei only partially, they increase the magnitude of the reduced potential of the two atoms, and hence increase the magnitude of the negative  $B$ .

When we are having an exchange of electrons between two closed shells, the situation is rather ambiguous from the strictly theoretical viewpoint. On the one hand, we have many exchanges between states which are mutually orthogonal. Thus the exchange integral between two filled  $d$  shells involves 40 exchanges between mutually orthogonal states, only 10 between states which are not mutually orthogonal. On the other hand, the large number of electrons in the closed shells insures a relatively large reduced potential, and therefore favors the dominance of  $B$ . The situation is perfectly clear, however, from the experimental viewpoint. Under all cases which have been observed, the exchange interaction between closed shells is a repulsive interaction. Thus in the interaction between inert gas atoms, between ions in ionic crystals, and between the inner cores in Cu, Ag, and Au, the overlapping of the charge distributions leads to a repulsion at all those distances of separation at which interactions have been observed. Since the transition metals Fe, Co, and Ni have a large number of electrons in the  $d$  shell, larger than the number of electrons in the outer closed shell of the inert gases, it appears likely that they will also have a repulsive exchange interaction, and that the repulsion will be greater the larger the number of exchanges. Since exchange occurs only between parallel spins, we conclude that the repulsive exchange interaction between incomplete  $d$  shells will be greater when the spins are aligned parallel than when aligned antiparallel.

We shall now review some of the consequences of the antiferromagnetic coupling of direct exchange.

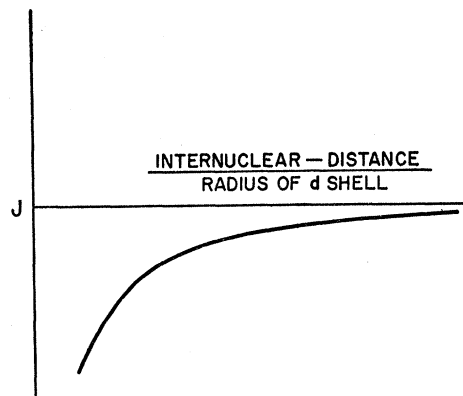


Fig. 2. Variation of exchange integral postulated by Zener.

We anticipate that metals will crystallize in a close-packed structure provided no counteracting tendency is present. One counteracting tendency, operating at high temperature, is the increased entropy associated with the larger amplitudes of vibration of loose-packed structures. This entropy effect is probably responsible for the close packed  $\rightarrow$  body centered cubic (b.c.c.) transition at high temperatures in Ti, Zr, and Fe. Another counteracting tendency must, however, be operating in the case of the transition metals of the V and Cr columns (V, Nb, Ta; Cr, Mo, W). These metals retain their loose b.c.c. lattice down to the lowest temperatures. One of the authors<sup>8</sup> has ascribed this b.c.c. structure to the direct exchange between adjacent  $d$  shells. In this structure it is possible for nearest neighbors to have an antiparallel alignment of spin, whereas in a close-packed lattice such an antiparallel arrangement is not possible. After this interpretation of the b.c.c. structure in the V and Cr columns was proposed, several investigations have appeared which corroborate this interpretation. These are discussed below.

(1) The above interpretation leads to the prediction of an ordered arrangement of spins in the V and Cr columns of the transition metals. An extensive search for such an ordered arrangement has been made by Shull. As we discussed in this conference, he has found negative results in all cases except Cr. Here he finds an ordered arrangement which disappears at 500°K. The experimental magnitude of the magnetic moments is, however, an order of magnitude less than the theoretical. The inconsistencies between theory and experiment can possibly be interpreted in terms of the intrinsic instability associated with an antiferromagnetic arrangement. As indicated in Fig. 3, when two spins which are coupled ferromagnetically become slightly uncoupled, they suffer a slight precession, whereas in the case of an antiferromagnetic coupling they undergo a large precession. This interpretation of Shull's negative results can be taken seriously only if the period of precession is comparable to or less than

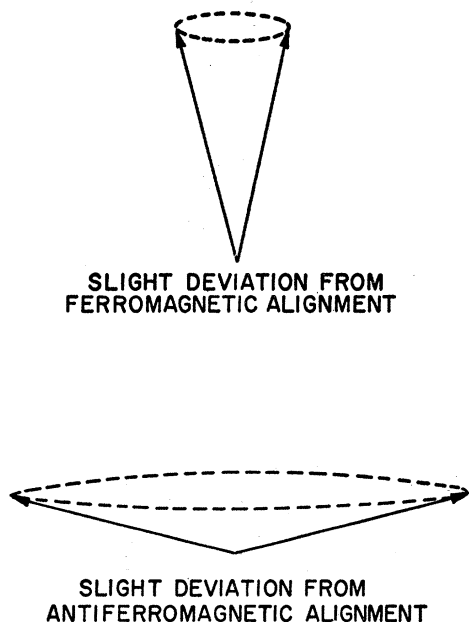


FIG. 3. Comparison of precession in cases of ferromagnetic and antiferromagnetic coupling.

the time of flight of a neutron through a single atom. In order to estimate the precessional frequency, we shall consider two spins of mechanical moment of momentum  $nh$  each, the energy  $J$  being required to change the relative orientation from an antiparallel to a parallel alignment. We then find that if the uncoupling energy is  $kT$ , and if  $kT$  is small compared to  $J$ , the precessional frequency  $\nu$  is given by

$$nh\nu \approx 2(JkT)^{\frac{1}{2}}.$$

Upon taking  $T$  as  $300^\circ\text{K}$ ,  $J$  as  $2kT$ ,  $n$  as  $5/2$  appropriate to the Cr  $d$  shell, we obtain the period of precession as  $1.4 \times 10^{-18}$  second. This period is of the same order as the time of transit of a neutron through a Cr atom, the neutron having a velocity suitable for diffraction studies. We thus see that the negative results of Shull may arise from the comparatively long time of transit of the neutrons through the individual atoms.

(2) An antiferromagnetic arrangement of spins should be accompanied by a rise in magnetic susceptibility with increasing temperature until the Curie temperature is reached. Such an increase has in fact been found by McGuire and Kriessman<sup>9</sup> in the case of Cr. In this metal the magnetic susceptibility continues to rise up to the highest temperature investigated, namely,  $1400^\circ\text{C}$ . At the upper part of this range the susceptibility rises at an accelerated rate as if a Curie temperature were not far above  $1400^\circ\text{C}$ .

(3) The metal Cr has been found by Friedberg<sup>10</sup> to have an anomalously low electronic specific heat at

<sup>9</sup> T. R. McGuire and C. J. Kriessman, Phys. Rev. **82**, 774 (1951); **85**, 452 (1952).

<sup>10</sup> Friedberg, Estermann, and Goldman, Phys. Rev. **85**, 375 (1952).

low temperatures. The electronic specific heat is linear in  $T$ , the coefficient of  $T$  being commonly denoted by  $\gamma$ , and is expressed in units of  $10^{-4}$  calorie/mole- $^\circ\text{C}$ . The  $\gamma$  of Cr is only 3, as compared to the value of 15 for V, to the left of Cr, and to the value of 42 for Mn, the metal to the right of Cr. This anomalously low value of  $\gamma$  for Cr is just what our model would predict. Whereas in the band description of metals it is commonly assumed that the potential for an electron is the same in every atom, it is of course only necessary to assume that the potential has the periodicity of the lattice. In particular, in our model, an electron with a positive spin ( $\alpha$ ) sees a lower potential on that simple cubic lattice occupied by atoms whose  $d$  electrons all have positive spins ( $\alpha$ ). Our model requires that the energy band is thereby split into two parts, the lower band for an  $\alpha$ -electron corresponding to the electron spending most of its time on  $\alpha$ -type atoms, the upper band corresponding to the electron spending most of its time on  $\beta$ -type atoms. The lower band is thus precisely filled by the 5 electrons in the  $d$  shell of the Cr atoms. The  $d$  electrons thus contribute essentially nothing to the specific heat. The only other metal in the Cr column

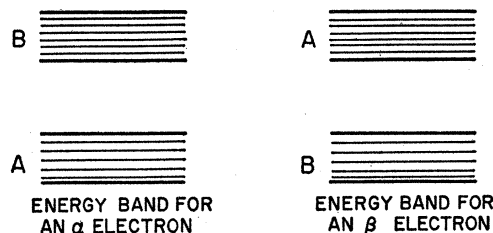


FIG. 4. Energy bands in chromium metal. Wave functions of  $A$  bands are concentrated on the  $A$  simple cubic lattice, those of the  $B$  bands on the  $B$  simple cubic lattice.

whose electronic specific heat has been measured is W. Whereas in all other metals the  $\gamma$  measured at high and at low temperatures agree, they are here in marked disagreement.<sup>11</sup> The high temperature measurement yields a low value of 5, in accord with our ideas, while the low temperature measurement yields a high value of 51, in discord with our ideas. This discrepancy in  $\gamma$  as measured at high and at low temperature is in fact in discord with any current theory of the electronic structure of the metals.

(4) One of the most convincing arguments for the intrinsic antiferromagnetic nature of the b.c.c. lattices of the V or Cr columns has been presented by Isenberg<sup>12</sup> through a theoretical analysis of elastic constants. Two independent elastic shear coefficients of cubic metals are  $C_{44}$  and  $(C_{11}-C_{12})/2$ . We shall define the elastic anisotropy factor by

$$A = 2C_{44}/(C_{11}-C_{12}).$$

<sup>11</sup> A. A. Silvidi and J. G. Daunt, Phys. Rev. **77**, 125 (1950).

<sup>12</sup> I. Isenberg, Phys. Rev. **83**, 637 (1951).

Isenberg has shown that, with neglect of very small terms, this factor may be written as

$$A = (8/9)[r^2W'']_1 / \{(8/3)[rW']_1 + [r^2W'']_2\}.$$

Here  $W$  refers to the mutual potential energy of the cores of two atoms at a distance  $r$  apart. The subscripts 1 and 2 indicate that the bracketed expressions are to be taken for first nearest and for second nearest neighbors, respectively. If now  $W$  represented a repulsive potential energy which decreased monotonically with  $r$ , we would conclude that the anisotropy factor  $A$  would be quite large. This conclusion would be reached by observing that  $rW''$  would be considerably larger for first nearest than for second nearest neighbors, and that  $rW'$  would be negative. Actually, such is indeed the case for the b.c.c. lattice of  $\beta$ -brass, where  $A$  is 8.8. It is quite impossible to make  $A$  unity by a reasonable repulsive  $W$ . A natural interpretation for the low values of  $A$  observed for tungsten and for molybdenum,<sup>25</sup> namely, 1.0 and 0.71, is to assume, that  $W$  is attractive for nearest neighbors, repulsive for next nearest neighbors, as indicated in Fig. 5. Such an interpretation makes sense only if an antiferromagnetic structure is postulated for  $W$ , nearest neighbors thereby having no direct exchange between their  $d$  shells, but next nearest neighbors having such exchange. Hsu<sup>13</sup> has found that the high binding energy for tungsten is given by such an antiferromagnetic structure, the binding energy coming primarily from the classical attraction of two interpenetrating diffuse negative charges in each of which is imbedded concentrated positive charges of like magnitude.

### C. Arising from an Exchange of Electrons within the Conduction Band

The sign of this exchange interaction is the same as of the exchange interaction discussed in Sec. A above, and hence tends towards a parallel alignment of the spins of all the conduction electrons. In contrast to the case of the exchange interaction of Sec. A this aligning tendency is opposed by the anti-aligning tendency of the kinetic energy. Thus the kinetic energy is a minimum when half the spins point in one direction, the other half in the other direction. Under ordinary conditions the anti-aligning tendency of the kinetic energy is dominant, resulting in a zero net spin. Bloch<sup>14</sup> has pointed out, however, that for a sufficiently low concentration of conduction electrons the aligning tendency of the exchange interaction is dominant, resulting in the magnetization of the conduction electrons. The critical electron density which separates the region where the kinetic energy dominates from the region where the exchange energy dominates is in the vicinity of the density of the conduction electrons in cesium. Wigner<sup>15</sup> has, however, pointed out that

<sup>13</sup> Yee-Chuang Hsu, Phys. Rev. **83**, 975 (1951).

<sup>14</sup> F. Bloch, Z. Physik **57**, 545 (1929).

<sup>15</sup> E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

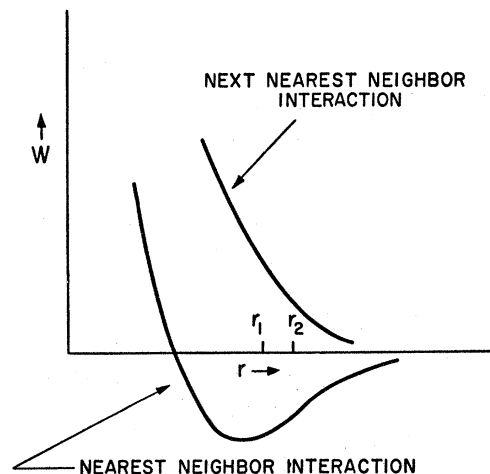


FIG. 5. Interactions postulated by Isenberg for tungsten.

such a magnetization of the conduction electrons would probably not take place, since at just about the same electron density the conduction electrons automatically become localized about lattice positions. Nonetheless, the exchange interaction arising from an exchange of electrons within the conduction band is of importance in helping to align the incomplete  $d$  shells of the transition metals, as is discussed later in this section.

### D. Arising from an Exchange of Electrons between the Conduction Band and the Incomplete $d$ Shells

Hund's rule of highest multiplicity applies to the coupling of the spin of an outer  $s$  electron to the spin of an incomplete  $d$  shell of isolated atoms, as well as to the coupling of the spins of the  $d$  electrons among themselves. When the outer  $s$  shell contains only one electron, the state of lowest energy will thus be that in which the spin of this  $s$  electron is aligned parallel with the spin of the inner incomplete  $d$  shell (see Table I). In Table I we consider the lowest configuration in which the outer  $s$  shell contains only one electron, and compare the two energies where the spin of this electron is parallel and antiparallel to that of the inner  $d$  shell.

In the model which we have adopted, the outer  $s$  electrons of the isolated atoms become conduction electrons in the condensed metallic state. The exchange interaction between a conduction electron and an inner incomplete  $d$  shell will therefore be ferromagnetic in nature. Each individual conduction electron tends to align the spins of the incomplete  $d$  shells in a direction parallel to its own spin. In the usual model of conduction electrons, equal numbers have spins pointing in one direction as in the opposite direction, and hence the net influence upon the spin of the incomplete  $d$  shells is zero. As soon as we relax the condition of equal numbers of conduction electron spins pointing in opposite directions, we find that the total energy of

TABLE I. Coupling energy  $\Delta E$  of spin of outer  $s$  electron to that of inner  $d$  shell.

	Cr	Mn	Fe	Co	Ni
Metal config-uration	$3d^5(^7S)4s$	$3d^5(^6D)4s$	$3d^7(^4F)4s$	$3d^8(^4F)4s$	$3d^9(^2F)4s$
$\Delta E$ , in ev	0.92	0.77	0.62	0.50	0.30

the system is lowered by first aligning the spin of the  $d$  shells, and then reversing the spins of some of the conduction electrons from an antiparallel to a parallel alignment.

The formal theory<sup>8</sup> of the above exchange interaction may be presented in a very simple manner. Towards this end we let  $E_{\text{spin}}$  be the spin energy per atom of a metal, the zero energy being taken as the unmagnetized state;  $S_d$  be the mean component per atom of the  $d$  shell spin along the magnetization direction, the unit of spin being a Bohr magneton; and finally  $S_c$  be the mean component per atom of the conduction electron spin along the magnetization direction. The spin energy may then be written as

$$E_{\text{spin}} = \left(\frac{1}{2}\right)\alpha S_d^2 - \beta S_d S_c + \left(\frac{1}{2}\right)\gamma S_c^2. \quad (1)$$

A minimization of this spin energy with respect to  $S_c$  leads to

$$E_{\text{spin}} = \left(\frac{1}{2}\right)(\alpha - \beta^2/\gamma)S_d^2 \quad (2)$$

for

$$S_c = (\beta/\gamma)S_d. \quad (3)$$

The present theory becomes formally identical to the Heisenberg-Slater theory through the following correspondence

$$J = (\beta^2/\gamma) - \alpha. \quad (4)$$

The reason for the success of Slater's theory now becomes evident. The "exchange integral"  $J$  is really the difference of two terms. One term  $\beta^2/\gamma$  arises from the indirect coupling via the conduction electrons. This term is always positive, and is independent of the amount of overlap of adjacent  $d$  shells. The second term  $-\alpha$  arises from the direct exchange between adjacent  $d$  shells. We assume this term to be always negative, and its magnitude decreases rapidly with decreasing overlap of adjacent  $d$  shells. The change in sign of the "exchange integral"  $J$  with decreasing amount of overlap thus arises naturally as a transition from the dominance of the direct exchange at a large overlap to the dominance of the indirect exchange via the conduction electron at a small overlap.

Whereas in the older theory the ferromagnetic coupling arose from the short-range direct exchange between adjacent  $d$  shells, in the present theory the ferromagnetic coupling via the conduction electrons is intrinsically a long-range type. We thus find a natural interpretation of the ferromagnetism of the Heusler alloys and of alloys of the type  $\text{CrPt}_3$ , materials in which the separation of the magnetic atoms is too large

to allow an appreciable direct coupling. A quantitative comparison of the predictions of the two theories for different Heusler alloys has been given by one of the authors.<sup>16</sup> The 16 percent difference in volume between the two Heusler alloys  $\text{Cu}_2\text{MnIn}$  and  $\text{Cu}_2\text{MnAl}$  would lead to an increase in 100 percent of the Curie temperature (in  $^\circ\text{K}$ ) of the latter over that of the former alloy according to the Heisenberg-Slater theory, an increase of only 20 percent according to the present theory. The observed increase is in fact just 20 percent. The success of the present theory in providing a qualitative interpretation of ferromagnetism in metals is paralleled by a corresponding success in providing a quantitative estimate of the magnetic coupling. Of the three coupling coefficients in Eq. (1), the last two may be readily estimated. The exchange coupling between the outer  $s$  and inner  $d$  electrons for isolated atoms is obtained from spectroscopic data. A comparison of the Hartree wave function for the  $s$  electrons with the cellular wave function for the metal shows how this exchange coupling is modified in the metal. The estimate of  $\beta$  for Ni is 0.48 ev per atom. The model of a free electron gas for the conduction electrons leads at once to an estimate for  $\gamma$ . This is 2.9 ev per atom for Ni. An estimate is thereby obtained for  $J$  by neglect of the direct exchange coefficient  $\alpha$ . The estimate so obtained for Ni is 25 percent higher than the observed value, thereby allowing for a small direct coupling.

### E. Arising from an Exchange of Valence States between Two Cations of the Same Transition Element

Because of their preoccupation with ionic solids of the NaCl type, physicists customarily think of the cations of ionic crystals as having a fixed degree of ionization, i.e., a fixed valency. Now ionic crystals can usefully be divided into two groups: one in which the cations have closed shells, of which NaCl is a typical example, the other in which the cation does not have a closed shell, a typical example of which is FeO. Crystals of the first class have an extremely small range of composition, and may, for most purposes, be thought of as existing only at the stoichiometric ratio. This narrowness in composition range arises from the fact that in order to create a deficiency in the cation lattice, one or more cations must become further ionized, and large energies are required to ionize a closed shell. Crystals of the second class have, on the whole, a comparatively wide range of composition, corresponding to a variable cation deficiency. This variable cation deficiency is possible only because of the comparative ease with which the cations in the ionic lattice may become further ionized. Common examples of the second group are found in the oxides, sulfides, selenides, and tellurides of the transition metals lying to the right of the Ti column in the periodic

<sup>16</sup> R. Heikes, Phys. Rev. 84, 376 (1951).

table. A mixture of the cation valency of the same transition element may also be produced by admixing a second cation of restricted valency. For example, if one replaces a small fraction of the Ni atoms in NiO by Li, one Ni<sup>++</sup> ion is forced to change to Ni<sup>+++</sup> for each Li atom introduced.

We are currently interested in the second group of crystals since, as has recently been pointed out by one of the authors,<sup>17</sup> the exchange of valence states between two cations of the same transition element leads to a ferromagnetic coupling of the cation spins. That this coupling is of a ferromagnetic nature may be seen from the following argument. Let  $\psi_1$  and  $\psi_2$  represent the two states indicated below,

$$\begin{aligned}\psi_1: & C^{++} C^{+++}, \\ \psi_2: & C^{+++} C^{++}.\end{aligned}$$

We shall suppose that each cation is in its lowest energy state, and hence in its state of highest multiplicity. Whereas each state  $\psi_1$  and  $\psi_2$  has the same energy, a state with still lower energy may be obtained by taking one of the linear combinations  $\psi_1 + \psi_2$  or  $\psi_1 - \psi_2$ , the appropriate linear combination depending upon the sign of the exchange integral. This energy will be lower the greater the exchange integral between these two states. Now the exchange integral will be greatest when the spins of the two cations are aligned parallel. The state of lowest energy therefore represents a ferromagnetic alignment of spins.

In actual ionic crystals, the distances between adjacent cations are usually too large to admit of an appreciable direct interaction. However, this exchange interaction is aided greatly by the intervening anions by a process which is called *double exchange*. In this process an electron jumps from the C<sup>++</sup> ion to the intervening anion, simultaneous with the jump of a second electron from the anion to the C<sup>+++</sup> ion.

An interesting feature of double exchange is that it promotes a mechanism not only for ferromagnetic coupling but also for electrical conductivity. If the concentration of C<sup>++</sup> and C<sup>+++</sup> ions is comparable, and if the temperature is sufficiently high, an electron leaving a particular C<sup>++</sup> ion by double exchange has an essentially equal probability of jumping to any of the C<sup>+++</sup> ions which are its immediate neighbors. Two features of the resulting electrical conductivity deserve special comment. (1) Since under the above conditions the frequency of jumping of an electron from a particular C<sup>++</sup> ion to a neighboring C<sup>+++</sup> ion is independent of temperature, the diffusion coefficient  $D$  of the  $d$  electron is likewise independent of temperature. Since now the electrical conductivity  $\sigma$  is related to  $D$  by the Einstein relation

$$\sigma \sim D/T,$$

we see that  $\sigma$  varies inversely as  $T$ . Any substance with such a temperature dependence we commonly call a

<sup>17</sup> C. Zener, Phys. Rev. **82**, 403 (1951).

metallic conductor. (2) In the absence of other pertinent exchange interactions, the magnitude of the double exchange determines both the Curie temperature  $T_c$  and the exchange frequency  $\nu$ , and hence  $\nu$  is determined uniquely by  $T_c$ . When use is made of this relation, one finds that the electrical conductivity at the Curie temperature for the case where the C<sup>++</sup> and C<sup>+++</sup> ions are of comparable concentration is essentially independent of the particular system, and has the order of magnitude given by

$$\sigma \sim e^2/ah,$$

where  $e$  is the electronic charge,  $a$  the lattice parameter. If one takes for the lattice parameter a typical value of 3A, one obtains for  $e^2/ah$  the value  $1.2 \times 10^{13}$  ohm<sup>-1</sup> cm<sup>-1</sup>. This is the order of magnitude of the conductivity of mixed valency crystals, such as magnetite,<sup>18</sup> manganese perovskites,<sup>4,5</sup> and chromium chalcogenides.<sup>19</sup>

#### F. Arising from an Exchange of Excited Valence States of Cations of the Same Transition Element

Our final exchange interaction, commonly known as super exchange, was first discussed by Kramers,<sup>20</sup> and later analyzed in detail by Anderson<sup>21</sup> and Van Vleck.<sup>22</sup> One of the authors<sup>19</sup> has recently given a detailed discussion of the physical significance of this exchange interaction, and discussed its application to a variety of systems.

In order to understand the physical basis of super exchange, it is wise to first review the proper description of a typical polar molecule such as NaCl. A perfectly polar molecule would be represented by Na<sup>+</sup>Cl<sup>-</sup>, and would have the ideal dipole moment of  $er$ , where  $r$  is the internuclear distance. Now most polar molecules have a dipole moment considerably less than the ideal value, indicating that the average charge on the anion and cation is considerably less than  $e$ . A possible method of representing the molecule, a method used extensively by Pauling,<sup>23</sup> is to define a polar and a nonpolar wave function as follows:

$$\begin{aligned}\psi_p &: \text{Na}^+ \text{Cl}^-, \\ \psi_{np} &: \text{Na} \text{Cl}.\end{aligned}$$

The appropriate wave function is then written as  $\psi_p + \beta\psi_{np}$ .

We now consider a slightly more complicated molecule of the type COC where C will denote a cation. The pure polar state would be represented by

$$\psi_p: \text{C}^+\text{O}=\text{C}^+.$$

A wave function more appropriate than  $\psi_p$  can be

<sup>18</sup> C. A. Domenicali, Phys. Rev. **76**, 460 (1949).

<sup>19</sup> R. Heikes (to be published in Acta Metallurgica).

<sup>20</sup> H. A. Kramers, Physica **1**, 182 (1934).

<sup>21</sup> P. Anderson, Phys. Rev. **79**, 350 (1950).

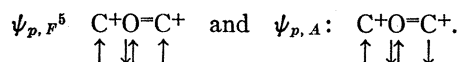
<sup>22</sup> J. H. Van Vleck, Grenoble Conference, 114 (1951).

<sup>23</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

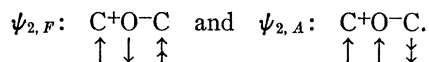
obtained by allowing for an admixture of the somewhat less polar states

$$\begin{aligned}\psi_1: & \text{C O}^- \text{C}^+, \\ \psi_2: & \text{C}^+ \text{O}^- \text{C}.\end{aligned}$$

We now consider the further complication of letting  $\text{C}^+$  be a transition metal cation having a nonzero electronic spin. The pure polar state will then be highly degenerate, the energy being independent of the relative orientation of the spins of the two cations. We shall consider in particular the two extreme states represented below:



The arrows beneath O<sup>-</sup> denote the spins of those two dumb-bell type  $p$  wave functions whose axes are parallel to the axis of the molecule. We shall now attempt to describe those semipolar states of the type  $\psi_2$  which combine with the above. Since we are concerned only with those states of lowest energy, we shall consider Hund's rule to apply to the spin configuration of both  $\text{C}^+$  and of C. Then if the  $d$  shell of  $\text{C}^+$  is less than half filled, the combining states of the type  $\psi_2$  are



We now make the important observation that these two states are not degenerate. The direct exchange interaction of the left-hand  $\text{C}^+$  with  $\text{O}^-$  will lower the energy of  $\psi_{2F}$  with respect to that of  $\psi_{2A}$ . The energy of the appropriate linear combination of  $\psi_{p,F}$  and  $\psi_{2,F}$  will therefore be lower in energy than that of the appropriate linear combination of  $\psi_{p,A}$  and  $\psi_{2,A}$ . We therefore conclude that when the  $d$  shell of  $\text{C}^+$  is less

than half filled, a ferromagnetic coupling exists between the cations. A similar analysis leads to the conclusion that when the  $d$  shell of  $\text{C}^+$  is half-filled or more than half filled, an antiferromagnetic coupling exists.

The first application of superexchange to particular systems was made by Néel.<sup>24</sup> He showed that the ferromagnetism of the ferrites could be interpreted in terms of this exchange.

### III. SUMMARY

The above-described six types of exchange interactions, taken in conjunction with our model of localized  $d$  electrons and lattice wave functions for the outer  $s$  electrons, are able to interpret the main features of magnetic coupling. The magnetic coupling giving rise to the magnetic moment of the isolated transition metal ions comes from the type of exchange described in Sec. A. The exchange coupling which aligns these isolated ionic moments is of type described in Sec. B in metals, of types in Sec. E and/or F in ionic lattices. The last type of exchange tends to align the  $d$  shell spins only in the case of less than half filled  $d$  shells, as in the case of CrTe. In case the  $d$  shells are half filled or more than half filled, as in the case of the ferrites, this exchange type is antiferromagnetic. The exchange type in Sec. B is also antiferromagnetic in nature. In any particular material several of these exchange interactions may be in simultaneous operation and may be comparable in magnitude. Such is the case, for example, in the chromium chalcogenides (Cr-S, Cr-Se, Cr-Te). An interpretation of the complex magnetic behavior found in these substances has been given by one of the authors.<sup>19</sup>

<sup>24</sup> L. Néel, Ann. phys. 3, 137 (1948).