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Magnetic Coupling in Crystalline Compounds. A Phenomenological Theory of Magnetism in 3*d* Metals

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Magnetic coupling processes are considered in terms of the orbitals which result from the splitting of the *d* levels by the crystalline field. It is shown that the antiferromagnetic and ferromagnetic structure properties of many crystalline compounds can be qualitatively accounted for on the basis of indirect coupling processes which depend on the overlap of magnetic cation *d* orbitals with *p* orbitals of intervening anions and on the electron spin occupation appropriate to the particular cations involved.

The orbital approach has also been used in considering the magnetic properties of the 3*d* metals and a coupling mechanism has been proposed which is consistent with much of the magnetic data relating to the iron group metals and their alloys.

INTRODUCTION

In part I indirect magnetic coupling processes in crystalline compounds are considered in terms of the properties of the orbitals which result from the splitting of the *d* levels by the crystalline field.

In part II the magnetic coupling properties of the 3*d* metals and their alloys are treated similarly in terms of the occupation and the energy splitting of the *d* orbitals.

I. MAGNETIC COUPLING IN CRYSTALLINE COMPOUNDS

A. Coupling between Ions in Octahedral Sites

The simplest type of compounds for the study of the magnetic coupling mechanisms between ions in octahedral sites are those of the perovskite type such as $LaMO_3$ and the trifluorides MF_3 where M represents an iron group element. These compounds are ideally cubic with one molecule per unit cell. The magnetic cation M is located at the corners of the cube and the anions lie near the centers of the cube edges between neighboring cations. In the perovskites of the type considered here the rare earth ion or its equivalent which is located at the center of the cube is nonmagnetic and plays no essential role other than that of determining the valence state of the magnetic ion.

Of these compounds a neutron diffraction study[1] was first made on the magnetic properties of the mixed system $La^{3+}Ca^{2+}(Mn^{3+},Mn^{4+})O_3$. It had been shown by Jonker and Van Santen[2] that this system was ferromagnetic in a region $0<Mn^{4+}<0.5$, from which it was concluded that the indirect magnetic interaction between a Mn^{3+} ion and a Mn^{4+} neighbor must be ferromagnetic. The neutron experiments showed the existence of a series of different antiferromagnetic structures as a function of composition, and it showed the transitions between these structures and structures involving the ferromagnetic properties.

Just prior to this work Goodenough and Loeb[3] had applied a hybrid orbital approach to the study of distortions in spinel type crystals and Goodenough[4] applied these same considerations to the above perovskite system and the resultant correlations of the spacially ordered hybrid orbitals with the observed magnetic structures were very striking. In the case of the ferromagnetic coupling between Mn^{3+} and Mn^{4+} ions there was unfortunately in this picture no obvious mechanism of magnetic coupling.

It appears now that the *d* orbitals that result from the application of crystal field theory[5] give a truer representation of the physical situation. It is on the basis of the spacial properties, the type of energy splitting and the electron occupation of these orbitals that the magnetic properties of crystals will be discussed.

The crystal field splits the 3*d* levels of an ion in an octahedral site into a lower triplet (t_{2g}) and an upper doublet (e_g). The three t_{2g} orbitals are of the type d_{xy}, d_{yz}, and d_{xz} and the two e_g orbitals are of the type d_{z^2} and $d_{x^2-y^2}$. The t_{2g} orbitals are square orbitals which point along the diagonals of the respective cube faces, the d_{z^2} orbital is concentrated along the z axis and the $d_{x^2-y^2}$ orbital is a square orbital whose lobes lie along the x and y edges of the cube. In a crystal of the perovskite type the two e_g orbitals of a metal atom on the corner of a cube point towards and overlap with one of the *p* orbitals of each of the six oxygen neighbors of the metal ion and the two nearest neighbor metal ions overlap the opposite ends of an intervening anion *p* orbital. It is thus to be expected that these orbitals would play the important role in the indirect magnetic exchange between the two neighboring cations and the intervening anion.

To consider the role of these orbitals in their overlap with their neighboring surroundings in crystals it is

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[1] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

[2] G. H. Jonker and J. H. Van Santen, Physica **16**, 337 (1950); **19**, 120 (1953).

[3] J. B. Goodenough and A. L. Loeb, Phys. Rev. **98**, 391 (1955).

[4] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).

[5] H. A. Bethe, Ann. Physik **3**, 133 (1929); J. H. Van Vleck, Phys. Rev. **41**, 208 (1932); W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); J. D. Dunitz and L. E. Orgel, J. Phys. Chem. Solids **3**, 20 (1957).

TABLE I. d-shell configuration and primary energy splitting for iron group ions.

Cations in compounds		Ti^{3+}	V^{3+} Ti^{2+}	Mn^{4+} Cr^{3+} V^{2+}	Mn^{3+} Cr^{2+}	Fe^{3+} Mn^{2+}	Co^{3+} Fe^{2+}	Ni^{3+} Co^{2+}	Cu^{3+} Ni^{2+}
Octahedral sites	e_g	00	00	00	↑0	↑↑	↑↑	↑↑	↑↑
$E(e_g)>E(t_{2g})$	t_{2g}	↑00	↑↑0	↑↑↑	↑↑↑	↑↑↑	↑↓↑↑	↑↓↑↓↑	↑↓↑↓↑↓
Tetrahedral sites	t_2	000	000	↑00	↑↑0	↑↑↑	↑↑↑	↑↑↑	↑↓↑↑
$E(t_2)>E(e)$	e	↑0	↑↑	↑↑	↑↑	↑↑	↑↓↑	↑↓↑↓	↑↓↑↓

necessary to consider their occupation by the electrons in the $3d$ shells of the ions of the iron group elements which enter into the compounds in question. The upper part of Table I shows the splitting in octahedral sites and the occupation of the orbitals for the ions of iron group elements.

The magnetic structure properties of the above mentioned perovskite system and of the corresponding compounds of chromium, iron and cobalt[6] as well as the more recently studied trifluoride compounds[7] CrF_3, MnF_3, FeF_3, and CoF_3 can be accounted for on the basis of the spacial distribution and the electron occupation of the e_g orbitals of the particular cations involved and on the basis of three associated types of indirect magnetic coupling.

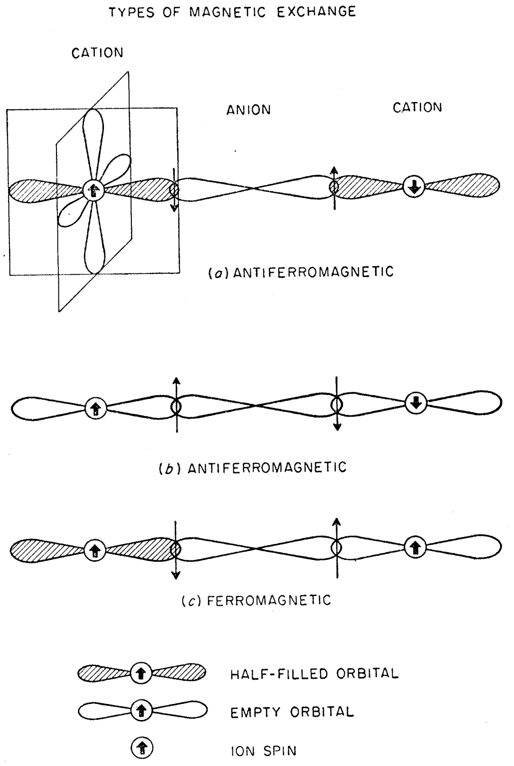

FIG. 1. Schematic representation of indirect exchange processes.

These three types of indirect coupling which result from the overlap of magnetic cation orbitals with intervening anion orbitals in crystalline compounds are listed below and they are also diagramatically illustrated in Fig. 1.

(1) Whenever half-filled orbitals of two magnetic cations overlap, respectively, the two ends of a given anion p orbital the magnetic coupling will be antiferromagnetic.

(2) Whenever empty orbitals of two magnetic cations overlap, respectively, the two ends of a given anion p orbital the magnetic coupling is likewise antiferromagnetic.

(3) Whenever an empty orbital of one magnetic ion overlaps one end of an anion p orbital and the other end of the same anion p orbital overlaps a half-filled orbital of another magnetic ion the magnetic coupling is ferromagnetic.

It would appear that (1) corresponds to the perturbation theory calculations which have been made by Anderson[8] and by Pratt[9] on the basis of Kramers'[10] earlier considerations and which has been termed superexchange. Although the first calculations of this type gave ferromagnetic coupling for ions with less than half-filled d shells, these conclusions were later modified to allow for possible antiferromagnetic coupling in this case (2) also. Case (3) must be considered as an interpretation of experimental observations but it is quite understandable on an intuitive extension of (a) and (b).[11]

These processes can be phenomenologically represented as indicating that an electron associated with overlapping orbitals of two neighboring ions must satisfy the condition for existing simultaneously on either ion. This condition requires (a) that the two electrons of an anion p orbital always remain antiparallel, (b) that when the anion p orbital overlaps an empty orbital of a magnetic cation that anion electron which spends time in the overlapping cation d orbital will tend to have its spin parallel to the cation spin, (c) in the case where the particular cation orbital is occupied by one electron regardless of whether or not the d shell is more or less than half filled the anion p electron which spends time in the overlapping cation d orbital will tend to have its spin antiparallel to the cation spin.

These principles have been expressed in terms of an indirect coupling process. As will be seen later it would

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[6] W. C. Koehler and E. O. Wollan, J. Phys. Chem. Solids **2**, 100 (1957).

[7] Wollan, Child, Koehler, and Wilkinson, Phys. Rev. **112**, 1132 (1958). Some of the considerations presented here were briefly reported in reference 7.

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

[9] George W. Pratt, Jr., Phys. Rev. **97**, 926 (1955).

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

[11] P. W. Anderson (to be published) has now written "A New Approach to the Theory of Superexchange Interactions" which treats theoretically the magnetic coupling processes herein presented. See also R. K. Nesbet, Ann. Phys. (N. Y.) **4**, 87 (1958).

TABLE II. Néel temperatures in perovskite and trifluoride compounds.

Trifluorides	T_N	Perovskites	T_N
CrF_3	80°K	$LaCrO_3$	320°K
MnF_3	43°K	$LaMnO_3$	100°K
FeF_3	394°K	$LaFeO_3$	750°K
CoF_3	460°K		

appear that similar considerations can be applied also to more direct coupling processes.

Two examples of magnetic structure types which develop in the perovskite and trifluoride compounds are shown in Fig. 2 where the symbols used to designate the magnetic structures are those used in the original papers. These figures represent the magnetic structures as interpreted in terms of the spacial properties of the e_g orbitals and the corresponding coupling processes (1), (2), and (3) listed above.

The *G*-type structure involves antiferromagnetic coupling between a given metal ion and all six of its nearest neighbors. If all the e_g orbitals in Fig. 1(a) are considered as half filled, then the indirect coupling would be of the type (1). The following are examples of this class: $LaFeO_3$, FeF_3, and CoF_3. On the other hand, if the orbitals were all empty one would obtain the same *G*-type antiferromagnetic structure by indirect coupling processes of type (2). The compounds $LaCrO_3$, $CaMnO_3$, and CrF_3 are of this class.

The *A* type of antiferromagnetic ordering is shown in Fig. 2(b). In this case there is ferromagnetic coupling within the plane and antiferromagnetic coupling between planes. This structure is observed for $LaMn^{3+}O_3$ and $Mn^{3+}F_3$. In Mn^{3+} one of the two e_g orbitals are empty and by proper ordering of these e_g orbitals one develops the observed ferromagnetic coupling within the plane according to process (3). It has been assumed here that the d_{z^2} orbital is half filled and the $d_{x^2-y^2}$ orbital is empty. The same structure could be developed on the opposite assumption. The antiferromagnetic coupling between planes under the present assumptions is of type (2). In this figure there is included a schematic representation of the displacement of the anions from the central position between the magnetic cations on the corners of the cube. This is the actual observed displacement of the anions in MnF_3 [12] and it makes the proposed type of orbital ordering very reasonable.

These examples serve to illustrate the possible indirect exchange processes in octahedrally coordinate compounds. Other types of antiferromagnetic ordering[13] have also been observed, and these can generally be accounted for on the basis of *d*-orbital exchange processes. This is true also of the ferromagnetic and ferrimagnetic ordering properties observed in some of these compounds.[14]

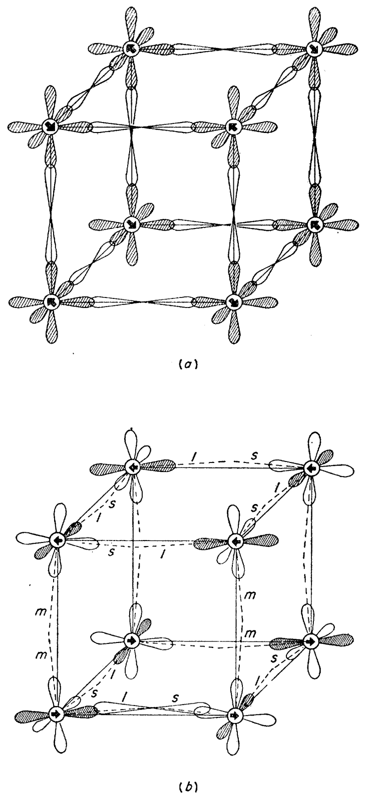

FIG. 2. Examples of *d*-orbital coupling in magnetic structures. (a) *G*-type antiferromagnetic structure which is observed when both e_g orbitals of all the cations involved are either half filled or empty. (b) *A*-type antiferromagnetic structure interpreted in terms of ordered arrangement of half-filled d_{z^2} orbitals and empty $d_{x^2-y^2}$ orbitals.

The approximate transition temperatures at which the various iron group perovskites and trifluoride structures order are shown in Table II. It will be noticed that the structures involving ions with empty e_g orbitals, those containing Cr^{3+} and Mn^{4+}, have relatively low Néel temperatures whereas those involving the ions Fe^{3+} and Co^{3+} with half-filled e_g orbitals have relatively high Néel temperatures. One would thus conclude that the type (2) indirect coupling ($e_0 - \infty - e_0$) involving empty orbitals is weaker than the type (1) coupling ($e_\uparrow - \infty - e_\downarrow$) involving half-filled orbitals.

B. Magnetic Coupling between Ions in Tetrahedral and Octahedral Sites

Compounds with the spinel type structure, of which so many have been studied in recent years, constitute the best source of information about this type of magnetic coupling.

The ideal spinel type structure is cubic with eight molecules per unit cell, and it can be characterized as a face-centered lattice array of oxygen atoms with metal atoms located in the interstices of the oxygen lattice. These sites, of which there are 48 in the unit cell, are of two types; there are 16 *A* sites in which the metal ions

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[12] M. H. Hepworth and K. H. Jack, Acta Cryst. **10**, 345 (1957).

[13] See reference 1 and Wold, Arnott, and Goodenough, J. Appl. Phys, **29**, 387 (1958).

[14] See reference 1 and U. H. Bents, Phys. Rev. **106**, 225 (1957).

are tetrahedrally coordinated to four oxygen neighbors and 32 B sites in which there is octahedral coordination to six oxygen neighbors. The 24 metal ions in the unit cell occupy half of the A sites and half of the B sites.

It was originally proposed by Néel that the A-B coupling in spinels was strongly antiferromagnetic and that the A-A and B-B couplings are weakly antiferromagnetic. Much of the work on spinels has been correlated with Néel's hypothesis and the results have been expressed where possible in terms of the coupling constants of these interactions.

Let us now consider whether or not the coupling mechanisms which were found to account for the magnetic structure properties of the simple perovskite and trifluoride type compounds will also account for the magnetic properties of spinels.

In these compounds there are ions in both octahedral and tetrahedral sites. For the ions in tetrahedral sites the crystal field splitting of the d shell is such as to make the doublet (e_g orbitals) of lower energy than the triplet (t_{2g} orbitals). The splitting and level occupation for ions in tetrahedral sites is also shown in Table I.

Now since in the spinels it has been observed that the important magnetic coupling in most cases seems to be that between the ions on A sites and those on B sites (A-B coupling) it would appear that the principal magnetic coupling would involve the t_{2g} orbitals of A ions and the e_g orbitals of B ions and their related overlap with the p orbitals of the intervening oxygen anions. The spacial arrangement of these orbitals is shown schematically for the B-site neighbors of a given A-site ion in Fig. 3(b).

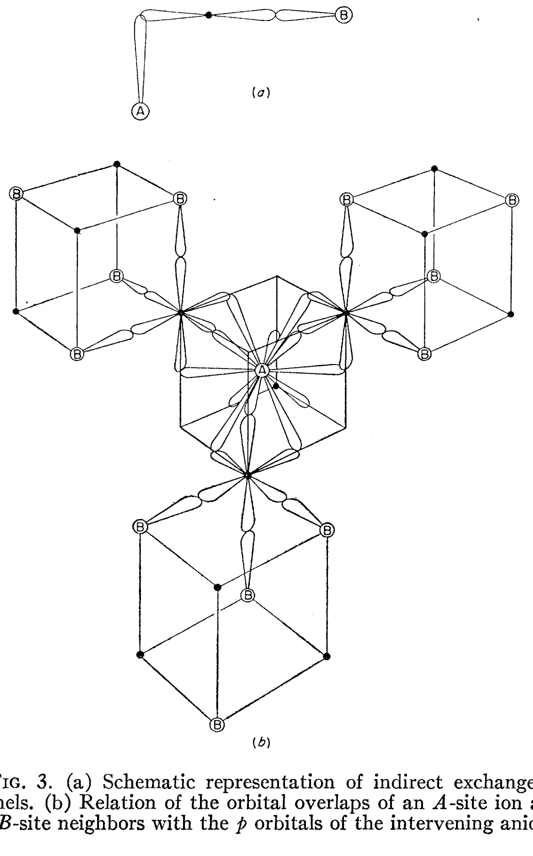

FIG. 3. (a) Schematic representation of indirect exchange in spinels. (b) Relation of the orbital overlaps of an A-site ion and its B-site neighbors with the p orbitals of the intervening anions.

Figure 3(a) shows schematically the orbital relationship of an A-site ion with a single B-site ion and the overlap of these orbitals with the two ends of a p orbital of the intervening anion. Now it would appear that this type of indirect coupling would in principle be the same as the linear ($e_g - \infty - e_g$) type coupling observed between ions in octahedral sites if as might be expected the primary requirement for such coupling is that the orbitals of two cations overlap a p orbital of an intervening anion. The right angle type of coupling shown in Fig. 3(a) is not to be confused with that involved when the right angle is centered on the anion which is assumed to give zero effect. If we accept this as essentially identical to the linear indirect coupling, except that it may differ in strength, then the types of coupling (1), (2), and (3) which were used in accounting for the magnetic properties of the perovskite type compounds would seem to be applicable here also. One would thus expect antiferromagnetic coupling in the spinels when cases (1) and (2) applied and ferromagnetic coupling in case (3).

From Fig. 3(b) one sees that there are 12 B-site ions (3 B-site ions are not shown) which are magnetically coupled to a single A-site ion by the mechanism of Fig. 3(a). If all the coupling orbitals indicated are half filled as would be the case for a compound like Fe_3O_4 whether it were normal or inverted, then all the magnetic A-B linkages would be antiferromagnetic. This would then appear to correspond to the strong A-B antiferromagnetic interaction introduced in molecular field theory.

It is evident now that if the indirect A-B coupling is correctly represented on the present picture, the assumption that this coupling should always be antiferromagnetic cannot be accepted. This will be true in a particular A-B indirect coupling bond only if the respective t_2 and e_g orbitals are either both empty or both half filled. On the present basis it would be suggested that, in spinels containing trivalent chromium ions with empty e_g orbitals in octahedral sites and iron ions, for example, with half-filled t_2 orbitals in tetrahedral sites, the A-B coupling would be ferromagnetic. The strength of this coupling might, however, be much weaker than the antiferromagnetic coupling involving half-filled orbitals for the ions on both A and B sites. It is known that mixed spinels involving chromium ions[15] have magnetic properties which cannot be accounted for on the basis of the usual molecular field approach. The whole approach to the preparation and study of such spinels might thus be modified if the

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[15] E. W. Gorter, Philips Research Repts. 9, 295 (1954).

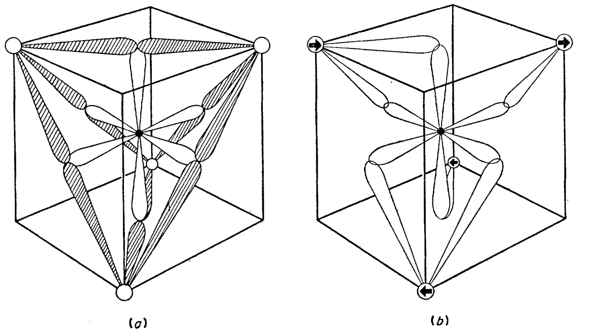

FIG. 4. (a) Direct linkage of the t_2 orbitals (cross hatched) of cations in tetrahedral sites and the relation of the t_2 orbitals to the p orbitals of an included anion. (b) Possible indirect coupling linkages for a tetrahedrally coordinated antiferromagnetic structure.

present suggestions regarding magnetic coupling in such systems are found to be essentially correct.

In addition to the A-B coupling it has usually been assumed in the molecular field approach that there are both A-A and B-B types of coupling. On the d-orbital picture there does not appear to be any obvious mechanism for an A-A type of coupling. In the case of the octahedral B-site ions, however, the direct overlap of the t_{2g} orbitals might be expected to give rise to a direct B-B exchange interaction. If one assumes that there is an exchange of d electrons between ions with overlapping t_{2g} orbitals and that the previously stated principles similar to (b) and (c) apply in this case also then the direct exchange between ions on octahedral sites would be antiferromagnetic when half-filled t_{2g} orbitals are involved. The overlap of empty orbitals would not be expected to give rise to coupling but the overlap of an empty orbital with a half-filled orbital might be expected on the present basis to give ferromagnetic coupling.

That this direct exchange is weak is suggested by the neutron diffraction data of Corliss and Hastings[16] on the $ZnFe_2O_4$ system in which all the tetrahedral A sites are occupied by the nonmagnetic Zn ions. This compound was found to show a tendency towards antiferromagnetic ordering at about 9°K. A broad unresolved band of antiferromagnetic type scattering was observed and the neutron pattern could be accounted for on the assumption of ferromagnetic sheets of random atomic thickness, some of which had one spin orientation and some the opposite orientation.

C. Magnetic Coupling between Ions in Tetrahedral Sites

In this class of compounds it is the t_2 orbitals that would be expected to participate in coupling processes. Figure 4(a) shows these orbitals in relation to four cations in tetrahedral coordination. In compounds of this type one may or may not find an anion in the center of such a group of cations. In fact it might appear at first sight that an anion would be superfluous as far as exchange is concerned since the cation orbitals point only to each other, and this would suggest that any exchange in such a configuration would be of the direct type between these cations. As had previously been pointed out, the direct exchange of a d electron between overlapping half-filled t_2 orbitals would on the present assumptions be expected to be antiferromagnetic. Such an exchange would, however, give rise to an antiferromagnetic structure only if there were distortions in the crystal or if other exchange processes were involved.

Consider now an anion to be brought into the picture with its p orbitals disposed as shown in Fig. 4(a). These anion p orbitals overlap the cation t_2 orbitals in a somewhat complicated pattern but they do indeed bring in the possibility of indirect coupling mechanisms of the type previously discussed. These orbital arrangements may at first sight seem rather unpromising as a basis for accounting for antiferromagnetic structures in such compounds but the apparent success of similar arrangements in accounting for the magnetic properties of the metals (see Part II) would suggest that serious consideration should be given to these orbital overlap properties. The antiferromagnetic spin arrangement shown by the arrows in Fig. 4(b) is one which is observed in some types of tetrahedrally coordinated compounds.[17]

Another somewhat different problem which may be tied in with a type $(t_{2g}-t_{2g})$ of direct exchange is that of the stabilization of the MnO type of antiferromagnetic structure. In the MnO structure the neighboring Mn^{2+} ions in a given sublattice are antiferro-

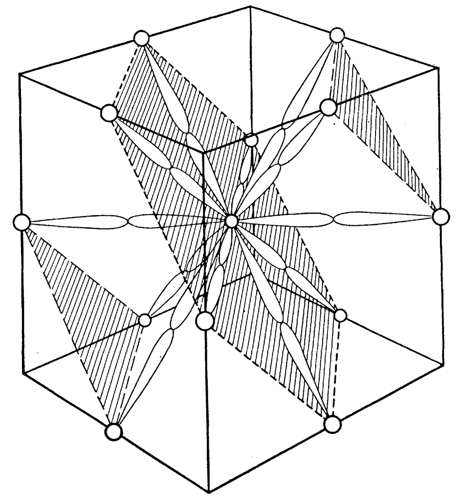

FIG. 5. Relationship of the t_{2g} orbitals of a given ion with its twelve nearest neighbors in the face-centered cubic structure. The shaded areas are for clarity of representation.

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[16] J. M. Hastings and L. M. Corliss, Phys. Rev. **102**, 1460 (1956).

[17] For example, the MnS (zincblende) antiferromagnetic structure, Corliss, Elliott, and Hastings, Phys. Rev. **104**, 924 (1956).

Table III. Proposed orbital occupation pattern for $3d$ metals.

STRUCTURES	Bcc	COMPLICATED Bcc	Bcc	Fcc (HEX)	Fcc
METALS	α-Cr	α-Mn	α-Fe	Co	Ni
E-ORBITALS	OO	↑O	↑↑	↑↓ ↑	↑↓ ↑↓
T-ORBITALS (HOLE = O)	↑↓↑↓↑↓○	↑↓↑↓↑↓○	↑↓↑↓↑↓○	↑↓↑↓↑↓○	↑↓↑↓↑↓○
$\langle\lvert\mu\rvert\rangle$	0.4	1.1	2.22	1.7	0.6

magnetically coupled via the intervening oxygen ions. The coupling in this case is to be associated with the half-filled e_g orbitals. The particular ferromagnetic sheet type structure which is known to exist in this compound is, however, only one of several possible ways of magnetically coupling the four sublattices together. This problem has received considerable attention and one proposal involves invoking magnetic dipole forces as the stabilizing factor.[18]

Now on the orbital approach one is impressed by the fact that the t_{2g} orbitals have just the required property of connecting the four sublattices. These orbitals are schematically represented in Fig. 5 where the circles represent the Mn ions in the MnO structure. Half of each d_{xy}, etc., orbital lies in the plane of a ferromagnetic sheet containing the central atom and the other half of these orbitals connects the central atom to the oppositely aligned magnetic sheets above and below the central plane on the cube diagonal.

Now the direct exchange of the type $(t_{2g}-t_{2g})$ would be expected to be antiferromagnetic for the half-filled orbitals of Mn^{2+}. This in itself would not stabilize a particular structure but if one considers that the crystal in the magnetically ordered state has a small rhombohedral distortion along the axis perpendicular to the ferromagnetic sheets, it is possible that this would strengthen the antiferromagnetic coupling between the layers and weaken it within the layers.

The magnetic structures of the other iron group oxides FeO, CoO, and NiO are based on the same ordering within each sublattice but the over-all structures differ in a fashion which is consistent with a $(t_{2g}-t_{2g})$ exchange which is modified by the different occupation patterns in this series of compounds.

II. PHENOMENOLOGICAL THEORY OF MAGNETISM IN $3d$ METALS[19]

A. Orbital Occupation and Magnetic Coupling in the Metals

In Part I it was shown how the indirect antiferromagnetic and ferromagnetic coupling in certain crystalline compounds may be determined to a considerable degree by the crystal field splitting and the resultant occupation patterns of the d orbitals of the magnetic cations involved.

The second part of this paper represents a similar approach to the interpretation of the fundamental properties of the $3d$ metals and their alloys. The reason for becoming involved with the metals is associated in part with observations relating to the e orbitals[20] of the ions of $3d$ elements in crystalline compounds. These observations led to a correlation of the orbital occupation pattern of 3+ ions with the corresponding $3d$ metals as shown by the bold arrows in Table III. The order of the entries have been made at this point without regard for the energy of splitting of the d orbitals. It is to be noted that the e-orbital occupation for chromium, manganese, and iron have been taken as those appropriate to ions in octahedral surroundings[21] whereas for the case of cobalt and nickel the e-orbital occupation is that appropriate to ions in tetrahedral sites (see Table I). The appropriateness of this assignment must be considered as a pure assumption at this stage of the development but an attempt will be made to show the reasonableness of this assumption in a later section.

Now the assumed occupation pattern of the e orbitals in the metals will be maintained if the remaining three electrons per atom over and above those shown in bold type are assumed in every case to enter with opposite spin into the t orbitals. It is known, however, that some of the outer electrons in the metals are in s states and hence it will be assumed that the partial occupation of these s states in all cases gives rise to holes in the t orbitals. In the ordered magnetic state these holes will be associated with the spin down electrons as indicated in Table III by the open circles.

The occupation of the orbitals as thus represented in Table III leads directly to a simple interpretation of the magnetic moment data for the $3d$ metals. The trend of the moments which result from the proposed occupation of the e orbitals only is plotted as the solid line in Fig. 6. In addition to these integral moment values there will be a contribution from the additional holes in the d shell which are here assumed in every case to be associated with an incomplete filling of the t orbitals. These holes are then considered as representing the fractional contribution to the observed moments. The trend of this contribution to the moment values is schematically represented by the cross hatched areas in Fig. 6. On this basis it is the holes in the t orbitals which give rise to the asymmetry of the magnetic moment data relative to iron and one notices from the figure that this asymmetry in the data appears to be a structure sensitive property.

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[18] F. Keffer and W. O'Sullivan, Phys. Rev. **108**, 637 (1957).

[19] A preliminary report of early considerations of Part II of this paper were given in Phys. Rev. **110**, 1205 (1958).

[20] In this part of the paper the d orbitals will be referred to as e orbitals and t orbitals, the cumbersome subscripts being omitted.

[21] N. F. Mott and K. W. H. Stevens, Phil. Mag. **2**, 1364 (1957), have proposed a d-level splitting which gives this e-orbital occupation.

Although we have given first this brief interpretation of the magnetic moment data of the metals in terms of the orbital occupations listed in Table III it is interesting from the writer's point of view to note that these moment data relations constituted only a byproduct and not a starting point in the consideration of the metals. At the outset an attempt was made to develop a magnetic coupling scheme for the metals along the lines pursued in considering the crystalline compounds.

In this connection the characteristics of the occupation pattern of the *e* orbitals of chromium, manganese, and iron as represented in Table III played an important role. Now since the *t* orbitals have been assumed to be similarly occupied in all the metals it is suggested that the differences in their magnetic properties is to be associated with the different occupation pattern of their *e* orbitals. It is then to be noted that chromium and manganese which are antiferromagnetic have empty *e* orbitals whereas for iron which is ferromagnetic both of the *e* orbitals are half filled. In the case of manganese which has one half filled and one empty *e* orbital, both the crystallographic and the magnetic structure properties are complicated.[22] This situation bears some similarity to that observed for Mn^{3+} ions in crystalline compounds in which the magnetic structure properties were found to be somewhat more complicated than those involved with a symmetrical filling of these orbitals.

In the case of iron and chromium the structures are nearly identical both being body centered cubic with spacing values which differ by only about half of one percent yet their magnetic properties are very different, iron being ferromagnetic with a large moment and chromium being antiferromagnetic with a small moment. It was on the basis of a consideration of these two metals that the ideas for the presently proposed theory of the 3*d* metals and their alloys was developed.

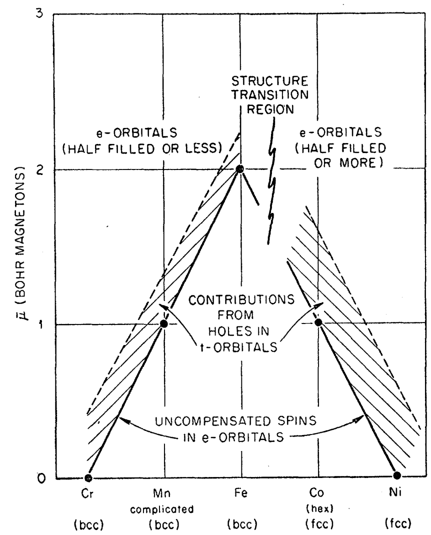

FIG. 6. Schematic representation of moment contributions in the iron group metals.

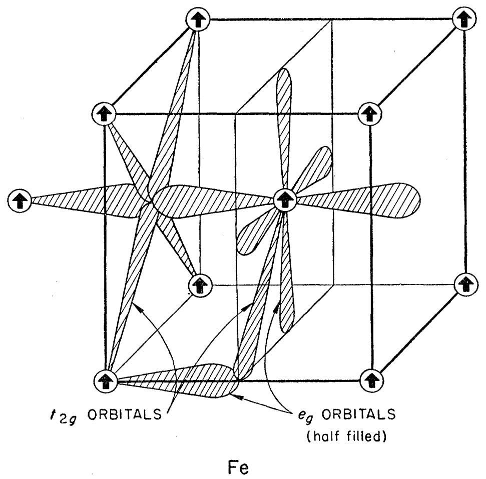

FIG. 7. Orbital relationships in the body-centered cubic structure of iron.

Iron

In the case of iron which has the body-centered cubic structure, the *t* and *e* orbitals would be expected to fit into the lattice as shown in Fig. 7. Every cube face and cube edge (cube face for body-centered ion) would constitute the meeting point of six orbital lobes which represent part of the five 3*d* orbitals. These orbital lobes for each of the six iron ions related to the left face of the cube are shown in Fig. 7 together with other orbital lobes which connect the central ion to the ion in the lower left-hand corner. As first contemplated this picture represented a rather unpromising situation but on further study it became apparent that this orbital arrangement might have just the desired characteristics to account for the magnetic properties of the bcc structure.

In what might be considered a somewhat naive approach the writer was led in the first step of the intuitive arguments to imagine the crystal to be made up of Fe^{3+} ion cores (spins in bold type in Table III) at each lattice point with three electrons per atom at hand to be returned to the crystal in a fashion consistent with the known ferromagnetic properties of iron. It was observed that if these three electrons per atom in iron were returned to *d* orbitals with their spins antiparallel to those on the 3+ ion cores, then the average moment per atom would be 2 μ_B which is close to the observed value no regard being taken at this point for the possible nature of the splitting of the *d* levels by the crystal field. As a step in the intuitive arguments, however, the three electrons per atom were imagined as returned to the crystal in the ferromagnetic

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[22] L. E. Orgel, J. Phys. Chem. Solids 3, 50 (1957), has proposed an empty *e* orbital in manganese as a means of accounting for the complicated crystallographic structure of the α form of this metal.

state as one electron per orbital meeting point there being just three such orbital meeting points per atom in the crystal.

If these three electrons per atom are then assumed to have an itinerant character, it would suggest the possibility of electron transfer processes in which these electrons could be thought of as resonating between half-filled orbitals, the process being governed by the probability of finding unoccupied states in these orbitals. Such a process suggests a magnetic coupling similar to that encountered in crystalline compounds. In that case two anion electrons were involved in the electron transfer process, and the coupling between two cations with half-filled orbitals overlapping a p orbital of an intervening anion was antiferromagnetic. In the present case of iron where a single electron is assumed to be involved in the process an intuitive application of the same general principles would lead to ferromagnetic coupling between ions with overlapping half-filled orbitals (spins in bold type in Table III).

Let us now examine these possible electron transfer processes in a little more detail. The iron crystal is assumed to be in the ferromagnetic state in which the atoms have net spin up. For the suggested orbital occupation pattern shown in Table III the moment value for iron would be somewhat greater than 2 μ_B per atom. Since the observed average moment per atom is 2.22 μ_B it will be assumed for the present that 0.22 spin down electrons per atom have been transferred from the t orbitals of the d band to the s band where their spins are assumed to be compensated. These holes in the t orbitals now give room for electron transfer processes of the type $(t_\uparrow - \downarrow - t_\uparrow)$ to take place, where the symbolism represents the resonant sharing of an electron between two half-filled t orbitals of neighboring atoms. One sees from Fig. 7 that if such processes are operative they would have the effect of ferromagnetically coupling the spins of first and second nearest neighbor atoms in each of the sublattices of the iron crystal via the overlap of their respective t orbitals.

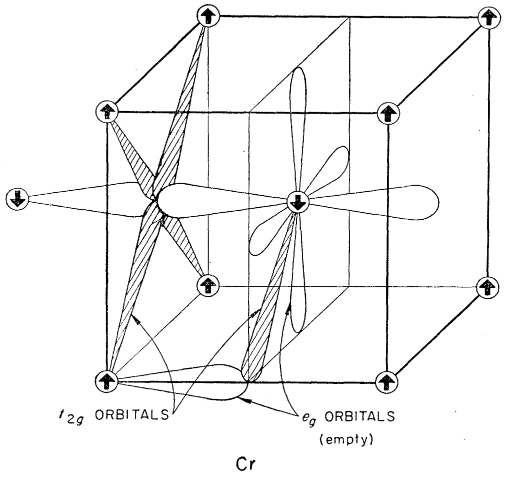

FIG. 8. Orbital relationships in the body-centered cubic structure of chromium.

If we consider now also that the half-filled e orbitals of an atom on one sublattice (body center) overlap the t orbitals of the atoms on the other sublattice a similar electron transfer process of the type $(t_\uparrow - \downarrow - e_\uparrow)$ can take place and this process will ferromagnetically couple the moments of atoms on one sublattice with those on the other sublattice. On the basis of the assumed splitting of the d orbitals shown in Table VI this latter process will be less probable than those of type $(t_\uparrow - \downarrow - t_\uparrow)$. The Curie temperature of iron would thus be expected to be determined primarily by the strength of the magnetic coupling of the spins within a given sublattice. It is interesting to note that similar processes of the type $(e_\uparrow - \downarrow - e_\uparrow)$ involving the overlap of the half-filled e orbitals of neighboring atoms would also be expected to be ferromagnetic. These are, however, assumed to be less probable than either of the other two. These and other points will be considered in a more detailed examination of the nature of the proposed spin correlation process in a later section.

It does appear, however, from these simple considerations that the ferromagnetic properties of iron are consistent with electron transfer processes of the type suggested and that also the average moment per atom is consistent with this picture.

Chromium

In chromium (bcc) the assumed occupation pattern of the d orbitals (Table III) differs from that of iron in that its e orbitals are empty whereas those in iron are half filled. Since chromium is known to be antiferromagnetic and iron is ferromagnetic, it seems logical to expect the difference in magnetic properties of these two metals to be associated with the difference in the occupation pattern of their e orbitals.

Let us now attempt to account for the antiferromagnetic properties of chromium on the basis of electron transfer processes of a type similar to those invoked in connection with the discussion of the ferromagnetic properties of iron. The orbitals for this case are schematically represented in Fig. 8 in which the spin orientations are those characteristic of the known antiferromagnetic structure of chromium.

This figure as in the case of Fig. 7 for iron is a schematic representation of the orbital occupation pattern before the three extra electrons per atom have been returned to the lattice. It is then interesting to note for this situation that if a spin down electron is introduced into the lattice at the meeting point of the orbital lobes in the face of the bcc structure and if this electron is allowed to make resonant transitions between the half-filled and empty orbitals consistent with the requirement of the Pauli exclusion principal and Hund's rule, it will appear to have the property of stabilizing the antiferromagnetic structure of chromium just as the same processes appeared to stabilize the ferromagnetic structure of iron.

Let us, however, now consider the situation when all the electrons have been returned to the crystal. We consider first the ferromagnetic coupling of the moments in one of the two sublattices (cube corners). The neutron diffraction measurements of Shull and Wilkinson[23] give an average moment of 0.4 μ_B per chromium atom. To obtain this moment value it will be assumed that an average of 0.4 electron per atom have been transferred from the *d* band to the *s* band. We now have a situation similar to that for the *t* orbitals of iron in which electron transfers of the type $(t_\uparrow-\downarrow-t_\uparrow)$ can be expected to operate. There is a very important difference in this case, however, in that on the present picture there is no permanent residual moment on a chromium ion as there was in the case of iron where the *e* orbitals were half filled. There is, however, a certain probability (~0.4) that a given atom will at any time have a moment of 1 μ_B. For the present then it will be assumed that electron transfer processes of the type $(t_\uparrow-\downarrow-t_\uparrow)$ ferromagnetically couple the spins in each of the two sublattices of chromium in the same fashion as such processes were assumed to couple the spins in the nearly identical bcc iron structure. A further examination of such a coupling scheme will again be deferred to a later section.

The antiferromagnetic structure of chromium must now be assumed to arise from the nature of the coupling of the spins in one sublattice (cube corners) with the spins in the other sublattice (body centers). Assuming as in the case of iron that electron transitions can take place between the *t* orbitals of the atoms on one sublattice with the overlapping empty *e* orbitals of neighboring atoms on the other sublattice one would have the situation in which the itinerant electron could be considered as making transitions between a half-filled *t* orbital where its spin would be expected to be antiparallel to the average net spin of the chromium ion and an empty *e* orbital where the electron would be expected to enter (because of Hund's rule) with its spin parallel to the net spin of the neighboring chromium ion. Such processes symbolized as of type $(t_\uparrow-\downarrow-{}_\downarrow e_0)$ would thus intuitively be expected to be of antiferromagnetic character. On the basis of such assumed processes then one would obtain exactly the observed antiferromagnetic structure of chromium. The strength of magnetic coupling and hence the Néel temperature would again be presumed to arise from the intrasublattice coupling of type $(t_\uparrow-\downarrow-t_\uparrow)$. Transitions to *e* orbitals would be less probable because of the higher energy of these orbitals but only a weak magnetic coupling of this type should be required to stabilize the antiferromagnetic structure.

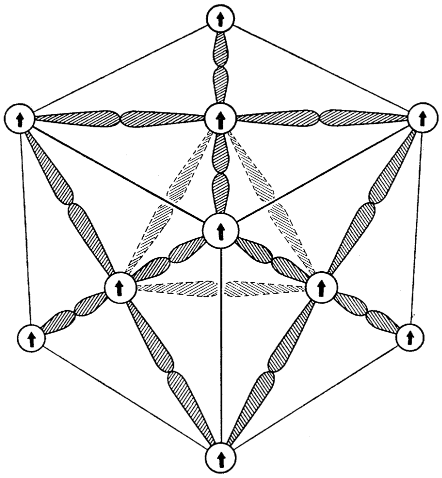

FIG. 9. The *t*-orbital relationships in the face-centered cubic structure of cobalt or nickel.

Manganese

The antiferromagnetic properties of α manganese would appear as for the case of chromium to be attributable to the existence in its orbital occupation pattern of an empty *e* orbital. The fact that there is only a single such empty orbital suggests a more complicated antiferromagnetic character than for chromium. The complicated character of both the crystallographic and the magnetic structure of α manganese has discouraged any further consideration of this metal at this time.

Cobalt

Since the 3*d* orbital representation and energy splitting in an hexagonal field is somewhat more complicated from the present point of view than that involved in other structures, it does not seem profitable to consider the hexagonal form of the metal at this time. Metallic cobalt is also quite stable in its fcc form and the magnetic moments of the two forms are nearly the same, and it seems preferable at this time to present the arguments relating to the magnetic properties of cobalt in terms of this structure. In the fcc form of the metal one would expect only the *t* orbitals to be directly involved in the magnetic coupling processes since these are the only orbitals in such a structure which would be expected to overlap appreciably the orbitals of neighboring atoms. The situation is shown schematically in Fig. 9 where the general nature of the *t*-orbital relationships is represented. Now the average moment per cobalt atom is observed to be about 1.7 μ_B and hence if the nonoverlapping *e* orbitals in this structure contain one uncompensated spin as indicated in the orbital occupation scheme presented in Table III one would ascribe the fractional moment of ~0.7 μ_B to holes in the *t* orbitals. Under these conditions the ferromagnetic properties of cobalt would be ascribable to

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[23] C. G. Shull and M. K. Wilkinson, Revs. Modern Phys. 25, 1 (1953).

electron transfer processes of the type $(t_\uparrow - \downarrow - t_\uparrow)$. In the fcc form of the metal these would be presumed to be the only important processes involved.

Nickel

In nickel which has the face-centered cubic structure the orbital occupation pattern in Table III shows the *e* orbitals to be completely filled and hence these orbitals would make no contribution to the magnetic moment. The observed moment of 0.6 μ_B per atom is then to be ascribed entirely to holes in the *t* orbitals. As in the fcc form of cobalt metal the ferromagnetic coupling process would then be presumed to be of the type $(t_\uparrow - \downarrow - t_\uparrow)$. There is a distinction between cobalt and nickel, however, in that each cobalt atom has at no time a moment of less than 1 μ_B arising from the uncompensated spin in the *e* orbital whereas for nickel on a dynamic picture the average moment of 0.6 μ_B per atom would represent the probability density of the uncompensated spins per atom. A further discussion of this situation which is similar to that encountered in the case of chromium is again deferred to a later section.

B. Regarding the Nature of the Proposed Electron Transfer Processes

Up to this point the magnetic moment and magnetic structure properties of the 3*d* metals have been shown to be consistent with the assumed orbital occupation scheme given in Table III and with the proposed coupling processes which operate in a fashion consistent with the applications of the Pauli principle and Hund's rule. An attempt will now be made to show in somewhat more detail how these processes might be expected to effect the spin correlations.

Let us first make a preliminary examination of the coupling processes of type $(t_\uparrow - \downarrow - t_\uparrow)$ in Fe and Co in which each atom is presumed to have a permanent moment associated with uncompensated spins in the *e* orbitals. Consider, for example, two neighboring Co atoms in a state *A* as represented in Table IV in which at a given instant atom (1) is in a neutral charge state with all *t* orbitals completely filled and atom (2) has a hole in an overlapping *t* orbital.

In the ferromagnetic state of the crystal represented by the aligned spins in the *e* orbitals one would expect these two neighboring atoms to be found equally likely in state *B* in which an unpaired electron is now found in a *t* orbital of atom (1). If the average state of the system as represented by a proper linear combination of states *A* and *B* has a lower energy than either state alone then the mechanism symbolically represented by $(t_\uparrow - \downarrow - t_\uparrow)$ would appear to have the required property of coupling the spins of neighboring atoms.

TABLE IV. Possible spin correlation process in cobalt.

State	*A*		*B*	
Atom	1	2	1	2
e	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
t	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\downarrow\uparrow$

TABLE V. Possible spin correlation process in nickel.

State	*A*		*B*	
Atom	1	2	1	2
t_{xy}	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\downarrow\uparrow$
t_{yz}	$\uparrow\downarrow$	$\uparrow$	$\uparrow\downarrow$	$\uparrow$

Consider now the same process in the case of chromium and nickel[24] where on a dynamic model there is no permanent moment associated with uncompensated spins in *e* orbitals but only the transient moment associated with holes in the *t* orbitals.

For this case consider two atoms as shown in Table V in which in state *A* two holes appear simultaneously in two *t* orbitals of the same atom (2). The unpaired electrons on this atom are thus coupled by Hund's rule. If at a later instant the system is found in another state *B* the unpaired spin on atom (1) must be instantaneously correlated with the spin on atom (2) to conserve angular momentum. Although such a process might give rise to spin correlations between neighboring atoms, it would appear to be energetically unfavorable because it requires atom (2) in state *A* to be in a rather high charge state. The state would also be statistically unfavored because it requires that two holes out of an average of $h_t = 0.6$ for nickel must first appear simultaneously on a single atom. Such a process as we shall see in a later section would not appear to be consistent with the linear variation of the Curie temperature data as a function of composition in the NiCu alloy system.

A further examination of the proposed coupling process for this case is thus required. Preliminary to these considerations let us recall the situation encountered in the binding of the hydrogen molecule. Here it is known that the singlet state (antiferromagnetic coupling of the spins) has the lowest energy because the electron density between the protons and the concomitant binding of the two atoms in the molecule is increased over that for the triplet state. In this system both electrons have identical space properties.

Consider, on the other hand, a helium positive molecular ion He_2^+ which is similar to the situation represented by two overlapping *t* orbitals, one taken instantaneously as filled and one as half filled, belonging, respectively, to two neighboring atoms which are otherwise neutral. The stability of the molecular ion He_2^+ would presumably arise from an increase in the electron charge density between the two positive nuclei as in the case of the hydrogen molecule. The simplest repre-

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[24] See J. H. Van Vleck, Revs. Modern Phys. **25**, 220 (1953), for related considerations.

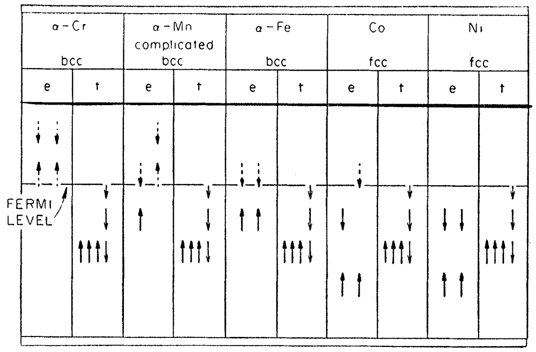
sentation of the molecular wave function for such a system would correspond to the antisymmetric combination of the two states in which two electrons in one or the other atom are in a singlet state, and the other electron is in a triplet state.

Although one might at first consider that in such a two atom system there is no suggestion of ferromagnetic coupling, it must certainly be true that a slow neutron scattering experiment would show the average spin state to consist essentially of two ions separated by a distance r, each having a net parallel spin of 0.5 μ_B.

This molecular system is then suggestive of the properties of the proposed coupling processes of type $(t_\uparrow - \downarrow - t_\uparrow)$ which have been considered in phenomenological terms as representing a spin down electron resonating between or being shared by the two overlapping half-filled t orbitals. The considerations regarding the properties of the wave functions of the He_2^+ ion are thus suggestive of the nature of the magnetic coupling in metals.

In this connection then let us consider the case of nickel in which the only uncompensated spins are presumed to be those associated with holes in t orbitals. In such a case the proposed process $(t_\uparrow - \downarrow - t_\uparrow)$ would appear to have the effect of correlating the spins on two neighboring atoms and in the paramagnetic state this might be considered as introducing a degree of short-range order. When considered as individual events such processes would proceed as effectively in the paramagnetic as in the ferromagnetic state of the crystal. This is obviously too restricted a view for a crystalline system in which more extensive interference effects would be expected. It is thus suggested by the intuitive arguments that the crystal in the ferromagnetic state has average wave function properties similar to those of a He_2^+ ion. The average spin dependent charge distribution would then be such that in the ferromagnetic state there would be a small increase in the charge density between the overlapping t orbitals over that which would be present in the paramagnetic state and this part of the charge distribution would have an excess of spin down electrons which are the shared electrons in the ferromagnetic state. The lower energy in this state would thus be associated with the small increase in electronic charge between the overlapping t orbitals and the spin dependence of this charge would be a consequence of the spin properties of the wave functions. Such a picture would thus seem to be consistent with the ferromagnetic properties of nickel. These considerations regarding the nature of the coupling processes of type $(t_\uparrow - \downarrow - t_\uparrow)$ in nickel would be pertinent also to the other $3d$ metals. In the case of iron and cobalt, however, there is the additional factor of the unpaired electrons in the e orbitals. The role of these electrons which is presumed to be related primarily to the strength of the magnetic coupling will be considered in a later section.

TABLE VI. Schematic representation of energy splitting of d orbitals in ordered magnetic state.



C. Energy Splitting of the d Orbitals

An attempt will be made in this section to qualitatively justify the assumed orbital occupation patterns shown in Table III. The proposed orbital occupations would seem to be consistent with an energy level diagram of the type shown schematically in Table VI for the ordered magnetic state. Consider first in this connection the case of nickel (fcc). The very nature of the structure in this case would seem to suggest the proposed type of energy splitting. The e orbitals which point along the cube edges would not be expected to have appreciable overlaps with the e orbitals of neighboring atoms because of the large cube edge spacing in this structure and hence the energy of the electrons in these orbitals would not be expected to be appreciably affected by the neighboring atoms. Consider the atoms to be brought in from large distances to form the crystal. In the free atom there are 8 $3d$ electrons and 2 $4s$ electrons of lower energy. When the d electrons begin to overlap the electrons in completely filled levels would tend to repel similar electrons on neighboring atoms, and hence there would be a distortion of the d functions tending to push these doubly filled levels into that part of space represented by the e orbitals where the overlaps are minimized. This has a tendency then to make the e orbitals completely filled. Anticipating the final situation we can now consider that the 2 $4s$ electrons have in the interim formed a conduction band which distributes electronic charge rather uniformly over the crystal. This uniform negative charge distribution has the effect of binding the positive nuclei in the crystal but this binding can presumably be further increased by concentrating more of this negative charge in the space between nearest neighbor atoms. This can presumably be accomplished if some of these s electrons are returned to overlapping d orbitals. The process must, of course, stop short of completely filling these orbitals because then the orbitals would become repulsive. It would thus appear reasonable to expect a splitting of the type proposed in Table VI.

In face-centered cobalt the situation is similar to that encountered in nickel except that in this case there is one less electron available. It must be assumed in this case then that more energy is gained by keeping the more nearly complete complement of electrons in the t orbitals where they are presumed to effect an advantageous charge distribution than would be gained by adding an extra electron per atom to a nonoverlapping e orbital. The situation relative to nickel may be reflected in a small increase in the number of holes in the t orbitals $[h_t(\text{Co})\sim 0.7,\ h_t(\text{Ni})\sim 0.6]$.

In the case of the body-centered cubic structures the nature of the orbital overlaps are more complicated as one sees from Fig. 7, for example, and arguments relative to the energy level splitting would seem to be less straightforward. It is presumably true here also that the electronic charge will tend to build up between atoms in such a way as to effect the maximum binding of the positive cores. In this structure the e orbitals would be expected to have the greatest overlap and hence a complete filling of these orbitals would tend to give the greatest repulsion. Electrons would thus tend to pair up first in the t orbitals in which the repulsive energy would be least. If this pairing up is carried too far even these orbitals will tend to become repulsive and raise the energy of the system. The optimum negative charge distribution between neighbors would then presumably be reached when a certain number of holes still remain in the t orbitals and a filling to this level would require $4s$ electrons also to enter the t orbitals. In the case of iron the proposed explanation of the ferromagnetic structure in terms of electron transfer processes between orbitals would not appear to be very sensitive to the exact nature of the splitting of the d orbitals. Whether the itinerant electrons spend more or less time in the t or in the e orbitals would not per se affect the ferromagnetic structure of the system. The proposed splitting is, however, more consistent with the over-all picture.

Another qualitative way of looking at the energy splitting is to assume that the itinerant electrons as represented by the light arrows in Table VI spend time and hence introduce negative charge in the between atom regions. The field splitting of the remainder of the d electrons represented in Table VI by the bold arrows which would result from such a charge distribution would then correspond to that required to give the orbital occupation pattern shown in Table III.

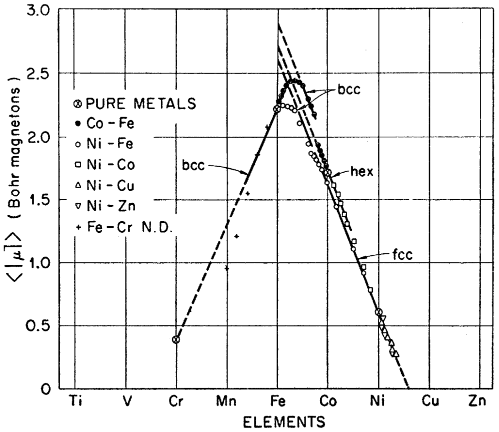


Fig. 10. Magnetic moments of iron group metals and alloys.

D. Ferromagnetic Alloys of 3*d* Metals

Face-Centered Alloys

The pertinent binary fcc alloys are those involving Fe, Co, Ni, Cu, and Zn. The data show that the average moments in such alloys vary almost linearly with the percent of alloying constituent on a plot of the type shown in Fig. 10 where the fraction of the added element is represented on a scale which depends on the distance apart of the elements involved.[25] The data break away from this approximate linear relationship when the structure changes from fcc to another crystalline form. Such a linear relationship of the average moments for the face-centered alloys involving Fe, Co, and Ni is consistent with the assumption that these elements in the alloys maintain approximately their individual character as determined primarily by the occupation of their respective e orbitals and that the number of holes h_t in the t orbitals is approximately a constant for this particular crystallograph structure.

Both these assumptions are consistent with the proposed occupation and splitting of the d levels and with the proposed ferromagnetic coupling processes which in the face-centered structures are of the single type $(t_\uparrow - \downarrow - t_\uparrow)$ involving the overlap of the t orbitals only. The assumption that there is no appreciable change in the individual occupation pattern of the e orbitals of the individual constituents is consistent with the proposed energy splitting of these orbitals. It seems reasonable to assume in addition that the electron transfer processes in the vicinity of a hole in two overlapping t orbitals would not be greatly affected by the fact that these orbitals belong to the same or to two adjacent $3d$ metals. Some effect on these processes would however be expected from the Hund's rule coupling relating to the difference in the e-orbital occupation of the particular constituents.

On this basis then the average magnetic moment per atom in the face-centered alloys would be expected to be quite well represented by a simple average of the magnetic moments of the pure constituents which have been assumed to be given by

$$\mu = M + h_t, \tag{1}$$

where M is the number of uncompensated spins in the e orbitals and h_t is the number of holes per atom in the t orbitals. The average atomic moment for an AB alloy

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[25] Data transcribed from Richard M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951).

would then be given by the relation

$$\mu_{AB}=n\mu_A+(1-n)\mu_B=nM_A+(1-n)M_B+h_t, \qquad (2)$$

where n is the fraction of element A and the appropriate values of M_A and M_B are $M_{\mathrm{Fe}}=2$, $M_{\mathrm{Co}}=1$, and $M_{\mathrm{Ni}}=0$, and h_t represents the average number of holes per atom in the t orbitals. This equation with $h_t=0.6$ gives the solid line in Fig. 10 which follows quite closely the NiCo and NiFe data for the fcc form of these alloys.

It is to be noticed that the line also passes through the data for Ni-Cu and Ni-Zn. Since copper and zinc have 1 and 2 electrons respectively in addition to those required to completely fill the d shell, these electrons could be expected to fill holes in the t orbitals of nickel until no more extra electrons are available than required to maintain an average of 0.6 s electrons per atom, and then the number of these holes per atom in the alloy would increase linearly with the percent of nickel atoms added. All the average moment values for the fcc alloys containing the elements Fe, Co, Ni, Cu, and Zn are thus seen to be well represented by Eq. (2).

Data relating to the individual moments of the constituents in these face centered cubic alloys were obtained in the neutron diffraction experiments of Shull and Wilkinson[26] on the NiFe system. For the alloy Ni_3Fe in the ordered state they obtained the moment values (most logical choice)

$$\mu_{\mathrm{Fe}}=(2.97\pm0.15)\mu_B,$$
$$\mu_{\mathrm{Ni}}=(0.55\pm0.15)\mu_B.$$

These values agree satisfactorily with the average moment data for this composition range and it is thus suggested for this case that the number of holes contributed to the t orbitals is effectively different for each constituent, $h_t(\mathrm{Fe})\sim0.9$ and $h_t(\mathrm{Ni})\sim0.6$.

Hexagonal (NiCo)

Over the small range for which the NiCo alloy system is stable in the hexagonal form the average moment data are consistent with an approximate constancy of the individual atomic moments. The slope of the data curve suggests a value of $h_t(\mathrm{Co})\sim0.7$.

Body-Centered (FeCo)

The FeCo alloy system is body-centered cubic in the composition range from pure iron to about 75% cobalt content. Considerable significance has been placed in the past on the maximum average moment value $\mu_{\max}(\mathrm{FeCo})=2.44\,\mu_B$ observed in this alloy system. It is difficult on the present basis to place any unusual significance on this value; it would appear to represent the maximum in a transition curve for this particular alloy system.

One notices for this system that the average moment data (Fig. 10) are nearly linear with composition for cobalt concentrations (0.75–0.5). Such a linear relation suggests again a constancy in the moments of the individual constituent atoms. As seen in Fig. 10 this line gives the following individual moment values in this alloy

$$\mu_{\mathrm{Fe}}=2.9\,\mu_B,$$
$$\mu_{\mathrm{Co}}=1.9\,\mu_B,$$

which compare very favorably with some unpublished results of Shull and Wilkinson which give

$$\mu_{\mathrm{Fe}}=(2.95\pm0.1)\mu_B,$$
$$\mu_{\mathrm{Co}}=(1.80\pm0.1)\mu_B.$$

One might, however, also make a similar extrapolation of the data for low cobalt content for which there is also a nearly linear relation of the average moment with composition. This line would predict the individual moment values to be $\mu_{\mathrm{Fe}}\sim2.22\,\mu_B$ and $\mu_{\mathrm{Co}}\sim3.1\,\mu_B$. These are the values which Lomer and Marshall[27] suggest for this composition range. On the basis of the concepts presented here there is no logical reason to assume a cobalt moment greater than 2 μ_B and hence if the holes in the t orbitals are assumed to remain nearly the same for cobalt and iron the moment assignments in this region would correspond more nearly to a monotonic drop-off from the high values at (0.5 Co-0.5 Fe) of $\mu_{\mathrm{Co}}\sim1.9$ and $\mu_{\mathrm{Fe}}\sim2.9$ down to values in the neighborhood of $\mu_{\mathrm{Co}}\sim1.2$ and $\mu_{\mathrm{Fe}}\sim2.2$ at the nearly pure iron end of the system. No attempt has been made to interpret the transition region in this alloy system and unfortunately no individual moment data are available for comparison with any theoretical predictions.

E. Magnetic Transition Temperatures

Certain properties of the magnetic coupling scheme here proposed would appear to have an important bearing on the energy of this coupling and hence on the transition temperatures of the 3d metals and their alloys. It is evident that nothing can be said on the basis of phenomenological arguments about the absolute magnitude of these temperatures, but it may be possible on the basis of such arguments to draw some conclusions regarding the relative transition temperatures in systems of similar crystallographic form.

The magnetic coupling as herein represented has been assumed to be associated in a basic way with what has been phenomenologically considered as processes of the type $(t\uparrow-\downarrow-t\uparrow)$. In the case of nickel for which the atomic moments are assumed to arise entirely from uncompensated spins or holes in the t orbitals the process has been qualitatively considered

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[26] C. G. Shull and M. K. Wilkinson, Phys. Rev. **97**, 304 (1955).

[27] W. M. Lomer and W. Marshall, Phil. Mag. **3**, 185 (1958).

as a coupling of the spin up electrons in the overlapping t orbitals by transitions made by the spin down electrons. The completely ordered ferromagnetic state of the system has been assumed (see Sec. B) to be represented by the time average of such processes over the whole crystal for which the effective coupling is presumed to arise from an average increase in the spin dependent charge density between the atoms which thus effects a lowering of the energy of the system. On this basis it would seem reasonable to expect within limits that the average coupling energy associated with pairs of neighboring spins would be a linear function of the average number of holes h_t per atom in the t orbitals.

In the case of iron and cobalt the effect of the uncompensated spins in the essentially noninteracting e orbitals must also be considered. These uncompensated spins are assumed to be effective only in so far as they modify the charge distribution associated with the basic coupling process $(t_\uparrow - \downarrow - t_\uparrow)$. The uncompensated spins in the e orbitals of the two atoms associated with this process can be considered to be coupled by Hund's rule to each of the spin up electrons phenomenologically represented as directly associated with the coupling process. In the case of nickel the resonating electron could thus be considered as coupling one unit of spin on each of the two atoms involved in the process. For cobalt with one uncompensated electron per atom in an e orbital the process would effectively involve a coupling of two units of spin on each atom and for iron with two uncompensated electrons in e orbitals there would be effectively three units of spin associated with each atom. The coupling situation as thus considered is pictorially represented in Table VII.

Now the simplest assumption with regard to the strength of the magnetic coupling in a single process would be that it would depend linearly on the effective number of spins associated with each of the two neighboring atoms involved in the process. The average strength of the coupling between spins on neighboring atoms would as we have previously indicated depend on the average number of such processes per atom which is linearly related to the number of holes per atom in the t orbitals. On the basis of these assumptions then the transition temperature which should be determined by the average spin coupling energy per atom pair would be given by the relation

$$T_c=\alpha h_t(M+1), \tag{3}$$

where h_t is the average number of holes per atom in the t orbitals, M is the number of uncompensated spins in the e orbitals of the metal being considered and α is a proportionality constant which would depend on the orbital overlap properties associated with a particular crystal type.

TABLE VII. Coupling processes and transition temperatures.

ELEMENTS	Cr(bcc)		Fe(bcc)		Co(fcc)		Ni(fcc)	
TRANSITIONS TEMPERATURES	475°K		1043°K		1396°K		640°K	
NEIGHBORING ATOMS	1	2	1	2	1	2	1	2
UNCOMPENSATED SPINS IN E-ORBITALS	0	0	↑↑	↑↑	↑	↑	0	0
COUPLING MECHANISM	↑ ↓ ↑		↑ ↓ ↑		↑ ↓ ↑		↑ ↓ ↑	
M + 1	1		3		2		1	
h_t IN Eq. (3) TO GIVE OBSERVED T_C	~0.4		0.33		0.67		0.6	
OBSERVED FRACTIONAL MOMENT VALUES	~0.4		0.22		0.7		0.6	

The Metals

For the case of face-centered cobalt and nickel the structures are sufficiently identical so that the constant α can be taken as the same for both. For this structure one obtains the value of h_t directly from the fractional part of the average magnetic moment per atom, $h_t(\text{Co})\cong 0.7$ and $h_t(\text{Ni})\cong 0.6$. With these values of h_t and the values of $M(\text{Co})=1$ and $M(\text{Ni})=0$ one should then obtain the relative values of T_c for these two metals. The relative number of holes required in Eq. (3) to give the observed values of T_c for these metals are listed in Table VII and one sees that the values are in good accord with those obtained from the moment data.

In considering the body-centered structures of chromium and iron it would be expected that a different constant α than that used for the face-centered structures would be required. It is interesting to note, however, that if the same value of α is used in Eq. (3) to determine the relative T_c values for both structure types one obtains agreement with the observed T_c values for the h_t values shown in Table VII. In the case of iron the h_t value thus obtained does not agree with the fractional moment value of 0.22 μ_B but for this structure h_t is not given directly by the fraction part of the moment. This is due to the fact that in iron the transitions from t orbitals to e orbitals increase the average value of h_t without affecting the observed fractional moment. In chromium similar transitions reduce the apparent h_t value. The large h_t value required to bring the transition temperature for iron in agreement with the other metals is thus not unreasonable but the qualitative agreement of the data with Eq. (3) with a single value of α for both structures may well be fortuitous.

Face-Centered Alloys

For the NiCu alloy system the average atomic moments and hence the number of holes h_t in the t orbitals is a linear function of nickel content for Ni$>$0.4. The Curie temperatures for this alloy system

(Fig. 11) are known also to vary linearly with composition and hence also with h_t over the same range. These data are thus in accord with Eq. (3), ($M=0$ for both constituents).

In the NiCo alloy system the average moment values which are given by Eq. (2) with $h_t \sim 0.6$ to 0.7 vary nearly linearly with cobalt content and the slope of the moment line is continuous with that of NiCu. The Curie temperature data for the NiCo system follow the upper dashed curve in Fig. 11. For such a system in which the constituents maintain to a considerable degree their individual moment values, it would not be expected that the Curie temperatures of the alloys would be given by a simple average of the Curie temperatures of the constituent metals. The observed type of curve might reasonably be expected on the present basis where the end points are accurately determined by Eq. (3).

The Curie temperature data for the NiFe system are given by the lower dashed curve of Fig. 11. In this case ($M_{\mathrm{Ni}}=0$, $M_{\mathrm{Fe}}=2$) it would be even more difficult than in the case of NiCo to determine the average interaction energy from that of the pure constituents among themselves. Nevertheless, it is interesting to note that the falloff of the Curie temperature curve in the limited composition range (0.75 Ni-0.25 Fe) to (0.5 Ni-0.5 Fe) can be qualitatively accounted for on the basis of a simple average of Eq. (3) for the two constituents when the observed change in the average individual h_t (see Fig. 11) values are taken into account.

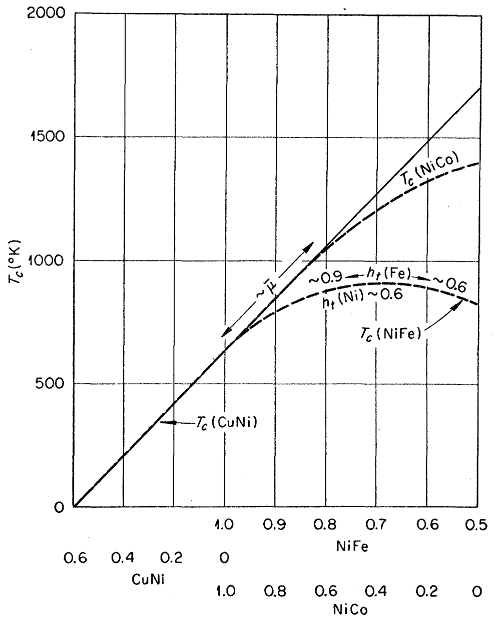

FIG. 11. Magnetic moment and Curie temperature data of face-centered cubic alloys of nickel as a function of composition.

It is interesting now in this connection to briefly speculate regarding the properties of the Ni-Pd alloy system and thus on the magnetic properties of palladium metal itself. If it is assumed that the energy splitting is such that the holes in the $4d$ shell of palladium are in the nonoverlapping e orbitals, then the fact that palladium has a moment $\mu=h_e\mu_B=0.6\mu_B$ but does not become ferromagnetic becomes understandable. On this assumption the Curie temperature data for the Ni-Pd alloy system are found to follow very qualitatively the curve obtained by a simple averaging of the coupling properties of the constituents as given by Eq. (3).

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