course qualitatively, even when their accurate structures are not known initially.

The most undesirable prediction derived from our theory may probably be that concerning the transverse dielectric constant; that is, K_x is far larger than is reasonable. But it is certain that this defect has arisen chiefly because no crystal anisotropy whatever is taken into account. If a crystal is spontaneously polarized in any one direction, there is no reason at all why it must still be cubic. In general, the crystal would preferably become strained, since the strains would stabilize all the more the specified axis of dipole orientation. Any amount of rotation of the axis of polarization away from the easiest direction would be realizable only when the transverse field is strong enough to overcome the potential barriers surrounding the easiest axis; this effect will certainly diminish the K_x value considerably.

In this respect, it seems very interesting to notice that in single crystals of $BaTiO_3$, the dielectric constant in the direction perpendicular to its spontaneous polarization is found to be far larger than the dielectric constant measured in the parallel field.[14]

I wish to express my hearty thanks to the staff of our laboratory in the Tokyo Institute of Technology, especially to Messrs. T. Oguchi, G. Shirane, and E. Sawaguchi for their very helpful discussions.

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Interaction between the *d*-Shells in the Transition Metals. IV. The Intrinsic Antiferromagnetic Character of Iron

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The principles developed in the previous papers of this series are applied to interpret the presence of ferromagnetism in b.c.c. iron, its absence in f.c.c. iron. It is found necessary to introduce a new principle, namely that for minimum energy the *d*-shell electrons are distributed among the atoms so as to maximize the total number of pairs of electrons having like spin within the individual atoms. This principle leads to the viewpoint that, at least on a local scale, the b.c.c. iron lattice consists of the superposition of two interpenetrating simple cubic lattices of atoms having *d*-shell spins of different magnitudes and of opposite direction. The same principles lead directly to the observed saturation magnetizations of all iron base alloys.

I. INTRODUCTION

In the previous papers[1] of this series the author has proposed that for the transition elements the magnetic structure of the *d*-shells of the individual atoms is essentially the same in the metallic as in the gaseous state, that ferromagnetic coupling between the incomplete *d*-shells in metals arises from an indirect coupling via the conduction electrons, and that the direct interaction between these shells is antiferromagnetic. These proposals have provided an unforced interpretation of the occurrence of ferromagnetism in the periodic table, of the occurrence of b.c.c. lattices in the transition metals, and have provided a quantitative calculation of the Weiss coupling factor. The essential validity of these proposals has been further strengthened by the observation of the antiferromagnetic behavior of the magnetic susceptibility of chromium by McGuire and Kriessman,[2] by the observation of the anomalously low value of the electronic specific heat of chromium at low temperatures by Friedberg,[3] by the computation of the binding energy of tungsten by Hsu,[4] by the analysis of the elastic constants of tungsten by Isenberg,[5] by the analysis of the Heusler alloys by Heikes,[6] and by the detailed analysis of the magnetic properties of alloys by Carr[7] in a forthcoming paper. Slater[8] has correlated the more usual band viewpoint with the atomistic viewpoint adopted in this series. In the second paper of this series it has been pointed out that, in the absence of *s* electrons, electrical conductivity by *d* electrons can also introduce ferromagnetic coupling. This relation between electrical conductivity by *d* electrons and ferromagnetic coupling has recently received further support from observations upon the ferrites. Below their Curie temperature a second critical temperature, or narrow temperature range, is found in which both the magnetic properties and the electrical conductivity suffer large abrupt changes. (Manganese ferrite,[9] iron

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ferrite,[10,11] nickel ferrite,[12] cobalt ferrite.[13]) An outstanding problem remains unsolved, namely, the structure sensitivity of the magnetic properties of iron. The b.c.c. phase of iron is ferromagnetic, the f.c.c. phase is not ferromagnetic. It is the purpose of the present paper to provide an understanding of this structure sensitivity.

The nonoccurrence of ferromagnetic coupling in f.c.c. iron cannot be dismissed merely by the observation that the transformation temperature from b.c.c. to f.c.c. iron lies above the Curie temperature of the former. If in the f.c.c. phase of the Fe—Co and of the Fe—Ni systems[14] one attempts to extrapolate the Curie temperature to the pure f.c.c. Fe phase, one finds this Curie temperature to lie at best in the vicinity of the absolute zero. Strong evidence of the absence of ferromagnetic coupling in the f.c.c. phase of iron is obtained from magnetic susceptibility measurements.[15]

An interpretation of the difference in the magnetic properties of the two phases of iron has been given by Néel[16] in terms of the original Heisenberg theory. In b.c.c. iron the nearest and next nearest neighbors are at distances of 2.48 and 2.86A, respectively. In f.c.c. iron corresponding neighbors are at distances of 2.52 and 3.58A, respectively. According to Néel, of these interatomic distances only 2.86A for next nearest neighbors in the b.c.c. phase lies within the appropriate range for ferromagnetic coupling. This interpretation suffers from the same disability as does the original Heisenberg theory, namely the lack of a theoretical basis for the existence of a range of interatomic distances within which the direct exchange interaction has the appropriate sign and magnitude for ferromagnetic coupling.

As one passes to the left along the first transition period from Ni through Co, Fe, Mn to Cr and V, the d-shell gradually expands. According to the previously developed viewpoint, the direct interaction between adjacent incomplete d-shells always tends to an antiferromagnetic alignment of spins. In Ni and Co, where the overlapping of adjacent d-shells is only very slight, the ferromagnetic indirect coupling via the conduction electrons dominates, leading to ferromagnetism. By the time Cr and V are reached, the overlap of adjacent d-shells is sufficiently great so that the direct antiferromagnetic coupling dominates, thereby stabilizing the b.c.c. lattice with respect to the f.c.c. lattice. Fe and Mn lie in the transition region between ferromagnetism and antiferromagnetism. The absence of ferromagnetism in f.c.c. iron leads us to suspect that a straightforward quantitative application of the above viewpoint would lead to the absence of ferromagnetism in all phases of iron, but that the b.c.c. phase possesses an intrinsic flexibility which, when properly considered, leads to ferromagnetism.

It is well recognized that exchange energy plays a dominant role in magnetism. The necessity for maximizing the negative exchange energy between electrons in the same d-shell assures us that the electrons in each incomplete d-shell will be distributed in the various quantum states so as to give the maximum possible net magnetic moment consistent with Pauli's exclusion principle. The negative exchange energy between the d-shell electrons and the conduction electrons gives rise to the indirect coupling between d-shells that leads to ferromagnetism. The positive exchange energy between electrons in adjacent d-shells gives the antiferromagnetic coupling that stabilizes the b.c.c. lattice of the transition metals in the V and Cr columns. The negative exchange energy between the conduction electrons themselves just about halves the coupling factor γ which appears in the author's formulation[1] of the theory of ferromagnetism. In previous discussions of ferromagnetism no attempt has been made further to increase the total negative exchange energy between electrons in the same d-shell by a transfer of d electrons from one atom to an adjacent atom. Simple considerations show that the total negative exchange energy will be increased by such a transfer if the atoms contain incomplete half d-shells.

As an example, we shall consider the particular case of iron. The outer configuration of the isolated Fe atoms is $3d^6 4s^2$. The necessity for minimizing the Fermi kinetic energy of the conduction electrons assures us that at least one $4s$ electron will be demoted into the $3d$ shell when the atoms condense to form the solid phase. The electronic configuration more appropriate to the metal is therefore $3d^7 4s$. In order to maximize the negative exchange energy between the electrons in the d-shell, we must place 5 electrons in one half-shell (Hund's rule). This distribution we shall symbolize as $(+++++,\,--)$. We now investigate the change in the negative exchange energy associated with the transfer of two electrons from the d-shell of one Fe atom to the d-shell of a second Fe atom. Such an exchange may be represented as

$$2(+++++,\,--)\rightarrow(+++++,)+(+++++,\,----). \quad (1)$$

Now the exchange energy within a given half-shell is proportional to the number of pairs which may be formed between the electrons in the half-shell. The exchange energy in the positive half-shells is unaltered by such a transfer. On the other hand, the total number of pairs in the negative half-shells is increased from 2 to 6. The negative exchange energy is therefore increased by the transfer (1).

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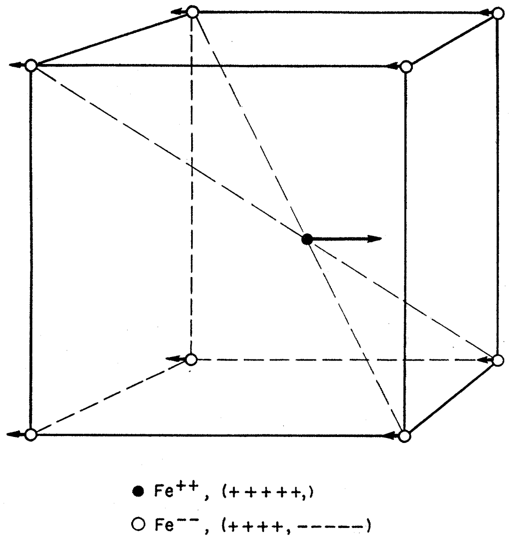

FIG. 1. Postulated spin structure of b.c.c. iron.

In the b.c.c. phase of iron, a maximizing of the total negative exchange energy within the *d*-shells will lead to the configuration shown in Fig. 1. The arrangement of the spins on a regular Cs Cl type lattice will minimize the electrostatic energy. The antiparallel arrangement of spins of the two simple cubic lattices leads to the observed saturation magnetic moment per atom. The saturation magnetic moment per atom of the arrangement of Fig. 1 is 2.0 μ_β, the observed value is 2.2 μ_β. The remaining 0.2 μ_β can arise from the polarization of the conduction electrons. This antiferromagnetic arrangement is consistent with the view that in iron the direct interaction between the *d*-shells and nearest neighbors is sufficiently large to overcome the indirect ferromagnetic coupling via the conduction electrons. The above considerations give a ready interpretation as to why the b.c.c. phase but not the f.c.c. phase of iron is ferromagnetic. No ordered arrangement of the charged atoms on a f.c.c. lattice will lower the electrostatic energy as much as on a b.c.c. lattice.

Two apparently serious objections might be raised against the above developed theory that the b.c.c. lattice is intrinsically polar in nature. The first objection is that the gain in exchange energy upon forming such a polar lattice will be more than offset by the rise in electrostatic energy. Upon taking the value of the exchange integrals computed by Slater[17] for nickel, we find the gain in exchange energy for a singly ionized lattice to be 0.9 ev per ion pair. In Sec. II we attempt to estimate the electrostatic energy. We find that it is not unreasonable for this electrostatic energy to be less than the above gain in exchange energy. The second objection is that such polarization should be detected by neutron diffraction, while Dr. Shull has informed the author that neutron diffraction reveals no such anomalies as would be anticipated from an ordered polar lattice in which the given atoms maintain the same polarity in a time at least as long as is required for a neutron to traverse a domain.† These negative results still allow the possibility of a polar lattice in which the polarity of a given atom fluctuates rapidly. Empirical evidence for a transfer of charge between atoms in alloys containing first row transition metals has been presented by Vogt,[18] for a transfer of charge between Mn atoms in Mn_2Sb by Guillaud,[19] and for a transfer of charge between Mn^{+++} ions in Mn_3O_4 by Verwey.[20]

II. ENERGETICS OF FORMATION OF POLAR LATTICES

In order to gain a physical insight into the factors determining the work required to polarize a b.c.c. lattice of like atoms, we shall first consider the case of a lattice of metal spheres. When the spheres are isolated, the work expended in removing a charge q from one sphere of radius R is $q^2/2R$, and a like work is expended upon placing this charge upon a similar second sphere. The work of polarizing the isolated atoms is therefore q^2/R per pair. When we now bring the polarized atoms together to form a CsCl type lattice, we gain back a certain amount of work. If we keep the charge on each sphere uniformly distributed, we gain back the energy 1.76 q^2/D, where D is the closest distance between oppositely charged spheres. Upon taking the spheres to be close packed, i.e., upon taking D to be $2R$, we find that 88 percent of the originally expended energy is gained back. The remaining 12 percent of the originally expended energy corresponds, in the case of spheres having the size of iron atoms, to 1.4 ev for q equal to the charge of one electron.

Essentially the same relation between net work and work of polarization is found for all atoms for which data are available. Thus in the case of the halogens the work of polarization is the ionization potential minus the electron affinity. By taking D as the sum of the radii of the halogen negative ion and of the positive ion of the next succeeding alkali metal, we obtain the data of Table I.

From the above examples, it appears that it would require less than 2 ev per atom pair to transfer an electron from the *d*-shell of each iron atom of one simple cubic lattice to the *d*-shell of each iron atom of the second simple cubic lattice, a redistribution of the conduction electrons being restrained. If we now allow the conduction electrons to be redistributed to minimize the energy, it appears reasonable that the net work will be lowered below the 0.9 ev per atom pair gained in the increase in the negative exchange energy.

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† *Note added in proof:* The most recent experiments of Dr. Shull do indeed indicate an antiferromagnetic structure in Cr.

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III. MAGNETIC STRUCTURES OF IRON BASE ALLOYS

The variation of the saturation magnetic moment in the b.c.c. alloys of iron with other first row transition metals is given by the rough rule that[21]

$$d\mu/dN=\mu_\beta, \tag{2}$$

where μ is the saturation magnetic moment per atom, and N is the average number of electrons. Once the average magnetic moment has reached 2.5 μ_β, further additions result in a reversal in sign of $d\mu/dN$. This rule may be most readily understood by tentatively adopting the viewpoint that equivalent lattice sites are occupied by the same number of electrons, irrespective of nuclear charge. Such a viewpoint is in accord with the strict application of the band model. The addition of atoms of atomic number less than that of iron results in a decrease in the average number of electrons. Since the positive ions have a complete half-shell, this decrease in number of electrons will occur solely in the negative ions, thereby resulting in an increase in the magnetic moment of the negative ions, in a decrease of magnetic moment of the negative ions, in a decrease the over-all moment by the amount given by (2). Similarly, the addition of atoms with atomic number greater than that of iron results in a decrease in the magnetic moment of the negative ions, and hence in an increase in the over-all magnetic moment by the amount given by Eq. (2). Once the negative ions have completed their second half-shells, further electrons must be accommodated by the positive ions. Since these additional electrons must now start a new half-shell, their spins will be opposed to those already on the positive ions, and they hence contribute to a decrease in the average magnetic moment. The maximum value (5/2) μ_β of the average magnetic moment thereby receives a natural interpretation.

Adherence to the above strict band model leads, however, to unreasonably large charges on the ions, as indicated by the second and third columns of Table II. Thus in Fe—V alloys vanadium atoms on the negative ion sites will have an excess of 5 electrons in the d shell. It is now reasonable to expect that most of these excess electrons will be redistributed on the neighboring negative iron ions. Such a redistribution of electrons among the negative ion sites, all of which have incomplete d shells with magnetic moments pointing in the same direction, will not change the over-all magnetic moment. The partial relaxation of unreasonably large negative charges will therefore not change the average magnetic moment, and hence leaves unaltered rule (2). In the case of Fe—Ni alloys, however, we must relax the unreasonably large charge on the positive Ni ions. This relaxation will be accomplished by a transfer of electrons from the Fe^{--} ions to the Ni^{++++} ions. These electrons will suffer a reversal of spin in this transfer, thereby resulting in a change in the over-all magnetic moment. A relaxation from a quadruply charged positive Ni ion to a doubly charged positive Ni ion will in fact precisely cancel the increase in average magnetic moment of 2 μ_β per nickel atom predicted by the strict band model. This expected deviation of the Fe—Ni alloys from rule (2) is precisely that found experimentally.

TABLE I. Energy of formation of polar lattice of halogen ions (energy in ev).

	Work of polarization	Madelung energy	Net work
Cl	9.0	8.0	1.0
Br	8.1	7.3	0.8
I	7.1	6.5	0.6

It is anticipated that the triple charge of Co^{+++} will relax at most only to a slight extent, since relaxation to Co^{++} would leave one d electron alone in a half-shell. That a slight relaxation does occur, with a concomitant slight reduction in the over-all magnetic moment, is indicated by the fact that ordering in a 50–50 Fe—Co alloy increases the average magnetic moment by about 4 percent.[22] In such an ordered alloy the iron atoms will occupy all the positive sites, the cobalt atoms all the negative sites.

Only the experiments upon the Fe—Mn alloys[23] are in conflict with the above theory. Observations up to 4 percent Mn indicate a variation of μ with Mn concentration about twice that given by (2). In view of the difficulty of being certain that a single phase is obtained in such alloys, the author is inclined to blame this disagreement upon the experiments rather than upon the theory.

In pure b.c.c. iron it is to be expected that the polarity of a given iron atom will rapidly fluctuate. Such fluctuations will however be eliminated in an ordered alloy when the alloying atoms have a distinct preference for one sign of polarity. Such will be the case, for example, in Fe_3Si and Fe_3Al, the alloying atoms here preferring to occupy the site of an Fe^{++} ion rather than that of an Fe^{--} ion. As indicated in Fig. 2, the negative Fe ions will occupy the corners of a simple cubic lattice. Half the centers will be filled by positive

TABLE II. Magnetic structure of disordered iron base alloys.

	Strict band model		Realistic model	
Alloy	→Site	←Site	→Site	←Site
Fe—V	V^-	V^{-----}	V^-	V^-
Fe—Cr	Cr	Cr^{----}	Cr	Cr
Fe—Mn	Mn^+	Mn^{---}	Mn^+	Mn^{--}
Fe	Fe^{++}	Fe^{--}	Fe^{++}	Fe^{--}
Fe—Co	Co^{+++}	Co^-	Co^{+++}	Co^{--}
Fe—Ni	Ni^{++++}	Ni	Ni^{++}	Ni^-

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[21] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), Fig. 10–11.

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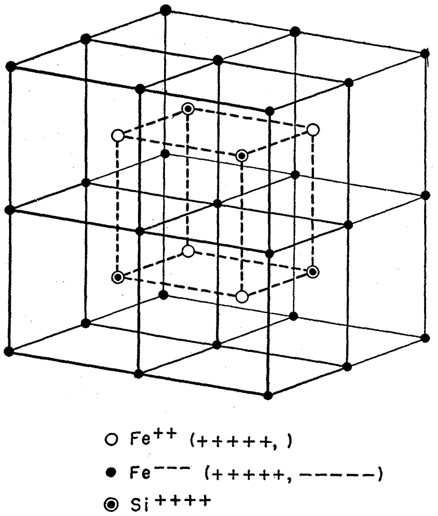

FIG. 2. Postulated spin structure of Fe_3Si.

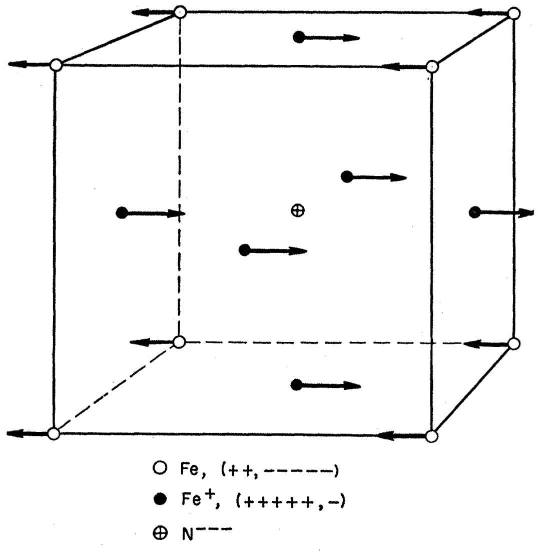

FIG. 3. Postulated spin structure of Fe_4N.

Fe ions, half by positive Si or Al ions.[24] In the case of Fe_3Si, Si has just enough valence electrons to fill completely the incompleted half *d* shells of the surrounding negative Fe ions. Such complete ionization of the Si atoms would give rise to the spin structure postulated in Fig. 2. Here only the Fe^{++} ions have a magnetic moment, of value 5 μ_β. The computed average magnetic moment is thus (5/4) μ_β per atom, in agreement with experiment.[25] The average magnetic moment of Fe_3Al has essentially the same value.[26] A more realistic computation would leave the negative iron ions with a slightly incomplete half-shell, the resulting decrease in the contribution of the *d* shells to the net magnetic moment being compensated by the magnetic polarization of the conduction electrons.

We shall finally analyze the ferromagnetism in f.c.c. iron induced by the solution of nitrogen. Face-centered cubic iron becomes ferromagnetic[27] when the center of each unit cube is occupied by a nitrogen atom. In contrast to Al, we expect each nitrogen atom to absorb three electrons from the neighboring Fe atoms. We thereby obtain a structure in which Fe^{+} ions occupy the faces, Fe atoms the corners of the unit cube. The removal of an electron from the *d* shell of an Fe atom results in a contraction of this shell, thereby reducing the direct antiferromagnetic interaction with the nearest neighbors having similarly contracted *d* shells. If we now assume that this reduction is sufficient to allow for a ferromagnetic coupling via the conduction electrons, while the interaction between the Fe^{+} ions and the neutral Fe atoms at the corners is still antiferromagnetic, we arrive at the spin structure shown in Fig. 3. The average magnetic moment per atom computed from this spin structure is (9/4) μ_β, in agreement with the observed value of 2.22.[28]

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[24] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), Fig. 7–2.

[25] See reference 24, Fig. 4–9:

[26] See reference 24, Fig. 7–8.

[27] See reference 24, Fig. 7–36.

[28] See reference 24, p. 240.