A THEORY OF FERROMAGNETISM

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The properties of ferromagnetic substances are in reasonably good accord with the theory of Weiss. In this theory it is postulated that the atomic magnets tend to be brought into parallel orientation not only by an applied magnetic field but also by an inner field which is proportional to the magnetization of the substance. The inner field is not due to magnetic interaction of the magnetic moments of the molecules, but to electrostatic interactions, which are related to the orientation of the magnetic moments of electrons through the Pauli principle. During the past twenty-five years many efforts have been made to develop a precise theory of the interactions that produce the inner field, and to account in this way for the observed magnetic properties of ferromagnetic substances, but these attempts have not been successful—no one has published a theory of the electronic structure of ferromagnetic substances that permits reasonably good predictions to be made of the values of the saturation magnetic moment and the Curie temperature.

I have now formulated a theory of ferromagnetism that seems to provide a simple explanation of the phenomenon. In the following paragraphs it is shown that the straightforward application of the theory to iron leads, with use only of spectroscopic data for the iron atom, to the predicted values 2.20 Bohr magnetons for the saturation magnetic moment per iron atom and 1350° K for the Curie temperature; these values are in reasonable agreement with the experimental values, 2.22 magnetons and 1043° K, respectively.

The theory can also be applied to cobalt and nickel, and to alloys. In this application, however, a complicating factor must be considered—
the contribution of two different values for the atomic magnetic moment. Satisfactory agreement between theory and experiment is obtained when the ratio of contributions of the two atomic moments has the value assigned to it in a discussion of the electronic structure of these metals that was published fifteen years ago.  

The Nature of the Theory.—In discussion of the transition metals the electrons may be divided into two classes, the conduction electrons and the atomic electrons. The conduction electrons are the electrons for which the exchange integrals between adjacent atoms are large, and the atomic electrons are the electrons for which the exchange integrals are small. Some investigators have thought that the electrons occupying 4s and 4p orbitals comprise the conduction electrons, and those occupying the 3d orbitals (plus those in inner shells) comprise the atomic electrons. The first quantum mechanical theory of ferromagnetism is that of Heisenberg. It was shown through the work of Hund, Heitler and London, and others that the exchange integral between electrons with antiparallel spin on the same atom usually has positive sign, whereas that between electrons with antiparallel spin on different atoms has negative sign. In consequence, atomic electrons align their spins parallel, to the extent permitted by Pauli’s principle. Moreover, it would be expected that atoms that have a magnetic moment, because of the presence of one or more unpaired electrons on each atom, would tend to align their moments antiparallel. The atomic moments of atoms in a crystal would then tend to divide into two classes, such that the moments of the neighbors of each atom are oriented antiparallel to the moment of that atom. This would give rise to antiferromagnetism (when the moments of the two kinds of atoms are equal) or to ferrimagnetism (when the moments are unequal). Heisenberg assumed, in order to account for the phenomenon of ferromagnetism, that under certain circumstances the exchange integrals of electrons with antiparallel spins on adjacent atoms are positive; the atomic moments would then tend to line up parallel to one another. Heisenberg’s theory is unsatisfactory in that there is no independent evidence in support of the assumption that exchange integrals between atoms are ever positive; this remains an ad hoc assumption. Moreover, the theory does not provide a reasonable explanation of the observed values of the saturation magnetic moment.

A somewhat different suggestion about the origin of ferromagnetism was made by Bloch. The conduction electrons usually occupy the low levels of a conduction band of orbitals in pairs, with opposed spins. Pauli pointed out that at temperature equilibrium a few of the pairs, occupying the uppermost levels, would be uncoupled by thermal agitation, one of the electrons being raised to a slightly higher level. These uncoupled electrons could then orient themselves independently in a magnetic field; Pauli in
this way explained the temperature-independent paramagnetism observed for the alkali metals and some other metals. Bloch observed that under some circumstances (proper ratio of exchange integrals to the density of states in energy) the exchange energy of the conduction electrons could accomplish some uncoupling, producing a set of conduction electrons occupying separate orbitals, and with parallel spins. The theory has been discussed further by Slater, who has suggested that a rather weak interaction between 3d orbitals on adjacent atoms would give rise to a narrow band of levels, with high density of states in energy, and that the conditions for ferromagnetism might be satisfied in this way. In order to account for the observed moment 2.22 magnetons per atom for iron, the assumption is made that 0.22 electron per atom is transferred from the 3d orbitals to the 4s orbital, constituting the main conduction band; the atomic moment is then ascribed to the hole of 2.22 unoccupied orbitals of the 3d subshell, which contains 5.78 electrons.

Recently it was pointed out by Zener that the atomic moments, in parallel orientation, might react with the electrons in the conduction band in such a way as to uncouple some of the pairs, producing a set of conduction electrons occupying individual orbitals, and with spins parallel to the spins of the atomic electrons. Zener assumed that the conduction band for the transition metals is formed by the 4s orbitals of the atoms, and that there is somewhat less than one conduction electron per atom in iron, cobalt, and nickel. Like Slater, he attributed the atomic magnetic moments to the partially filled 3d subshell.

The new theory is based upon the assumption that there are about six conduction electrons per atom in the transition metals. In the first discussion of the new metallic valences the value 5.78 was assigned as the normal metallic valence of the atoms chromium, manganese, iron, cobalt, and nickel. This value was obtained by subtracting from the total number of outer electrons of iron (eight electrons, outside of the argon shell) the number 2.22 of unpaired electrons, as indicated by the value 2.22 for the saturation magnetic moment of iron. It now seems probable that the valence is equal exactly or nearly exactly to six. In the resonating-valence-bond theory of metals it is assumed that the 3d, 4s, and 4p orbitals of an atom hybridize to form bond orbitals, which are combined with bond orbitals of other atoms in the crystal, with use of Bloch functions, to produce orbitals that are occupied by electron pairs. These orbitals are closely similar to those used for occupancy by single electrons or by two electrons with opposed spins in the usual electron theory of metals. It might be expected that as many atomic orbitals could be combined in this way into orbitals for conduction electrons (bonding electrons) as satisfy the criterion of large overlapping, characteristic of good bond orbitals. The best bond orbital that can be formed from
3d, 4s, and 4p orbitals is a 3d⁴4s⁴4p⁴ orbital, for which the bond strength has value 3.000. Two equivalent orbitals orthogonal to the first one can be constructed. It has been found that a fourth, a fifth, and a sixth of nearly equal strength can also be made, but that a seventh orbital, orthogonal to the other six, is a much poorer bond orbital. Hence it seems not unreasonable to assume that only six bonds will be formed by an atom in a metal, and that the remaining orbitals may be occupied by electrons which interact only weakly with electrons on other atoms.

In iron, cobalt, and nickel there are some unpaired atomic electrons, giving rise to an atomic magnetic moment. There are also six electrons per atom which occupy a conduction band—these are the valence electrons. It is assumed that the direct interaction of the atomic electrons on neighboring atoms is small, and that the exchange integral is, as is customary, negative. If this interaction is larger than the interaction with the conduction electrons, which will be discussed immediately, the moments on adjacent atoms will tend to align themselves in the antiparallel orientation, and the substance will be antiferromagnetic. If the direct interaction energy of the moments is smaller than the possible interaction energy with the conduction electrons, however, the substance will be ferromagnetic.

The conduction electrons occupy metallic orbitals which are formed by linear combination of atomic bond orbitals, which are dsp hybrids. A metallic electron, which may be considered to move from atom to atom through the crystal, interacts with the electrons producing the atomic moment of each atom to the extent that a bond orbital of the atom contributes to the metallic orbital. The exchange integral for the interaction is positive in sign, according to Hund’s principle, and the interaction results in stabilization if the spin of the metallic electron is parallel to the atomic moment, and in destabilization if the spin is antiparallel. There is, then, the possibility of stabilization of the metal crystal if the atomic moments are aligned parallel to one another, and a significant number of metallic electrons, occupying separate metallic orbitals, align themselves with spins parallel to the atomic moments. If the energy of interaction of a metallic electron with an atomic moment is \(-\epsilon\) for parallel spin and \(+\epsilon\) for antiparallel spin, the width of the conduction band, at the top of the doubly occupied conduction levels, that can be occupied by single electrons, with parallel spin, will be equal to 2\(\epsilon\). The energy of uncoupling the first pair of electrons (occupying the topmost level) is zero, so that a gain in stabilization through the change in energy \(-2\epsilon\) will be achieved by uncoupling this pair of electrons. The gain in energy for the last pair is, however, zero, and the average change in energy is \(-\epsilon\) per electron pair, or \(-\epsilon/2\) per electron. If \(n\) conduction electrons are thus uncoupled, the ferromagnetic crystal will be stabilized through this interaction by the
energy change $-n\epsilon/2$. The energy required to reverse the direction of an atomic moment is equal to $2n\epsilon$; accordingly the energy of interaction of the atomic moments and the uncoupled conduction electrons acts in the way corresponding to a Weiss field.

Quantitative calculations can be made on the basis of the assumption that the density of levels in energy for the conduction band is given by the simple expression for the free electron in a box, and the interaction energy $\epsilon$ of a $d_{sp}$ hybrid conduction electron and the atomic moment can be calculated from the spectroscopic values of the energy of interaction of electrons in the isolated atom. The results of this calculation for iron are discussed in the following section.

Application of the Theory to Iron.—We assume, in essential accordance with earlier conclusions,5,6,8 that six of the eight outer electrons of the iron atom are valence electrons, occupying $d_{sp}^{3}$ orbitals, and the remaining two are atomic electrons.

The electron configuration of the atom in the metal is accordingly assumed to be $3d^{4}s^{4}p^{2}$. This assumption differs considerably from the usual assumption that the electron configuration is close to $3d^{8}$—for example, Slater's assumption that the configuration is $3d^{7}3s^{1}$. It is interesting to note, however, that the normal state10 of the isolated iron atom is not based on the configuration $3d^{8}$ but on the configuration $3d^{10}$; its Russell-Saunders symbol is $^{3}\!D$. The first excited state is $3d^{6}4s^{1}F$, and the third configuration to appear, with increasing energy, is $3d^{5}4s^{2}p$. There are, in fact, twenty-eight Russell-Saunders states that appear in the FeI spectrum below the first state, $3d^{8}^{3}F$, that is assigned to the configuration $3d^{8}$. The spectroscopic data indicate that the $4s$ atomic orbital is more stable than the $3d$ orbital by about 1.2 ev, and that the energy of a $4p$ electron is only about 1.4 ev greater than that of a $3d$ electron. The configuration $3d^{4}s^{4}p^{2}$ accordingly lies about 4 ev above the normal configuration, $3d^{4}s^{3}$, and only 1.6 ev above the configuration $3d^{8}$. The bond energy of six valence electrons can, of course, easily effect the promotion to the assumed configuration $3d^{4}s^{4}p^{2}$.

The exchange energy $-\epsilon(4s, 3d)$ of a $4s$ electron and a $3d$ electron with parallel spin can be calculated from the separation of the states $3d^{4}s^{1}F$ and $3d^{4}s^{1}F$. The separation of these states (averaged over the levels with different values of total moment $J$) is 4947 cm$^{-1}$. In the $^{3}\!F$ state the $4s$ electron has spin parallel to the spins of three $3d$ electrons, and in the $^{1}\!F$ state it has spin antiparallel to the spins of these three $3d$ electrons. The value of the exchange energy per electron is accordingly $-4947/6 = -825$ cm$^{-1}$. For $-\epsilon(3d, 3d)$ one sixth of the difference in energy of $3d^{4}s^{2}^{3}D$ and $3d^{4}s^{2}^{3}D$ was used; its value is $-4826$ cm$^{-1}$. The evaluation of $-\epsilon(4p, 3d)$ as $-470$ cm$^{-1}$ is similar, although somewhat less straightforward, because it involves averaging over a number of Russell-
Saunders states. Assuming that the valence electrons at the top of the band have the average hybrid character 3d4s4p2, the interaction energy of one of these valence electrons and an atomic electron, assumed to be approximately a 3d electron, is found to be \(-2707\) cm\(^{-1}\), or \(-0.334\) ev, with probable error about 10%.

The interaction energy of the valence electron with the two atomic 3d electrons, with parallel spins, is accordingly \(-0.67\) ev, and the width of the energy band that would be occupied by uncoupled valence electrons is 1.34 ev. The number of orbitals in this band can be calculated from the equation for the distribution of energy levels for an electron in a box. The number of levels per atom is

\[
n_0 = 4\pi V (2m)^{1/2}E^{1/2}/3h^2,
\]

where \(V\) is the atomic volume, \(m\) is the mass of the electron, \(E\) is the kinetic energy of the electron, and \(h\) is Planck's constant. For iron, with \(V = 11.72 \times 10^{-24}\) cm\(^3\), and six electrons per atom, which can occupy three orbitals, in pairs, the value of \(E\), the energy of the top level occupied by conduction electrons if they are all paired, is calculated to be 23.3 ev. Differentiation of this equation leads to the equation

\[
dn = 2\pi V (2n)^{1/2}E^{1/2}dE/h^2
\]

as the number of levels \(dn\) with the width in energy \(dE\). Substitution of the value 1.34 ev for \(dE\) leads to the value 0.26 for \(dn\). Accordingly we predict that 0.26 of the conduction electrons will be uncoupled by interaction with the atomic moments, and will align themselves parallel to these moments.

The experimental values of the gyromagnetic ratio and the observed magnetic moments for paramagnetic compounds of transition metals show that the orbital moment is nearly completely quenched. On multiplying 2.26 by the ratio 1.946/2.000 of the gyromagnetic ratio to the spin value, the predicted value of the saturation magnetic moment per atom for iron is obtained as 2.20 magnetons, in excellent agreement with the experimental value, 2.22 magnetons.

The calculated energy of interaction of an atomic moment and the Weiss field (0.26 uncoupled conduction electrons per atom) for magnetic saturation is 0.135 ev, or 3070 cal. mole\(^{-1}\). According to the Weiss theory the Curie temperature is equal to this energy of interaction divided by 3\(k\), where \(k\) is Boltzmann's constant. The effect of spatial quantization of the atomic moment, with spin quantum number \(S\), is to introduce the factor \((S + 1)/S\); that is, the Curie temperature is equal to \(n\epsilon(S + 1)/3Sk\). For iron, with \(S = 1\), the predicted value for the Curie constant is 1350°K, in rough agreement with the experimental value, 1043°K.

\textit{Cobalt and Nickel.}—The discussion of the magnetic properties of cobalt
and nickel is somewhat more complicated than that for iron, because of the necessity of giving consideration to the metallic orbital. It has been pointed out that on the basis of the resonating-valence-bond theory of metals a metallic structure, showing large electronic conductivity, can occur only if many of the atoms in the metal have available one orbital not ordinarily occupied by an electron; this orbital can act as receptor for an additional electron, permitting the unsynchronized resonance of the shared electron pairs in the metal. When the metallic orbital is occupied by an electron the atom has a negative charge, and another atom in the metal has a positive charge; it is the motion of these negative charges and positive charges through the metal that gives rise to electronic conduction. (A discussion of the relation between metallic conductivity and negatively charged and positively charged atoms in the metal on the basis of the conventional electronic theory of metals has been given by Slater.)

An atom of cobalt, with six valence electrons and three atomic electrons, essentially 3d electrons, can have the spins of the atomic electrons parallel by utilizing all of its orbitals; a metallic orbital is made available only if two of the atomic electrons have opposed spins. The metal can be described as having some atoms with resultant spin quantum number 3/2 and some atoms with spin 1/2. In the same way the atom of nickel can be described as having some atoms, without a metallic orbital, with spin 1 and some atoms, with a metallic orbital, with spin 0. The number of atoms without a metallic orbital has been estimated to be 28%. In the following calculations we use the value 28.5%, which is obtained from the value 28.57 for the electron number that marks the upper boundary of the ferromagnetic region, as given by the intercept of the curve of values of saturation magnetic moment corrected by extrapolation for isoelectronic sequences to the value 0°K for the Curie temperature (Taglang).

With this assumption and use of the value 1.94 for the g-factor the average magnetic moment per atom of cobalt is calculated to be 1.52 magnetons. The spectroscopic data for cobalt do not provide very reliable values for the interaction energies of 3d, 4s, and 4p electrons. The data for chromium and manganese, when compared with those for iron, indicate that the interaction energies increase by 5% with unit increase in the atomic number. We accordingly use the value 0.70 ev for ε, which leads to 0.20 uncoupled valence electrons per atom. The predicted saturation magnetic moment for cobalt is thus 1.72 magnetons, in good agreement with the experimental value 1.71 magnetons. The value of the Curie temperature is calculated with use of the average value of the magnetic moment per atom and the average value of $(J + 1)/J$ to be 1190°K, which is somewhat smaller than the experimental value 1393° K.

In nickel 28.5% of the atoms, without a metallic orbital, have two atomic electrons with parallel spins, and magnetic moment 1.94 (corre-
sponding to \( J = 1 \), with \( g = 1.94 \). The value of the interaction energy \( \epsilon \) is 0.74 ev, and the calculated number of uncoupled valence electrons per atom is 0.064. The saturation magnetic moment per atom is thus calculated to be 0.617, in good agreement with the observed value 0.606 magnetons. The calculated value of the Curie temperature, 367° K, is considerably smaller than the observed value, 631° K.

For alloys of iron, cobalt, nickel, and copper the calculated values of saturation magnetic moments agree closely with the observed values; in particular, the maximum value of about 2.48 magnetons at electron number about 26.3 is reproduced by the theory. There is, however, only rough agreement between the observed and calculated values of the Curie temperature.

An obvious refinement of the simple theory for cobalt and nickel and their alloys can be made which leads to a significant increase in the calculated value of the Curie temperature. The foregoing calculation for nickel, for example, is based upon the assumption that the uncoupled valence electrons spend equal amounts of time on the nickel atoms with \( J = 1 \) and the nickel atoms with \( J = 0 \). However, the stabilizing interaction of the spins of the valence electrons and the parallel atomic moments would cause an increase in the wave function for the valence electrons in the neighborhood of the atoms with \( J = 1 \) and the parallel orientation. This effect also produces a change in the shape of the curve of saturation magnetization as a function of temperature. The details of this refined theory will be published later.

The simple theory accounts for the deviation of the slope of the curve of saturation magnetic moment against average electron number from the values +1 and −1 by about 10% as resulting from an induced moment contributed by the conduction electrons. This explanation was suggested and given empirical support by Forrer\textsuperscript{13} and Taglang.\textsuperscript{12}

Gadolinium.—For gadolinium the saturation magnetic moment is 7.12 magnetons and the Curie temperature is 290° K.\textsuperscript{14} There is little doubt that three of the ten outer electrons of gadolinium are valence electrons and the other seven are atomic electrons occupying 4f orbitals, with spectroscopic state \( ^8S \). These seven atomic electrons would give rise to the magnetic moment 7.00 magnetons, and the small increment may be attributed to uncoupled valence electrons.

Spectroscopic data are not available to permit an independent estimate of the magnitude of the interaction energy of a valence electron and the seven atomic electrons. If we assume the value 0.31 ev for this quantity, \( \epsilon \), the calculated value of the Curie temperature, 290° K, is equal to the observed value, and the calculated value of the saturation magnetic moment, 7.19 magnetons, is slightly greater than the observed value, 7.12. The small disagreement might be explained as resulting from a small
contribution of orbital moment, reducing the g-factor from 2 to 1.98; the value $1.95 \pm 0.03$ for the g-factor has been reported from microwave resonance absorption measurements of gadolinium metal in the paramagnetic region.\(^7\)

**Other Interactions.**—In the foregoing calculations the direct exchange interactions of the atomic electrons on neighboring atoms have been neglected. These exchange interactions are expected in general to tend to cause the atomic moments on adjacent atoms to align themselves in the antiparallel orientation. If these interactions and other interactions (such as those involving an unsymmetrical distribution of the electrons in an electron-pair bond between adjacent atoms) are less important than the interactions that stabilize the parallel orientation of the atomic moments the substance will be ferromagnetic at low temperatures, and the value of the saturation magnetic moment will be that calculated by the above methods. However, the neglected interactions, although they are not expected to change significantly the saturation magnetic moment, could have a large effect on the calculation of the Curie temperature.

It has been pointed out by Bozorth\(^8\) that not all of the alloys of the iron-group transition metals have ferromagnetic saturation moments that correspond to the simple theory of six valence electrons and 0.715 metallic orbital per atom. It is likely that the exceptional alloys show ferromagnetism or antiferromagnetism—that in these alloys the interactions that stabilize antiparallel orientation of the moments of adjacent atoms are stronger than those favoring parallel orientation. Until these interactions have been subjected to quantitative treatment the theory of ferromagnetism, ferrimagnetism, and antiferromagnetism will remain incomplete.

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6 Slater, J. C., *Phys. Rev.*, 36, 57 (1930); 49, 537, 931 (1936); 52, 198 (1937).
13 Forrer, R., *J. de Physique*, 10, 181 (1939); 17, 74 (1940).
EQUAL RATIOS OF ENERGIES OF NUCLEAR EXCITED STATES OF EVEN-EVEN ISOTOPES

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The purpose of this note is to point out a regularity in the measured energies of some excited states of isotopic nuclei with even numbers both of neutrons and protons (N and Z). The experimental data indicate that although the addition of two or four neutrons to an even-even nucleus changes the energies of its excited states, in most instances it does not alter the ratio between the energies of its first and second excited states.

In order to describe this relation, as well as some similar ones, let $E_m(A)$ and $E_n(A')$ denote the energies of the mth and nth excited states of two even-even isotopes with mass numbers $A$ and $A' = A + 2$ or $A + 4$, and further, let

$$r_m(A) = \frac{E_m(A)}{E_1(A)}.$$  

In this note, if $r_n(A')$ is equal within 3% to $r_m(A)$, the nth level of isotope $A'$ will be said to correspond to the mth level of isotope $A$. This correspondence will be expressed symbolically as $n \sim m$. (The correspondence is not symmetric.) For six of the nine pairs of isotopes on which data are available, $2 \sim 2$. The distribution of correspondences among the remaining pairs is: $2 \sim 3$ and $3 \sim 4$ for one pair; $3 \sim 2$ for another. There is only one pair, Pb$^{204}$ and Pb$^{208}$, for which no correspondence is observed. It is possible to conclude from experimental evidence which will be discussed in a subsequent paragraph that the spins of the second excited states of these Pb isotopes are not equal. In view of this fact, the absence of a correspondence between these states might be expected. On a graph of $E(A)$ vs. $E(A')$ the correspondence $2 \sim 2$ would entail that the points $(E_1(A), E_1(A'))$ and $(E_2(A), E_2(A'))$ lie on a straight line through the origin.

The experimental data are summarized in table 1. The energies of at least two excited states of many even-even isotopes can be obtained from decay schemes. All elements with two or more such isotopes whose levels were found in a recent paper1 or in the new Table of Isotopes2 are listed in

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