SOME MODIFICATIONS AND APPLICATIONS OF THE PAULING THEORY OF FERROMAGNETISM

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ABSTRACT

The Pauling theories of ferromagnetism and metal structure are discussed and compared with other theories. The results of Pauling are derived with the inclusion of previously neglected temperature effects. The metallic band structure assumed by Pauling is also modified and the modification is shown to lead to better agreement with the results of previous investigations.

The ferromagnetic alloys are studied with the use of the Pauling theory. It is demonstrated that the simple theory is inadequate for the treatment of alloys, and an improved model is proposed. Calculations based upon this model provide qualitatively correct predictions of the behavior of the Curie temperature of many ferromagnetic alloys. Explanations of the abnormal behavior of the iron-vanadium and nickel-chromium alloys are offered.

The effects of non-uniform electron distribution in ferromagnetic crystals are considered. An expression for the Curie temperature is derived. If reasonable values of the parameters which describe the non-uniformity are inserted in this expression, the result is an increase in the predicted Curie temperature of nickel and a decrease in that of iron, both of which are improvements. Some methods of estimating the values of the parameters are discussed.

It is concluded that the Pauling theory, with appropriate modifications, will accurately describe ferromagnetic behavior.

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I. INTRODUCTION

The semi-empirical theory of ferromagnetism developed by Pierre Weiss (1) in 1907 has served ever since as the guide for theoretical explanations of ferromagnetic behavior. The Weiss theory is a simple extension of the Langevin theory of ferromagnetism, which assumes that a paramagnetic material consists of large numbers of independent molecular dipoles which orient themselves in a magnetic field according to the Boltzmann distribution law. The result obtained by Langevin (2) for the average moment per molecule was

$$M = \mu L\left(\frac{\mu H}{kT}\right) = \chi H$$

where μ is the permanent dipole moment and χ the susceptibility of each molecule, H is the field intensity, and L(x), the Langevin function, is equal to coth x - 1/x.

The discovery of Weiss is based upon the observation that a distinction must be made between the external applied field H and the "local" field H_1 to which the molecular dipoles are exposed. Lorentz (3), using a simple model, calculated the contribution to the local field made by the alignment of molecular dipoles, obtaining the equation

$$H_\ell = H + \frac{4\pi M}{3} \cdot \frac{n}{V} \qquad (1)$$

where n/V is the number of molecules per unit volume. The correct expression for the magnetic moment per atom is

$$M = \chi' H_\ell = \chi H \qquad (2)$$

where χ' is the molecular susceptibility.

If the equation for H_1 is substituted in Equation (2) the resulting expression is

$$M = \frac{\chi'}{1 - \frac{4\pi n}{V}\chi'} H$$

If there is some temperature at which $\chi' = \frac{3V}{4\pi n}$, then M will be finite even when the external field H is zero and the spontaneous magnetization which is characteristic of ferromagnetism will result. The dependence of χ' upon temperature for a system of independent dipoles is given by $\chi' = A/T$, according to the Langevin theory. This ensures that ferromagnetic behavior will occur at some critical point, but the value of the constant A is far too small either in the classical Langevin theory or in its quantum-mechanical counterpart to account for the observed ferromagnetism of iron, cobalt, nickel or gadolinium.

Ignoring this difficulty, Weiss assumed that an equation analogous to Equation (1) could be written

$$H_l = H + \alpha M$$

where α is a constant sufficiently large to account for the observed ferromagnetic Curie temperatures. With the proper choice of α Weiss was able to obtain reasonably good agreement between his predictions and the experimentally observed variation of magnetization with temperature. The introduction of quantized states of angular momentum does not alter the basic results obtained by Weiss with the use of classical physics.

The Weiss theory is not an explanation of ferromagnetism, since it depends upon the assumption of a mysteriously high Weiss field. The excellence of agreement with experimental results has suggested, however, that a correct physical treatment should result in the Weiss equations or something closely resembling them. The principal quantitative theories of ferromagnetism have in fact satisfied this requirement.

The Heisenberg theory of ferromagnetism (4) was the first to offer an explanation of the large value of the Weiss field. According to Heisenberg the field arises from quantum mechanical exchange forces. Heisenberg assumed that the electrons in a ferromagnetic crystal were tightly bound to their respective atoms so that an approximation could be made resembling the Heitler-London treatment for molecules. In the Heisenberg discussion it is assumed that the tendency to form "ionic" structures is small and that orbitals on different atoms are essentially orthogonal. The energy due to the exchange effect between electrons i and j is then given by

$$V_{ij} = -2 J_{ij} \underset{\sim}{S}_i \cdot \underset{\sim}{S}_j$$

where J_{ij} is the exchange integral for electrons i and j, and S_i is the spin angular momentum vector of atom i(5). In order to account for ferromagnetism it is necessary to assume that J_{ij} is a positive quantity, since if the exchange integral is positive the ground state of the system is the one of highest multiplicity. Many attempts have been made to justify this assumption, but it remains an entirely arbitrary one and is probably incorrect in most cases. As Pauling (6) has pointed out, the two-center exchange integrals which are encountered in molecular theory are almost always negative. Bethe (7) has shown that positive exchange integrals may exist over rather limited ranges of interatomic distance. Slater (8) has shown correlations between magnetic properties and the ratio of interatomic distance to atomic radius. The results of Pauling's theory of ferromagnetism suggest strongly that Slater's correlations are accidental to ferromagnetic behavior.

It is instructive to briefly consider the method which Heisenberg used in attempting to solve the problem of ferromagnetism, since it illustrates the complexity of a model in which all of the effects depend upon the relative orientations of neighbors, so that the energy of the system is determined only when the orientation of each dipole is specified.

When coupling exists between the dipoles the crystal may be treated as a large molecule in which the total spin of the crystal is conserved. The quantum numbers S', describing the total spin of the crystal, and $M_{S'}$, describing the spin component along the z axis, have physical significance. Just as in the case of simple molecules (9) one may use the atomic functions as unperturbed wave functions. The perturbation, which is the exchange energy V_{ij} summed over all neighboring atoms, makes it necessary to find the proper zero-order wave functions by forming linear combinations of the atomic functions. Specification of $M_{S'}$ is not sufficient to describe the energy of the crystal, since each set of states of a given $M_{S'}$ contains components from various spectroscopic states of the crystal which do not have the same energy. Even when S' and $M_{S'}$ are specified the energy of the crystal is not uniquely determined; the dependence of the perturbing potential upon the arrangement of neighboring spins allows variation of the total energy. Faced with the problem of finding the energy as a function not only of S' but also as a function of the orientation of the individual dipoles, Heisenberg was forced to make drastic simplifications.

The most important of these simplifications circumvents the solution of the perturbation problem discussed above. It is assumed that for any given total crystalline spin S' the energy distribution in Gaussian about the average for all ω (S') states consistent with the given S'. The number of states between W(S') and W(S') + x + dx is

$$\frac{\omega(S')}{(2\pi)^{1/2}\Delta_{S'}} e^{-x^2/2\Delta_{S'}} \, dx \qquad (3)$$

The average value of W(S') and the Gaussian spread constant $\Delta_{S'}$ have been evaluated (10) only for the case in which the individual atomic spins are all 1/2. For other cases Heisenberg makes the assumption that all states with the same S' have the same energy. The substitution of expression (3) for the density of states into the partition function makes possible a calculation of the magnetic moment as a function of temperature. In order to do this it is necessary to make the further assumption that all states of a given $M_{S'}$ have $S' = \left| M_{S'} \right|$, which is a good approximation for large S'. The evaluation of the magnetic moment is described by Van Vleck (10). If unimportant higher order terms are neglected the result has the same form as that of the Weiss theory, containing a parameter J which is related to the exchange integrals J_{ij}, and is equal to J_{ij} if all of the integrals are assumed to have the same value, as Heisenberg does. The value of J is chosen to give the best value of the Curie temperature, since no simple method of evaluating J exists. The curve in which the fractional saturation is plotted against T/T_c, where T_c is the Curie temperature, naturally agrees with experiment to the same extent as does the Weiss theory. The Heisenberg result is explicitly a function of the number of nearest neighbors for each atom, as might be expected from the form of the perturbation. In this respect Heisenberg's theory would appear to be more sophisticated than the theories to be discussed below, since the latter do not directly depend upon the crystal structure.

The assumptions involved in the Heisenberg calculation are not satisfactory. Even if the exchange integral were positive the use of the Gaussian distribution largely invalidates the results. It is interesting to note that Stoner (11) has shown that the method of Heisenberg is equivalent to taking the potential of each atom as

$$V_i = -2J \sum_{\substack{\text{neighbors} \\ \text{of } i}} \underset{\sim}{S}_i \cdot \underset{\sim}{S}_j = -\left(\frac{zJM}{N\beta}\right) S_{z_i}$$

where β is the Bohr magneton, z is the number of nearest neighbors, and S_{z_i} is the z component of spin of the i th atom. It is therefore clear that Heisenberg is employing a disguised averaging technique of the sort which is of importance in the theory of Pauling. The original model of Heisenberg is a complex one, but the results are misleading if one does not realize that the actual calculation is based not upon the starting model but upon a much simpler one.

The Theory of Slater and the Structure of Metals

The Heisenberg model depends upon the same approximations as does the Heitler-London theory of molecules, and it is not surprising that the same objections should be raised to the Heisenberg theory as have been raised to other simple valence bond approximations. As in the case of simpler molecules the metallic crystal has been discussed from two points of view, one of which is the valence bond model, the other the molecular orbital model. The principal proponent of the former approach to metallic problems has been Pauling (12, 13), while one of the most important advocates of the latter model has been Slater (8). Theoretical chemists have tended to prefer molecular orbital theory for the treatment of complex molecules because of the relative simplicity of the calculations involved. For the same reason the molecular orbital method has been the principal technique used in quantitative calculations of metallic properties.

The simplest molecular orbital theory, or "band theory", of metals makes use of linear combinations of atomic orbitals just as in the treatment of molecules. There is one energy level for each atom in the crystal and in the absence of interatomic exchange perturbations all of the levels arising from one kind of atomic orbital are degenerate. The introduction of interatomic electron interaction terms removes the degeneracy and produces a spreading of the levels into a more or less quasi-continuous set of levels called a band. Each wave function spreads throughout the crystal after the fashion of molecular orbitals. The problem is to find the positions and shapes of the bands arising from each of the atomic energy levels.

The band structure which Slater and most other physicists have concluded is the correct one for iron, cobalt, and nickel consists of a rather narrow band arising from all of the 3d atomic orbitals and a broad "valence" band of 4s and 4p orbitals. The existence of a narrow band implies a very small splitting of degeneracy; it is to be expected that the wave functions of such a band will be very much like atomic wave functions. On the other hand, the wave functions associated with a very wide band will produce electron densities which are much different from the unperturbed atomic densities. According to Slater there is 0.6 electron in the broad valence band of iron, cobalt, and nickel. The remaining electrons are in the "atomic" d band, and do not contribute significantly to the cohesive energy of the crystal. This aspect of the Slater model will be discussed in greater detail in the following section.

Slater has given much attention to the problem of explaining ferromagnetic behavior on the basis of his model of metal structure. Slater objects to the Heisenberg-Van Vleck treatment for the reason that the Heitler-London method is completely inaccurate when dealing with polyatomic molecules or crystals if overlap integrals between orbitals on different atoms are assumed to be equal to zero, as is generally done in the very simple valence bond treatments, and which is implicit in the derivation of the equation for V_{ij}. The energy of the system in such a case involves overlap integrals which may be small but are so numerous that they cause a serious error, according to Slater (14). He concludes that the energy band method is superior to the Heitler-London method for the explanation of crystal properties.

One of the well-known problems associated with molecular orbital interpretations of molecular structure is the incorrect behavior of MO functions at large internuclear separations. The MO approximation weights ionic and covalent structures equally; as interatomic distances grow larger this becomes an increasingly absurd prediction. Slater recognizes this difficulty and points out that the large ratio of the interatomic distance to the size of the d orbitals in ferromagnetic elements makes it important to introduce correlation of electron positions. He is at present studying the effect of introduction of excited states in the variation function with the aim of producing "correlation through configuration interaction". If these "anti-ionic" terms prove to be as important as Slater suggests it is difficult to explain his denunciation of the Heisenberg-Van Vleck treatment. If the ratio of interatomic distance to d orbital size is large, as Slater claims, the overlap integrals are smaller than Slater originally supposed so that even large numbers may not contribute appreciably to the energy of the system.

Because of uncertainty about his model Slater has restricted himself to some general observations about the way in which ferromagnetism arises. The fundamental requirement, according to Slater, is the existence of a narrow d band. In order to understand this requirement it is necessary to consider the effect of exchange interactions upon band structure.

The very simple band theory assumes that two electrons of opposite spin can be assigned to each energy level, starting with the lowest level and working upward in the case of a system in the ground state. Whenever there is a difference in energy between states of positive and negative spin component this scheme is unsatisfactory. The effect of a magnetic field or an exchange stabilization of the kind proposed by Heisenberg must be described by a modified band system in which bands of positive and negative spin are separated from one another by an amount equal to the average difference in energy between a positive and negative spin function. Where no exchange perturbation exists the two bands are exactly superposed and the behavior is that of a simple band. When the perturbation is introduced the positive-spin band is lowered and the negative-spin band raised on the energy scale and therefore, unless both bands are full, there will be more positive spins than negative spins in the ground state of the perturbed system. The size of the excess of positive spin for any given displacement of the positive band relative to the negative band will depend upon the density of levels in the bands, the excess being greater when the density is greater. It is for this reason that Slater insists upon the necessity of narrow d bands for any significant ferromagnetic behavior. In one form or another this requirement appears in all of the theories of ferromagnetism.

The Slater model of ferromagnetism may now be briefly described. There is a narrow band formed from the five d orbitals of each atom. Exchange interactions between spins cause a displacement of all of the positive spin energies relative to the negative and produce a net magnetic moment. Recently Slater has made modifications of his theory (15) which bring it into closer agreement with that of Pauling.

The significance of the change will be discussed in the conclusion of this thesis.

The Collective Electron Theory of Stoner

Following the work of Heisenberg and the various modifications of his theory by others the next important quantitative treatment of ferromagnetism was that of Stoner (16). The Stoner theory is based upon the Slater model of ferromagnetic metals, and the stabilization energy is assumed to arise from the positive exchange interactions among d electrons. None of the magnetic moment arises from the valence band. The principal innovation of the Stoner theory is the treatment of all of the d electrons as freely circulating electrons. This is the extreme opposite of the Heisenberg assumption of Heitler-London bonds between atoms, giving rise to the ionic structures which are forbidden in the Heisenberg theory and destroying all correlation.

In a model of this sort the most obvious method of attack is to treat the d electrons as a free electron gas. Stoner introduces greater flexibility by assuming that the density of energy levels is proportional to the square root of the energy as in the free electron model, but with an arbitrary proportionality constant. This is equivalent to the often-used modification of the free electron model in which an effective mass is substituted for the true electron mass. As Stoner points out, it is only necessary for the band form to resemble the free electron band form up to and somewhat beyond the top of the electron distribution, and this requirement is fairly well satisfied by band structures which have been computed by fairly accurate theoretical methods.

Stoner treats the statistical problem of ferromagnetism with the use of Fermi-Dirac statistics, assuming various arbitrary values for the ratio of the exchange field to the width of the d band. As expected, there is a critical value of the ratio below which no ferromagnetism occurs; at this value of the ratio the density of levels is so small (i. e., the band is so wide) that the stabilization energy is not sufficient to cause any displacement of electrons from the negative band into the positive one. The form of the Stoner theory deviates somewhat from that of the Weiss theory when the d band is wide compared with the exchange energy, because of the differences between Fermi-Dirac and Boltzmann statistics. The difference disappears when the band is infinitely narrow since the two forms of statistics then predict the same distribution; even when the band is wide the deviation from Weiss form is never very great. Van Vleck (5) has compared the Stoner and Heisenberg theories and points out that the predicted results of the two extreme models both agree fairly well with experiment, so that one may be reasonably certain that although the correct model lies somewhere between the extremes the answer does not change very much. This conclusion is of course predicated upon the existence of positive interatomic exchange integrals.

The Hypothesis of Zener

One of the striking things about most of the theoretical publications on ferromagnetism which were based on Heisenberg's exchange principle was the great trouble taken to justify the positive sign of the exchange integral, without which all ferromagnetism seemed impossible. Only recently has a plausible suggestion been made concerning another mechanism of exchange stabilization which does not contradict so many of the basic ideas about molecular structure. In 1951, Zener (17) proposed that the stabilization of states of non-zero moment arises from an exchange interaction between the electrons of the valence band and those of the d band, and that this exchange is related to the intra-atomic exchange coupling which gives rise to alignment of spins in isolated atoms. This exchange integral is, of course, positive. Zener further proposed that "the exchange integrals between d shells of adjacent atoms are always the same sign as in the H_2 molecule", that is, negative rather than positive, and that instead of contributing to the ferromagnetic effect they are actually the cause of a reduced ferromagnetic behavior or even antiferromagnetism. Finally Zener proposed that the d bands were filled according to Hund's rule for atoms, which is equivalent to the assumption of narrow d bands which is characteristic of all ferromagnetic theories. In this model the atomic band interacts with the valence band to cause some unpairing of valence electrons. The unpaired electrons then cause alignment of the d band moment.

Zener did not attempt to develop a quantitative theory, since it was his belief that no accurate values existed for the exchange energies. His nearest approach to a quantitative statement was the development of the expression

$$E = \tfrac{1}{2}\left\{\alpha - \beta^2/\gamma\right\} S_d^2$$

where E is the energy of stabilization, S_d is the magnetic moment arising from the d electrons, β^2/γ is a parameter determining the strength of the coupling of valence electrons to d electrons, and α is the anti-ferromagnetic Heisenberg coupling coefficient. The form of this equation is exactly that of the Weiss theory. When $\beta^2 < \alpha\gamma$, an antiferromagnetic behavior is predicted.

Zener retains the model of Slater and Stoner for metallic structure, placing all of the d character in the narrow band and assuming about 0.6 valence electron.

The Pauling Theory of Metals

The assumption that there is only about 0.6 valence electron in iron, cobalt and nickel has not been questioned by physicists. It is possible to explain much of the behavior of the saturation magnetic moment in ferromagnetic alloys with the use of such a model (15). The major objection to the idea of 0.6 valence electron was raised in 1938 by Pauling (12), who pointed out that the bond distances in crystals of iron, cobalt, and nickel were not very much different from the single-bond covalent radii observed in simple compounds of these elements. Pauling observed that the interatomic distances in these three metals were all about 2.50A, and suggested that there are about six bonds per atom in each of these elements, just as there are in the octahedral complexes such as $Fe(CN)_6^{\equiv}$. The bonding orbitals in these complexes are assumed to have d^2sp^3 hybridization. In the metals larger amounts of d character might lead to greater stability. In any case, no more than six strong bonds can be formed from the available orbitals. It would seem difficult to account for either the cohesive energy or the bond distances in these metals with the assumption of only 0.6 valence electron, and it is likely that the view of Slater must be modified.

Given approximately six electrons in the valence band, Pauling had to account for the observed magnetic moments. At the time of this work the valence electrons were not supposed to contribute to the magnetic effect. It was imperative, therefore, to introduce the familiar narrow band in which positive exchange interactions of some sort would occur. Pauling postulated that, if the valence orbital hybridization involved n d orbitals, then the remaining (5-n) d orbitals form a narrow band in which positive interactions could occur. If such a band has the proper energy relationship to the valence band, the atomic band will not be entirely filled and there will be a resultant moment.

It is convenient to modify Pauling's original diagram of this band structure in order to show the d band interaction, as discussed earlier. Figure 4 (Part III) shows the separate bands for orbitals of positive and negative spin. In iron the positive band is partly filled and the negative band is empty. In cobalt, with one more electron per atom, the positive band is completely filled and the negative band partly filled. In nickel the filling of the negative band has proceeded further. In this very simple model the number of valence electrons and the relative positions of the atomic and valence bands are assumed to remain constant from one element to the next.

The number of orbitals in the atomic band was estimated by Pauling from the variation of magnetic moment with composition in the binary alloys of iron, cobalt, and nickel. Pure iron has a saturation moment of 2.22 Bohr magnetons. The addition of cobalt or nickel contributes electrons to the positive d atomic band until it is filled. The magnetic moment is a maximum here. From the average position of the experimentally observed maxima in the curves of magnetization plotted against electron number Pauling determined that the atomic band contained 2.44 d orbitals. This is of course a crude approximation, implying that the magnetic moment is only a function of electron number. Actually there is considerable variation in the observed magnetic moments of various alloys with the same electron number, and in all cases there is a plateau rather than a maximum in the curve of magnetic moment plotted against electron number. Both of these phenomena can be accounted for by a more detailed theory of ferromagnetism based upon this early Pauling model.

One of the striking differences between this model and that of the physicists occurs in the explanation of the magnetic moment of iron. In Pauling's arrangement iron has a moment because of 2.22 electrons per atom which are in the atomic band. In the Slater model there is a hole of magnitude 2.22 in the d band.

The Pauling Theory of Ferromagnetism

It seems quite reasonable that the next step should be the combination of the best elements of the Zener theory of ferromagnetism and the Pauling ideas of metal structure. The combination was effected by Pauling in 1953, producing the first theory which is capable of predicting both the saturation magnetic moment and the Curie temperature with the adjustment of only one parameter. All other theories of the Weiss form have two parameters which must be fixed for such a determination and are therefore worthless for that purpose.

The Pauling theory of ferromagnetism (6) is based upon the following assumptions:

1. There are nearly six valence electrons per atom as in the earlier Pauling model.

2. The electrons in the valence band interact with the electrons in the d band, as in Zener's hypothesis, to produce ferromagnetism.

3. The Heisenberg antiferromagnetic exchange term is negligible compared with the ferromagnetic exchange term.

4. The positive exchange energy between the valence electrons and the atomic electrons is equal to the Hund's rule stabilization energy in the isolated atom. The value of this energy may be determined from tables of atomic spectroscopic levels.

5. The valence electrons are treated as a free electron gas.

6. The number of atomic electrons and atomic orbitals is slightly different from the number given in the 1938 Pauling theory, since a certain amount of moment is now contributed by uncoupling of valence electrons. This number is the only undetermined parameter in the Pauling theory. It will be demonstrated in Part III that the choice made by Pauling is not necessarily the best one.

In the cases of cobalt and nickel there is a certain amount of difficulty in explaining the atomic moments because in each case the moment per atom cannot be a whole number if each atom is assumed to have the same moment. This problem had arisen even in the physicists' theories, and both Mott and Jones (18) and Pauling (6) resolved the problem by assuming that the elements are mixtures of atoms of different spins. In the case of cobalt the mixture would be composed of 28.5^{o}/o atoms with spin 3/2 and 71.5^{o}/o with spin 1/2. In nickel there would be 28.5^{o}/o with spin 1 and 71.5^{o}/o with spin 0. The percentages happen to be the same because nickel, with one more electron than cobalt, has a magnetic moment almost exactly one Bohr magneton less. Pauling (13) has discussed the structural significance of these mixed atomic moments. The empty "metallic" orbital in the atoms of lower spin permits formation of ionic structures, greatly increasing the possibility of resonance stabilization and giving rise to metallic conduction properties.

7. The atomic band is assumed to be very narrow, so that Hund's rule holds, and so that each atom can be treated independently. Each atom has a moment which can be treated as "permanent" because the Hund's rule interaction energy between d electrons is assumed to be much larger than kT_c.

The method of calculation in the Pauling theory is quite simple compared with the methods of any of its predecessors. Heisenberg's difficulty arose from assumptions of direct interactions between atoms, which required calculations in terms of an overall crystalline quantum number. The Pauling theory postulates the existence of individual permanent atomic moments in a sea of partially unpaired valence electrons. The permanent atomic moments are not directly coupled to one another and the individual atomic spin quantum numbers therefore retain their meaning.

The energy of the system is a function only of the net permanent magnetic moment component along the z axis, and the orientation of these moments is determined, as in the Langevin-Weiss theories, according to the Boltzmann distribution law.

The valence electrons obey Fermi-Dirac statistics and must be treated accordingly. Fortunately, as will be shown in Part II, the distribution in a free electron gas is almost independent of temperature in the temperature range to be considered, so that the calculation of the number of unpaired valence electrons is simple.

Results of the Pauling Theory

The dependence of magnetization upon temperature predicted by the Pauling theory can be expected to be fairly correct because the Pauling theory has the same form as that of Weiss. The agreement with observed magnetic moment is quite good, but the number of electrons assumed to be in the atomic band is flexible to a certain extent, and is implicitly chosen to give the correct total magnetic moment. In the case of iron it seems reasonable to assume that there are about six valence electrons and therefore about two atomic electrons. In cobalt and nickel, faced with the non-integral average atomic moments discussed above, Pauling estimates the relative amounts of each kind of atomic spin from Taglang's extrapolation (19, 20) of the residual moments of isoelectronic sequences to the electron number at which all residual moment disappears. The validity of such extrapolations will be discussed in the conclusion of Part III.

The ultimate test of the Pauling theory would seem to lie in its ability to predict the Curie temperatures of the elements and alloys. The results are not entirely satisfactory. The Curie temperature predicted for iron is somewhat higher than the observed value. The predicted Curie temperature for cobalt is somewhat lower, and that for nickel much lower than the experimental value. The alloys also show large deviations in Curie temperature, though the magnetic moments predicted are in fair agreement with experiment.

The subject of the following chapters is a series of attempts to improve upon the basic model presented by Pauling, especially with regard to the prediction of Curie temperatures.

The first topic discussed is the accurate treatment of the temperature dependence of magnetization in the original Pauling model. The detailed techniques of calculation will be introduced at this point.

The second topic is a discussion of experimental data for the magnetic elements and alloys. Modifications of the Pauling theory will be made in order to provide better results for the predicted Curie temperatures.

The third topic is a discussion of inhomogeneous electron distributions in ferromagnetic crystals and their effect upon the Curie temperature.

II. SOME EFFECTS OF TEMPERATURE IN THE PAULING THEORY OF FERROMAGNETISM

The results which Pauling obtains are based upon certain simplifying assumptions which have been outlined in the introduction. One of these assumptions is the negligibility of temperature effects other than that concerned with alignment of atomic spins in the Weiss field. There are two possible ways in which such an assumption can lead to error in the Pauling calculation for iron. First, it involves the neglect of a contribution to the susceptibility from the thermally-induced uncoupling of the conduction electrons. Second, the effect of temperature upon the lattice itself has been neglected. Since there are no direct interactions between conduction electrons in the Pauling theory the latter effect is of significance only insofar as it changes the effective atomic volume of the metal and alters the relationship describing the density of energy levels.

The results of Pauling will now be rederived with the inclusion of these corrections.

Pauling makes the assumption that there are six "valence electrons" per atom in the ferromagnetic crystal and that these behave as free conduction electrons enclosed in a box. According to the W.K.B. approximation (21) there is assigned to each energy level in such a system a volume h^3 in phase space. The number of levels enclosed in a volume V in real space and $\frac{4\pi}{3}(2m\epsilon')^{3/2}$ in momentum space is therefore given by the familiar formula

$$n = \frac{(2m\epsilon')^{3/2}}{h^3} V \cdot \frac{4\pi}{3}$$

The Pauling theory is based upon the Weiss formalism. The large value of the "local" susceptibility which is required for a ferromagnetic effect in iron is obtained by assuming that the six conduction electrons in d^3sp^2 orbitals are stabilized by alignment parallel with the two 3d atomic electrons. This in turn results in the alignment of the atomic moments in the "Weiss field" provided by the spin of the unpaired conduction electrons. If this is to be true Weiss magnetism the local field must be directly proportional to the net atomic moment; the unpairing of valence electrons must be proportional to the net atomic moment. The two atomic electrons on each iron atom which are assumed by Pauling to take no part in conduction or binding are the source of what might be called the "essential" magnetic moment. The magnetic moment provided by the conduction electrons is "accidental" in the sense that it is a byproduct of the manner in which Pauling obtains the Weiss field but is not necessary for the more general Weiss theory. The atoms may have their spin magnetic moments oriented with respect to the z axis in the manner usually associated with the component of angular momentum in atoms. It is assumed that the orbital magnetic moment is quenched so that the entire contribution to the moment arises from electron spin.

The net z component per atom of atomic spin is called J_z. Since the spin quantum number S of each atom is 1, the net z component for the crystal is

$$J_z = \frac{N_U - N_D}{N_T}$$

where $(N_U - N_D)$ is the difference between the number of atoms with $S_z = +1$ and the number with $S_z = -1$. There may of course be atoms with $S_z = 0$, but these do not contribute to J_z. The magnetic moment produced by a net spin J_z is gJ_z, where g, the gyromagnetic ratio, is assumed temporarily to be equal to 2, the value for pure spin contribution. The quantity gJ_z will be called M_S, and the net magnetic moment per atom produced by the unpairing of conduction electrons will be designated by the symbol M_V. The subscript ∞ following any of these symbols designates the value of the variable at saturation.

It is assumed that there is an interaction energy 2Q which is associated with the reversal of spin of one conduction electron in the presence of the two atomic electrons of the iron atom. Pauling (6) describes the method of determining Q from spectroscopic data for atomic states. The existence of a net atomic spin results in the stabilization of conduction electrons with spin 1/2 relative to those with spin -1/2 by an amount $\frac{M_S}{M_{S\infty}} \cdot 2Q = M_S Q$.

The problem of the unpairing of conduction electrons in a field was treated by Pauli (22) for the case of an external magnetic field. Pauli proposed this as a mechanism for temperature-independent paramagnetism. The magnetic field produced by the alignment of atomic spins is about 10^{-4} as great as the exchange energy field and may be neglected in the discussion of ferromagnetism. However, the formalism of the Pauli theory is valid for any field in which reversal of spin involves a constant energy change.

In connection with the investigation of the effects of temperature it will be necessary to make an extension of the simple Pauli formula, which was originally derived for a system of electrons in the ground state. When the temperature is not absolute zero the criterion of minimization of internal energy which is used in the Pauli treatment is no longer correct.

If the Fermi-Dirac distribution is used in the analysis of the free-electron model it is easily shown (23) that the mean energy of a distribution of unpaired electrons at absolute zero is

$$\overline{E}_o = 3/5\, E_o' = 3/10\, \frac{h^2}{m}\left(\frac{3N_o}{4\pi}\right)^{2/3}$$

where E_o' is the highest occupied level. At temperatures near absolute zero the approximate expression

$$\overline{E} = \overline{E}_o\left[1 + \frac{5}{12}\pi^2\left(\frac{kT}{E_o'}\right)^2\right]$$

may be used (23). The total energy of the system is $N_o\overline{E}$. It can also be shown (Appendix 1) that the entropy of this system to the same degree of approximation is

$$\frac{N_o\overline{E}_o}{T}\cdot\frac{5}{6}\pi^2\left(\frac{kT}{E_o'}\right)^2$$

so that the free energy is

$$F(N_o) = N_o\overline{E}_o\left[1 - \frac{5}{12}\pi^2\left(\frac{kT}{E_o'}\right)^2\right] .$$

If one considers a distribution of N_o electrons with spin + 1/2 and n_o electrons with spin -1/2, then in the absence of an external field the free energy of the entire system is $F = F(N_o) + F(n_o)$. If a field which differentiates energetically the two components of spin is applied, the free energy of the system is increased by a term Gn_o, so that one finds

$$F = N_o \cdot \tfrac{3}{5} E_o' \left[1 - \frac{A}{E_o'^2}\right] + n_o \cdot \tfrac{3}{5} \epsilon_o' \left[1 - \frac{A}{\epsilon_o'^2}\right] + G n_o \quad .$$

The requirement for the equilibrium condition is that $dF = 0$, subject to the restriction that $N_o + n_o = \eta$. Substituting the values of E'_o and ϵ'_o as functions of N_o and n_o and introducing the Lagrange multiplier λ, one gets

$$\varphi = \tfrac{3}{5}\left[N_o^{5/3} + n_o^{5/3}\right] - \tfrac{3}{5}\frac{A}{\alpha}\left[N_o^{1/3} + n_o^{1/3}\right] + G n_o + \lambda\left[N_o + n_o - n\right]$$

where
$$\alpha = \frac{\hbar^2}{2m}\left(\frac{3}{4\pi}\right)^{2/3} \quad .$$

Taking the customary partial derivatives with respect to N_o and n_o, equating these to zero and eliminating λ, one obtains

$$\alpha\left(N_o^{2/3} - n_o^{2/3}\right) - \tfrac{1}{5}\frac{A}{\alpha}\left(N_o^{-2/3} - n_o^{-2/3}\right) = G \quad .$$

If $(N_o - n_o) \equiv \delta$ is small, binomial expansions can be made in terms of the parameter δ, giving the equations

$$G \cong \alpha \cdot \frac{2\delta}{3} n_0^{-1/3} + \frac{1}{5}\frac{A}{\alpha}\frac{2\delta}{3} \cdot n_0^{-5/3}$$

$$\delta = \frac{G}{\frac{2}{3}\alpha n_0^{-1/3} + \frac{2}{15}\frac{A}{\alpha} n_0^{-5/3}}$$

$$\cong \left[\frac{G}{\frac{2\alpha}{3} n_0^{-1/3}} - \frac{18\,A\,G}{60\,\alpha^3 n_0} \right]$$

If the term n_o is replaced by $\frac{\mathfrak{n}}{2}$ and A and α are replaced with their correct expressions one then obtains the equation

$$\delta = G \left\{ \frac{12m}{\hbar^2}\left(\frac{\mathfrak{n}}{V}\right)^{1/3}\left(\frac{\pi}{3}\right)^{2/3} - \frac{64\pi^2 V m^3 k^2 T^2}{9\mathfrak{n}\hbar^6} \right\}$$

This is an expression first obtained by Bloch (24) in a different and more complicated manner. The numerical values of the constants may be substituted to give the expression

$$M_V = \frac{\beta \delta V}{N_T} = \beta \frac{G V}{N_T}\left\{ 2.20 \times 10^{-14}\left(\frac{\mathfrak{n}}{V}\right)^{1/3} - 1.03 \times 10^{7}\, T^2 \left(\frac{V}{\mathfrak{n}}\right) \right\} \quad (1)$$

where $\frac{V}{\mathfrak{n}}$ is of the order of 10^{-22}. In none of the crystals to be considered does the temperature exceed about 10^3, so that the temperature-dependent term is negligible. The remaining term is that obtained by Pauli and Pauling. In the case of ferromagnetism the energy term G is equal to QM_S as has been shown earlier. It will be observed that the Weiss requirement of linear dependence of M_V upon M_S is met by this equation.

The other correction to be considered is the inclusion of the dependence of the effective atomic volume upon temperature. Equation (1) shows that M_V varies as $V^{2/3}$. Since V can be written approximately as $V_o (1 + \gamma T)$ where γ is the coefficient of cubic expansion and V_o is the volume at absolute zero, and since $\gamma T \ll 1$, one may write

$$V^{2/3} \cong V_o^{2/3} \left(1 + \frac{2\alpha T}{3}\right)$$

The inclusion of the factor γ results in an increase in the predicted Curie temperatures of all of the crystals considered, as shown in Table 1.

Because of the volume change there should be a free energy term corresponding to the PΔV work. This has been neglected in the Pauli derivation because the value of the product $\frac{\gamma k T}{E'}$ is clearly much smaller than the first temperature-dependent term in the free energy.

Table 1.

Substance	Coefficient of Expansion	Uncorrected Curie Temp.	Corrected Curie Temp.
Iron	3.5×10^{-5}	1350°	1390°
Cobalt	3.6×10^{-5}	1190°	1240°
Nickel	3.8×10^{-5}	367°	370°
Gadolinium	0	--	--

Calculation of Temperature-Magnetization Curves

The orientation of the atomic moments in the Weiss field as a function of temperature must now be taken into account. A Weiss field of strength $\frac{M_V Q}{2\beta S}$ gauss is created by the unpairing of valence electrons. That is, the energy required to "turn over" an atom with spin of magnitude +1 in the presence of a single conduction electron is equivalent to twice the interaction energy of an atom with spin +1 with a field of strength $\frac{Q}{\beta S}$. This energy is equal to $2M_V Q$ and therefore the partition function for the system is

$$f = \left(\sum_{S_z=-1}^{S_z=+1} e^{-\frac{M_V Q}{kT} S_z} \right)^{N_T}$$

where there are N_T atoms in the crystal. The atoms are independent of one another so that the device of raising the single-atom partition function to the power N_T is a valid one.

The atomic susceptibility χ of a system with partition function f is given by

$$\chi = \frac{kT}{N_T H} \frac{\partial}{\partial H} \ln f$$

where H is the Weiss field intensity. Making use of the proper partition function and the definition of magnetic moment, the magnetic moment which arises from the atomic moments alone can be written

$$M_S = 2 S B_S\left(\frac{2\beta H}{kT}\right) = 2 S B_S\left(\frac{M_V Q}{kTS}\right) = M_{S\infty} B_S\left(\frac{M_V Q}{kTS}\right)$$

where $B_S(u)$, the Brillouin function, is

$$B_S(u) = \frac{(S+\frac{1}{2})\coth(S+\frac{1}{2})u - \frac{1}{2}\coth\frac{u}{2}}{S}$$

This equation provides a second relationship between M_V and M_S, the first being the equation

$$M_v = \frac{M_S}{M_{S_\infty}} M_{V_\infty}\left(1 + \frac{2\gamma T}{3}\right) \qquad (2.)$$

which has already been derived.

The solution of these simultaneous equations for M_V and M_S is customarily carried out graphically. The function $B_S\left(\frac{M_V Q}{kTS}\right) = \frac{M_S}{M_{S_\infty}}$ is plotted* against $\frac{M_V Q}{kTS}$ and the line through the origin with slope $\frac{kTS}{M_{V_\infty}Q(1+\frac{2\gamma T}{3})}$ is drawn for some value of T. The intersection of the two curves directly gives the value of $\frac{M_S}{M_{S_\infty}}$ for the value of T used. The total magnetization, $M = M_S + M_V$, is calculated from the known value of M_S and Equation (2.).

As the temperature increases the slope of the straight line also increases until its intersection with the Brillouin curve occurs at the origin. This point corresponds to the Curie temperature, which may be calculated by equating the slope $\frac{kTS}{M_{V_\infty}Q(1+\frac{2\gamma T}{3})}$ with the slope of the Brillouin function at the origin. The limiting slope of the Brillouin function is easily shown to be $(S+1)/3$. The Curie temperature is therefore given by the equation

$$T_c = \frac{M_{V_\infty}Q}{k}\frac{(S+1)}{3S} \Big/ \left[1 - \frac{2}{3}\gamma\frac{M_{V_\infty}Q}{k}\frac{(S+1)}{S}\right]$$

The Curie temperature of iron calculated in this manner has

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*For the shape of the curve see Seitz (23).

been given in Table 1. The complete magnetization curve of iron is given in Figure 1.

If one temporarily neglects the term involving the coefficient of expansion it is seen that the magnetization curve which is to be expected is that of the Weiss curve for J = 1, since

$$\frac{M}{M_\infty} = \frac{M_s + M_v}{M_{s\infty} + M_{v\infty}} = \frac{M_s}{M_{s\infty}} .$$

As long as the magnetic moment arising from unpairing of conduction electrons is directly proportional to the net atomic moment with a temperature-independent constant there can be no improvement upon the magnetization curve predicted by the most general Weiss theory. The Weiss magnetization curve deviates somewhat from experimentally observed values in the high temperature region, where the absolute value of the slope is too small. The inclusion of the expansion coefficient will provide a correction in the right direction, since the slope is of the form

$$\frac{d(M/M_\infty)}{d(T/T_c)} = \frac{d(M_s/M_{s\infty})}{d(T/T_c)}\left[1 + cT\right]$$

where c is a small positive constant. The correction is not sufficient, however, to make the curve coincide with the experimentally observed results.

Gyromagnetic Ratio

The assumption that the value of the gyromagnetic ratio is 2 has been made throughout the equations derived above. Pauling indicates that in iron the gyromagnetic ratio is actually 1.946, and he introduces this factor by multiplying the value of M_∞ by the fraction $\frac{1.946}{2.000}$. Since the forces involved in the Pauling theory are electrostatic and not magnetic the value of g does not enter except in the final evaluation of the magnetic moment. The Weiss field and the Curie temperature depend only upon the net number of atomic electrons aligned in the positive direction of the z axis, and not upon the net moment. The treatment of Pauling is a consistent method of correcting the value of M_∞, since the experimentally observed gyromagnetic ratio may be expected to involve contributions from atomic and conduction electrons in proportion to the net number of each kind aligned with the field. It is not necessary to take into account possible differences in the gyromagnetic ratios of the two kinds of electrons, though such differences might be expected to exist, because, provided that the Pauling theory is correct (and that the modifications which are made in the present study are not very large in their effect) the ratio of the net number of aligned atomic electrons to the net number of aligned conduction electrons is independent of temperature, and the intensity of magnetization at any temperature will be correct provided that M_∞ has been corrected in the manner described above. The Pauling theory in effect predicts that the gyromagnetic ratio should be independent of temperature.

Treatment of Other Metals

Pauling makes the assumption, based upon a consideration of metallic properties (6, 13), that 28.5°/o of the atoms in nickel have atomic spin 1 while the remaining 71.5°/o have no resultant spin angular momentum. Similarly, 28.5°/o of the atoms in cobalt are assumed to have spin 3/2 while the remainder have spin 1/2. This assumption may be introduced formally by slight modifications of the preceding treatment. If there are several different "kinds" of atoms in a given crystal, each comprising a fraction r_i of the total number of atoms N_T, and if there is associated with each kind of atom a spin S_i, then the partition function for the system is

$$f = \prod_i \left(\sum_{S_z = -S_i}^{S_z = +S_i} e^{-\frac{M_v Q}{kT} S_z} \right)^{r_i N_T}$$

where Q is the interaction energy of a conduction electron with an atomic spin of magnitude 1. Taking the usual derivative of f with respect to H, one finds

$$\frac{M_s}{M_{s\infty}} = \frac{2}{M_{s\infty}} \left\{ \sum_i S_i r_i B_{S_i} \left(\frac{M_v Q}{kT} \right) \right\}$$

where $M_{s\infty} = \frac{2}{N_T} \left\{ \sum_z n_z S_z \right\}$.

The Curie temperature is then given by

$$T_c = \frac{2 M_{v\infty} Q}{3 k M_{s\infty}} \left[\sum_i r_i S_i (S_i + 1) \right]$$

since $M_v = \frac{M_s}{M_{s\infty}} M_{v\infty}$ as in the case of iron.

The application of this equation gives somewhat different results from those of Pauling in the case of cobalt, leading to a Curie temperature of 1160° K without correction for volume expansion. The averaging method used by Pauling is completely accurate in the case of nickel since the contributing moments are $S = 1$ and $S = 0$, and the latter leads to a constant factor in the partition function.

Figures 2 and 3 show the temperature-magnetization curves for cobalt and nickel.

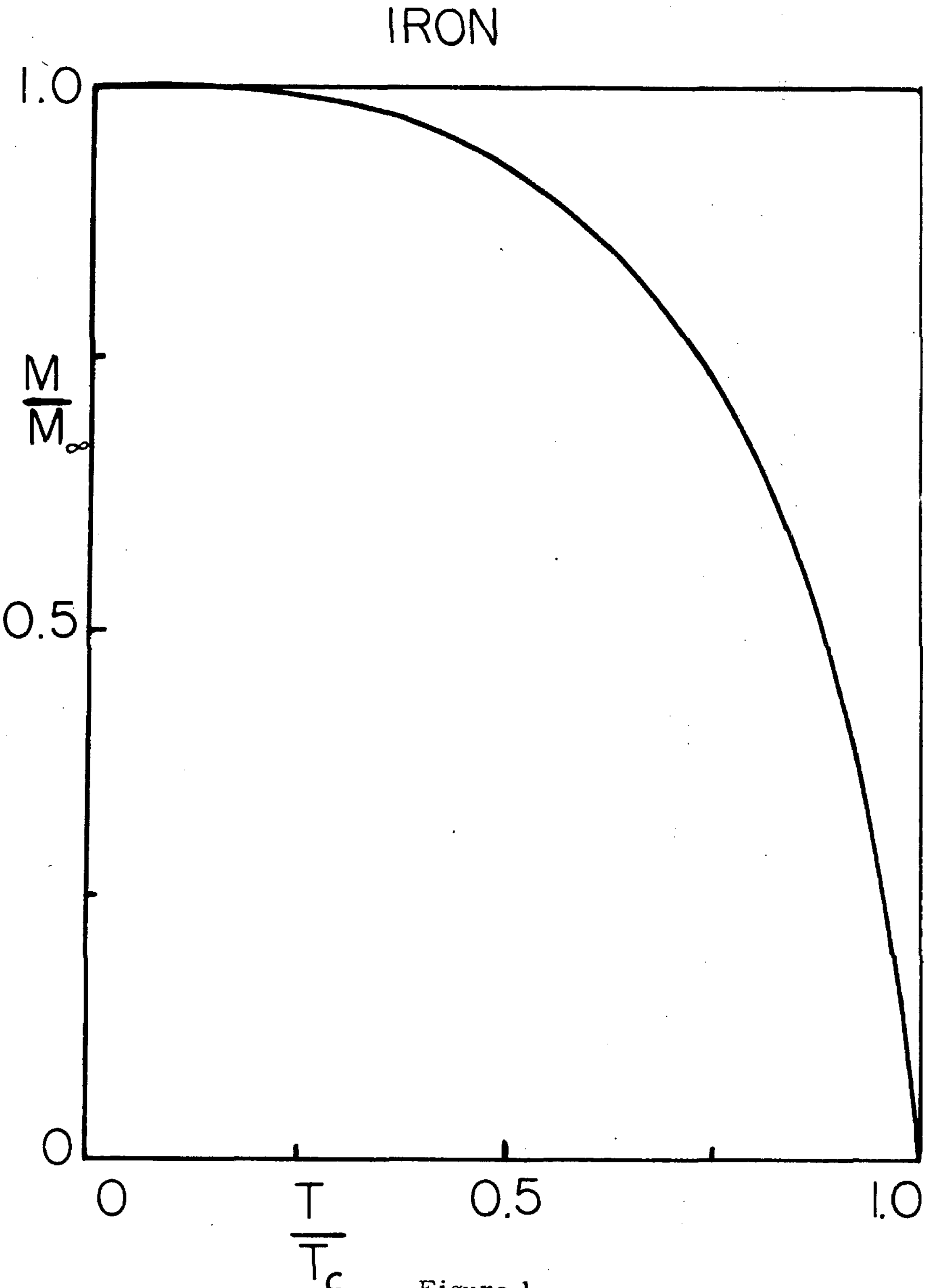

Figure 1.

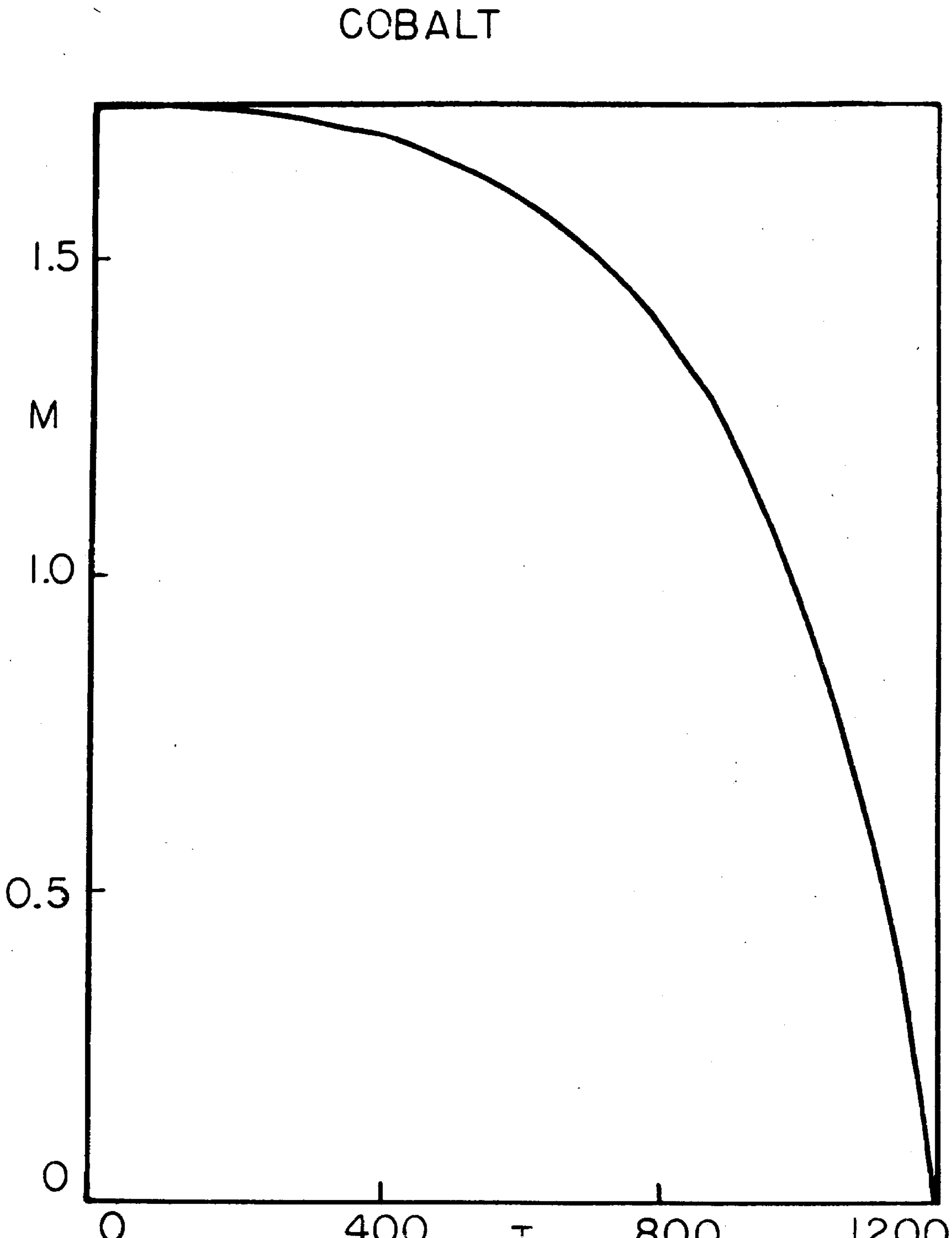

Figure 2.

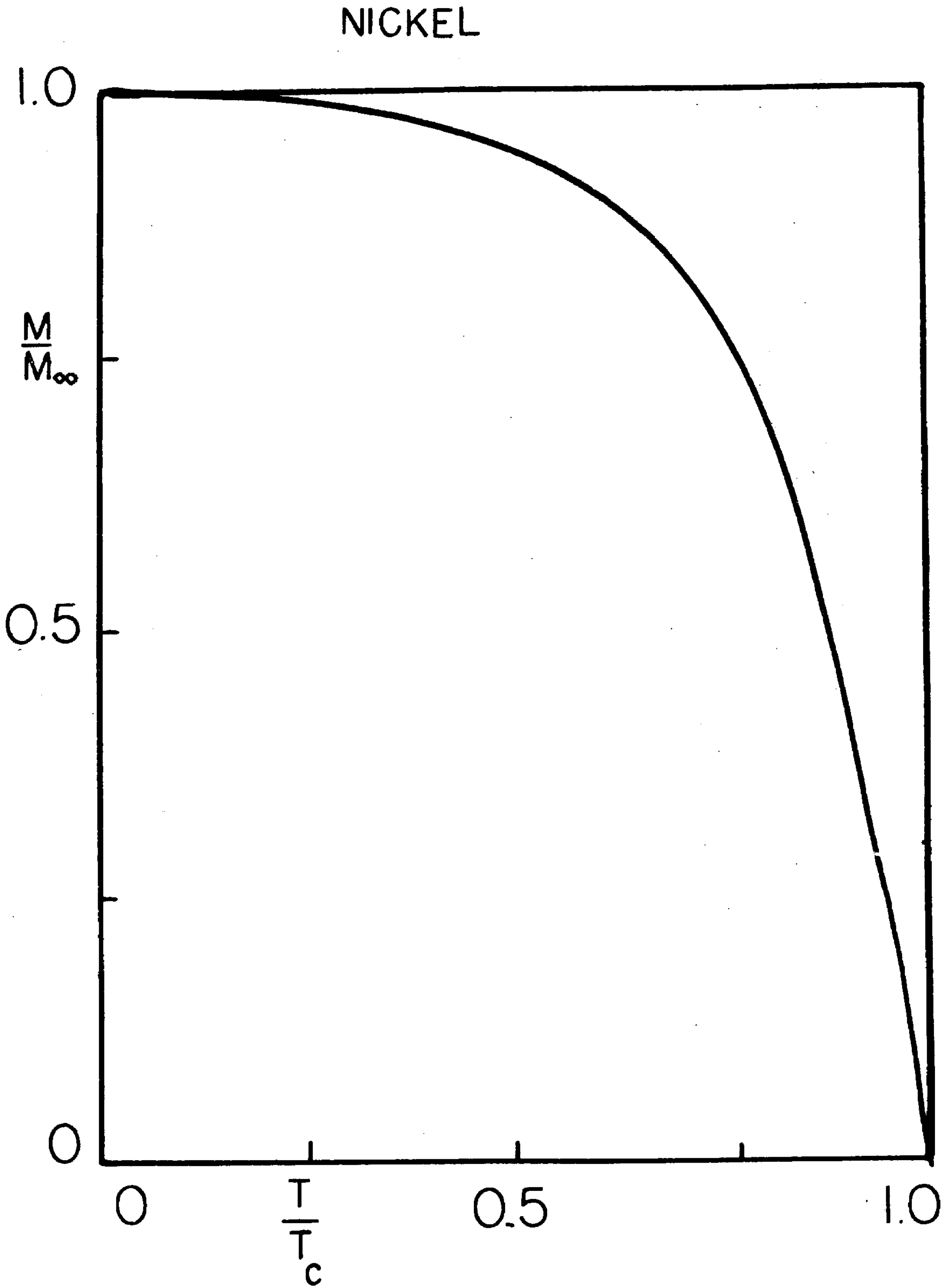

Figure 3.

III. FERROMAGNETIC ALLOYS AND BAND STRUCTURE

The preceding calculations are all based upon the assumption that the valence bond orbitals have d^3sp^2 hybridization, and that there are exactly six valence electrons per atom. In the case of iron, which will be considered first, the interaction energy for a valence electron with an atomic electron can be estimated with fair accuracy (6), since the tables of spectroscopic levels for iron are complete. Pauling computes the interaction energy between a d electron and an s electron, a d electron and a p electron, and a d electron and another d electron. He then weights these energies according to the d^3sp^2 hybridization to find the average interaction energy of a valence electron.

It was pointed out in the introduction that the assumption of d^3sp^2 hybridization was arbitrary. The fact that the predicted Curie temperature of iron is too high by 350^o suggests that the choice was not correct. In order to determine what the hybridization should be, Pauling's calculation was repeated with varying amounts of d character in the valence band. It was assumed that no more than six strong bonds could form whatever the hybridization. The variable affecting the result most is the interaction energy, which decreases as the amount of d character in the valence orbitals is decreased. It was not required that the valence band have six electrons. Instead, the relative numbers of electrons in the valence band and the atomic band were adjusted to give the proper value of the saturation magnetic moment. This procedure was repeated for each choice of hybridization until that choice which gave the correct Curie temperature was found.

The variation of the Curie point with hybridization is shown in Table 2.

Table 2

Valence band d character	No. of valence electrons	$M_{S\infty}$	T_c
0.0	0.26	2.26	23.2°K
1.0	2.17	2.17	312.
2.0	5.92	2.08	756.
2.5	5.95	2.05	1045.

The proper Curie point is predicted when the valence electrons have hybridization $d^{2.5}sp^{2.5}$. There are 5.95 valence electrons in the valence band and 2.05 atomic electrons. There are now 2.5 atomic orbitals per atom, rather than the 2.0 of Pauling's theory. This is a satisfying development, since the band model now agrees with that first assumed by Pauling in 1938, in which the atomic band had 2.44 orbitals. This ensures that the predicted behavior of the magnetic moments of alloys will be at least as accurate as that of the early Pauling model. In the recent Pauling paper on ferromagnetism there is implied an atomic band structure for iron which is different from that of cobalt. This is contradictory to most of what is usually assumed about the band structure of the ferromagnetic elements, including the assumptions of the 1938 Pauling paper. It will therefore be assumed instead that iron, cobalt, and nickel all have 2.5 atomic orbitals and $d^{2.5}sp^{2.5}$ valence bond hybridization.

The calculation of the Curie temperatures of cobalt and nickel can now be made using this band structure. Since he was unable to obtain accurate values for the interaction energies because of the incompleteness of the spectroscopic tables for these elements, Pauling estimated that the energies were 5°/o and 10°/o higher respectively than those of iron. The use of these values to calculate the Curie point does not result in any improvement over the results of Pauling. In fact, the results are worse (about 400 degrees lower for cobalt). This is not surprising, since the amount of d character in the bonds is smaller than that in the d^3sp^2 bonds of Pauling. It is interesting to note, however, that d^3sp^2 bonds are actually impossible in cobalt because more than two d orbitals must be used up to accommodate the number of atomic electrons which Pauling calculates are in the d band. Even if there were only enough d orbitals in the atomic band to hold the atomic electrons, 2.285 atomic orbitals would be needed, and the valence hybridization in cobalt could be, at best, $d^{2.715}sp^{2.285}$. The value Pauling finds for the Curie temperature of cobalt is therefore too high even according to his own model.

The weakest point in this argument seems to lie in the choice of interaction energies, and those of cobalt and nickel were reexamined. It was found that Pauling's estimate is somewhat low, and that the successive increases in energy from iron to cobalt and cobalt to nickel might be as high as 13°/o rather than the 5°/o estimated by Pauling. Nonetheless it appears certain that the spectroscopic levels cannot be sufficiently far apart to account for the large energies required to give the proper Curie temperatures for cobalt and nickel. The principal object of the investigation is the study of the behavior of the alloys, and it is clear that no meaningful calculation of the Curie temperatures of the alloys can be made if the Curie temperatures of the pure elements are not correct. It was therefore decided to adjust the interaction energies of cobalt and nickel to give the proper magnetic moments and Curie temperatures using the band structure decided upon above. The experimental data on behavior of alloys are plentiful and full of anomalies, so that the ability of the Pauling theory to predict this behavior represents a significant test despite the added arbitrariness of the selection of an interaction energy. The physical justification of this step will be discussed in the conclusion of the thesis.

The interaction energy values chosen for cobalt and nickel were 0.80 e.v. and 0.93 e.v. respectively (compared with 0.58 e.v. for iron). The number of valence electrons found for both cobalt and nickel is 5.53. This seems an unusual coincidence, and the question arises as to why iron has 5.95 valence electrons rather than 5.53. The answer appears to lie in the fact that the stable phase for iron below the Curie point is the α or body centered phase, while cobalt and nickel exist in a face centered γ phase. Iron undergoes a transition from the α phase to the γ phase some distance above the Curie point. It is interesting to note that although the paramagnetic moments predicted from the slopes of the curves of susceptibility plotted against temperature disagree with the results in the ferromagnetic region, the ratio of the slope of the paramagnetic curve of the α phase of iron to the slope of the paramagnetic curve of the γ phase of iron is close to what would be predicted if there were a change from 5.95 valence electrons to

5.53 valence electrons. There is an apparent increase in atomic magnetic moment from 2.05 Bohr magnetons to 2.47 Bohr magnetons when iron undergoes the α-γ transition. It seems quite likely, therefore, that the number of valence electrons associated with γ phases in iron, cobalt, and nickel is 5.53.

The first attempt to test the ideas outlined above was made on the alloy which is 50°/o iron and 50°/o nickel. (All alloy compositions are given in atom per cent.) Since this is a γ phase it was assumed that there are 5.53 valence electrons. Assuming that all atoms have the same average moment and that the interaction energy of the alloy is the average of the iron and nickel energies, the answer obtained for the magnetic moment is in fair agreement with experiment. The predicted Curie temperature, however, is about 1400°K, close to that of cobalt, and far different from the observed value of 835°. The problem is easily stated: Since the electron number is the same for this alloy as it is for cobalt, and since the average interaction energy is about the same as that of cobalt, how can the Curie temperature of the alloy be almost six hundred degrees less than that of cobalt, especially since the experimental magnetic moments are about the same?

The solution of the problem requires a closer examination of the hypothesis of band structure. A fundamental assumption of the Pauling theory is the existence of narrow atomic bands; iron will have 2.5 d + orbitals and 2.5 d- orbitals in two bands separated by the Hund's rule interaction energy for d electrons. Now suppose that one atom of nickel replaces an atom of iron. An atomic level is lost from the iron band and one nickel atomic level appears. But since nickel has a higher atomic number this level will be an "impurity level" below the main iron band. This result has been established by many theoretical investigations (25). As more nickel atoms are added the number of levels in the nickel band increases and the number in the iron band decreases. In the equimolar mixture it is not unreasonable to suppose that the arrangement is as shown in Figure 5, in which the Ni+ band is lowest, followed by the Fe+ band, then the Ni- band, and finally the Fe- band. The wave functions in the nickel bands are largely concentrated upon nickel atoms, since the nickel potential wells are deeper. In order to keep the crystal microscopically neutral the functions in the iron bands will then have to be concentrated upon the iron atoms.* Thus, the alloy should be treated as a mixture of two kinds of atoms with the interaction energies of iron and nickel respectively. If there are 5.53 valence electrons there will be 3.47 atomic electrons just as in cobalt. Filling in the atomic bands in the usual order one places 1.25 electrons in the Ni+ band, 1.25 in the Fe+ band, and 0.97 in the Ni- band. The permanent atomic moment is therefore 1.53, just as in cobalt, but the moment interacts with the valence electrons as though there were 0.28 Bohr magnetons of moment arising from the nickel atoms and 1.25 from iron. Since the interaction energy of iron is low compared with that of nickel there is a considerable lowering of the Curie temperature from that predicted by the simple model just discussed, in which iron and nickel were assumed to contribute

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*A somewhat similar model for alloys has been suggested by Slater (15).

half each to the interaction energy. The Curie temperature predicted is now 1030° and the magnetic moment is about 0.1 Bohr magneton too high. One may leave matters as they stand or one may take the logical step of assuming that the bands are not entirely separated, but overlap at some point. This would reduce both the magnetic moment and the Curie temperature. It is clear that the only overlap which can affect the result would occur between the Fe+ and Ni- bands. Assuming that the levels in the bands are evenly distributed, one can adjust the overlap to give the correct magnetic moment. The Curie temperature predicted is then 960°K, which is just 11°/o higher than the correct value.

At this point it is necessary to explain some of the details of calculation. Non-integral moments must still be resolved into sums of integral moments. In cobalt and nickel the individual moments used are 3/2 and 1/2 and 1 and 0 respectively, just as in the earlier work. The atomic magnetic moment of iron, 2.05 Bohr magnetons, is resolved into moments of 2 and 3, or, in alloys where the moment of iron falls below 2.0, into moments of 2 and 1. In most cases the results seem to be relatively independent of the manner of choosing the components.

The partition function and the definition of ferromagnetic susceptibility in terms of the partition function must be modified somewhat when there are atoms possessing different interaction energies with the field. The Curie temperature is given by

$$T_c = \frac{2}{3k}\left[\sum_i r_i Q_i \frac{M_{V_i\infty}}{M_{S_i\infty}} S_i(S_i+1)\right],$$

an equation closely resembling that used for cobalt in Part III.

The atomic volume used is the weighted mean of the atomic volumes of the elements.

The essential point of the preceding paragraphs is that one must consider atomic bands of alloyed metals as being filled "in series" rather than "in parallel". The exact manner in which bands fill will of course depend upon the order in which they are arranged relative to one another. It is to be expected that in a binary alloy composed of two elements which are several atomic numbers apart, the bands of the element of higher atomic number will no longer alternate with those of the other, but will both lie below (Figure 6). Such an alloy would be expected to have a much lower magnetic moment than an isoelectronic alloy of elements closer together in the periodic table. Examples of this sort of alloy will be discussed in the next section.

A study of the binary alloys of ferromagnetic elements has been made using the methods described. The Curie temperature and magnetic moment were calculated for various compositions with an arrangement of bands which will be described for each alloy. In the relatively few cases, like that of the 50°/o iron-50°/o nickel alloy, in which both the calculated moment and Curie point were high, sufficient overlap of the bands was introduced to correct the magnetic moment. In these cases the values of M_∞ and T_c are given both with and without the correction. The graphs of the results show the corrected Curie temperatures. The experimental data, unless otherwise noted, were taken from Bozorth's book on ferromagnetism (26). The calculations were not made for composition regions where two phases are stable. Such omissions are noted below.

Cobalt-Nickel (Table 3, Figure 7). The application of this method was first made to the system cobalt-nickel because no overlap is necessary at any point in order to obtain the proper magnetic moment. The order of the atomic bands is Ni+, Co+, Ni-, Co-. There is little doubt that the number of valence electrons is 5.53 since the alloy and the two elements all have the γ structure. The predicted Curie temperatures are in excellent agreement with observed values, no point deviating from the correct value by more than 5°/o. The predicted moments are a little too low, but never by more than 0.06 Bohr magneton.

Iron-cobalt (Table 4, Figure 8). The arrangement of bands is Co+, Fe+, Co-, Fe-. A small amount of overlap is introduced between the Fe+ and Co- bands to obtain a better value of the moment. The Curie temperatures predicted for the middle composition range are much higher than the experimentally observed temperatures, and exhibit a fairly sharp maximum at 60°/o cobalt, while the experimental curve shows a broad plateau from about 20°/o to 70°/o cobalt. The phase diagram, however, shows that in this composition range the ferromagnetic boundary is also a phase boundary. The temperature-magnetization curves (27) have the usual Weiss form up to the Curie temperature, but do not fall smoothly to zero at that point. Instead there is a sudden drop in magnetic moment because of the transition to a non-magnetic phase. Forrer (28) has extrapolated the temperature-magnetization curves for these alloys in the manner in which they would be expected to behave if the phase change did not occur. He obtains a new, higher, value which is the true Curie temperature for the γ phase. The Pauling theory would naturally be expected to give this answer rather than the experimentally observed value.

Table 4 and Figure 8 compare the predicted Curie temperatures with those obtained by Forrer. The agreement is certainly not as good as in the case of cobalt-nickel alloys, but there are several impressive points of agreement. The maximum Curie temperature does occur at $60^{o}/o$, as the theory predicts. This is rather remarkable in view of the fact that the magnetic moment reaches its maximum at a cobalt concentration of $40^{o}/o$, and has dropped considerably from its maximum value by the time the $60^{o}/o$ composition is reached. It is interesting to compare these results with those predicted by the simple interpretation of the Pauling theory which failed so badly in the iron-nickel alloy first discussed. The maximum Curie temperature, as shown in Figure 4, occurs at about $40^{o}/o$. The Curie temperature in this simple model is determined almost entirely by the magnetic moment, and the maxima of the magnetic moment and the Curie temperature must occur at the same place. This strict dependence is not observed experimentally. A second and more striking example of the independence of magnetic moment from Curie temperature is given by the behavior of pure cobalt upon the addition of small amounts of iron. The Curie temperature goes down, but the magnetic moment rises. The behavior predicted by the theory developed in this chapter is not very satisfactory in this region. A decrease in Curie temperature is indeed predicted when small amounts of iron are added, and there is good agreement with experiment for concentrations of iron up to about $5^{o}/o$. Beyond that, however, the predicted values increase rapidly, while the experimental Curie point continues to decrease. Nonetheless, the fact that this behavior should be predicted at all seems significant.

Iron-nickel (Table 5). The calculation is made only for the pure γ phase, and it is assumed that there are 5.53 valence electrons. As indicated earlier the band structure chosen is Ni+, Fe+, Ni-, Fe-. The behavior of the Curie temperature is fairly good from pure nickel to 40°/o iron. At higher iron concentrations the predicted Curie temperature levels off. This is another example of a region in which Curie temperature drops and magnetic moment continues to rise, and once again the theory predicts the observed effect, but without sufficient magnitude to obtain a quantitatively correct answer. The principal problem in dealing with alloys of iron with cobalt and nickel arises from the structural differences of iron, which give rise to complicated phase changes which cannot be easily compensated for by means of a simple model.

The remaining alloys considered are those in which one element is ferromagnetic and the other is not.

Iron-chromium (Table 6, Figure 9). It is known that chromium has no ferromagnetic properties. Therefore it is assumed that there are 6.00 valence electrons in chromium, and that the number of valence electrons in the alloy system is the weighted average of 6.00 and 5.95, since these alloys have the α structure. The order of the atomic bands is Fe+, Cr+, Fe-, Cr-. It is to be noted that since the only filled band is an iron band it is not necessary to know the interaction energy of chromium. The predicted Curie temperatures agree very well with experiment except at extremely low values, where the predicted values are somewhat too large.

Nickel-chromium (Table 7). This alloy presents a problem which has not been entirely solved, though Slater (15) has recently offered an explanation which seems to be very much like that given here, except that it is developed in terms of the Slater model of metals. The magnetic behavior of alloys of nickel with copper and zinc has long been explained by assuming that the excess atomic electrons of the copper or zinc fill the hole in nickel's atomic band. This explanation serves just as well in the present theory as in the older ones. A more unusual case is that of the alloys of nickel and aluminum. These behave like the nickel alloys with copper and zinc. It appears that the three valence electrons of aluminum are in a band which lies so much higher than the atomic band of nickel that the valence electrons of aluminum leave the valence band to fill the nickel atomic band instead.

The nickel-chromium alloys might reasonably be expected to behave like the iron-chromium alloys. In that case the number of atomic electrons would decrease with increasing chromium concentration. In the alloys with iron this leads to a decrease in atomic moment, but nickel alloys would show a very large increase in moment as chromium was added because the size of the hole in the atomic band would increase. This is not observed. Instead, the magnetization decrease as a function of electron number is almost exactly the same as that obtained by the addition of copper, which has a completely filled atomic d shell of five electrons. This suggests that the six valence electrons of chromium are in a band which, like that of aluminum, is relatively far above the atomic band of nickel (Figure 6). The five valence electrons fill the hole in the nickel band.

Since the difference in atomic numbers is so great, the order of the atomic bands is Ni+, Ni-, Cr+, Cr-, with a large space between Ni- and Cr+. The magnetic moment and Curie temperature decrease linearly and vanish, according to theory, at 8°/o chromium. The observed decreases are also linear and magnetization vanishes at 13°/o chromium.

Cobalt-chromium: The same argument seems to apply to these alloys as to nickel-chromium alloys. The bands are Co+, Co-, Cr+, Cr-. The calculated vanishing point for ferromagnetic behavior is at 20°/o chromium; the experimental value is 25°/o. There is a phase change at about 10°/o chromium which introduces a discontinuity in the Curie temperature. It is not possible to make calculations for the ε phase which forms above this point. The extrapolation of the γ phase Curie temperatures gives a vanishing point at about 20°/o chromium, as found in the calculation.

Iron-vanadium (Table 8). In view of the behavior of cobalt-chromium alloys, it seems likely that the arrangement of atomic bands in iron-vanadium alloys would be similar. The order Fe+, Fe-, V+, V-, is accordingly used. In analogy with cobalt-chromium the vanadium valence band is situated above the iron valence band and the vanadium electrons fill the iron atomic bands. The Curie temperature and magnetic moment of this system both rise upon the addition of vanadium because the Fe+ band must first be completely filled before the Fe- band can begin to be filled. The predicted maximum in the Curie temperature occurs at 8°/o vanadium and is actually observed at 5-1/2°/o vanadium. This rise has always been considered as an anomaly in the behavior of alloys.

The accompanying predicted rise in magnetic moment is not reported, but the magnetic moment data (29) have been "corrected" to account for carbon impurities which apparently affect the magnetic moment rather seriously, though leaving the Curie temperature relatively unchanged. There seems to be good reason to doubt the accuracy of these corrections.

The vanishing point of ferromagnetism is predicted to be at 37°/o vanadium. There is difficulty in obtaining reliable experimental values for the vanishing point because of the carbon impurities and phase changes.

Nickel-copper (Table 9, Figure 10). Dealing with an alloy of two elements adjacent in the periodic table, it can be assumed that the valence bands are more or less superimposed, and one returns to the treatment of cobalt-nickel and similar alloys. There are 5.53 valence electrons and the arrangement of atomic bands is Cu+, Ni+, Cu-, Ni-. The only band not entirely filled is Ni-, so that as in all the other cases the non-ferromagnetic atom has no moment associated with it and one does not need to know its interaction energy with the valence electrons. The Curie temperature and magnetic moment decrease linearly both in theory and in fact. The predicted vanishing point for magnetic behavior is 53°/o copper, rather than the observed 60°/o.

Gadolinium-magnesium. This alloy presents a complicated problem. The permanent magnetic moment of gadolinium is undoubtedly to be ascribed to the seven 4f electrons, leaving three valence electrons. There are two valence electrons in magnesium. The relative positions of the atomic bands are not easily determined. So long as comparisons are made between 3d bands one may be fairly certain that those belonging to an element of higher atomic number lie lower. This is not true of a comparison between bands composed respectively of 4f and 3d orbitals. In such a case it is entirely possible for the arrangement to be Gd+, Mg+, Gd-, Mg-. If this is so, the magnetic properties are entirely due to the Gd+ band, which remains completely filled as the amount of magnesium increases, though of course the number of levels in the band decreases. This behavior is accidental, arising because the 4f shell in gadolinium is half filled.

For this reason the behavior of the system is describable in terms of the simple theory which fails for all the other alloys. In that approach the interaction energy of magnesium is zero, and the interaction energy of the alloy is therefore the interaction energy of gadolinium multiplied by its per cent concentration. Exactly the same result is predicted by means of the more complicated model simply because the filling of Gd bands never changes. That is the assumption, in fact, which ruins the simple theory in all of the other alloys.

The equimolar alloy of gadolinium and magnesium is predicted on this basis to have a Curie temperature of 124° and a magnetic moment of 3.58 (uncorrected for gyromagnetic ratio). The observed Curie point is 103° (30). The mixture of composition Gd_9Mg is predicted to have a Curie point at 254° and a magnetic moment of 6.37. Gaume-Mahn (30) found a Curie temperature of

267° for an alloy which she estimated to have the composition Gd_9Mg. Pauling has pointed out (31) that this value is actually consistent with the composition $Gd_{12}Mg$, which would have a predicted magnetic moment of 6.55. It is difficult to tell whether these computations should be trusted to have such high accuracy. At low concentrations of magnesium the method should be fairly accurate, just as it is for the other alloys, since Pauling chose the interaction energy of gadolinium to give the proper Curie temperature. Nonetheless it is hazardous to draw conclusions until further information is available to determine the arrangement of atomic bands. In particular the experimental magnetic moments should be determined.

The model introduced in the preceding pages seems to describe the general form of behavior of magnetic alloys reasonably well. It is more than an *ad hoc* model, for it arises as a logical consequence of the original postulates of Pauling and introduces nothing which is not fairly well established with regard to band behavior, though no doubt the picture is oversimplified.

It is observed that over a large range of alloy compositions (though by no means for all compositions) the predicted magnetic moments of the various kinds of atoms remain fairly constant. Iron has a moment of about 2.5 in many of the alloys, nickel exhibits a moment of 0.4 to 0.6, and cobalt has a moment in the neighborhood of 1.5. This seems to agree with the unpublished results of recent experiments at the Oak Ridge and Brookhaven National Laboratories reported by Slater (15).

One can now critically examine Taglang's studies of the magnetic moments of isoelectronic sequences. For example, Taglang adds cobalt to an equimolar mixture of iron and nickel. The reason for the depression of the Curie point in the iron-nickel binary alloy has been given. The magnetic moment is slightly depressed for the same reason, namely, that the effective interaction energy is lower for a mixture of iron and nickel than for pure cobalt. The effect upon the Curie temperature is profound, but the effect upon the saturation moment is small because the atomic moment is essentially unchanged and only the contribution from uncoupled valence electrons is altered.

Taglang plots the magnetic moment against the Curie temperature for this sequence, finds a linear dependence and extrapolates to $T_c = 0$, thus obtaining a residual magnetic moment which is to be identified with the quantity M_S in the Pauling theory. This treatment rests on the assumption that the equation for the dependence of T_c on M_S is

$$T_c = aM_V = a(M - M_s).$$

M_S is a constant and therefore if one plots the total moment M against T_c the point at which T_c vanishes is that at which $M = M_S$. Unfortunately this equation is incorrect. Speaking very generally, T_c is proportional to the number of valence electrons uncoupled and also to the interaction energy. But M_V is directly proportional to the interaction energy, and therefore T_c is proportional to the square of M_V. Of course, when M_V is large the dependence will look linear over a small range of variation of M_V, but Taglang's extrapolation to zero over such large distances is likely to be somewhat in error. The quadratic dependence will certainly result in an answer smaller than Taglang's, both for the moments to be associated with individual isoelectronic sequences and for the electron number at which ferromagnetism vanishes. Taglang's residual moment for the cobalt isoelectronic sequence is 1.57. It is not at all unlikely that the correct extrapolation would give the answer 1.53 which is deduced from the calculations of this chapter.

Table 3

Cobalt-Nickel

^{o}/o Ni	M_∞(Calc.)	M_∞(Obs.)	T_c(Calc.)	T_c(Obs.)
10	1.59	1.61	1340° K.	1350° K.
20	1.48	1.52	1270	1300
30	1.37	1.42	1190	1240
40	1.26	1.32	1138	1180
50	1.14	1.20	1060	1120
60	1.05	1.09	985	1040
70	0.92	0.98	900	950
80	1.81	0.86	864	870
90	0.71	0.73	726	770

Table 4

Iron-Cobalt

^{o}/o Co	M_∞ (No Overlap)	M_∞(Obs.)	T_c (No Overlap)	T_c(Final)	T_c(Obs.)
10	2.38	2.34	1320° K.	1235° K.	1150° K.
20	Phase transition				
30	2.71	2.46	1780	1530	1300
40	2.61	2.46	1790	1620	1363
50	2.45	2.40	1700	1630	1400
60	2.30	2.30	1660	1660	1410
70	2.15	2.17	1560	1560	1340
80	Phase transition				
95	1.76	1.80	1390	1390	1370

Table 5

Iron-Nickel

°/o Ni	M_∞(Calc.)	M_∞(Obs.)	T_c(Calc.)	T_c(Obs.)
50	1.65*	1.65	960° K.	835° K.
60	1.46	1.50	960	870
70	1.24	1.30	875	870
80	1.03	1.07	800	845
90	0.82	0.85	745	760

*The composition 50°/o iron-50°/o nickel is the only one requiring introduction of overlap. (See text.)

Table 6

Iron-Chromium

°/o Cr	M_∞(Calc.)	M_∞(Obs.)	T_c (Calc.)	T_c (Obs.)
2	2.17	2.12	1030° K.	1050° K.
5	2.10	2.05	1010	1040
10	2.00	1.90	960	990
20	1.78	1.65	851	910
50	1.11	0.90	535	550
60	0.88	0.65	431	430
80	0.45	--	218	73

Table 7

Nickel-Chromium

°/o Cr	M_∞(Calc.)	M_∞(Obs.)	T_c(Calc.)	T_c (Obs.)
2	0.47	--	480° K.	510° K.
4	0.30		310	430
8	0.00		--	--

Table 8

Iron-Vanadium

°/o V	M_∞(Calc.)	T_c(Calc.)	T_c (Obs.)
2	2.28	1110° K.	1060° K.
5	2.37	1210	1090
7	2.42	1260	1060
10	2.33	1200	--
20	1.45	620	--

Table 9

Nickel-Copper

°/o Cu	M_∞(Calc.)	M_∞(Obs.)	T_c(Calc.)	T_c(Obs.)
10	0.49	0.50	516° K.	510° K.
20	0.37	0.38	394	390
30	0.26	0.28	274	310
40	0.15	0.20	155	215

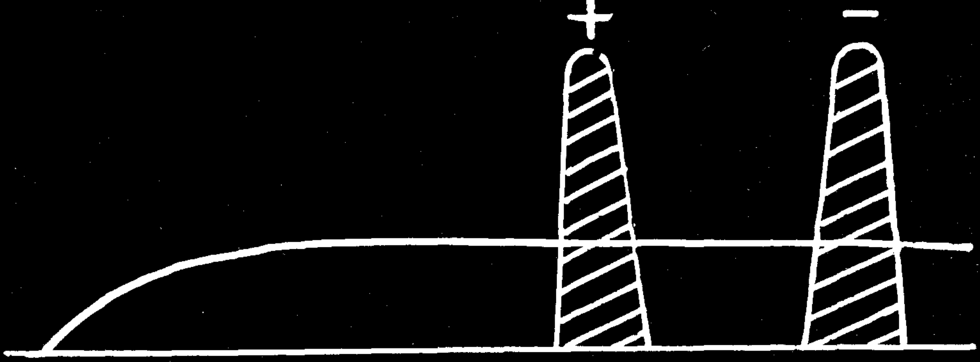


Figure 4

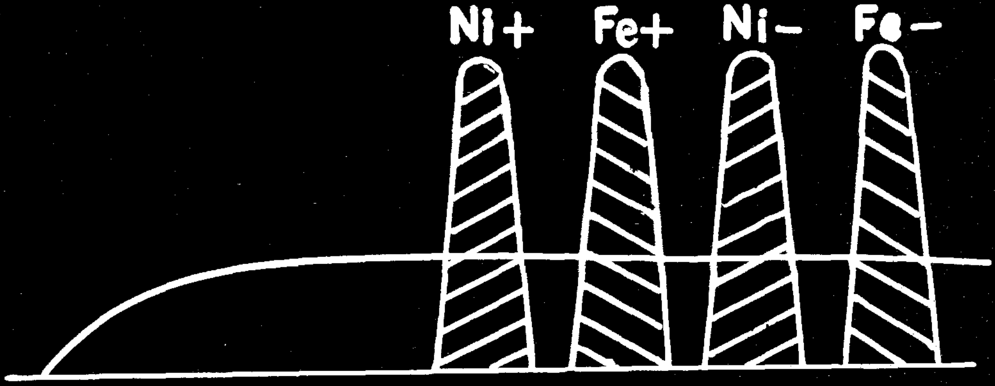


Figure 5

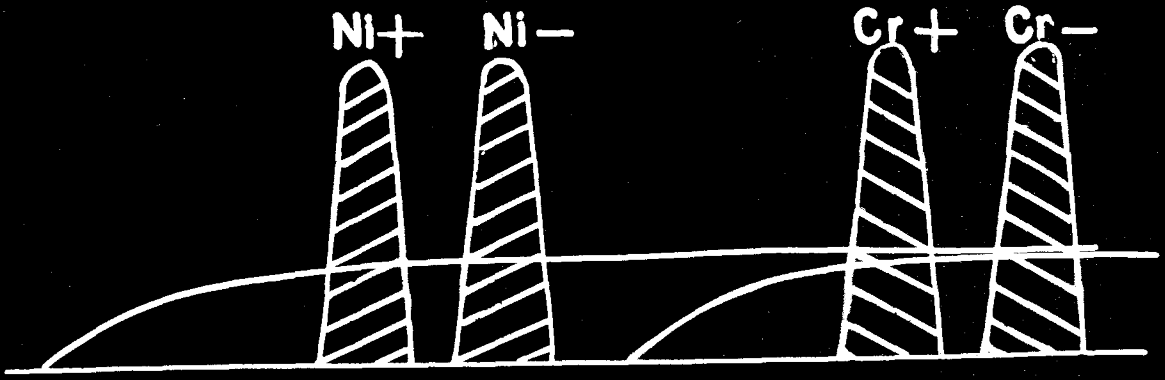


Figure 6

Figure 7

COBALT - NICKEL

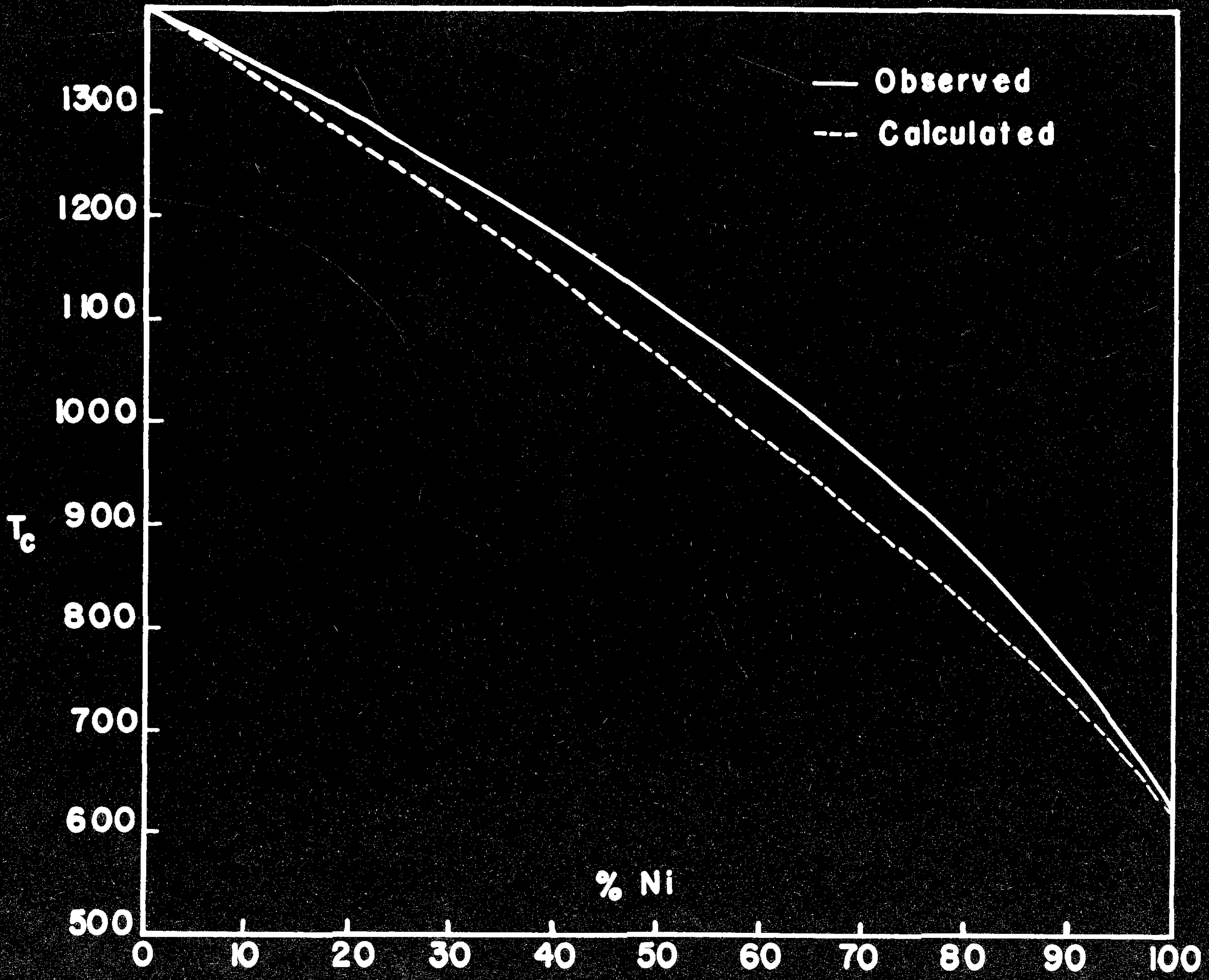
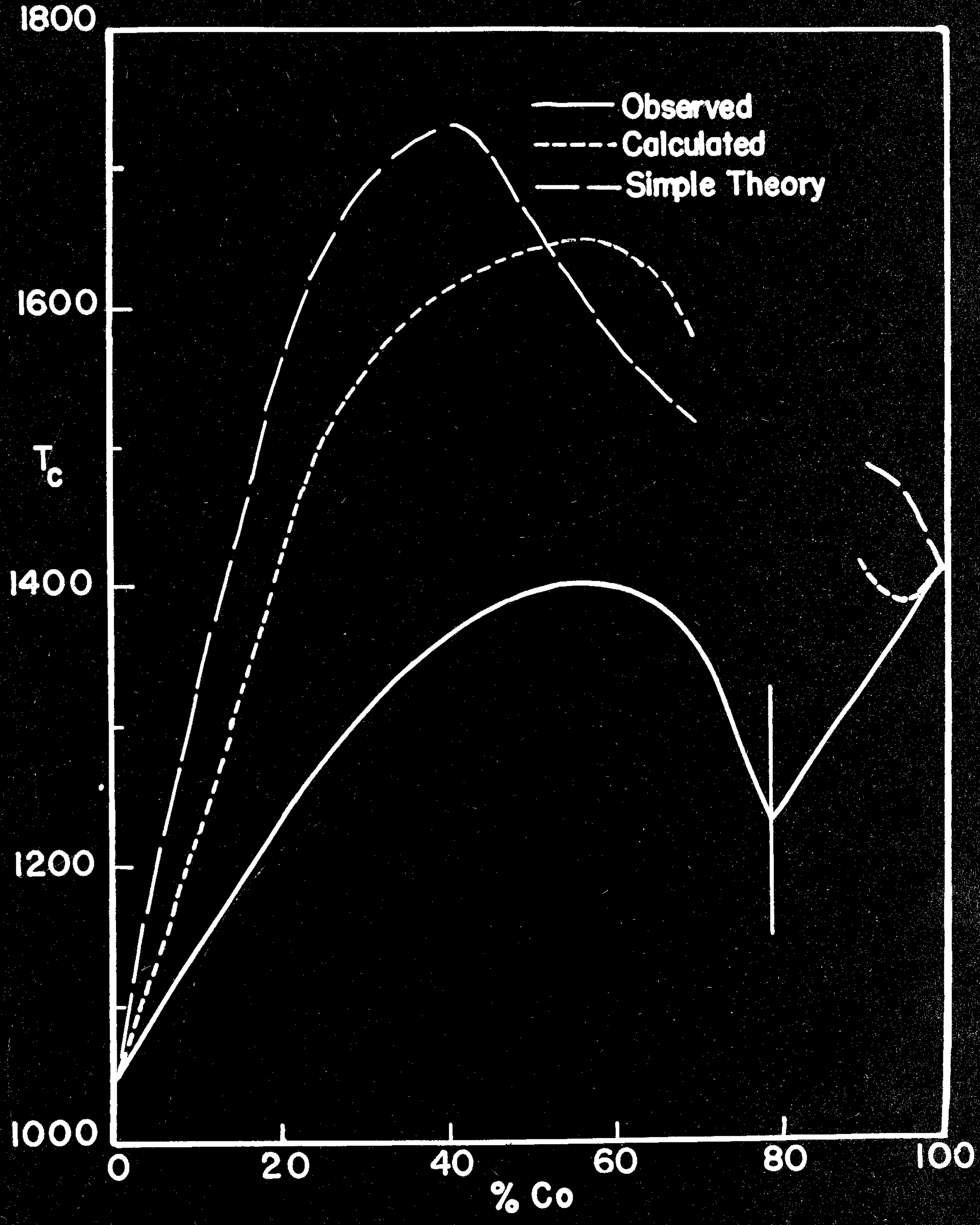


Figure 8

IRON-COBALT



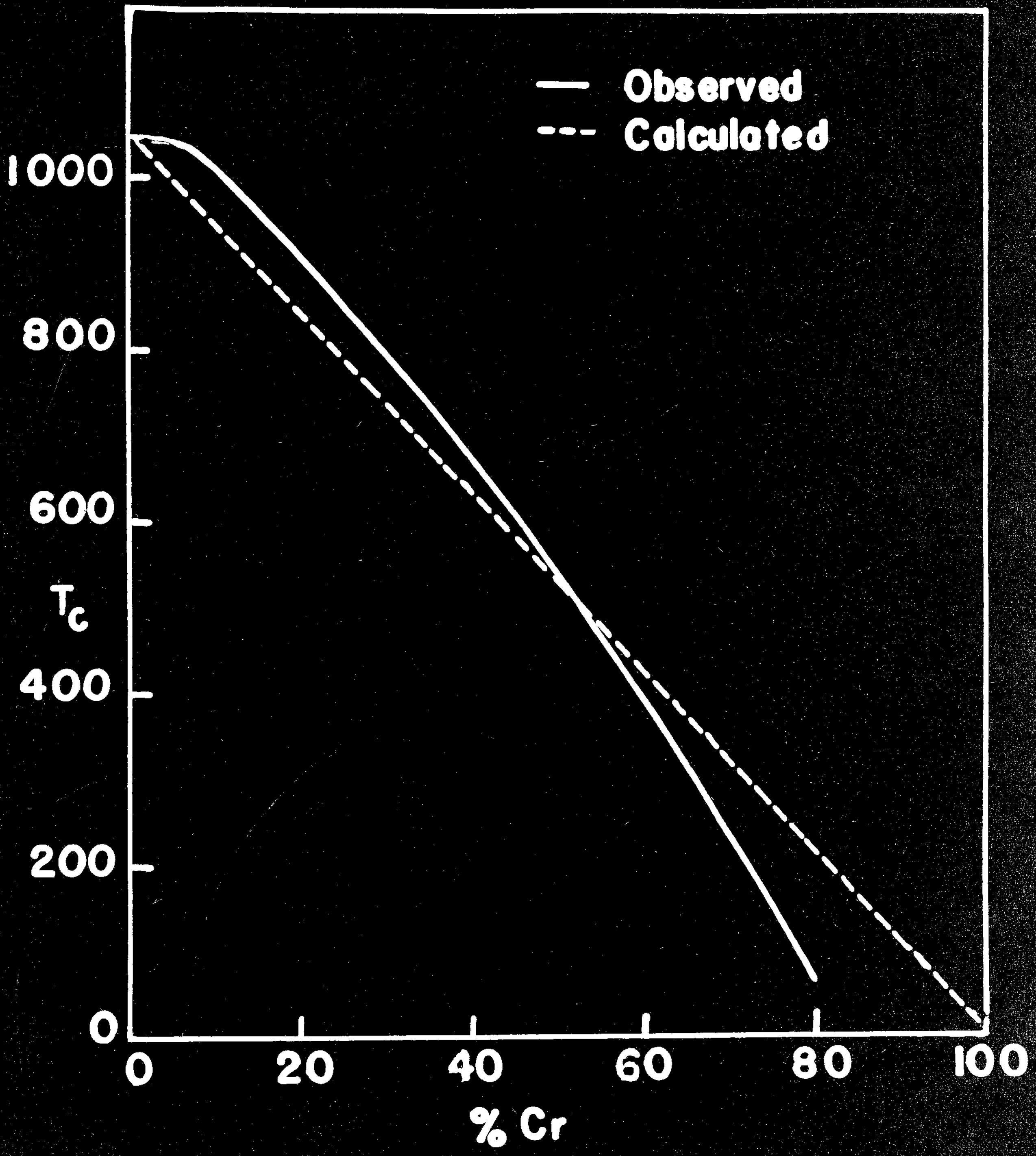
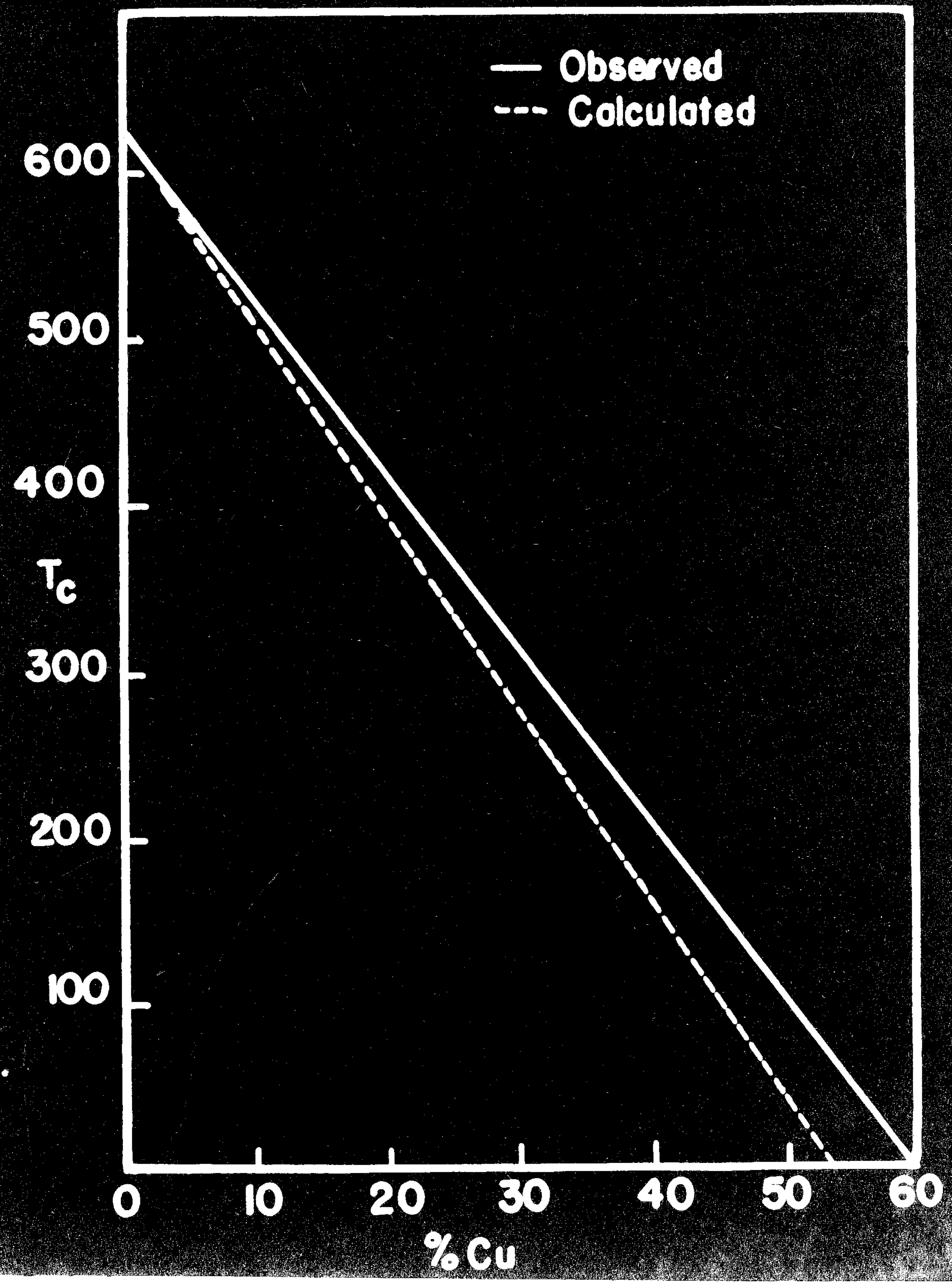


Figure 9

IRON - CHROMIUM

Figure 10

NICKEL-COPPER



IV. THE EFFECTS OF INHOMOGENEOUS ELECTRON DISTRIBUTION

In his paper on ferromagnetism Pauling suggested that his theory might be refined by a consideration of the non-uniform probability distribution of electrons in crystals of ferromagnetic substances. In the simple theory it is implied that the conduction electrons spend equal amounts of time in all parts of the crystal. This is a bad assumption, because a conduction electron with a given direction of spin spends a greater amount of time in regions where its spin is aligned parallel with the spin of the neighboring atomic electrons than in regions where the spin is aligned anti-parallel. This chapter describes a method of modifying the Pauling theory to take into account the non-uniform electron density.

One of the major advantages of the simple theory of ferromagnetism is the ease of calculation of the partition function for the crystal. Since the electron density is assumed to be uniform each atomic moment may be considered to be interacting with the Weiss field independently of the other atomic moments. If the idea of uniform electron distribution is abandoned the simple form of the partition function discussed in the preceding chapter must, strictly speaking, also be abandoned. The density of conduction electrons in a given small region of the crystal depends upon the degree of alignment of atomic spins in that region. The extent of further alignment depends upon the density of conduction electrons. Consequently, further alignment will tend to occur in regions where the existing amount of alignment is greater. The atomic spins are no longer independent, and the partition function must describe the crystal as one large system, rather than as N_T independent ones.

In order to make the calculation feasible it is assumed that the local interactions are small, and that a single value of M_V is sufficient to describe the energy of the entire crystal. The quantity M_V takes into account the changed uncoupling effect of the unequal distribution of valence electrons, but averages this effect over the entire crystal. The partition function has the same form under these restrictions as it does in the simple theory.

Calculation of M_V

The case in which the atomic moment is 1 will be considered first. It is assumed that the probability of finding a conduction electron with spin + 1/2 in the neighborhood of a given atom is R_1 times greater if the atom has atomic spin component $S_z = 0$ than if it has $S_z = -1$, and R_2 times greater if the atom has $S_z = +1$ than if it has $S_z = -1$.

If the number of atoms with $S_z = 1$ is called N_U, the number with $S_z = 0$ is called N_0, and the number with $S_z = -1$ is called N_D, then the conduction electrons with spin + 1/2 are stabilized by an amount of energy proportional to

$$\frac{R_2 N_U - N_D}{R_2 N_U + R_1 N_0 + N_D}$$

Electrons with spin - 1/2 have a greater probability density in the neighborhood of atoms with $S_z = -1$ and a smaller probability density in the neighborhood of atoms with $S_z = +1$. The value of M_V is assumed to be proportional as in the simpler theory to the difference between the two oppositely displaced energy curves for the conduction electrons of spin + 1/2 and - 1/2.

$$M_V = \frac{\alpha}{2}\left\{\frac{R_2 N_U - N_D}{R_2 N_U + R_1 N_0 + N_D} + \frac{N_U - R_2 N_D}{N_U + R_1 N_0 + R_2 N_D}\right\} \qquad (1)$$

The expression is symmetric with respect to interchange of N_U and N_D. It reduces to the simple form of the earlier theory when $R_1 = R_2 = 1$. M_V is then proportional to M_S, the net magnetic moment component per atom in the z direction:

$$M_S \equiv \frac{2(N_U - N_D)}{N_T} ;$$

$$M_V = \frac{\alpha}{2} M_S \qquad \text{when} \quad R_1 = R_2 = 1.$$

The partition function provides one relationship between M_V and M_S. A second expression is necessary in order to fix M_V and M_S as a function of temperature. The quantity M_S is a single-valued function of M_V in the simpler theory. If Equation (1) is restated in terms of M_S, it is found that this is no longer true. Instead the equation has the form

$$M_V'\left\{R_1^2 N_0^2 + R_2(N_T - N_0)^2 + R_1(R_2+1) N_0 (N_T - N_0) + \frac{(R_2-1)^2}{4}(N_T - N_0)^2\right\}$$
$$= M_V' \frac{(R_2-1)^2}{4} N_T^2 M_S^2 + M_S\left\{R_1 N_0 N_T (R_2+1) + 2 R_2 N_T (N_T - N_0)\right\}$$

where $M_V' = \frac{M_{S\infty}}{M_{V\infty}} M_V$.

The quadratic equation in M_s may be solved for M_s, giving

$$M_s = \frac{-R_1 N_0 N_T (R_2+1) - 2 R_2 N_T (N_T - N_0) \pm \sqrt{\begin{aligned}&[R_1 N_0 N_T (R_2+1) + 2 R_2 N_T (N_T - N_0)]^2 \\ &+ M_V'^2 (R_2-1)^2 N_T^2 [R_1^2 N_0^2 + R_1 (R_2+1) N_0 (N_T - N_0) \\ &\qquad + \frac{(R_2-1)^2}{4} (N_T - N_0)^2 + R_2 (N_T - N_0)^2]\end{aligned}}}{\frac{M_V'}{2} N_T^2 (R_2-1)^2}$$

If M_V is small this can be expanded to give

$$M_s = \frac{\frac{2}{M_V'} \cdot \frac{M_V'^2}{2} \left\{ R_1^2 N_0^2 + R_1 [R_2+1] N_0 [N_T - N_0] + \left[\frac{(R_2-1)^2}{4} + R_2 \right] [N_T - N_0]^2 \right\}}{R_1 (R_2+1) N_0 N_T + 2 R_2 N_T (N_T - N_0)}$$

It is now possible to expand the denominator in terms of powers of $\frac{N_O}{N_T}$. It was found necessary to retain terms of the second power. This gives the equation

$$M_s = \frac{M_V'}{2 R_2 N_T^2} \left\{ R_1^2 N_0^2 + R_1 (R_2+1) N_0 (N_T - N_0) + \left[\frac{(R_2-1)^2}{4} + R_2 \right] [N_T - N_0]^2 \right\}$$
$$\times \left\{ 1 - \frac{[R_1 (R_2+1) - 2 R_2]}{2 R_2} \frac{N_0}{N_T} + \left[\frac{R_1 (R_2+1) - 2 R_2}{2 R_2} \right]^2 \frac{N_0^2}{N_T^2} - \dots \right\}$$

which can be written in the form

$$M_s = \frac{M_v'}{N_T^4}\left\{c_1 N_T^4 + c_2 N_0 N_T^3 + c_3 N_0^2 N_T^2 + c_4 N_0^3 N_T + c_5 N_0^4\right\}$$

where

$$c_1 = 4R_2^2\left[\frac{(R_2-1)^2}{4} + R_2\right]$$

$$\begin{aligned} c_2 = {} & 4R_2^2\left\{R_1(R_2+1) - 2\left[\frac{(R_2-1)^2}{4} + R_2\right]\right\} \\ & -2R_2\left\{R_1(R_2+1) - 2R_2\right\}\left\{\frac{(R_2-1)^2}{4} + R_2\right\} \end{aligned}$$

$$\begin{aligned} c_3 = {} & 4R_2^2\left[R_1^2 + \frac{(R_2-1)^2}{4} + R_2 - R_1(R_2+1)\right] \\ & -2R_2\left[R_1(R_2+1) - 2R_2\right]\left[R_1(R_2+1) - 2R_2 - \frac{(R_2-1)^2}{2}\right] \\ & +\left[\frac{(R_2-1)^2}{4} + R_2\right]\left[R_1(R_2+1) - 2R_2\right]^2 \end{aligned}$$

$$\begin{aligned} c_4 = {} & \left[R_1(R_2+1) - 2R_2\right]^2\left[R_1R_2 + R_1 - \frac{(R_2-1)^2}{2} - 2R_2\right] \\ & -\left[R_1^2 + \frac{(R_2-1)^2}{4} + R_2 - R_1(R_2+1)\right]\left[2R_2\right] \\ & \times\left[R_1(R_2+1) - 2R_2\right] \end{aligned}$$

$$\begin{aligned} c_5 = {} & \left[R_1(R_2+1) - 2R_2\right]^2\left[R_1^2 + \frac{(R_2-1)^2}{4}\right. \\ & \left. + R_2 - R_1(R_2+1)\right] \end{aligned}$$

In order to provide a single-valued relationship between M_V and M_S an average value of M_S must now be calculated for each value of M_V. When the power series expansion of M_S is valid the equation is

$$\overline{M}_s = \frac{M_V}{N_T^4}\left[c_1 N_T^4 + c_2 N_T^3 \overline{N_0} + c_3 N_T^2 \overline{N_0^2} + c_4 N_T \overline{N_0^3} + c_5 \overline{N_0^4}\right]$$

With the values of R_1 and R_2 which are used in these equations, $\frac{d^2\overline{M}_s}{dM_V^2}$ is a positive quantity in regions near the origin. Hence the criterion for the Curie temperature is that the slope of the curve $\frac{\overline{M}_s}{M_{s\infty}}$ must be equal to that of the Brillouin function at the origin. This is a necessary condition, since if the slope is smaller there is bound to be an intersection of the two curves at some point other than the origin and some magnetization will be predicted. The condition is also sufficient because the positive second derivative ensures that if there is no intersection at the origin there will be no intersection elsewhere in the approximately straightline region of the Brillouin curve. Since the Brillouin function undergoes a sharp decrease in slope as the argument increases there is no danger of an intersection anywhere, and no non-trivial solution exists. The criterion for the Curie temperature is therefore given by the limiting slope

$$\frac{1}{M_{s\infty}}\left[\frac{d\overline{M}_s}{dM_V}\right]_{M_V=0} = \frac{1}{N_T^4 M_{s\infty}}\Big[c_1 N_T^4 + c_2 N_T^3 \overline{N_0} + c_3 N_T^2 \overline{N_0^2} + c_4 N_T \overline{N_0^3} + c_5 \overline{N_0^4}\Big]_{M_V=0}$$

In order to evaluate this derivative it is necessary to determine the average values of the powers of N_O at $M_V = 0$. In iron all values of N_O from 0 to N_T are consistent with $M_V = M_S = 0$. The only restriction is that $N_U - N_D = 0$. Since the energy of all states with $M_V = 0$ is the same it is sufficient to consider the degeneracy associated with a given value of N_O. The degeneracy is given by

$$\omega(N_o) = \frac{N_T\,!}{(N_o\,!)\left(\frac{N_T - N_o}{2}\,!\right)^2},$$

Therefore we obtain

$$\overline{N_o} = \frac{\sum\limits_{N_o=0}^{N_T} N_o\,\omega(N_o)}{\sum\limits_{N_o=0}^{N_T} \omega(N_o)}.$$

To evaluate $\overline{N}_O$ the sums are approximated by integrals and the factorial function is replaced by Stirling's formula, giving

$$\overline{N_o} = \frac{\int \frac{N_o\;dN_o}{N_o^{N_o}\left(\frac{N_T-N_o}{2}\right)^{N_T-N_o}}}{\int \frac{dN_o}{N_o^{N_o}\left(\frac{N_T-N_o}{2}\right)^{N_T-N_o}}}.$$

The limits of the integrals will depend upon the substance being considered. In the case of iron at the Curie temperature the limits are 0 and N_T. In the case of nickel the lower limit is 0.715 N_T and the upper limit is N_T. The customary method (10) of evaluating integrals of this sort involves writing the integrals as

$$\int e^{f(x)}dx.$$

If f(x) has a sharp maximum at x_o it is then possible to expand f(x) about x_o and retain only the first two non-vanishing terms in the expansion. Since the maximum is a sharp one the limits of the integration may be taken as $-\infty$ and $+\infty$ and the integral becomes

$$e^{f(x_0)}\int_{-\infty}^{\infty} e^{\frac{1}{2}f''(x_0)(x-x_0)^2}\,dx\,.$$

In the case of iron this method works quite well, but there is some question in the case of nickel concerning the validity of the use of the Gaussian approximation to the integral. Another method has therefore been devised for the evaluation of the integrals which depends upon somewhat different approximations and does not require alteration of the limits of integration.

The case of iron will be considered first. The function $\overline{N}_O$ may be written as

$$\overline{N}_0 = \frac{\int_0^{N_T} e^{g(N_0)}\,dN_0}{\int_0^{N_T} e^{f(N_0)}\,dN_0}$$

where

$$g(N_0) = (1-N_0)\ln N_0 + (N_0-N_T)\ln\left(\frac{N_T-N_0}{2}\right)$$

$$f(N_0) = -N_0\ln N_0 + (N_0-N_T)\ln\left(\frac{N_T-N_0}{2}\right)$$

In the same manner as described above for Van Vleck's method $g(N_O)$ and $f(N_O)$ are expanded about their respective maxima, giving the equation

$$g(N_0) = g(N_0^*) + \frac{g''(N_0^*)}{2}(N_0-N_0^*)^2 + \frac{g'''(N_0^*)}{6}(N_0-N_0^*)^3 + \ldots$$

and an analogous equation for $f(N_O)$.

The maxima of $g(N_O)$ and $f(N_O)$ must now be found. Taking the first derivatives one obtains the equations

$$g'(N_o) = \frac{1}{N_o} + \ln\left(\frac{N_T - N_o}{2N_o}\right)$$

$$f'(N_o) = \ln\left(\frac{N_T - N_o}{2N_o}\right)$$

The maximum of $f(N_O)$ therefore occurs at $N_O^* = N_T/3$. It is clear that the term $1/N_O$ in the expression for $g'(N_O)$ may be neglected in the neighborhood of the maximum, and $g'(N_O^*)$ is identical with $f'(N_O^*)$. Similarly it is found that

$$g''(N_o^*) = -\frac{1}{(N_o^*)^2} - \frac{1}{N_T - N_o^*} - \frac{1}{N_o^*}$$

$$f''(N_o^*) = -\frac{1}{N_T - N_o^*} - \frac{1}{N_o^*}$$

$$g'''(N_o^*) = \frac{2}{(N_o^*)^3} - \frac{1}{(N_T - N_o^*)^2} + \frac{1}{(N_o^*)^2}$$

$$f'''(N_o^*) = -\frac{1}{(N_T - N_o^*)^2} + \frac{1}{(N_o^*)^2}$$

In each case the difference between $g^n(N_O^*)$ and $f^n(N_O^*)$ is a number which is very small compared with either of the derivatives. Therefore all of the derivatives of $g(N_O)$ evaluated at N_O^* may be set equal to all of the derivatives of $f(N_O)$ evaluated at N_O^*. The only terms of the expansions for which this is not true are the constant terms of each. Consequently the expression for $\overline{N}_O$ may be written

$$\overline{N}_0 = \frac{e^{g(N_0^*)}\int_0^{N_T} e^{\frac{f''(N_0^*)}{2}(N_0-N_0^*)^2 + \frac{f'''(N_0^*)}{6}(N_0-N_0^*)^3 + \ldots} dN_0}{e^{f(N_0^*)}\int_0^{N_T} e^{\frac{f''(N_0^*)}{2}(N_0-N_0^*)^2 + \frac{f'''(N_0^*)}{6}(N_0-N_0^*)^3 + \ldots} dN_0}$$

$$= \frac{e^{g(N_0^*)}}{e^{f(N_0^*)}} = e^{\ln(N_0^*)}$$

$$= N_0^* = \frac{N_T}{3},$$

By similar arguments one finds that $\overline{N_O^m} \cong (N_O^*)^m$ provided that m is small compared with N_T so that the term m/N_O which appears in the first derivative of the function analogous to $g(N_O)$ is negligible.

In the case of nickel one may use exactly the same analysis except that the lower limit of the integrals is $0.715\ N_T$. The maximum for this region is at the lower limit $N_O^* = 0.715\ N_T$. The function $g(N_O)$ is decreasing in value in this region very rapidly with increasing N_O, and one finds that the above method once again gives the result that $(\overline{N_O^m}) \cong (N_O^*)^m$.

The evaluation of these average values of powers of N_O makes it possible to determine the Curie temperature provided that the values of R_1 and R_2 are known. In order to demonstrate roughly the nature of the corrections provided by this modification it may be assumed that the values of R_1 and R_2 are the same for iron as for nickel, and that R_2 is equal to R_1^2. The possible change in the predicted Curie temperature of nickel shown in Table 10 is not very great if one makes this assumption, but every choice of R_1 results in a decrease in the predicted Curie temperature of iron and an increase in that of nickel. This has also been found to be true over a very wide range of the parameters R representing considerable deviations from the restriction $R_2 = R_1^2$.

Table 10

R_1	$T_C(Fe)$	$T_C(Ni)$
1.00	1395° K.	370° K.
1.50	1281	374
1.81	1168	377
2.00	1100	378
2.16	1045	379
4.00	630	383

An examination of Equation (1) shows that one effect of making R_2 greater than 1 is to decrease the uncoupling of valence electrons. This is the predominant effect in iron, and the Curie temperature decreases. In nickel, however, the presence of large numbers of atoms with $S_z = 0$ tends to concentrate the valence electrons in the region where uncoupling is possible when R_2 is greater than R_1. In such a case, increasing R_2 will, up to a certain point, increase uncoupling, and the Curie temperature will be raised. In the following section some methods of estimating the relationships between R_1 and R_2 will be discussed.

The case of cobalt differs from those of iron and nickel in the magnitudes of the spin components involved. The components are ± 3/2 and ± 1/2, and three parameters, $R_{3/2}$, $R_{1/2}$, and $R_{-1/2}$ are required. The factor of increased probability of finding a conduction electron of spin +1/2 near an atom with spin component i is R_i. In this case

$$M_V = \frac{\alpha_{Co}}{2}\left\{\frac{3R_{3/2}N_{3/2} + R_{1/2}N_{1/2} - R_{-1/2}N_{-1/2} - 3N_{-3/2}}{R_{3/2}N_{3/2} + R_{1/2}N_{1/2} + R_{-1/2}N_{-1/2} + N_{-3/2}}\right.$$

$$\left. + \frac{3N_{3/2} + R_{-1/2}N_{1/2} - R_{1/2}N_{-1/2} - 3R_{3/2}N_{-3/2}}{N_{3/2} + R_{-1/2}N_{1/2} + R_{1/2}N_{-1/2} + R_{3/2}N_{-3/2}}\right\}$$

The procedure for finding a relationship between M_S and M_V is somewhat more complicated than that for iron and nickel. It is necessary to find average values for both $N_{1/2}$ and $N_{-1/2}$ in order to evaluate $\overline{M}_S$. It is found that the state of extremely high degeneracy at the Curie temperature is that for which $N_{1/2}$ equals $N_{-1/2}$. With this restriction the sum $(N_{1/2} + N_{-1/2})$ behaves in exactly the same manner as does N_O in the treatment of nickel.

The application of this modified theory to cobalt results in a negligible change in the Curie temperature, as might be expected from the metal's intermediate position and structure.

The saturation magnetic moment predicted for nickel and cobalt in this theory are slightly different from those given by Pauling, but the changes are not significant ones. The reason for the change is readily seen by an examination of Equation 1 . In the case of iron, if both N_D and N_O are set equal to zero one obtains the result that $M_V = \alpha$, which is exactly the same as in Pauling's simpler theory. This is to be expected because in the limiting case in which all atomic spins are aligned the increased probability density of conduction electrons about aligned atoms merely results in a homogeneous distribution of conduction electrons regardless of the values of R_1 and R_2. For nickel, however, the value of N_O at saturation is $0.715\ N_T$ and M_V has a value different from the saturation value given by Pauling. Using the value $R_1 = 2.16$ which was most suitable according to Table 1, an increase of 0.006 in the saturation moment of nickel is obtained. Cobalt shows an increase of 0.01 Bohr magnetons.

V. SOME PROBLEMS RELATED TO THE ESTIMATION OF THE PARAMETERS R_i

The use of the approximation that R_2 is equal to R_1^2 in the equations of the preceding section is not entirely satisfactory, since it is assumed that the parameters R_i are the same for iron as for nickel and that they are independent of the numbers N_U and N_D. An attempt will be made in the following pages to determine the variation of these parameters with variation of N_U and N_D and of the substance being considered.

The choice of a model for the crystalline potential is limited largely by the difficulty of solving all but the simplest problems involving periodic potentials. In the problem to be considered the potential is not strictly periodic and it will therefore be necessary to make rather drastic simplifications in order to arrive at a model for the potential for which a solution can readily be found*. It is usual to replace the periodic Coulomb potential of the atoms in a crystal by a periodic potential whose unit is a well of some attractive shape and of finite depth (21, 32). In practice it is seldom possible to use anything more complicated than a square well or a sinusoidal potential. The model chosen for this discussion will be a square well potential.

The electrons referred to in the work of Pauling as "conduction electrons" are presumably sufficiently near the tops of the

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*It is to be noted that numerous discussions have been given (25, 33) of impurities in periodic potentials. Some of these discuss the case of random impurities. These discussions always draw some rather general conclusions about the behavior of energy levels but never give the behavior of the wave functions themselves, or even solve the problem for the energy levels.

periodic potential wells to behave as nearly free electrons. It will be assumed that these conduction electrons form a discrete energy band and that the separation of this band from lower-shell bands is sufficiently great so that one may consider the filling of the conduction band as a separate problem. The potential in which the conduction electrons move is then considered to be an almost periodic square well potential, the aperiodicity being introduced by the differences in depths of the wells corresponding to the differences in stabilization energies of conduction electrons in the neighborhood of atoms with different values of the atomic spin component.

To estimate roughly the depth of these wells one might utilize the first ionization energy which is 7.90 e.v. in the case of iron, 7.86 e.v. for cobalt, and 7.63 e.v. for nickel. Since the potential is coulombic, $-1/2\,\overline{V} = \overline{T}$, so that the magnitude of the depth of the well is twice that of the ionization energy. In making calculations it was assumed that the nickel potential is 10°/o greater than the iron potential. It is only necessary to know the ratio of the potentials.

The "ideal" problem which it would be desirable to solve involves a potential which, in the cases of iron and nickel, has square wells of three different depths (Figure 11). The first of these is of depth V, the second of depth V-Q, and the third of depth V-2Q, where Q is the stabilization energy defined in Part II of this thesis, and V is the number estimated in the preceding paragraph. The solutions should then be calculated for all possible numbers of each type of well, and for all possible permutations of arrangement for these given numbers. The problem which will be solved instead is based upon rather crude approximations to these ideal potentials. The periodicity will be essentially ignored, as in the treatment of Pauling's original theory.

It is noted that the potential shown in Figure 11 may be divided into three regions. For energy levels in region III the solutions are sinusoidal in all three wells. The probability of finding an electron in well A compared with the probability of finding it in well B for the energy levels in region III will be estimated by use of the W.K.B. method. In region I this procedure is unsatisfactory because the wave function is sinusoidal in A and exponential in B and C, so that the potential is not constant over many wavelengths and there is in fact no approximate wavelength which can be assigned to the wave function in B and C. In region I the problem may be simplified by allowing the inter-well width to approach zero while the depth of the wells remains constant. In the limit the barriers between the wells may be ignored, and the problem reduces to one in which a well of depth Q and width equal to the aggregate width of wells of type A is set in the bottom of an infinite-walled box whose width is that of the aggregate of wells of both types A and B. It is assumed that for levels in region I the presence of wells of type C may be neglected, since the exponential function in well C will be small compared to that in well B. It is likely that the limiting problem in which the inter-well width is zero will exhibit in its solution the same dependence upon the number of deeper wells present as does the more complicated problem from which it was derived, provided that the periodicity of the original potential does not produce marked perturbation of the free electron levels.

The Problem of a Well in the Bottom of a Box

The potential in the problem to be solved is shown in Figure 12. The determination of eigenvalues involves the solution of a transcendental equation, and is generally accomplished by means of a graph. This method is unsatisfactory where immense numbers of levels are to be considered, so that it is necessary to develop approximate algebraic expressions for the desired quantities.

In the usual method of solution (34) the potential is divided into three regions. In the first and third of these the wave functions are exponential; in the middle region they are sinusoidal. Because of the symmetry requirements these solutions may be written immediately as

$$u_1 = A_1 e^{\mathcal{H}x} + A_2 e^{-\mathcal{H}x}$$

$$u_2 = B_1 \cos kx$$

$$u_3 = A_2 e^{\mathcal{H}x} + A_1 e^{-\mathcal{H}x}$$

where

$$\mathcal{H} = \frac{\sqrt{2m(V-E)}}{\hbar} \qquad k = \frac{\sqrt{2mE}}{\hbar}$$

The application of the usual continuity conditions for the function and its first derivative at boundaries yields the requirement that

$$\tan ka \tanh(N\mathcal{H}a) = \frac{\mathcal{H}a}{ka}$$

for symmetric solutions and that

$$-\tanh(N\mathcal{H}a)\cot ka = \frac{\mathcal{H}a}{ka}$$

for the alternating antisymmetric solutions.

In this problem the argument ($N\mathcal{H}a$) is quite large and $\tanh(N\mathcal{H}a)$ is essentially equal to one. The simplified equations

$$\tan ka = \frac{\mathcal{H}a}{ka} \qquad -\cot ka = \frac{\mathcal{H}a}{ka} \tag{1}$$

are of course the familiar conditions arising in the problem of the potential step. It is noted also that the requirement that $u_3(b)=0$ implies that $A_2/A_1 = e^{-2\mathcal{H}b}$, so that A_2 is approximately zero and may be neglected. Considering only the positive half of the potential, which is entirely sufficient because of the symmetry, one then has

$$u_2 = B_1 \cos kx \qquad u_3 = A_1 e^{-\mathcal{H}x}$$

The problem is to find the quantity P_1, the probability of finding a particle in the well for $E < Q$. This is given by

$$\frac{B_1^2 \int_0^a \cos^2 kx \, dx}{B_1^2 \int_0^a \cos^2 kx \, dx + A_1^2 \int_0^b e^{-2\mathcal{H}x} dx}$$

$$= \frac{B_1^2\left(\frac{a}{2} + \frac{1}{4k}\sin 2ka\right)}{B_1^2\left(\frac{a}{2} + \frac{1}{4k}\sin 2ka\right) - \frac{A_1^2}{2\mathcal{H}}\left(e^{-2\mathcal{H}b} - e^{-2\mathcal{H}a}\right)}$$

$$\cong \frac{\frac{a}{2} + \frac{1}{4k} \sin 2ka}{\frac{a}{2} + \frac{1}{4k} \sin 2ka + \frac{A_1^2}{B_1^2 \cdot 2\mathcal{H}} e^{-2\mathcal{H}a}}$$

Let $\xi = ka$ and $\eta = \mathcal{H}a$. At the boundary x = a, $B_1 \cos \xi = A_1 e^{-\eta}$ and therefore $\frac{A_1^2}{B_1^2} = \frac{\cos^2 \xi}{e^{-2\mathcal{H}a}}$.

Therefore

$$P_1 = \frac{\left(\frac{a}{2} + \frac{1}{4k} \sin 2\xi\right)}{\left(\frac{a}{2} + \frac{1}{4k} \sin 2\xi\right) + \frac{\cos^2 \xi}{2\mathcal{H}}}$$

Since both $\frac{1}{4k} \sin 2\xi$ and $\frac{\cos^2 \xi}{2\mathcal{H}}$ are small compared with a/2, and

$$\frac{c + \delta}{c + \delta + \epsilon} \cong \frac{c}{c + \epsilon} \qquad \text{where } \delta \text{ and } \epsilon \text{ are both} \ll c,$$

it follows that

$$P_1 \cong \frac{a}{a + \frac{\cos^2 \xi}{\mathcal{H}}} = \frac{\eta}{\eta + \cos^2 \xi}$$

It is assumed that the corresponding three-dimensional potential well is such that the three-dimensional problem is separable in Cartesian coordinates. The probability of finding a particle in a three-dimensional well is

$$P = P_x P_Y P_z = \left(\frac{a}{a + \frac{\cos^2 \xi_x}{\mathcal{H}_x}}\right)\left(\frac{a}{a + \frac{\cos^2 \xi_y}{\mathcal{H}_y}}\right)\left(\frac{a}{a + \frac{\cos^2 \xi_z}{\mathcal{H}_z}}\right)$$

The significant variable is the ratio of finding the particle in the well, per unit volume of the well, to the probability of finding it outside the well, per unit volume of the remaining part of the box:

$$R = \frac{P/a^3}{\frac{1-P}{a_m^3 - a^3}} = \frac{a_m^3 - a^3}{a^3} \; \frac{P}{1-P}$$

The quantization condition for the problem is given almost exactly by $\eta = \xi \tan \xi$. This implies that $\frac{\xi^2 + \eta^2}{\xi^2} = \frac{1}{\cos^2 \xi}$ and therefore that

$$R(E) = \frac{a_m^3 - a^3}{a^2} \sqrt{\frac{2m\,V}{\hbar^2}} \cdot \frac{1}{\frac{E_x}{\sqrt{V - E_x}} + \frac{E_y}{\sqrt{V - E_y}} + \frac{E_z}{\sqrt{V - E_z}}}$$

There are of course many values of E_x, E_y, and E_z which satisfy the requirement that $E_x + E_y + E_z = E$. Since all three directions are equivalent, $\overline{E}_x = \overline{E}_y = \overline{E}_z$ for a given value of E. As long as the three energy components deviate from $\overline{E}_x$ by an amount small compared with $V - \overline{E}_x$, the value of R(E) remains unchanged. The values of E_x, E_y, and E_z will therefore be replaced by E/3, a reasonable approximation for all but a relatively small number of states all of which occur when E is nearly equal to V. It is therefore found that

$$R(E) \cong \frac{a_m^3 - a^3}{3a^2} \sqrt{\frac{2m}{\hbar^2}} \; \frac{V(V - E')^{1/2}}{E'}$$

The density of even levels in the one-dimensional problem will now be considered. Equation (1) may be written $\eta = \xi \tan \xi$, and it is further observed that $\xi^2 + \eta^2 = \frac{2mV_0 a^2}{\hbar^2}$. A graphical solution which is often used involves plotting η against ξ , so that the correct solutions are the intersections of the function $\xi \tan \xi$ with the circle of radius $c = \sqrt{2mV_0}\frac{a}{\hbar}$. The function $\xi \tan \xi$ is of course multivalued in η , one branch of the function in the first quadrant occurring in each of the intervals $n\pi$ to $(n + 1/2)\pi$. The odd functions provide the solutions between $(n + 1/2)\pi$ and $(n+1)\pi$, and since the odd and even levels alternate it is sufficient to consider only one set in order to determine the density of all levels.

It is clear that there can be at most one intersection of each branch of the function $\xi \tan \xi$ with the circle in the first quadrant. Since branch n occurs in a specified range of ξ such that $(n + 1/2)\pi > \xi > n\pi$, it follows that the solutions must be distributed according to the same rule. There must be one even energy level for every interval of π in ξ . Furthermore, the smallest possible interval between successive even levels is $\frac{\pi}{2}$.

It is possible to calculate the density of levels in this system. Because of the large value of c, the radius of the circle, the successive solutions are closely spaced along the circle with respect to the polar angle θ. It is therefore permissible to assume that for two successive solutions the slope of the circle at both intersections is the same. The slope is $\frac{d\eta}{d\xi} = -\frac{\xi}{\eta}$. Therefore if one solution is given by the points (ξ_0, η_0) then a point in the neighborhood is given by

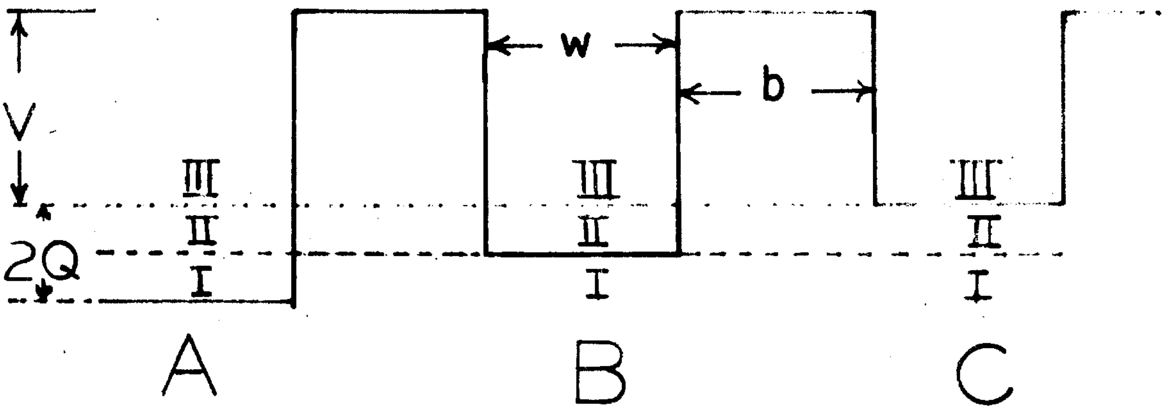

Figure 11

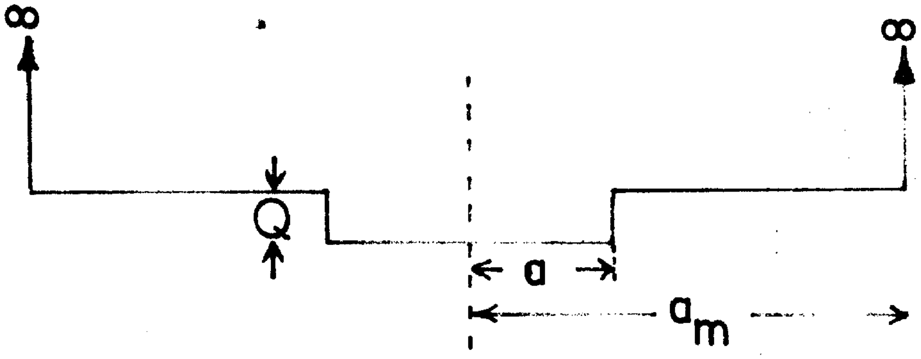

Figure 12

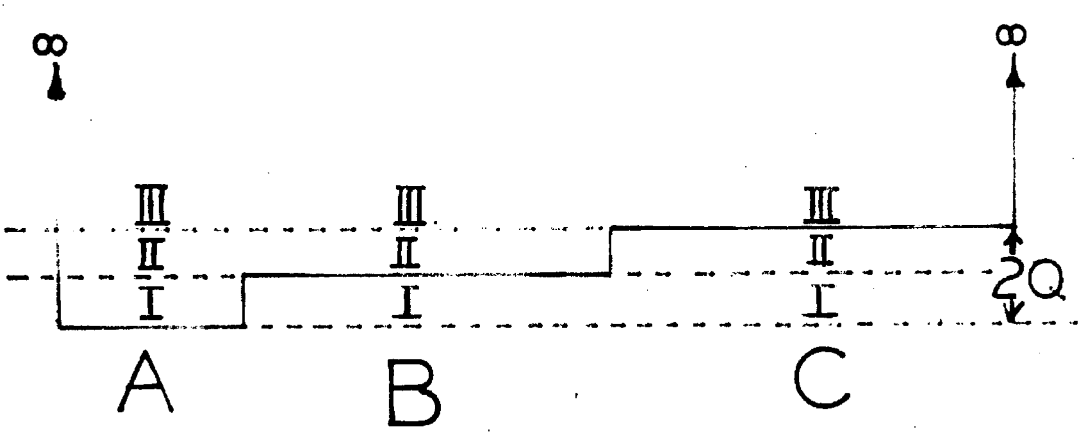

Figure 13

$$\eta = -\frac{\xi}{\eta_0}\left(\xi - \xi_0\right) + \eta$$

The function $\xi \tan \xi$ has the slope

$$\frac{d\eta}{d\xi} = \tan \xi + \xi \sec^2 \xi \quad .$$

If it is temporarily assumed that the next solution occurs at $\xi + \pi$, then the slope of this function at the next intersection will be

$$\tan\left(\xi_0 + \pi\right) + \left(\xi_0 + \pi\right) \sec^2\left(\xi_0 + \pi\right)$$

and in the neighborhood of this intersection the function is approximated by the straight line

$$\eta = \left[\tan \xi_0 + (\xi_0 + \pi) \sec^2 \xi_0\right]\left[\xi - \xi_0 - \pi\right] + \eta_0 + \pi \tan \xi_0 \quad .$$

At the point of intersection which represents the desired new solution

$$\left[\tan \xi_0 + (\xi_0 + \pi) \sec^2 \xi_0\right]\left[\xi - \xi_0 - \pi\right] + \pi \tan \xi_0$$
$$= -\frac{\xi_0}{\eta_0}\left(\xi - \xi_0\right)$$

$$\left(\xi - \xi_0\right) = \frac{\pi\left[(\xi_0 + \pi)\sec^2 \xi_0\right]}{\tan \xi_0 + (\xi_0 + \pi)\sec^2 \xi_0 + (\xi_0/\eta_0)}$$

For all but a negligible number of levels near the mouth of the well $\xi_0 \sec^2 \xi_0 \gg \frac{\xi_0}{\eta_0}$, so that one obtains

$$\xi = \xi_0 + \frac{\pi(\xi_0+\pi)\sec^2\xi_0}{\tan\xi_0+(\xi_0+\pi)\sec^2\xi_0}\left\{1 - \frac{\xi_0}{\eta_0\left[\tan\xi_0+(\xi_0+\pi)\sec^2\xi_0\right]}\right\}$$

Since $\xi_0 \gg \pi$ for all but a small number of levels at the bottom of the well the term $(\xi_0+\pi)$ may be replaced by ξ_0. Since $\sec^2\xi_0 = 1+\tan^2\xi_0$ it is also permissible to neglect the term $\tan\xi_0$ in the denominator. If one now takes into account the odd levels, one of which may be assumed to be half way between each of the even levels, one obtains the final expression

$$\xi_{n+1} - \xi_n \cong \frac{\pi}{2}\left[1 - \frac{1}{\eta_n \sec^2\xi_n}\right]$$

The assumption used to obtain this result, that $\xi_{n+2} - \xi_n \cong \pi$, is seen to lead to a consistent answer.

It is concluded from this analysis that the infinite-well density function, in which the spacing is exactly $\frac{\pi}{2}$ in ξ, is entirely adequate for the description of the density of levels in the finite well.

The potential for the ferromagnetic crystal is based upon that of the preceding calculation and takes the form shown in Figure 13. In region III, containing about 97°/o of the levels, it is permissible to use the WKB approximation. In region I the dependence of R upon a has already been determined. In region II it is necessary to combine the approximations used in regions I and III. First, wells of types A and B are grouped together and compared with wells of type C, in which the solutions are exponential, using the method previously applied to region I. The inequality in probability density in well A compared with well B, which has relatively little effect upon the result, can be estimated by use of the WKB approximation.

It is not easy to decide on an adequate averaging process for R. Electrons in lower levels with large values of R probably have a more profound effect upon atomic alignment than their relatively small numbers would suggest, because of the production of very large "local" Weiss fields in the neighborhood of these electrons. The use of an average value of M_V does not permit a direct description of this effect, but it may be possible to take some account of the influence of electrons in levels having high values of R by using the quantity $\overline{R}$ in the equations relating M_V and M_S:

$$\overline{R} = \frac{\int_0^Q R(E)\rho(E)\,dE + 3N_T \cdot 0.97}{3N_T} = \beta Q^2 a(a_m^3 - a^3) + 0.97$$

$$\rho(E) = \frac{16\pi a^3}{h^3}(2m)^{3/2}E^{1/2} \tag{2}$$

The number 0.97 arises from the electrons in levels of region III. No attempt is made to obtain a value of $\overline{R}$ from this equation. Instead the single parameter β is fixed and assumed to remain constant for all of the elements. All that can be said in defense of this assumption is that β does not contain terms which are dependent upon a, a_m, or Q. The fact that the completely determined constant which has been replaced by the parameter β is not of the right order of magnitude to give reasonable values of $\overline{R}$ is not surprising considering the change involved in transforming the potential of Figure 11 to that of Figure 13. One can only hope that the original assumption involved in that transformation is correct, namely, that the functional dependence of R upon a is preserved. If appropriate values of Q, a_m and a are inserted, all of the R_i are determined once β is chosen. Table 11 lists the values of these quantities which were used. The well width w is taken as the cube root of the effective atomic volume at the Curie temperature. R_1 is calculated by using the total width of wells of types A and B as the value of a, and the total width of wells of all three types for a_m. R_2 is calculated using the total width of wells of type A as the value of a, and the total width of wells of types A and B for a_m. The true value of R_2 is calculated by multiplying the result of the latter calculation by the value of R_1 previously calculated, since what has been calculated here is the ratio of the probability of finding a particle in well A compared with that for finding it in B, while R_2 was originally defined as the ratio of A relative to C.

The extension to the case of cobalt involves the use of wells of four different depths. Consequently there are two regions analogous to region II of Figure 13 in which weighting factors like that of Equation (2) must be applied. The same value for β is assumed for cobalt as for the other elements, and three numbers, $R_{3/2}$, $R_{1/2}$ and $R_{-1/2}$, are calculated.

Many values of β were inserted in Equation (2) in order to observe the variation in the predicted Curie temperatures. Some values of R_1 and R_2 for iron and nickel and the corresponding Curie temperatures predicted are shown in Table 11. As in the earlier results with the assumption that $R_2 = R_1^2$, the predicted Curie temperature of iron changes rapidly relative to that of nickel. When the predicted Curie temperature of iron is set at 1080° K the Curie temperature of nickel is predicted to be 457° K and that of cobalt is predicted to be 1271° K. These are of course improvements both upon the results of the simple Pauling theory and the results of Chapter II, but it is difficult to tell whether the effect is actually large enough to account for the necessary correction.

Table 11a

	R_1		R_2	
	$a_m \times 10^8 N_T^{-1/3}$	a	$a_m \times 10^8 N_T^{-1/3}$	a
Fe	2.27	0.874 a_m	1.99	0.794 a_m
Ni	2.25	0.950 a_m	2.14	0.550 a_m

Table 11b

$Q^2(\mathrm{Fe}) \times 10^{-31} N_T^{4/3}$	$R_{1_{Fe}}$	$R_{2_{Fe}}$	$R_{1_{Ni}}$	$R_{2_{Ni}}$
2.96	2.50	7.51	1.98	8.92
2.43	2.05	5.11	1.70	6.17
2.24	1.89	4.37	1.60	5.30

Table 11c

$Q^2(\mathrm{Fe}) \times 10^{-31} N_T^{4/3}$	T_c(Fe)	T_c(Ni)
2.96	1330° K.	469° K.
2.43	1130	457
2.24	1080	457

VI. CONCLUSION

The conclusion to be drawn from the preceding discussion, especially that of Part III, is that the Pauling model of metals and the Zener theory of ferromagnetism are, when properly combined and modified, reasonably adequate descriptions of ferromagnetic behavior. It seems unlikely that such a large amount of experimental evidence could be even qualitatively explained by the Pauling theory if it were not nearly correct. The problem of the Curie temperatures of the alloys is by no means solved, but it seems certain that this model is a step in the right direction.

The question arises as to the way in which the differences between the Pauling model and that of Slater, Stoner and other physicists can be reconciled. Slater himself (15) has recently pointed out that there is a sharp dip in density in the middle of his "atomic" d band and that this separates the d band into an upper and a lower part which may be identified respectively with the atomic and valence d orbitals of Pauling. One must also reexamine the concept of "valence electron" which has perhaps been a little more inflexible than necessary.

When identical atoms are brought together to form a crystal it is supposed by physicists and chemists alike that there is a narrow relatively unperturbed atomic band and a widened valence band which is formed from the strongly overlapping bonding orbitals of the atoms. All that is actually required of a "valence level" is that it be energetically more stable than the isolated atomic wave function from which it was formed. It is not essential that electrons in these levels behave as a free electron gas. The lower part of Slater's d band seems to satisfy the requirement for a valence band. If it is reasonably broad it will contribute a significant amount to valence stabilization, and the entire valence band might be treated roughly as a hybrid of d, s, and p orbitals. The difference between the Slater and Pauling models may actually be largely one of nomenclature.

What will happen if the valence electrons are not treated as free electrons? The first variation which comes to mind is that used by Stoner. Suppose that one chooses an effective mass for the electron, as Stoner did, in order to give better results for the Curie temperatures of cobalt and nickel. A step very much like this has, in fact, already been taken by means of the adjustment of the interaction energy described in Part III. Since all effects in the Pauling theory depend upon the uncoupling of valence electrons, and the number of valence electrons uncoupled is proportional to the product of the interaction energy and the density of levels, the alteration of the interaction energy produces an effect nearly equivalent to that produced by multiplication of the valence band level density by a constant factor, which is equivalent to choosing a new effective mass for the electron. The only difference between effects arises because the Curie temperature is proportional to the first power of the density and the second power of the interaction energy, while the number of valence electrons uncoupled is proportional to the first power of each. This results in a small variation in the total moment when the product of the density and the square of the interaction energy is kept constant and the interaction energy is varied.

It is clear that even if the original Pauling theory were entirely successful in predicting the Curie temperature of iron it would not be possible to state with certainty that the valence electrons were free electrons. It could only be concluded that the product of the true level density and the square of the true interaction energy was about the same as that of the free electron density and the square of the atomic interaction energy. Provided that this product is kept constant it makes relatively little difference what values of the effective mass and interaction energy are used. The principal assumption which is made in varying the band structure of iron to find the best value of the Curie temperature is not that the electrons are free, but that the ratios of the interaction energies of d electrons with s electrons, with p electrons, and with other d electrons remain constant whatever the actual values of the interaction energies.

The 0.6 electron per atom which physicists call the valence electrons are generally believed to behave as free particles, so that the Zener model could not be used to explain ferromagnetism if these were actually the only valence electrons. If that were so, the amount of uncoupling would not be enough to give the high Curie temperatures of the ferromagnetic elements. One must conclude both from this argument and from the evidence of bond distances that bonding stabilization is contributed by about six electrons per atom. From the calculations involving cobalt and nickel it is further concluded that these electrons are not entirely free. This modification removes the principal objection of physicists to the Pauling model.

One could abandon the assumptions made in Part III and methodically investigate the behavior of the alloys with the use of various values of the valence band hybridization, interaction energy, and effective electron mass. The best answer cannot lie far from the one used in Part III, because about 2.5 atomic orbitals are necessary to account for the behavior of the magnetic moments of the alloys. Similarly, one could adapt the calculations of Part IV to the problem of alloys and perhaps account for some of the deviations from experimental results. The major conclusion, however, would probably remain unaltered. Ferromagnetism is to be attributed primarily to interactions of electrons in narrow bands with electrons in relatively wide bands. The electrons in the wide bands are not necessarily free electrons, but may be discussed in terms of an effective electron mass. The number of orbitals in the narrow d band is about 2.5; the number of electrons in the wider band is about 6.0. With minor modifications, this model will probably be capable of adequately describing the properties of the ferromagnetic elements and all of their alloys.

APPENDIX 1

ENTROPY OF A FERMI GAS NEAR ABSOLUTE ZERO

It is necessary to evaluate the number of possible distributions corresponding to the most probable configuration of a free electron gas at some temperature T near absolute zero. For a Fermi-Dirac system (35)

$$\ln \Omega_{D_0} = \sum_{j} \left[- g_j \ln(1-f) + N_j \ln(f-1) \right]$$

where $f = \frac{1}{e^{(E-E')/kT}+1}$, and $g_j = 2\pi V \frac{(2m)^{3/2}}{h^3} \sqrt{E} = c\sqrt{E}$

In the integral approximation,

$$\ln \Omega_{D_0} = c \int_0^\infty E^{1/2} \left[-\ln(1-f) + f \cdot \left(\frac{E-E'}{kT} \right) \right] dE.$$

We follow the method of Sommerfeld and Bethe (36) for evaluation of integrals of this sort. Integrating by parts, we find

$$\ln \Omega_{D_0} = -\frac{2}{3} c \int_0^\infty \frac{E^{3/2}}{1-f} \frac{df}{dE} dE - \frac{c}{kT} \int_0^\infty \left[\frac{2}{5} E^{5/2} - \frac{2}{3} E' E^{3/2} \right] \frac{df}{dE} dE.$$

An integral of the form $\int_0^\infty \alpha(E) \frac{df}{dE} dE$ can be expanded as a power series in kT. Taking only the first two terms, the value of the integral is

$$\alpha(E') + \frac{\pi^2}{6} (kT)^2 \left(\frac{\partial^2 \alpha}{\partial E^2} \right)_{E=E'}$$

Therefore we have

$$\ln \Omega_{D_0} \cong \frac{2}{3} c \left[\left(\frac{E^{3/2}}{1-f} \right)_{E'} + \frac{\pi^2}{6} (kT)^2 \frac{\partial^2}{\partial E^2} \left(\frac{E^{3/2}}{1-f} \right)_{E'} \right]$$

$$+ \frac{c}{kT} \left[\left(\frac{2}{5} E^{5/2} - \frac{2}{3} E_0' E^{3/2} \right)_{E'} \right.$$

$$\left. + \frac{\pi^2}{6} (kT)^2 \frac{\partial^2}{\partial E^2} \left(\frac{2}{5} E^{5/2} - \frac{2}{3} E' E^{3/2} \right)_{E'} \right]$$

Since only first order corrections are to be considered it is sufficient to set $E' = E_0'$, the value of E' at absolute zero. The only first order term in T arises as one part of

$$\frac{c}{kT} \left[\frac{\pi^2}{6} (kT)^2 \frac{\partial^2}{\partial E^2} \left(\frac{2}{5} E^{5/2} - \frac{2}{3} E' E^{3/2} \right)_{E'} \right],$$

The remaining terms are either of higher order or are temperature-independent and therefore are part of the entropy at absolute zero, which is zero.

The equation which results is

$$\ln \Omega_{D_0} \cong \frac{c}{kT} \frac{\pi^2}{6} (kT)^2 E_0'^{1/2} = 2 N_0 \cdot \frac{3}{2} \frac{\pi^2}{6} \frac{kT}{E_0'}$$

Therefore we have

$$F = H - TS = H - kT \ln \Omega_{D_0} =$$

$$N_0 \cdot \frac{3}{5} E_0' \left[1 + \frac{5}{12} \pi^2 \left(\frac{kT}{E_0'} \right)^2 \right] - \frac{N_0}{2} \pi^2 E_0' \left(\frac{kT}{E_0'} \right)^2$$

$$= N_0 \cdot \frac{3}{5} E_0' \left[1 - \frac{5}{12} \pi^2 \left(\frac{kT}{E_0'} \right)^2 \right].$$

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PROPOSITIONS

1. It is proposed that the enzyme ascorbic acid oxidase functions by direct combination with oxygen and not by the reversible oxidation of cuprous ion, as is generally believed. Evidence is presented for this conclusion, and it is suggested that all naturally occurring copper-containing proteins which have a deep blue color in $5^{\circ}/o$ solution be investigated for possible ability to unite with oxygen.

2. It has recently been stated (1) that the binding of zinc by the hormone ACTH is favored by high concentrations of hydrogen ion, though other proteins are well known to have a decreased affinity for metals at low pH. It is proposed that this conclusion is incorrect, and it is shown that the experimental data upon which it is based, when correctly interpreted, account satisfactorily for the observed results without requiring the abnormal behavior of ACTH.

3. The Doppler effect for scattering by periodic structures may be discussed most conveniently by the introduction of a four-dimensional reciprocal lattice.

4. It is proposed that the number of valence electrons characteristic of the γ phases of iron, cobalt, and nickel is 5.53.

5. It is suggested that the method used by Taglang (2) to determine the atomic moments of isoelectronic sequences of ferromagnetic alloys is not accurate because the assumed linear relationship between magnetic moment and Curie temperature doesnot exist. The values of the atomic moment obtained by Taglang are shown to be too high.

6. It is proposed that the magnetic behavior of iron-vanadium alloys be reinvestigated with the use of carbon-free metals. It is predicted that a rise in the magnetic moment will be observed upon the addition of small amounts of vanadium to pure iron.

7. It is suggested that the hemocyanin of the horseshoe crab, Limulus polyphemus, is used almost entirely for reserve oxygen storage, much like the myoglobin of vertebrates.

8. It is proposed that the conclusions reached by Huxley and Stampfli (3) concerning the current distribution on the surface of internodes in single nerve fibers are not justified by the experimental technique employed. A modified experiment is proposed which would provide the information necessary to draw such conclusions.

9. The statement that the introduction of metallic orbitals in the Pauling theory of metals is necessary for the explanation of metallic conduction is incompatible with the statement that the Pauling theory can be shown to be identical with the simple Bloch theory.

10. It has recently been discovered (4) that the rapid decomposition of diazomethane can produce unique and complex fracture patterns in spherical Pyrex containers, and that these patterns can be recorded by a suitable experimental arrangement. With a knowledge of the tensile strength of Pyrex it has been possible to evaluate the line integral of the pattern over the surface of the sphere, to obtain a value of the heat of formation of diazomethane of 40.3 kcal., in excellent agreement with the estimated experimental value of 40.4 kcal.

11. A recent review article (5) on the formation of Liesegang rings discusses the "quantum-mechanical" explanation of the phenomenon. The original paper (6) upon which this discussion is based contains several fundamental errors, and it is proposed that there is no basis for a discussion of the Liesegang phenomenon in terms of quantum mechanics.

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