In the case of the hydrogen compounds, the formulas for $G_{22}$ are:

$$G_{22}/m=\tfrac{1}{8}(2+\mu)(\lambda_3+\lambda_4)+\tfrac{1}{8}(2-\mu)[(\lambda_3-\lambda_4)^2 -8D^2/\mu m^2]^{\frac{1}{2}}+\tfrac{1}{4}\lambda_1+D/m \quad (7)$$

and

$$\tfrac{1}{4}\lambda_1+\tfrac{1}{2}\lambda_3+\tfrac{1}{4}\mu\lambda_4<G_{22}/m\leqslant\tfrac{1}{4}\lambda_1+\tfrac{1}{2}\lambda_3+\tfrac{1}{4}\mu\lambda_3, \quad (8)$$

the minimum occurring for $D=0$ and the maximum for $D=m\mu(\lambda_3-\lambda_4)/(2+\mu)$. Here again we would not expect $G_{22}$ to be very close to the lower limit.

The numerical values of the bond constant calculated for various molecules are given in Table I.

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# The Ferromagnetism of Nickel

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By using metallic energy levels extrapolated from copper to nickel, the energy difference between a nonmagnetic and a ferromagnetic state with permanent magnetic moment is calculated for nickel, and it is shown that the ferromagnetic state is the stable one. Both saturation magnetic moment and Curie point are calculated, in agreement with experiment within the limits of error of the calculation. Extrapolation further into the iron group, though less justified than to nickel, indicates that ferromagnetism should persist in that group down approximately to iron. The criterion for ferromagnetism previously suggested by the author, the existence of inner unfilled electron shells (the 3*d*), small in proportion to their distance apart, is justified. The calculation is not made according to Heisenberg's method, which is considered to be unsuitable for application to ferromagnetism, except in its general principle of explaining the energy of orientation of elementary magnets in terms of exchange energy.

TWO different approaches have been made to the theory of ferromagnetism, that of Heisenberg[1] and that of Bloch.[2] The former operates with wave functions of the Heitler and London type, localized around the atoms of the crystal, while the latter uses plane waves traveling through the whole crystal. Neither theory has met with great success, except in the fundamental point of explaining the large energy of orientation of the elementary magnets, or magnetic spins, within a ferromagnetic crystal in terms of exchange energy rather than magnetic energy. This fundamental principle is surely correct, but Heisenberg's theory postulates the existence of a positive sign for certain exchange integrals which, in every case where they have been calculated, have negative sign, and Bloch's theory does not permit ferromagnetism except for lattice spacings much larger than those observed in the ferromagnetic metals. Neither theory has been applied specifically to the metals which are known to be ferromagnetic, and neither one gives any suggestion of why just iron, cobalt, and nickel should have these properties.

Several years ago the writer[3] pointed out that a necessary condition for ferromagnetism appeared to be the possession by the atoms in question of an incompleted inner shell of electrons, capable therefore of taking on a magnetic moment by proper orientation of the spins, and small enough so that the shells of neighboring atoms overlapped very little, so that these shells did not take part in the cohesion. The reason is that the theory of valence and cohesion demands, in agreement with experiment, that the stable state be that in which the spins are neutralized, so as to produce no net magnetic moment. The electrons responsible for ferromagnetism cannot then be those engaged in cohesion, but must be much more like those in free atoms, in which the condition of stability is known to be just the opposite: the stable state is in general that of highest multiplicity, or that with the maximum magnetic moment. It was at that time pointed out that the incom-

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[1] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928). See also Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford, 1932.

[2] F. Bloch, Zeits. f. Physik **57**, 545 (1929). For discussion of both theories, see A. Sommerfeld and H. Bethe, *Handbuch der Physik*, Vol. 24, second edition.

[3] J. C. Slater, Phys. Rev. **36**, 57 (1930).

pleted groups of $d$ electrons in the transition groups were appropriate for ferromagnetism, and it was found that of all the elements of these groups, those with the greatest distance between the $d$ shells in proportion to their size, and therefore the least overlapping, were just iron, cobalt and nickel. The recent discovery of the ferromagnetism of gadolinium, in which the $4f$ group is presumably effective, fits in with this rule, as Bethe[4] has pointed out.

Recent advances in the theory of electronic energy levels within a metallic crystal[5] have made it possible to carry Bloch's type of theory much further than before. In the reference just mentioned, it was shown to be possible to understand ferromagnetism in terms of this type of theory, and to see why those elements with non-overlapping unfilled shells should be likely to show it. Until the present time, however, energy levels for a ferromagnetic crystal have not been calculated, and consequently no detailed comparison of the theory with experiment could be made. Such computations have still not been carried out, but the calculations of Krutter[6] on energy bands in copper makes possible an extrapolation to the next element, nickel, which has the same face-centered cubic crystal structure, with a good deal of assurance. Similar computations are now being made by Dr. Manning for iron, and when they are completed an interpolation for the whole iron group will be possible. In the meantime, however, it was thought worth while in the present paper to develop the method of calculation, and apply it to the ferromagnetism of nickel, using the extrapolated energy bands. The result is to show definitely that nickel should be ferromagnetic, and to calculate saturation magnetic moment and Curie point in good agreement with experiment. Thus for the first time the theory of ferromagnetism has advanced far enough to make one fairly sure of its correctness. At the same time, with much less justification, the calculations have been extrapolated all the way to iron. The extrapolation indicates definitely that only a few metals preceding nickel in the periodic table should be ferromagnetic; as a matter of fact, it would predict the limit of the ferromagnetic elements to lie about at iron rather than between iron and manganese, but the calculation depends on the small difference between large quantities, and a small error in the extrapolation could shift the limit to its correct position. It is hoped to remedy this when the calculations for iron are completed. It is worth noticing that while the present calculations are made by the general method of electrons traversing the whole crystal, there seem to be good reasons to doubt whether any calculations of Heisenberg's type, depending on wave functions surrounding the individual atoms, could lead to the correct result in any simple way.

The writer is indebted to Mr. R. H. Fowler, Professor J. H. Van Vleck and Professor Francis Bitter for illuminating discussions regarding the question of ferromagnetism.

## UNFILLED ENERGY BANDS AND FERROMAGNETISM

The wave functions of an electron in a periodic potential field representing a crystal are modulated waves, behaving around each nucleus like an atomic wave function, but changing phase from one atom to another. In the case of rather tightly bound electrons like the $3d$ electrons concerned in ferromagnetism, the wave function is very much like an atomic one, falling to a rather low value in the region midway between atoms. The energy level is no longer a sharp one, as in an atom, but is spread out into a band, the spreading being greater and greater as the overlapping gets greater. Thus in the $3d$ functions the spreading is not very great. In copper, it amounts to about 0.4 atomic unit, or about 5.5 volts. Since there are five types of $d$ electrons (corresponding in the atomic case to the five degenerate states given by $m=2, 1, 0, -1, -2$), there will be five bands in the crystal, but these overlap in a complicated way. For our present purposes we need only the distribution in energy of the levels. This is given in Fig. 1, where $f(E)$, the number of states between $E$ and $E+dE$, divided by $dE$, is plotted as a function of $E$, for the five $3d$ bands combined. The total area under the curve then gives the total number of electrons which can be accommodated in the band; this is $10N$, where $N$ is

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[4] See article in *Handbuch der Physik*, Vol. 24, see p. 596.

[5] J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934).

[6] H. Krutter, Phys. Rev. **48**, 664 (1935).

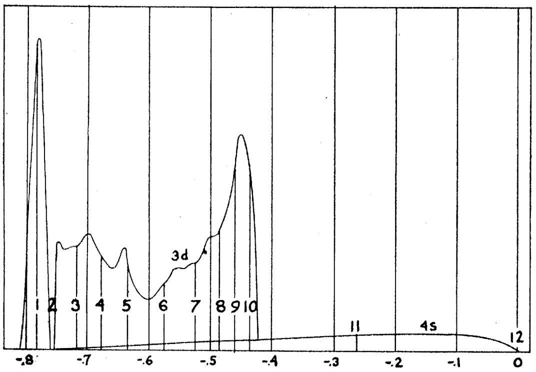

FIG. 1. Distribution of states in energy, for copper. $f(E)$, number of levels per unit energy range, plotted against $E$, in atomic units, lowest energies to the left. $3d$ and $4s$ bands shown separately. Vertical lines indicate the portion of bands filled by 1, 2, . . . 12 electrons, respectively.

the number of atoms in the crystal, since each band can hold one of each spin per atom. The values of Fig. 1 were found by starting with Krutter's calculations, extending them from the particular directions of propagation for which he found them to all directions of propagation by a method of interpolation, and tabulating the number of states for each range of energy of 0.01 atomic unit. The method will be described in a forthcoming paper. The fluctuations noted in the curve of Fig. 1 are partly of significance, partly a result of the approximate method of calculation used.

Overlapping the band of $3d$ electrons is another band, also shown in Fig. 1, arising from the $4s$ level of the atom, with interaction with the $4p$ and other higher levels. This band, capable of holding 2 electrons per atom, has wave functions of a very different character, large in the regions between atoms, and acting there very much like plane waves. Electrons in this band act like free electrons, and possess high electrical conductivity, in contrast to the $3d$'s. At the same time they contribute strongly to the cohesion, as in Wigner and Seitz's[7] calculation of cohesion in sodium, and in Fuchs's[8] calculation of the cohesion in copper, where wave functions very similar to the present ones were used.

As a first approximation to the structure of the metal, we may suppose that levels are filled, beginning with the lowest energies, high enough up so that all the electrons of the crystal are accommodated. There will be two electrons per state up to a certain energy, none above. In Fig. 1, lines are drawn indicating the maximum energy if there are 1, 2, 3 ⋯ 12 electrons in the $3d$ and $4s$ bands combined. The case of 11 corresponds to copper, whose atom has 10 $3d$ and 1 $4s$ electrons. It is seen that the metallic $3d$ band is filled, and that the $4s$ contains one electron per atom. If now the energy levels remained the same for the preceding elements, the case of 10 electrons would represent nickel, 9 cobalt, and 8 iron, respectively. We shall not try to estimate the changes in the energy levels, but shall wait until the case of iron is actually calculated. We see that the ferromagnetic elements contain less than one $4s$ electron per atom (explaining partly the poorer conductivity of these metals compared with copper, as Mott[9] has pointed out), but that nickel contains only about 9.5 electrons in the $3d$ band, cobalt about 8.5 and iron about 7.5. These missing electrons in the $3d$ band are necessary for ferromagnetism. But as long as the electron arrangement is as we have described, with each state either occupied by two electrons of opposite spins or empty, there will be no net magnetic moment, and the metal cannot show ferromagnetism.

We must, then, go to a higher approximation to find any net magnetic moment. A similar situation arises in the structure of atoms. As a first approximation, we assign to each electron a set of quantum numbers, $n$, $l$, $m$, and a spin quantum number, and assume that, as in a central field of force, the energy of each depends on $n$ and $l$. We then assume that the energy levels in the central field are filled far enough up to accommodate all the electrons, deducing in this way which of the quantum states are occupied in the normal state of the atom. As a next step, however, we consider the vectorial interaction of electrons, resulting in the multiplet structure. The electrostatic interaction is already taken into account if we set our central field up properly, and the same is true in the metal if the periodic field is chosen properly. But we must consider the changes of energy resulting from orientations of the orbits (change in $m$) and from orientations of spins. The energy

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[7] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[8] K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935).

[9] N. F. Mott, Proc. Phys. Soc. **47**, 571 (1935).

of a state proves to be, to the first order of perturbation theory, given by the energy neglecting orientations, minus the sum of certain exchange integrals over all pairs of electrons having parallel spins.[10] The integral is positive; with the result that the energy depends on the arrangement of spins, and that the minimum energy corresponds to the state where as many electrons as possible have spins parallel to each other. Now suppose there are $(10-n)$ electrons per atom in the $3d$ shells, $(10-n)N$ in the whole crystal. If these are divided, as we have assumed, into equal groups of each spin, there will be $(5-n/2)N$ of each spin. With each spin there will then be $\frac{1}{2}\{(5-n/2)N\}\{(5-n/2)N-1\}$ pairs, or, neglecting 1 compared with $N$, the total number of exchange integrals will be $\{(5-n/2)N\}^2$. Suppose on the other hand that there are only $(5-n/2-\mu/2)N$ electrons with negative spin, but $(5-n/2+\mu/2)N$ of positive spin, leaving the same number of electrons as before, but with a net positive spin of $(\mu/2+\mu/2)=\mu$ electrons per atom. Then there will be approximately

$$\tfrac{1}{2}\{[(5-n/2+\mu/2)N]^2+[(5-n/2-\mu/2)N]^2\} = [(5-n/2)N]^2+[\mu N/2]^2$$

exchange integrals, an increase of $(\mu N/2)^2$ integrals. Since these terms are to be subtracted, there will be a decrease of energy, and a tightness of binding, if the spins set themselves parallel, resulting in a magnetic moment. The maximum possible moment is determined by the condition that the number of electrons of either spin in the $3d$ bands must be between zero and five. The second limiting condition is the significant one in the ferromagnetic case, and as a result we see that the maximum value of $\mu$ equals $n$. In this case, all states of positive spin are filled, but there are $nN$ electrons missing from the states of negative spin. The exchange energy in this case is less than that in the case of zero spin by $(nN/2)^2$ times the average exchange integral between two electrons.

We have just seen that the total energy of the crystal is decreased, on account of exchange effects, if as many spins as possible set themselves parallel, resulting in a permanent magnetic moment. There is, however, a compensating effect, which may be less or greater than the exchange effect depending on circumstances. If we go from the state of balanced spins to that of unbalanced spins, we remove $\mu N/2$ electrons from states of minus spin, and add them to the states of plus spin. In the balanced state, the lowest $(5-n/2)N$ levels of each spin were occupied, up to a certain definite energy level. In the process of unbalancing, the $\mu N/2$ electrons of negative spin are removed from energies lower than this maximum value, and are raised in energy so as to occupy levels of positive spin above this maximum value. Thus there is a net increase of energy. This increase is likewise approximately proportional to $\mu^2$; for the number of shifted electrons is proportional to $\mu$, and the energy difference through which they must be raised is, at any rate for small $\mu$, approximately proportional to $\mu$. The net effect of this energy increase and the energy decrease due to exchange will then be positive or negative depending on the relative magnitude of the effects, but in any case it will generally remain of the same sign independent of the magnitude of $\mu$, so that either the state of balanced spins will be the most stable, or it will be the least stable and the unbalancing will go the whole way, resulting in an unbalanced spin of $n$ electrons per atom. This latter case is that for ferromagnetism.

The magnitude of the exchange integral is not very different for different atoms, and for most atoms the increase in energy on account of shifting the electrons to higher levels, increasing the binding energy, is far greater than the decrease of exchange energy when going into a magnetic state. (Algebraic rather than absolute values of the energies are here referred to.) Thus most metals are nonmagnetic. For the ferromagnetic elements we must seek those whose unfilled energy bands are as little split up as possible, so that as little energy change as possible will result from a rearrangement of electrons within the band. Thus we are led back to our former criterion of nonoverlapping unfilled shells, for it is just here that the splitting will be small. Furthermore, the whole calculation, based on the top part of the band being unfilled, the bottom part filled, is one for which the method of periodic wave functions is particularly suited, but for which Heisenberg's method

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[10] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

of atomic wave functions could be adapted only with great difficulty.

## Calculation of Exchange Integral

To get the exchange effect, we need only find the average value of the exchange integral between two $3d$ electrons in the lattice. Such an exchange integral between two wave functions $a_i$ and $a_j$ is by definition

$$\int a_i^*(1)a_j^*(2)(e^2/r_{12})a_j(1)a_i(2)dv_{12}, \qquad (1)$$

where 1 and 2 represent the coordinates of two electrons. We divide the volume into $N$ polyhedral cells, each surrounding an atom, and integrate separately over each pair of cells. Thus the integral is the sum, as $p$ and $q$ range from 1 to $N$, of the integral in which $dv_1$ ranges over the interior of the $p$th cell, $dv_2$ over the $q$th cell. Within the $p$th cell, according to the modulation of the wave function described by Bloch, the function $a_i$ is equal to its value at the corresponding point of the central cell, multiplied by the factor $\exp(i\mathbf{k}_i\cdot\mathbf{R}_p)$, where $\mathbf{k}_i$ is the vector wave number describing this stationary state, $\mathbf{R}_p$ is the vector from the center of the central cell to the corresponding point of the $p$th cell. Similar relations hold for the other functions. Thus our integral becomes

$$\sum_{p=1}^{N}\sum_{q=1}^{N}\exp\left(i(\mathbf{k}_j-\mathbf{k}_i)\cdot(\mathbf{R}_p-\mathbf{R}_q)\right)$$

times the integral in which $dv_1$ ranges over the $p$th cell, $dv_2$ over the $q$th, and where we replace $a_i$ and $a_j$ by their values at corresponding points of the central cell. Let these values in the central cell be $u_i$, $u_j$; then the exchange integral becomes

$$I=\sum_{p=1}^{N}\sum_{q=1}^{N}\exp\left(i(\mathbf{k}_j-\mathbf{k}_i)\cdot(\mathbf{R}_p-\mathbf{R}_q)\right)\int_p\int_q u_i^*(1)u_j^*(2)(e^2/r_{12})u_j(1)u_i(2)dv_{12}. \qquad (2)$$

A single term is the potential of a charge density $eu_i^*(1)u_j(1)$ in the $p$th cell, on a charge of density $eu_j^*(2)u_i(2)$ in the $q$th cell, times the appropriate exponential. First we shall consider the terms $p=q$, which prove to be the leading terms. For this case, $\mathbf{R}_p-\mathbf{R}_q=0$, so that the exponential reduces to unity, and the integral becomes simply $N\int u_i^*(1)u_j^*(2)(e^2/r_{12})u_j(1)u_i(2)dv_{12}$, integrated through the central cell only. Now within this cell, the functions $u_i$ and $u_j$ are very much like atomic $d$ functions, on account of the relatively small perturbations of the $d$ electrons of different atoms on each other. The normalization, however, is different, each function being approximately $1/N^{\frac{1}{2}}$ times the corresponding atomic function, so that the square of the function, integrated over the $N$ cells, can equal unity. Thus the exchange integral finally is seen to be approximately $1/N$ times the corresponding atomic integral, which we shall call $J$.

Next we consider the case $p\neq q$. Two different cases arise, depending on whether $u_i$ and $u_j$ refer to the same value of the quantum number corresponding to the atomic quantum number $m$, or not. If they do, $u_i$ and $u_j$ are approximately equal to each other within the cell, and their product integrates to $1/N$ over the cell, so that the charge density $eu_i^*(1)u_j(2)$ is a charge of approximate amount $e/N$, distributed through the $p$th cell. Its potential at the $q$th cell will then be approximately $(e/N)(1/|\mathbf{R}_p-\mathbf{R}_q|)$, plus terms in higher inverse powers of $|\mathbf{R}_p-\mathbf{R}_q|$, arising from the fact that the charge distribution really has multipole components as well as a total charge. We shall see, however, that the whole effect is very small, and the multipole terms can consequently be neglected. On the other hand, if $u_i$ and $u_j$ refer to different $m$ values, the functions will be approximately orthogonal to each other, their product will integrate almost to zero, over the cell, the charge distribution will consist practically only of multipoles (beginning with a quadripole), and we may neglect its potential completely. We are left, then, only with the case of equal $m$ values, in which the contribution to the integral is the potential of a charge $e/N$ on an equal one at distance $|\mathbf{R}_p-\mathbf{R}_q|$. We may then convert the sum over $p$ and $q$ in (2) into a single sum in which the $p$th cell is at the origin, obtaining

$$I=J/N+N(e^2/N^2)\sum_q\left(\exp\left(i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{R}_q\right)\right)/R_q, \qquad (3)$$

if $u_i$ and $u_j$ refer to the same $m$ value, while

$I=J/N$ otherwise. It is to be noted that $J$ is different for different pairs of $m$ values of the two wave functions.

We shall not attempt to evaluate $I$ from (3) for each separate combination of functions $u_i$ and $u_j$, but only to find the average over all possible combinations, recognizing that this may involve us in certain errors in the final result. In reference 10 it was shown that the exchange integrals between two $d$ functions can be written in terms of two parameters, $F^2$ and $F^4$, which can be evaluated from atomic wave functions, or from observed atomic spectra. In the table of coefficients $b^k(lm_l;\ l'm_l')$ on p. 1312 of that reference, the necessary coefficients are given for different combinations of the $m$'s. When we average over the 25 combinations of the five $m$ values with each other, we find from that table that

$$\bar{J}=2/35(F^2+F^4). \qquad (4)$$

For nickel, we can estimate the quantities $F^2$ and $F^4$ from the observed spectrum. The $(3d)^8(4s)^2$ configuration of Ni I involves energy separations determined by just these quantities. Taking the observed multiplet separations for this configuration, we can fit $F$ values to it. The fit is not very good, but to a rough approximation we have $F^2=80{,}000\ \text{cm}^{-1}$, $F^4=50{,}000\ \text{cm}^{-1}$. To indicate the order of accuracy, we give in Table I the energy differences between the multiplets, as obtained by taking the center of gravity of the observed multiplets, and we compare with the values determined from these parameters. Using these values of the $F$'s, we have $\bar{J}=7430\ \text{cm}^{-1}$ approximately.

Next we wish to average the second term of (3) over all pairs of wave functions. We recall that this term is present only when $u_i$ and $u_j$ have the same $m$ values, which occurs only 1/5 of the time, so that we wish 1/5 of the average over $i$ and $j$ of this term. Strictly, the quantities $\mathbf{k}_i$ and $\mathbf{k}_j$ should be allowed to range over a polyhedral cell in the $k$ space, but it will make only a small error if instead we allow them to range over the interior of a sphere of the same volume. It is easy to show that the average of $\exp(i\mathbf{k}\cdot\mathbf{R})$ over the interior of a sphere of radius $K$ in $k$ space is $3(\sin KR-KR\cos KR)/(KR)^3$. Thus the average of the second term of (3) is

$$\frac{1}{5}(e^2/N)\sum_q\left\{\frac{3\sin KR_q-KR_q\cos KR_q}{(KR_q)^3}\right\}^2\bigg/R_q. \qquad (5)$$

TABLE I.

| | OBSERVED | COMPUTED |
|---|---|---|
| $^3F-{}^1D$ | 12,550 cm$^{-1}$ | 13,250 |
| $^3F-{}^3P$ | 14,750 | 15,950 |
| $^3F-{}^1G$ | 21,150 | 20,750 |
| $^3F-{}^1S$ | not obs. | 51,600 |

Here $K$ is to be so chosen that $(4/3)\pi K^3$ is the volume of one cell in $k$ space. If $R$ is the distance from an atom to its nearest neighbors in a face centered lattice, it is not hard to show that this leads to $KR=6^{\frac{1}{3}}2^{\frac{1}{6}}\pi^{\frac{2}{3}}$. Inserting this value, the bracket above becomes 0.000352 for the case where $q$ is one of the nearest neighbors, and it is much less for more distant neighbors. The nearest ones are then the only ones which need be considered, and since there are 12 of them, the expression (5) becomes approximately

$$(12/5)(0.000352)(e^2/N)/R. \qquad (6)$$

The distance $R$ from an atom to its nearest neighbor is about 4.67 atomic units in Ni. Inserting this value, and converting to cm$^{-1}$, the expression (6) becomes $36\ \text{cm}^{-1}/N$. It is thus evident that the terms for $p\neq q$ are almost negligible in finding the exchange integral, which arises almost entirely from the atomic integral. Adding our two expressions, we have $\bar{I}=7466\ \text{cm}^{-1}/N$, and

$$\begin{aligned}&\text{Exchange energy of magnetic state}-\text{exchange}\\&\quad\text{energy of nonmagnetic state}\\&\qquad=-(n^2/4)(7466)N\\&\qquad=-1866\ n^2\ \text{cm}^{-1}\ \text{per atom.}\end{aligned} \qquad (7)$$

On account of the discrepancies between the observed multiplets and those calculated from our $F$ values, we may expect this value to be uncertain to between five and ten percent. We must recall, furthermore, that it represents only an average value, and that the exchange energy for particular pairs of wave functions can differ widely from the average.

## CALCULATION OF CHANGE IN BINDING ENERGY

We must next find the change of binding energy involved in shifting $nN/2$ electrons from the states of negative spin to those of positive spin, remembering that they must go into states previously unoccupied. Since the binding energy is known only in the form of numerical calculations, as summarized in Fig. 1, this calculation must be made numerically, not analytically. In terms of the function $f(E)$ plotted in Fig. 1, giving the number of states per unit energy range, the total energy of the electrons between two energy values, assuming them to fill all energy states between the limits, is $\int Ef(E)dE$ between these limits, or rather a corresponding summation, since $f(E)$ has been computed for discrete values of $E$. We must find the energy in two cases: (1) the state of no net spin, in which all states are filled from the bottom of the band to an energy such that there are $n/2$ states per atom of each spin vacant above this value; and (2) the state of maximum spin, in which all states of positive spin are filled, but in which states of negative spin are filled only to such an energy that there are $n$ states per atom of this spin vacant above this value. These energies have been computed, as a function of $n$, by obvious numerical methods, and their difference $E_2-E_1$ has been found, giving the increase in binding energy in going to the ferromagnetic state.

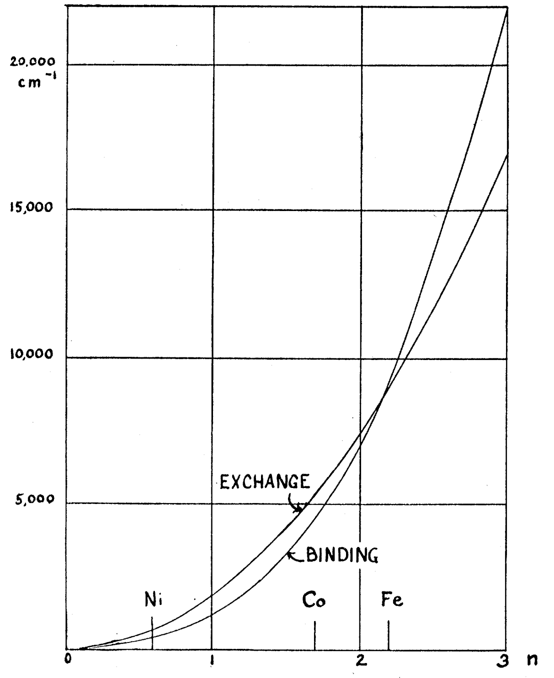

Fig. 2. Magnitudes of exchange and binding energy changes between ferromagnetic and nonferromagnetic states (in cm$^{-1}$ per atom), as function of $n$ (number of net electrons spins per atom). The condition for ferromagnetism is that the exchange energy term be greater numerically than the binding energy term.

## Net Energy Change from Nonmagnetic to Magnetic State

We have now found that on account of the exchange effect, as given in (7), the energy of the crystal decreases by 1866 $n^2$ cm$^{-1}$ per atom when the electrons change from the state of no net spin to the state of maximum spin. On the other hand, the energy arising from binding increases by the amount $E_2-E_1$, as discussed in the last paragraph, when the same change is made. The absolute values of these two quantities, as functions of $n$, are plotted in Fig. 2. It is seen that, for small $n$'s, the increase in binding energy is less than the decrease in exchange energy, so that the net result is a decrease of energy, the ferromagnetic state is more stable than the nonmagnetic state, and the metal should be ferromagnetic. On the other hand, as $n$ increases, the two curves are seen to cross, so that for too large a value of $n$ (too small a total number of electrons in the $d$ shell, or in the atom), the increase in binding energy becomes greater than the compensating decrease in exchange energy, so that the state of zero spin is the most stable one. The question now is, in which part of the curve is nickel located? We have already pointed out that, according to our extrapolated copper energy bands, nickel should contain about 9.5 electrons per atom in the $3d$ bands, so that $n=0.5$. Mott[9] has shown that according to experiment $n$ is nearer 0.6. This is near enough our theoretical results so that the uncertainty in the extrapolation could easily account for the difference. In either case, Fig. 2 very definitely shows that nickel should lie in the ferromagnetic part of the curve. It is tempting, as we have remarked above, to extend the extrapolation further down the iron group, using these same curves for cobalt and iron, though of course they are really not accurate, since both the exchange energy (as computed from the spectrum) and the binding energy (as computed from the metallic energy bands) will really change as we go from atom to atom, and furthermore cobalt and iron have different crystal structures from copper and nickel. We have seen that approximately $n=1.5$ for cobalt, 2.5 for iron. Mott[9] has shown that experimentally $n=1.7$ for cobalt, 2.2 for iron, approximately. These values of $n$ are all obtained from the observed saturation magnetic moments of the metals. From Fig. 2, on which the values 1.7, 2.2 are indicated, it is seen that the curves cross at approximately the $n$ value for iron, instead of between iron and manganese (that is, for $n>2.2$) as they should from the observed ferromagnetism of iron. But the error is one which we can easily attribute to the errors in our extrapolation. Both curves rise rapidly with $n$, and comparatively small changes in them would shift the intersection by the required amount. We may reasonably say, then, that our theory not only predicts the ferromagnetism of nickel, but also predicts that the phenomenon of ferromagnetism should persist for some distance down into the iron group of elements, approximately as far as it is observed experimentally, and then should cease.

## Magnetic Energy and Curie Point of Nickel

Let us adopt for nickel the value 0.6 for $n$, as indicated by experiment. Then we find the exchange energy to be $1866\ (0.6)^2\ \text{cm}^{-1}=672\ \text{cm}^{-1}$. The difference in binding energy between the two states is found to be 401 $\text{cm}^{-1}$. The net decrease in energy on going from the nonmagnetic to the ferromagnetic state is thus 271 $\text{cm}^{-1}$ per atom. This of course is at the absolute zero of temperature, for with both nonmagnetic and ferromagnetic states we have considered only the lowest possible energy level, all electrons being in the lowest state consistent with the given total spin. This quantity is not susceptible of experimental measurement, but it is closely related to the Curie point. For nickel, the Curie temperature $\theta$ is about 630° absolute, and the corresponding energy $k\theta$, where $k$ is Boltzmann's constant, is 440 $\text{cm}^{-1}$, when converted to spectroscopic units. This is obviously of the same order of magnitude as the quantity found theoretically. We can, however, make a more definite comparison, on the basis of available theories of ferromagnetism. For the present, we shall not try to replace these theories of the temperature variation of the magnetic moment by a more suitable theory based on the present model.

In the Weiss theory of ferromagnetism* in the absence of an external magnetic field, one writes the internal magnetic field in terms of the magnetic moment per unit volume as $\mathbf{H}=N\mathbf{I}$, where $N$ is an empirical constant, large compared with unity, and $\mathbf{I}$ is the magnetic moment per cc. The magnetic energy per unit volume is then $-\frac{1}{2}\mathbf{H}\cdot\mathbf{I}=-\frac{1}{2}NI^2$ in the magnetic case, as compared with a nonmagnetized state. The formula for the Curie point on this theory can be written $\theta=\sigma_{m0}{}^2N\rho/3mR$, where $\sigma_{m0}$ is the magnetic moment per gram molecular weight (equal to our $n$, times the Bohr magneton, times Avogadro's number), $\rho$ is the density, $m$ the molecular weight, $R$ the gas constant per gram molecular weight. In an obvious way $\sigma_{m0}$ can be written in terms of $I$, the magnetic moment per unit volume, so that $\theta$ is plainly proportional to the same quantity $NI^2$ appearing in the energy per unit volume. In fact, if we multiply this magnetic energy by the volume of an atom, to get the energy per atom, we have very simply

$$k\theta=\tfrac{2}{3}\ \text{magnetic energy per atom (Weiss).} \qquad (8)$$

We can proceed similarly in the Heisenberg theory.† The magnetic energy of the whole crystal is then written in terms of certain exchange integrals (not to be confused with our exchange integrals) denoted by $J$, a number of nearest neighbors $z$, and a total spin $S'$ of the crystal, equal to $NS$, where $S$ is the spin of one atom, $N$ the number of atoms in the crystal. It is then, as given by Van Vleck's formula (22) equal to $-zJS'^2/N$. The Curie point, on the other hand, is given by Van Vleck's formula (37) as $\theta=2zJS(S+1)/3k$. Thus we are led to the relation

$$k\theta=\tfrac{2}{3}S(S+1)/S^2\ \text{times magnetic energy per atom (Heisenberg).} \qquad (9)$$

It is observed that Heisenberg's result approaches Weiss's in the limit $S=\infty$, as it does in other respects. However, as Van Vleck

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* See for example E. C. Stoner, *Magnetism and Atomic Structure*, p. 75.

† See for example Van Vleck, *Electric and Magnetic Susceptibilities*, p. 328.

points out, the experimental results for nickel are best represented by $S=1/2$, leading to $\frac{2}{3}S(S+1)/S^2=2$. Thus we may expect the Curie energy to be somewhere between $\frac{2}{3}$ and twice the energy of magnetization at the absolute zero, with the probabilities favoring the latter value. The experimental Curie energy 440 $\text{cm}^{-1}$ is 1.62 times the magnetization energy 271 $\text{cm}^{-1}$ which we have found. The agreement seems entirely satisfactory, considering the nature of the approximations which we have made.

## ELECTRONIC SPECIFIC HEAT OF NICKEL AT LOW TEMPERATURE

It has been recently observed by Keesom[11] that the electronic contribution to the specific heat, which, being proportional to the temperature, outweighs the contribution of the lattice vibrations at low temperatures, is many times the normal amount in nickel. Both Keesom and Mott have suggested that this arises from the large concentration of energy levels in the neighborhood of the top of the Fermi distribution, on account of the $3d$ levels. We can easily test this hypothesis. Sommerfeld and Bethe (reference 2, p. 430) show that the specific heat per gram molecular weight on account of free electrons in a normal metal is $C_v=(2\pi^2/3)N(\zeta_0)k^2T$, where $N(E)dE$ represents the number of energy levels of one spin in $dE$, if we are dealing with a gram molecular weight, and $\zeta_0$ is the maximum energy occupied at the absolute zero. Thus his $N$ is half our distribution function $f$. For a ferromagnetic metal, however, at low temperatures all levels of positive spin are filled, so that they do not contribute to the specific heat, and we count only electrons of negative spin. This removes the factor 2 in the formula above. Furthermore, $\zeta_0$ must be taken to be the maximum energy of electrons with negative spin, when the electrons of positive spin occupy the whole band. In this case, from the numerical data from which Fig. 1 is drawn, we find that $N(E)$ is 26.15 times Avogadro's number, if energy is expressed in atomic units. Substituting this value, and appropriate constants, we find $C_v=0.0011T$ calories per mole per degree. Keesom's experimental value is $0.001744T$. The agreement is not very good, but still it is correct in order of magnitude. To get better agreement, the peak in Fig. 1 at energy $-0.45$ atomic unit would have to be about half again as high as it is, presumably being correspondingly more narrow. This does not seem impossible, though it is unlikely. In any case, the high specific heat is definitely connected with the high peak in the $3d$ distribution curve of Fig. 1, verifying again this general feature of our curve.

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[11] Keesom and Clark, Physica 2, 513 (1935); W. H. Keesom, Proc. Roy. Soc. **A152**, 12 (1935); N. F. Mott, Proc. Roy. Soc. **A152**, 42 (1935). I am much indebted to Mr. R. H. Fowler for calling my attention to these references.

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# A Note on Positron Theory and Proper Energies

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The origin of the infinite light-quantum proper energy which follows, according to Heisenberg, from the creation of matter by the field of the photon, is examined in some detail. We are led to investigate the inconsistencies which appear on the incorporation of the Dirac positron theory into the formalism of the quantum theory. These inconsistencies make it impossible to regard with confidence any predictions of the theory for which a consideration of the singularities of the density matrix is essential. It is shown that when the off-diagonal distance in the density matrix is taken different from zero, the proper energy of a light quantum and the electromagnetic energy of an electron are, in order $e^2$, finite, and that the off-diagonal distance plays in these calculations the part of a generalized electron radius.

IN a field free vacuum, the infinite distribution of electrons in negative energy states envisaged in Dirac's theory of the positron clearly should contribute nothing to the expectation values of observables of the system (charge and

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