

The Ferromagnetism of Nickel

II. Temperature Effects

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With the model proposed in an earlier paper, the temperature variation of the ferromagnetism of nickel is discussed. By application of Fermi statistics to the electrons in the d bands, the free energy is computed as a function of temperature and magnetic moment. At each temperature, the value of magnetic moment for which the free energy is a minimum is the value which will actually be found, and this decreases with increasing temperature, going to zero at the Curie point, in satisfactory agreement with experiment. The value of the free energy itself at the minimum, as a function of temperature, is compared with experimental values derived from the observed electronic specific heat of nickel, and the agreement is again satisfactory. To get agreement of both quantities with experi-

ment, it is necessary to use a smaller exchange integral than was suggested in the earlier paper, but plausible reasons are suggested for thinking that this should be done anyway. It is found that even at the absolute zero not quite all of the spins are parallel to each other, the minimum in the free energy curve coming at a little less than the maximum possible magnetic moment. It is suggested that this small effect becomes much more pronounced as iron is approached in the series of ferromagnetic elements, explaining the fact that alloys of iron and cobalt show the highest saturation moments of any ferromagnetic substances, the moment then decreasing in iron and even more in alloys of iron with lighter elements.

IN a previous paper, the writer has shown¹ that the ferromagnetism of nickel can be accounted for by the model of a metal in which each electron moves in a stationary state throughout the whole metal, modulated by the periodic lattice. It was shown that the energy of the electrons of such a metal changes for two reasons when the metal goes, at the absolute zero of temperature, from a nonmagnetic state with equal numbers of electrons of each spin, to a magnetized state with as many as possible of the electrons having one spin, the remainder the opposite spin. In the first place, work is required to produce this change, because electrons of negative spin must be lifted from lower, occupied states up to the higher, unoccupied levels, in order to allow them to change to positive spin. In the second place, energy is gained because of exchange, which, as in atoms, gives a lower energy the more pairs of electrons there are with the same spin. The first effect is ordinarily enough to outweigh the second, resulting in a nonmagnetic normal state, but in the ferromagnetic elements the electrons concerned are in a narrow d band; it requires a comparatively small amount of energy to produce the necessary electron displacement, and as a result the magnetized state has a lower energy at absolute zero, and is the

stable state. This was shown to be the situation for nickel, where the work required to produce the rearrangement of electrons was computed by use of energy levels extrapolated from calculations on copper, and where the necessary exchange integral was estimated from observed atomic spectra. The calculation was not extended to temperatures above the absolute zero, however. An estimate of the Curie point was made in terms of the energy difference between the magnetized and nonmagnetized states at the absolute zero, but this cannot be regarded as reliable. It is the purpose of the present paper to discuss the temperature variation of the ferromagnetism, thus presenting the essentials of a complete theory.

Experimentally, there are two phenomena to be explained. In the first place, the saturation magnetization decreases with temperature. At the absolute zero, for nickel, the magnetization corresponds to almost exactly 0.6 electron spin per atom. As the temperature increases, this decreases, very slowly at first, then very rapidly, falling to zero at the Curie point. Secondly, the specific heat shows anomalies definitely connected with the ferromagnetism. If a Debye function is subtracted from the observed specific heat,² the difference is large, and must be at-

¹ J. C. Slater, *Phys. Rev.* **49**, 537 (1936).

² E. Lapp, *Ann. de physique* **12**, 442 (1929). Miss Lapp considers the electronic specific heat to drop to zero above

tributed to the specific heat of the free electrons. This electronic heat is proportional at low temperature to the temperature, then begins to rise more rapidly, going to a sharp peak at the Curie point, after which it falls to an approximately constant but by no means negligible value, of the order of magnitude of $\frac{1}{2}R$.

These phenomena may be best discussed by means of the free energy $\Psi = U - TS$. We regard this as a function of two variables, the temperature, and the magnetic moment μ (measured in electrons spins per atom). It is a well-known property of the free energy that for equilibrium it takes on a minimum value, in a system at constant volume, and constant temperature. Thus if we have a family of curves of Ψ as a function of μ , for different temperatures, the minimum of the curves (which alone represents a physically realizable state) will come at maximum μ for the absolute zero of temperature, but will shift inward toward smaller μ as the temperature increases, reaching $\mu = 0$ at the Curie point (which is determined by this fact), and remaining at zero for all higher temperatures. From this behavior we can at once derive the well-known law giving the temperature variation of the paramagnetic susceptibility. By symmetry, the free energy must be an even function of μ , or of the magnetic moment I of the whole crystal (which is proportional to μ). Thus the first term in the power series expansion of Ψ as function of I , apart from a constant, is a term in I^2 . Furthermore, the coefficient of this term is positive for temperatures above the Curie point, negative below, so that, if T_c is the Curie temperature, the expansion of Ψ for small I near T_c is $\Psi = a(T - T_c)I^2$. In the presence of an external magnetic field H , the free energy is diminished by an additional term HI . For equilibrium, the derivative of the whole free energy with respect to I must be zero. Thus $\partial\Psi/\partial I = 0 = 2a(T - T_c)I - H$, $I = H/(2a(T - T_c))$, expressing the fact that the metal is paramagnetic above the Curie point (I is proportional to H , with a positive coefficient), and that the paramagnetic susceptibility is inversely pro-

portional to the temperature interval above the Curie point. This well-known law is thus seen to follow quite independently of the model. It is evident, however, that the constant a bears no necessary relation to the saturation magnetic moment at the absolute zero, in contradiction to the Weiss theory.

In addition to the magnetic moment, the free energy Ψ is of great value in discussing the specific heat, on account of the relation $C_v = -T(\partial^2\Psi/\partial T^2)_v$. Since C_v for the free electrons equals $0.001744T$ at low temperatures, in calories per g mole,³ Ψ must be a quadratic function of the temperature, so that its second derivative will be constant. We may take the entropy $S = -(\partial\Psi/\partial T)_v$ to be zero at the absolute zero, so that Ψ , apart from an additive constant, is given by the expression $-0.000872T^2$ for low temperatures. For higher temperatures, the free energy can be found by integrating the experimental values of C_v/T twice with respect to temperature. This has been done numerically. The result, then, gives the actual value of free energy at the minimum of each curve of Ψ against μ . In our comparison of theory with experiment, we shall compare the free energy curve, rather than the specific heat.

Using the model of the previous paper, the free energy of the electrons has been computed as a function of T and μ . The method will be described in the Appendix. Briefly, we consider the electrons to be a mixture of two gases, one consisting of the electrons of each spin, with energy levels as given by the model. The free energy of the electrons of each spin is calculated by application of Fermi statistics, the two are added, the exchange energy is subtracted, and the result is a correct deduction of the free energy from the model used. It should be stated that the calculation is largely numerical, and that it depends on small differences of large quantities, so that its accuracy is not great. When the calculation was carried out, using distribution function and exchange integral of the previous paper, it was at once found that the Curie point came out several times too high. This was unexpected, for a discussion in the

the Curie point, and treats the remaining specific heat, which persists above this point, as an "unknown" term. It seems likely that most of this "unknown" term is also of electronic origin, and we have included it in our calculations.

³ 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).

earlier paper indicated that the Curie temperature, when translated into energy units, should be of the same order of magnitude as the energy difference between the magnetized and unmagnetized states at the absolute zero, and this relation was found to hold for the observed Curie temperature and the calculated energy difference. That argument, however, was based on the Weiss and the Heisenberg theories of the temperature variation of ferromagnetism, and when the present theory is worked out it appears that the Curie temperature is much larger in comparison with the energy difference at absolute zero than on those theories. To get agreement with experiment, it was thus necessary to reduce decidedly the energy difference between magnetized and unmagnetized states, and this could be done in either of two ways, by reducing the exchange integral or by modifying the distribution of stationary states so as to increase the energy expended in raising electrons of negative spin to unoccupied states of positive spin. Both methods were investigated, and it was found that agreement with experiment could not be secured in any easy way by the second method, but that the first alone sufficed to bring the results into good agreement with experiment. In the earlier paper, the exchange energy was taken to be $-1866\mu^2 \text{ cm}^{-1}$, where μ is expressed in Bohr magnetons per atom. Expressed in thermal units this is $-5320\mu^2 \text{ cal. per g mole}$. In place of this value it was found necessary to use the value $-3315\mu^2 \text{ cal. per g mole}$, only 0.62 of the previous figure. A very plausible argument can be given for supposing such a change to be correct, however, as will be indicated in a later paragraph.

Using the revised exchange integral, the values of free energy plotted in Fig. 1 were calculated. In this figure the free energy Ψ , in calories per g mole, is plotted as a function of μ , for a variety of temperatures. On each curve the temperature is indicated, as a fraction of the Curie temperature. It will be observed, in accordance with expectation, that each curve below the Curie temperature has a minimum for some value of μ . Furthermore, as the temperature increases, this value of μ decreases from the value 0.6 which it has at the absolute zero (the curves being adjusted to give this value)

to the value zero at the Curie point. To compare with experiment, the dotted line of Fig. 1 is the experimental curve which should pass through the minima, and the circles represent the particular points on the curve where the minima should be found for the various temperatures. To compute the dotted curve, we have found the free energy for each temperature, by the method described above, and have plotted it against the observed saturation magnetic moment, marking the points of the curve corresponding to particular temperatures. Since the free energy is roughly proportional to T^2 , this curve resembles the familiar curve of μ as function of T^2 , with abscissa and ordinate interchanged. When now we compare the dotted curve with its circles with the minima of the theoretical curves, the agreement is surprisingly satisfactory. The minima of the theoretical

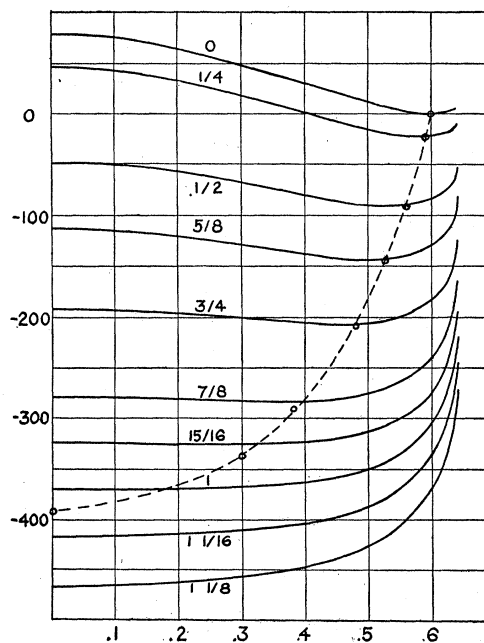


FIG. 1. Theoretical electronic free energy of nickel, in calories per g mole, as function of magnetic moment, in Bohr magnetons per atom, for different temperatures, expressed as fractions of the Curie temperature (approximately 630° Abs.). Minima give equilibrium values of magnetic moment and free energy. Dotted curve gives experimental relation between free energy and magnetic moment, obtained from specific heat and saturation magnetization, circles representing points on dotted line corresponding to the various temperatures plotted, therefore being experimental positions of minima.

curves at low temperature seem to show a slight tendency to come at too small values of μ , but it is hard to tell whether this tendency is real or not, on account of the difficulty of the calculation and the inaccuracy in the curves. The values of free energy at the minima, at low temperature, agree practically perfectly, showing that the calculated specific heat is almost exactly right (in contrast to the cruder calculations of the previous paper, where the agreement was only as to order of magnitude). In fact, in the Appendix the free energy is expressed analytically as a function of temperature, and the specific heat at low temperature found by differentiation, with agreement to about two percent with Keesom's experimental value. At higher temperatures, it will be seen that the experimental and theoretical free energies depart appreciably from each other, the experimental points lying lower, indicating that the experimental specific heat is greater than the theoretical. This is not surprising, for it is entirely possible that other terms in the specific heat, not of electronic origin at all, are becoming appreciable at these temperatures, as often happens with metals. Even if this is not the case, the agreement is probably within the error of the calculation and of experiment.

The net result, then, is agreement between theory and experiment both in the magnetic moment as a function of temperature, and in the free energy. It would be more convincing to calculate magnetic moment directly by finding the minima of the curves, and to find a theoretical free energy, differentiate it twice, and thus get a theoretical specific heat curve, to compare with experiment. The difficulties with this program are entirely practical. It has been stated that the calculations were difficult to carry out accurately, for the two terms in the energy, the exchange term and the other one, almost exactly cancel, and the net result is the difference of almost equal quantities. With curves as uncertain as these are, an attempt to find the minima numerically is seen from Fig. 1 to be impracticable. The free energy as function of temperature could be found more accurately from the ordinates of the minima, but to get the specific heat we should have to differentiate this curve twice numerically, and this would introduce great errors. We must

thus be content with the type of comparison with experiment which we have used. It seems entirely satisfactory, however, within the limits of error.

Two points in connection with the calculation deserve further comment. In the first place, as has been stated, it was necessary to use an exchange integral only 62 percent of the value found in the previous paper. Not only this, but the value of the integral is found rather accurately from the requirement that the Curie point agree with the experimental value, for a very few percent in the exchange integral make a large proportional change in the small difference between exchange and binding energies, which much more nearly cancel than in the previous paper. The earlier value of the integral, however, was derived from empirical spectrum terms, and it is not legitimate to change it as drastically as this without justification. One fact was overlooked in the previous paper, however. The integral was found from a configuration of nickel in which there were 8 d electrons, whereas in the metal there are about 9.4 d electrons per atom. The increased number of electrons in the d shell in the metal will increase the shielding on each electron, causing the orbits to increase in size, and will thereby decrease the exchange integral, which is very sensitive to orbital dimensions. The amount of change cannot be estimated from available nickel terms, but in the next element, cobalt, such an estimate can be made. In Co I we have two configurations, $3d^74s^2$ and $3d^84s$, both leading to the terms 4F and 4P , analogous to the 3F and 3P in nickel, used in determining the exchange integral in the previous paper. The interval between the centers of gravity of these multiplets is about 14,700 cm^{-1} in the $3d^74s^2$ configuration, but only about 10,500 cm^{-1} , or 71 percent as great, in $3d^84s$. If this figure of 71 percent can be accepted for the decrease in the integral on adding one electron to the shell, the integral for nickel should have been $(0.71)^{1.4} = 0.62$ times as great as first estimated, in exact agreement with the factor which we found necessary to fit the magnetic observations. Since the earlier value of the exchange integral was estimated to be accurate only to five or ten percent, this exact agreement of course is fortuitous.

The second interesting point may be seen by reference to Fig. 1. It has been previously supposed⁴ that at the absolute zero all electron spins were parallel to each other. On the other hand, the curve for $T=0$ in Fig. 1 shows a minimum at a value of μ slightly less than that corresponding to all spins being parallel. The figure is drawn on the assumption that there are empty spaces in the d shell corresponding to 0.64 electron per atom; in this case the minimum energy is for a state with 0.62 electron of positive spin, 0.02 of negative spin, giving the net spin of 0.60, as observed. This minimum is real, not a result of inaccuracies in computation, as an analytical investigation of the theoretical nature of the curves in this neighborhood shows. The writer knows of no theoretical method of discovering whether this is in agreement with the facts or not. The shape of the curve near the minimum could be investigated only by studying the change of saturation moment in fields much stronger than can be obtained, in which case theoretically the moment could eventually be increased to a true saturation of 0.64 magneton per atom, but this is outside the range of experimental fields. There is, however, a very interesting possibility opened up by this effect. It is well known that the saturation moments of Ni, Co, and Fe at the absolute zero correspond, respectively, to 0.6, 1.7, and 2.2 magnetons per atom. If the number of s electrons per atom remains approximately unchanged in this series, we should expect the saturation moment to increase by one unit in going from one atom to the next, so that it should be about 2.7 for iron, rather than 2.2. It is now attractive to suppose that when the calculations for iron are carried out it may be found that the minimum of the curve, at absolute zero, lies not where the moment is 0.60/0.64 of its maximum possible value, but at the smaller proportion 2.2/2.7. That is, we suppose that as the end of the series of ferromagnetic elements is reached, the curve of Ψ versus μ at absolute zero does not suddenly change from a curve like that for nickel, with maximum energy at $\mu=0$, to a curve of the non-magnetic type with a minimum at $\mu=0$, but that rather the minimum already present in

nickel gradually moves in toward $\mu=0$. This is in accordance with the observed facts for alloys. In the first place it is found that the highest saturation moments are found, not in iron, but in iron-cobalt alloys, which contain a smaller number of holes per atom in the d shell than iron, and at first sight would be expected to have smaller moments. Presumably the effect of which we are speaking begins to be important between these alloys and iron itself, cutting the moment of iron below its expected value, without greatly affecting the iron-cobalt alloys. In the second place, alloys of iron with lighter elements, as chromium and manganese, have more holes per atom in the d shell than iron, and might be expected to show greater saturation moment. As a matter of fact they show less. An observation interpreted by Weiss⁵ and his colleagues by the assumption that the moments of the chromium or manganese atoms set themselves opposite to the moments of the iron atoms, an assumption which has no place in the present type of theory. Rather we may assume that, in spite of having more holes in the d shell than iron, the tendency of the minimum of the free energy curve toward $\mu=0$ is so marked in these alloys that the moment is really less than iron, not greater. These remarks are illustrated by Fig. 2, in which the saturation moments of the alloys of Ni-Cu, Ni-Zn, Ni-Co, Fe-Ni, Fe-Co, Fe-V, and Fe-Cr are shown.

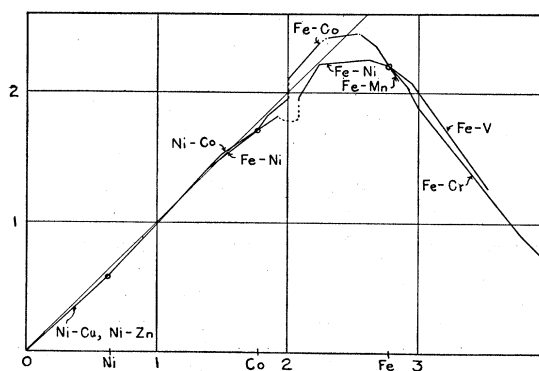


FIG. 2. Saturation magnetic moments of ferromagnetic alloys at absolute zero, in Bohr magnetons, as function of number of empty holes in d shell, arbitrarily taken to be 0.64 in Ni, 1.78 in Co, 2.78 in Fe. Data from references 5.

⁵ P. Weiss, "Recherches récentes sur le magnétisme," Congrès International d'électricité (Paris, 1932); M. Fallot, "Ferromagnétisme des alliages de fer," Thesis (Paris, 1935). The curves for Fig. 2 are taken from these references.

⁴ N. F. Mott, Proc. Phys. Soc. **47**, 571 (1935); J. C. Slater, reference 1.

Fe-Mn, Fe-Cr, and Fe-V are plotted as a function of the number of holes in the d shell, equalling the maximum possible magnetic moment if as many spins as possible were parallel. It will be seen that up to about halfway between Co and Fe, all the alloys lie very nicely on a line which is approximately the 45° line, indicating almost maximum possible moment, but

that at this point the curve breaks away, starting to decrease, which we interpret to mean that only part of the available spins are parallel in the state of minimum free energy.

The writer is greatly indebted to his colleague Professor Francis Bitter for interesting discussions, and particularly for assistance in locating references in the ferromagnetic literature.

APPENDIX

We first find the free energy ψ of a system of electrons all of the same spin, the energy being a sum of one-electron energies of the various electrons. A stationary state of the system is denoted by the values of the n_i 's, the number of electrons in the i th orbital, where by the exclusion principle n_i is limited to the values 0, 1. If there are N_0 electrons, we have

$$N_0 = \sum_i n_i. \quad (1)$$

If the one-electron energy of an electron in the i th state is ϵ_i , the total energy E is

$$E = \sum_i n_i \epsilon_i. \quad (2)$$

Then according to Gibbs the free energy is given by the equation

$$\exp(-\psi/kT) = \sum \exp(-E/kT), \quad (3)$$

where the summation is to be extended over all stationary states of the combined system; that is, over all combinations of the n_i 's consistent with (1) and the exclusion principle. By using (2), Eq. (3) becomes

$$\exp(-\psi/kT) = \sum_i \prod_i \exp(-n_i \epsilon_i/kT), \quad (4)$$

where again each n_i is to range over the values 0, 1, subject to the condition (1). Introducing an index z , we have

$\exp(-\psi/kT) =$ coefficient of term in z^{N_0} in

$$\begin{aligned} & \prod_i (1 + z \exp(-\epsilon_i/kT)) \\ &= \frac{1}{2\pi i} \oint \frac{dz}{z^{N_0+1}} \prod_i (1 + zx_i), \end{aligned} \quad (5)$$

where $x_i = \exp(-\epsilon_i/kT)$. We evaluate the integral (5) by the method of steepest descents. To do this, we first find the minimum of the integrand along the real axis; then we know that the integral is given by a constant times the value of the integrand at this point. To find the minimum of the integrand, we take the logarithm and differentiate:

$$\begin{aligned} \frac{d}{dz} \left\{ \sum_i \ln(1 + zx_i) - (N_0 + 1) \ln z \right\} \\ = \sum_i \frac{x_i}{(1 + zx_i)} - (N_0 + 1)/z = 0, \end{aligned}$$

from which, neglecting unity in comparison to N_0 ,

$$N_0 = \sum_i \frac{1}{(1/z)e^{\epsilon_i/kT} + 1}. \quad (6)$$

We recognize in (6) the familiar condition in the Fermi statistics determining the number of particles as the sum of the number in the various stationary states, and see that in the usual notation we should let

$$z = \exp(\zeta/kT). \quad (7)$$

Substituting this value of z in (5), and again neglecting unity compared to N_0 , we have

$$\exp(-\psi/kT) = \text{constant} \times \exp(-N_0 \zeta/kT) \prod_i (1 + \exp((\zeta - \epsilon_i)/kT)),$$

and

$$\psi = \text{constant} + N_0 \zeta - kT \sum_i \ln(1 + \exp((\zeta - \epsilon_i)/kT)). \quad (8)$$

The formulas we have derived are convenient when most of the energy levels are empty. In our case, however, most of the states are filled, only the top states of the d band being empty, and it is better to rewrite the formulas so that the essential contributions to the sums come from the holes, not the filled levels. Thus assume there are only N_1 empty stationary states, so that $N_0 + N_1$ equals the total number of stationary states, which is assumed finite (as in the d bands). Then in place of (6) we have

$$\begin{aligned} N_1 &= \sum_j \left\{ 1 - \frac{1}{\exp((\epsilon_j - \zeta)/kT) + 1} \right\} \\ &= \sum_i \frac{1}{\exp((\zeta - \epsilon_i)/kT) + 1}. \end{aligned} \quad (9)$$

The quantity being summed in (9) is approximately equal to unity for the states empty at absolute zero, for which ϵ_i is greater than ζ , but is approximately zero for the states occupied at absolute zero. In place of (8) we have

$$\begin{aligned} \psi(N_1, T) &= \text{constant} + (N_0 + N_1 - N_1)\zeta \\ &\quad - kT \sum_i \ln(\exp((\zeta - \epsilon_i)/kT)) \\ &\quad - kT \sum_i \ln(1 + \exp((\zeta - \epsilon_i)/kT)) \\ &= \text{constant} + \sum_i \epsilon_i - N_1 \zeta \\ &\quad - kT \sum_i \ln(1 + \exp((\zeta - \epsilon_i)/kT)). \end{aligned} \quad (10)$$

The quantity being summed in (10) is again approximately zero for the states occupied at absolute zero, but is approximately equal to $\zeta - \epsilon_i$ for the states unoccupied at absolute zero. Thus at absolute zero, leaving out of account the

first two terms in (10), which are constants, we see that ψ is equal to the negative of the sum, over unoccupied states, of ϵ_i ; that is, to the work required to remove the electrons from these states, starting with all states filled.

By using the numerical distribution of stationary states in the d band described in the previous paper, the quantity ψ from (10) has been computed for a variety of temperatures as a function of N_1 . Actually ζ rather than N_1 was used as the fundamental parameter, N_1 being calculated in terms of ζ from (9), and ψ from (10). Finally ζ was eliminated by plotting ψ as a function of N_1 , interpolating to get the values at suitable values of N_1 .

As mentioned earlier in the paper, the free energy is a quadratic function of T at low temperatures; it was consequently found convenient for some purposes to plot ψ as a function of T^2 , for various values of N_1 . When this was done, it was found that the curves were very nearly straight lines over the range of temperature used, and that they could be expressed with great accuracy by quadratic functions of T^2 . Furthermore, by a fortunate chance, the coefficient of the term in T^4 was almost the same function of N_1 as the coefficient of the term in T^2 , so that it was accurate enough to take the same coefficient in each case. As a result, it was possible to write

$$\psi(N_1, T) = f(N_1) - g(N_1) \{T^2 - 3.35 \times 10^{-7} T^4\}, \quad (11)$$

where $f(N_1)$ and $g(N_1)$ are empirical functions of N_1 , and the coefficient of the T^4 term is empirical.

Now we are ready to consider the actual crystal. Let there be N atoms in the crystal, so that there are $10N$ states for d electrons, $5N$ of each spin. Assume there are $(10-n)N$ electrons in these states, of which $(5-n/2 + \mu/2)N$ have positive spin, $(5-n/2 - \mu/2)N$ negative spin, so that there are $(n/2 - \mu/2)N$ electrons missing from states of positive spin, $(n/2 + \mu/2)N$ from those of negative spin. Then we may write the whole free energy as the sum of functions (11) for these two spins. This gives the contribution to the free energy coming from the one-electron energies of the electrons. From it must be subtracted the exchange energy, which as shown in the previous paper is quadratic in μ , and whose coefficient has

been already seen to be 3315 cal. per g mole. Thus we have as the complete free energy $\Psi(\mu, T)$ of the crystal

$$\begin{aligned} \Psi(\mu, T) &= \psi((n/2 - \mu/2)N, T) + \psi((n/2 + \mu/2)N, T) - 3315\mu^2 \\ &= \{f((n/2 - \mu/2)N) + f((n/2 + \mu/2)N) - 3315\mu^2\} \\ &\quad - \{g((n/2 - \mu/2)N) + g((n/2 + \mu/2)N)\} \\ &\quad \quad \quad \times \{T^2 - 3.35 \times 10^{-7} T^4\} \\ &= F(\mu) - G(\mu) \{T^2 - 3.35 \times 10^{-7} T^4\}. \end{aligned} \quad (12)$$

Values of $F(\mu)$ and $G(\mu)$ as functions of (μ) , computed for $n=0.64$, are given in Table I. They are the values from

TABLE I.

μ	$F(\mu)$	$G(\mu)$	μ	$F(\mu)$	$G(\mu)$
0	75.3	0.001311	0.49	11.2	0.001062
0.04	74.5	1309	.50	9.7	1050
.08	72.8	1305	.51	8.1	1038
.12	70.0	1295	.52	6.7	1026
.16	66.2	1285	.53	5.5	1014
.20	61.4	1270	.54	4.0	1000
.24	55.6	1251	.55	2.8	985
.28	49.1	1230	.56	1.7	970
.32	41.6	1206	.57	1.0	952
.36	34.0	1180	.58	.5	934
.40	26.5	1148	.59	.2	912
.44	19.5	1112	.60	.0	888
.48	12.8	1072	.61	.3	861
			.62	1.0	830
			.63	2.0	785
			.64	4.1	624

which Fig. 1 was constructed. The values have been smoothed, but probably are not accurate to the last significant figure given. The constant in $F(\mu)$ is adjusted so that the energy of the stable state at absolute zero is zero. The unit for $F(\mu)$ is calories per gram mole, and for $G(\mu)$ calories per gram mole per degree². It is to be noted that the value of $G(\mu)$ for $\mu=0.60$ should give the coefficient of T^2 in the actual free energy near the absolute zero, and should agree with half the experimental value of C_v/T , or has been stated above should be 0.000872. Our value, 0.000888, differs from this value by about two percent, as has been previously stated.