THE MAGNETIC PROPERTIES OF IRON, NICKEL AND COBALT ABOVE THE CURIE POINT, AND KEESON'S QUANTUM THEORY OF MAGNETISM.

BY EARLE M. TERRY.

IN 1905, Langevin[1] proposed a kinetic theory of magnetism by means of which he was able to account in a remarkable way for many of the thermo-magnetic phenomena of both para- and dia-magnetic bodies. Assuming that the molecules of a paramagnetic substance are, as in a gas, free to orient themselves in all directions and that, with respect to an external field, the distribution of directions of their magnetic axes under the influence of thermal agitation follows the Maxwell-Boltzmann law, he derived, by purely statistical methods, the law previously obtained experimentally by Curie,[2] that the susceptibility is inversely proportional to the absolute temperature.

Introducing the idea of an internal magnetic field proportional to the intensity of magnetization, Weiss[3] has extended the method of Langevin to ferro-magnetic substances, and obtained a relation between intensity and temperature, which, when put in the form of corresponding states, represents the experimental facts with a fair degree of accuracy. He has further shown that in the region of "induced ferro-magnetism," *i. e.*, in the temperature interval immediately above the magnetic transformation point, called the "Curie Point," the susceptibility should follow a modified form of Curie's Law, namely, inversely proportional to the excess of temperature above the transformation point where the constant of proportionality is the same as would have held for the substance, if, by suppression of the mutual actions between molecules, it had remained paramagnetic.

As a result of their study of magnetic properties at very low temperatures, Weiss and Kammerlingh Onnes[4] found that the saturation values of the magnetic moments per gram atom for Fe, Ni, and Co are to one another in simple ratios; namely, 11 : 3 : 9. To the aliquot part common to the magnetic moment of the gram atoms, Weiss has given

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[1] Langevin, Ann. de chem. et phys. (8), 5, p. 70, 1905.

[2] Curie, Oeuvres, p. 255, 1908.

[3] Weiss, Arch. des Sci. phys. et nat. (4), Vol. 31, p. 5, 1911.

[4] Weiss and Kammerlingh Onnes, Comm. phys. Lab. Leyden, No. 114, p. 3, 1910.

the name of gram-magneton and this quantity, divided by the Avogadro number, gives the moment of the ultimate magnetic corpuscle which he has called the magneton. This he supposes, for magnetism, to play a rôle analogous to the electron for electricity. His theory further shows that the number of magnetons per molecule is related to the Curie constant in a simple manner, so that it is easy to test the existence of the magneton by determining whether or not the number per molecule is an integer. Using the results of Pascal,[1] Weiss and Foëx,[2] Leibknecht and Wills,[3] Miss E. Feytis[4] and others, he found that the ferromagnetic substances at high temperatures and their salts at ordinary temperatures give, for the number of magnetons per molecule, numbers which rarely depart from integers by more than one or two per cent. Similar results were obtained for a large number of alloys of iron, nickel and cobalt.

On the other hand, Honda[5] and his co-workers, after examining a large number of substances, both elements and compounds, have amassed a large amount of data showing that Curie's law is not a general law of nature and that the existence of the magneton, at least as based on the simple theory of Weiss, is open to serious question.

In the cryogenic laboratory at Leyden, Kammerlingh Onnes[6] and his co-workers have extended their thermo-magnetic studies to very low temperatures with a view to testing the validity of Curie's law in this region and have found that, as regards their departures therefrom, substances may be divided into three general groups:

1. The relation, $\chi T =$ constant, holds down to the temperatures of liquid nitrogen, but below this, χT continually decreases.

2. The product χT diminishes at once starting from room temperature. The relation $(T + \Delta) =$ constant holds with fair accuracy as far as liquid nitrogen temperatures but below this, unsystematic deviations appear.

3. Susceptibility changes very little with temperature and, in the interval between liquid nitrogen, and liquid hydrogen, is almost independent of temperature.

Kunz[7] has shown that the elementary magnet in the Weiss-Langevin theory is not the magneton mentioned above but is a much larger aggregate consisting of a definite number of atoms: *e. g.*, Fe, 2; and Ni, 6.

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[1] Pascal, Ann. de Chim. et Phys., Vol. XVI., p. 531, 1909.

[2] Weiss and Foëx, Archiv. des Sci. phys. et nat., Vol. XXXI., 1911, p. 4 and 89.

[3] Liebknecht and Wills, Ann. des Phys., I., p. 178, 1900.

[4] Miss E. Feytis, Comptes rendus, Vol. CLII., p. 708; 1911.

[5] Honda, Science Reports Tohoku Univ., Vol. 4, p. 215, 1915.

[6] K. Onnes, Perrier, Oosterhuis, Leyden Comm. No. 5, 116, *122a*, *129b*, *132e*, *134d*.

[7] Kunz, Phys. Rev., Vol. XXX., p. 359; 1910.

Stifler[1] has studied cobalt and found, for the atoms per elementary magnet, four.

The classical work of Curie was carried out at a time when the subject of pyrometry was in its infancy and his temperature scale is in error by at least twenty degrees. Weiss and Foëx could not extend their work to melting point temperatures of the ferro-magnetic substances, because oxidation and errors from the effects of the hydrogen atmosphere which filled their furnace chamber make their results open to question. The same criticisms may be made of the word of Honda whose experimental equipment was quite similar except that he used an atmosphere of nitrogen. Moreover, in the work of Weiss and Foëx, certain deviations from Curie's law are apparent in the case of iron, nickel, and cobalt. Since it is of extreme importance, from the standpoint of the magneton theory, to have accurate information regarding the thermo-magnetic behavior of these cardinal magnetic substances, the present investigation was undertaken with these objects in view:

1. To extend the work up to the melting point.
2. To eliminate errors due to effects of oxidation by working in a good vacuum.
3. To eliminate the effects of occluded gases by melting the specimens in a vacuum before testing.
4. To improve previous temperature measurements.

Method of Measurement.—The method which seemed best adapted for the purpose is that of Faraday in which the magnetic susceptibility is deduced from the mechanical force exerted upon a specimen in a non-uniform field. For an object of small dimensions placed in the plane of symmetry between the poles of a magnet, the force F in a direction X at right angles to the field H is given by the expression

$$F = m\chi H \frac{dH}{dx}, \qquad (1)$$

where m is the mass of the specimen, and χ its susceptibility referred to unit mass. If this is to be an absolute method, it is obviously necessary to determine both the field strength and its gradient over the volume occupied by the specimen. However, if a body of known susceptibility is available, the product $H(dH/dx)$ may be determined for a particular place in the field by substituting it for the test specimen and measuring the force upon it. This method was followed in the present work.

The force F was measured by means of a modified form of the Curie balance as shown in Fig. 1. The specimen m was supported at the desired

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[1] Stifler, PHYS. REV., Vol. XXXIII., p. 268; 1911.

point in the field by means of a slender porcelain tube carried by an aluminum arm and counterpoised by an adjustable threaded lead nut *W*. When the magnet *NS* is energized, the specimen is urged toward the stronger part of the field and the couple due to this force is counter-

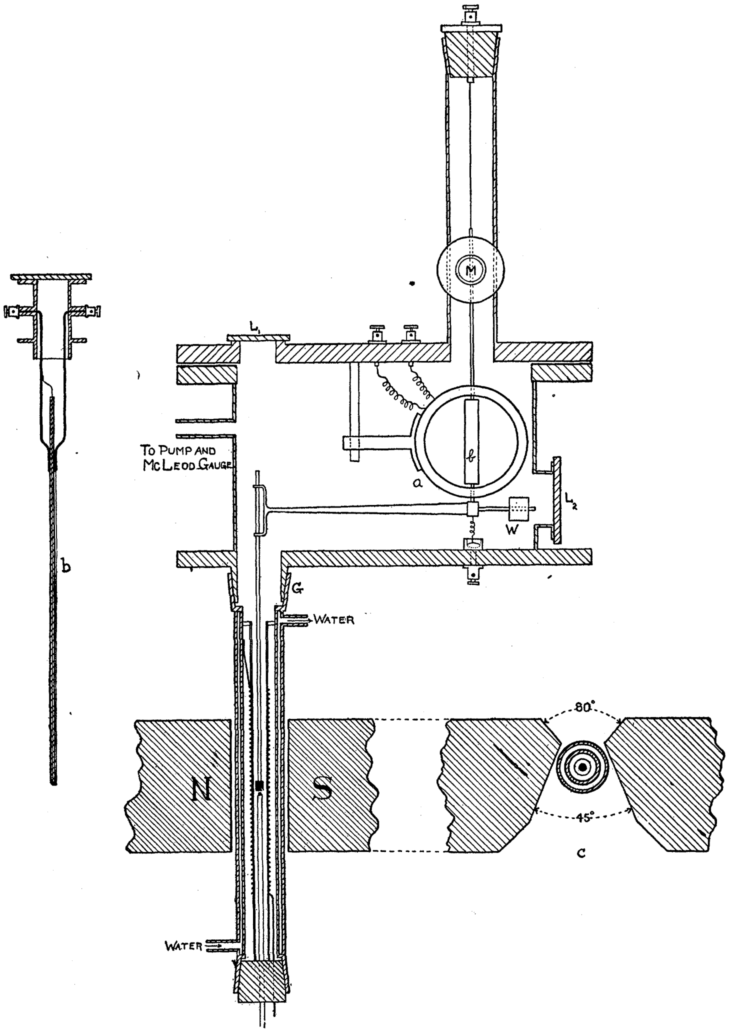

Fig. 1.

balanced by the electrodynamic action between the currents supplied to the coils *a* and *b*, the former of which is fixed while the latter is mounted on the moving system. A spot of light focused by the concave mirror *M* on a distant scale indicates when a balance has been obtained. The substitution of the coils and optical lever for the torsion fiber and divided head constitutes the principle modification of the original Curie balance. Since the torque is proportional to the current in each coil, this form of instrument may be used for large ranges of forces and has the advantages of high sensitivity and easy control when mounted within a vacuum chamber. Current is led to the moving coil by means of the suspending phosphor bronze ribbon, and away by a small copper wire dipping into a mercury cup below.

Experimental Details.—The furnace consisted of a tube of Berlin porcelain 8 mm. internal diameter and 20 cm. in length closely wound over a distance of 15 cm. with a .5 mm. tungsten wire. Outside of this tube there was placed another porcelain tube, not shown in the figure, and the whole mounted inside a water-cooled jacket. This container was supported from the bottom of the vacuum chamber by means of the ground joint G. An input of 750 watts sufficed for a temperature of 1500° C.

Temperature was measured by means of an Heraeus platinum platinum-rhodium thermo couple supported by a porcelain tube mounted upon the plug which closed the lower end of the furnace chamber. The junction was held immediately below the specimen. In its calibration, the following melting points were used: Cadmium, 320.9° C.; antimony, 630° C.; gold, 1062° C.; and nickel[1] 1452° C. In using the first two of these, the test specimen was swung to one side of the furnace and a tiny crucible of pure magnesia containing a small particle of the melt specimen was lowered through the window L_1, till it hung beside the test specimen. A vacuum was then obtained and the temperature gradually raised. The specimen was illuminated by light from a nearby arc reflected into the furnace by means of a prism placed upon L_1 and observed by a telemicroscope. The gold and nickel points were obtained by means of the apparatus shown in *b*, Fig. 1. The melt specimen, in the form of a narrow strip of foil, was supported by platinum wires at the end of a slender porcelain tube inserted through L_1 and made tight by means of a ground joint. The foil was used as a fuse in an electric circuit containing a relay which actuated a buzzer when the melt occurred. It is to be observed that the thermocouple was thus calibrated in the same furnace and under exactly the same conditions as when used for the measurement of temperature.

In the early part of the work, a tungsten-iron couple was used with good results. By properly adjusting the current and voltage, it is possible by forming an arc between them, to weld tungsten and iron wires in the

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[1] Burgess and Waltenberg, Bulletin Bureau Standards, Vol. 10, p. 79, 1914, have shown that nickel possesses a very sharp melting point and, for work in a vacuum, it furnishes a very satisfactory standard temperature.

air. Such a thermo element has an inversion point near 300° C. and gives a thermoelectric power about twice that of platinum platinum-rhodium. It is satisfactory for work in a vacuum or hydrogen.

The magnet employed was a powerful one weighing 800 lbs. and required 4 K. W. for full excitation. It had pole pieces 10 cm. in diameter and was mounted upon a carriage which rested upon two rows of steel balls running in grooves. It could thus be easily moved to and from the test specimen by means of a slow motion screw operated from the observation table two meters distant. Since the pull upon the specimen depends upon its location in the field, it is necessary to work with it always at the same position. The point selected for this purpose was the one for which the pull is greatest, since it is easy to find and gives maximum sensitivity. As the force is proportional to both the magnitude and gradient of the field, it is desirable to have their product constant over as large an interval as possible to minimize the error due to variations in location of the specimen. By giving the pole faces the peculiar shape shown in *C*, Fig. 1, it is possible to obtain an $X-F$ curve with a very broad peak. A careful study of the particular field used in this work, carried out by means of a small travelling flip coil, showed that the slope of the H^2-X curve varied by less than one per cent. over a distance of 1 cm. in the neighborhood of the position of maximum pull. Since the specimens used never exceeded 4 mm. in diameter, the error due to faulty location is very small. The method followed in each case was to energize the magnet at the normal working field, usually 9,000 gauss, and measure the force for a series of magnet positions on each side of the position desired and from the curve determine the point of maximum F.

The vacuum was obtained by a molecular pump and read on a McLeod gauge. Since the porcelain furnace tubes occlude large quantities of air and water vapor, it was necessary to bake them out at low temperatures for a long time, *e. g.*, several days. By taking proper precautions in this respect, it was possible to operate at the melting point of iron with a pressure which seldom exceeded .0005 mm. of Hg. The pump was run continuously during all measurements. Two dishes containing P_2O_5 were placed within the vacuum chamber near the opening to the furnace —a precaution absolutely essential to the life of a tungsten furnace and the constancy of a platinum thermo-couple used within it.

Current was supplied to both the magnet and furnace from storage batteries and controlled by water-cooled rheostats, which made possible the maintenance of very constant fields and temperatures.

Standardization of the Curie Balance.—As standard substances, four solutions, nickel nitrate, nickel sulphate, cobalt nitrate, and cobalt sulphate, were used, whose susceptibilities were determined by the Quincke absolute method. For this purpose, the magnet was placed with its yoke in a vertical position and pole tips of 4 cm. diameter attached with a gap of 6 mm. The field strength was measured by three small independent flip coils with different numbers of turns and different diameters wound on carefully turned vulcanite spools. Their diameters were measured by means of a travelling microscope. The ballistic galvanometer was standardized in terms of a mutual inductance wound on a marble spool and certified by the U. S. Bureau of Standards. The change in level of the solution was read by a microscope travelling vertically with the apparatus so arranged that the capillary tube in which the liquid under test was placed travelled with it, which enabled the readings to be taken always through the same spot in the tube to eliminate errors due to unequal capillarity. A jacket through which water of constant temperature circulated surrounded the capillary tube and maintained the temperature of the solution under test invariable. The outstanding discrepancies in the constant of the Curie balance, as determined by these four different solutions, never exceeded one half of one per cent.

The Test Specimens.—The iron used in this investigation was Burgess electrolytic and was part of the same deposit used in a previous investigation[1] and is known to have a purity, as regards other metals, of 99.98 per cent. The nickel and cobalt were obtained from Kahlbaum in the form of powders guaranteed to be cobalt and nickel free respectively. All specimens were freed from occluded gases by melting in vacuo in crucibles cut from plates of pure magnesia from the Berlin Porcelain Factory. This is believed to be a very important precaution, as a large evolution of gas at the melting point is evidenced by a vigorous boiling which lasts for several seconds and then subsides. In fact, experience has shown that it is quite impossible to obtain consistent results at high temperatures unless gases are thus eliminated. This has also been noted by Burgess[2] in his work on the temperatures of the Ar_2 and Ar_3 points for iron. Several samples of electrolytic iron melted in vacuo prepared by Yensen[3] were also tested.

Results.—The results for beta iron are given in Table I. and shown graphically in Fig. 2.

It is to be noted that iron in this region obeys Curie's law only approximately, for, when the reciprocal of susceptibility is plotted against

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[1] Terry, PHYS. REV., Vol. XXX., p. 133.

[2] Burgess, Bull. Bur. Stds., Vol. 10, p. 315, 1914.

[3] Yensen, Bulletin, Univ. of Ill., No. 72.

temperature, instead of a straight line, a curve with a marked upward concavity is obtained.

Table I.

Beta iron. Susceptibility as a function of temperature.

Temp.	$\chi\cdot 10^{-6}$.	$\frac{1}{\chi}\cdot 10^4$.	Temp.	$\chi\cdot 10^{-6}$.	$\frac{1}{\chi}\cdot 10^4$.
796	1,514	.0661	860	379.0	.2638
806	1,111	.0900	874	327.2	.3056
815	862.5	.1160	878	297.6	.3360
826	701	.1426	889	267.5	.3739
840	532	.1879	896	241.4	.4141
849	456	.2193	907	205.4	.4861
854	427	.2342	916	180.7	.5534

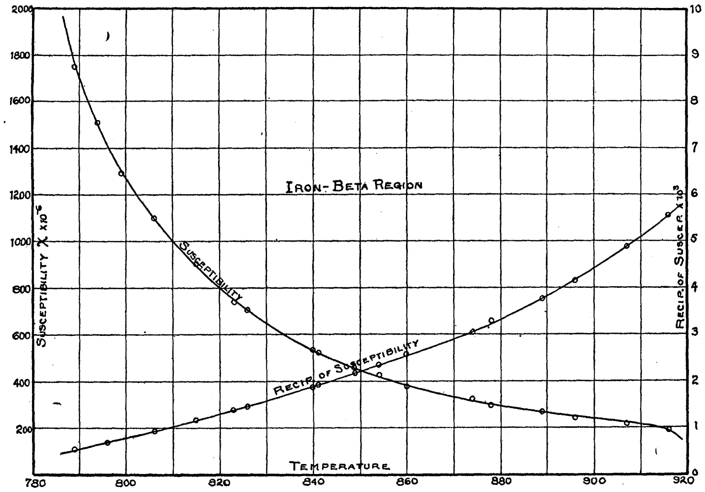

Fig. 2.

Electrolytic Iron Melted in Vacuo, Beta Region.

The results for iron in the gamma and delta regions are given in Table II. and plotted in Fig. 3.

It is to be noted that in the gamma region, Curie's law is not even approximately obeyed. We have here an interval of nearly five hundred degrees throughout which the susceptibility remains almost constant. At 1407° C. there is an abrupt increase when the transformation to the delta form occurs. Throughout the delta region, which extends to the melting point (1530° C.), the susceptibility decreases approximately linearly with the temperature. Electrolytic iron, as deposited, shows slightly greater values of susceptibility in the gamma and smaller in the delta regions than the same iron after being melted in vacuo. The melting point is less sharply marked also, for fusion apparently begins at 1500° C. and extends over an interval of about twenty-five degrees. These specimens consistently clung to the supporting porcelain rod after melting so that observations on molten iron were obtained over a small interval. The susceptibility shows a marked decrease on melting and has values approximately corresponding to an extension of the curve for the gamma region. Iron which had previously been melted in vacuo showed a sharp melting point and always dropped from the support.

TABLE II.

Iron. Gamma and Delta Regions.

Temp.	$\chi \cdot 10^{-6}$.	Temp.	$\chi \cdot 10^{-6}$.	Temp.	$\chi \cdot 10^{-6}$.
929	26.95	1197	25.54	1409	37.60
961	26.81	1224	25.37	1412	37.96
991	26.71	1245	25.19	1417	37.82
1026	26.40	1285	24.98	1425	37.69
1056	26.38	1343	24.58	1432	37.20
1071	26.32	1359	24.55	1442	36.72
1086	26.20	1370	24.39	1464	35.44
1109	25.96	1374	24.30	1483	34.38
1125	25.93	1400	24.40	1502	33.04
1145	25.87	1400	24.83	1515	31.93
1151	25.85	1400	29.87	1532	30.49
1164	25.76	1403	35.58		

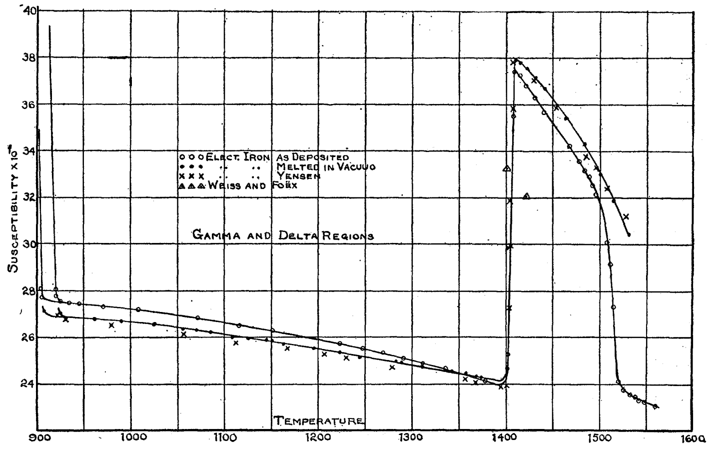

Fig. 3.

Gamma and delta iron. Susceptibility as a function of temperature.

A special study was made of the transformation from the beta to gamma and gamma to delta regions, the results of which are shown in Fig. 4.

These were carried out by causing the temperature to change very slowly while susceptibility changes were followed closely. As water cooled rheostats were used and the furnace and magnet currents were supplied by storage batteries, it was possible to control conditions very accurately. The rate of change of temperature seldom exceeded 10 degrees per half hour in the neighborhood of a transformation point. To insure accurate temperature readings, the thermo couple was calibrated during each run. For example, at the beta-gamma transformation, a gold melt specimen was introduced beside the test specimen as explained above. The susceptibility curve for rising temperature was then obtained and extended up to the melting point of gold (1062° C.), after which the curve for decreasing temperature was taken. For the gamma-delta transformation, the thermo couple was checked at the nickel point in the same manner.

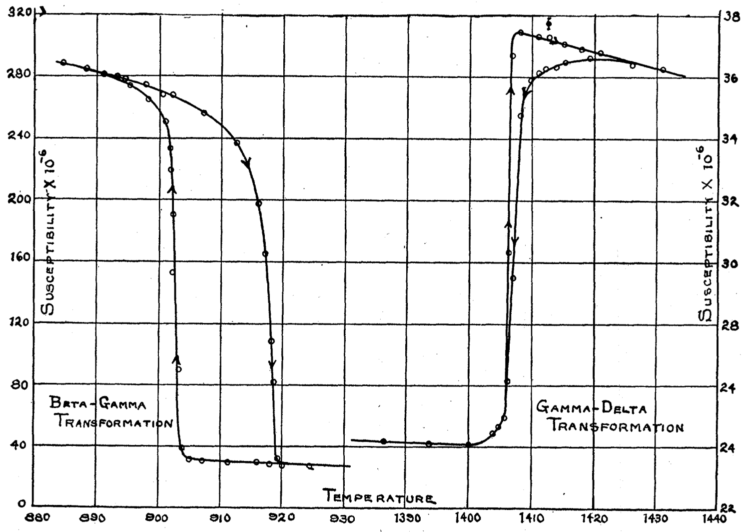

Fig. 4.

Beta-gamma and gamma-delta transformation in iron.

It is to be observed that these transformations are of entirely different characters magnetically. For the former, there is a marked hysteresis. The steepest part of the curve occurs at 918° C. on rising and at 903° C. on falling temperatures. For the latter, no real hysteresis can be detected. The steep part of the curve on falling coincides with that on rising within the limits of experimental accuracy. A marked peculiarity, however, is the fact that on cooling the return to the gamma state is not abrupt but begins rather gradually. This peculiarity was always found, even though the specimen had been heated to within a few degrees of the melting point. The results given here for the beta-gamma transformation correspond qualitatively to those obtained by Burgess[1] for the heat changes. He gives for the temperature at which maximum rates of absorption and evolution occur 898° C. and 909° C. respectively.

The results for nickel are given in Table III. and plotted in Fig. 5. Of the three metals studied, nickel alone shows a tendency to obey Curie's law, but for limited regions only. Starting at the transformation point, 370° C., the curve for the reciprocal of susceptibility shows a marked concavity upward till about 500° C. when there is an interval of 400° for which it is remarkably straight. Between 900° C. and 1000° C. it curves downward after which it continues straight up through the melting point. On this basis, there appear to be three distinct regions of beta nickel. It is interesting to observe that on passing through the melting point (1452° C.) there is no change whatever in the magnetic behavior.

TABLE III.

Temp.	$\chi\cdot10^{-6}$.	$\frac{1}{\chi}\cdot10^{4}$.	Temp.	$\chi\cdot10^{-6}$.	$\frac{1}{\chi}\cdot10^{4}$.
381	820.	.1219	782	13.06	7.650
383	723.	.1383	807	12.53	7.980
385	678.	.1478	820	11.72	8.530
387	611.	.1638	849	11.12	9.000
391	498.	.2008	866	10.61	9.425
393	377.	.2653	890	10.13	9.870
403	283.	.3530	924	9.495	10.53
411	219.	.4570	961	8.845	11.31
416	183.7	.5460	1010	8.214	12.18
420	177.2	.5645	1033	7.842	12.75
423	149.2	.6700	1051	7.734	12.93
435	126.7	.7890	1074	7.550	13.24
445	102.3	.9800	1099	7.318	13.66
467	74.90	1.334	1107	7.275	13.74
491.5	56.85	1.760	1147	6.968	14.35
508	47.90	2.046	1172	6.774	14.76
519	44.00	2.274	1187	6.730	14.86
556	32.56	3.068	1217	6.532	15.31
562	31.70	3.155	1242	6.388	15.64
612	23.98	4.170	1261	6.304	15.86
674	18.88	5.390	1295	6.110	16.37
687	17.57	5.690	1329	5.968	16.75
723	15.43	6.480	1357	5.854	17.07
747	14.51	6.890	1378	5.752	17.38
755	13.94	7.175	1407	5.645	17.70
777	13.52	7.390	1431	5.540	18.04

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[1] Burgess, Bulletin, Bureau of Standards, Vol. 10, p. 315, 1914.

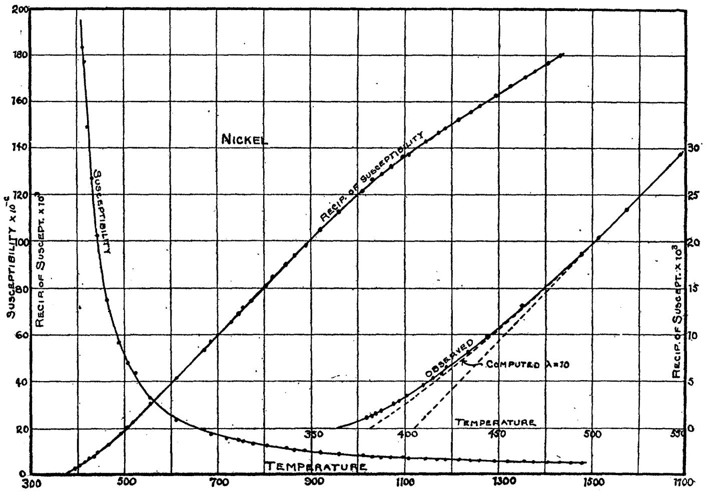

Fig. 5.

Susceptibility as a function of temperature for nickel.

The results for cobalt are given in Table IV. and plotted in Fig. 6. Beta cobalt is similar in its magnetic behavior to beta iron. Starting with the relatively high transformation point of 1100° C. the curve for the reciprocal of susceptibility has a gradual upward curvature throughout the entire region up to the melting point (1485° C.). At this point, the susceptibility curve shows a slight knick, continuing regular, however, as far as the observations were carried.

Table IV.

Temp.	$\chi \cdot 10^{-6}$.	$\frac{1}{\chi} \cdot 10^{4}$.	Temp.	$\chi \cdot 10^{-6}$.	$\frac{1}{\chi} \cdot 10^{4}$.
1100	6010	.01663	1450	54.48	1.836
1144	777	.1287	1479	48.02	2.167
1178	403	.2482	1490	35.42	2.824
1206	294.5	.3395	1517	32.10	3.130
1237	224.7	.4450	1528	29.10	3.436
1267	161.2	.6205	1533	25.95	3.854
1296	133.2	.7508			
1327	104.7	.9615			
1331	102.0	.9800			
1362	88.4	1.131			
1396	72.08	1.387			
1416	63.92	1.564			

Discussion of Results.—These results are in marked contrast to those obtained by Weiss and Foëx,[1] who found Curie's law to hold in all cases. For beta iron, cobalt, and nickel at low temperatures they found, however, that the points for the reciprocal of susceptibility against temperature do not lie on a single straight line but on two straight lines with well defined points of intersection; *e. g.*, 828° C. for iron, 412° C. for nickel, and 1241° C. for cobalt, and they accordingly speak of beta$_1$ and beta$_2$ regions. My experiments have been repeated a great many times and in no case have I ever found evidence of two straight lines but always a smooth curve. For gamma iron, their departures from Curie's law were greatest but there seemed to be a tendency to obey it while my results show that not only is Curie's law not obeyed but the small curvature in the susceptibility plot is in the opposite direction. Delta iron was beyond the temperature range of their apparatus and they were unable to determine the shape of the curve in this region. The transformation temperature which I have obtained, 1407° C., is eight degrees higher than the value given by them. It is obviously then impossible to deduce a Curie constant for these metals or assign a definite number of magnetons to the atom according to the Weiss theory.

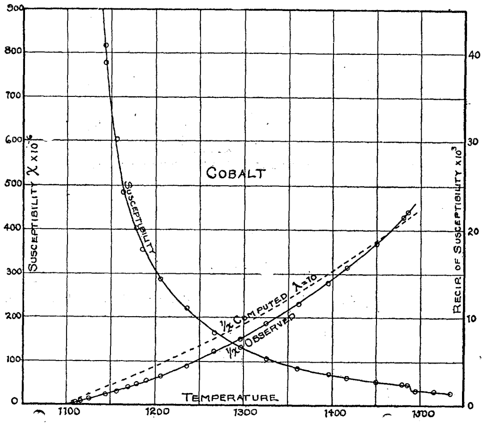

Fig. 6.

Susceptibility of cobalt as a function of temperature.

Keesom's Quantum Theory of Magnetism.—Keesom,[2] following the method of Debye[3] for specific heats, has introduced the quantum theory into the theory of magnetism and obtained an expression for the variation of susceptibility with temperature which, while it does not represent the facts accurately, gives a much better agreement than any other theory thus far proposed. He supposes that the amount of thermal energy which the molecules possess at a given temperature T is to be obtained from a consideration of the equilibrium of a system of rotating molecules with black radiation at that temperature and assumes that Planck's formula, with the addition of a zero point energy, gives the rotational energy in the same manner, as for a linear oscillator. He supposes

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[1] Weiss and Foëx, Arc. des Sc. Phys. et Nat., Vol. XXXI., p. 89, 1911.

[2] Communications, Phys. Lab. Leyden. Sup. No. 32.

[3] Debye, Ann. der Phys., Vol. 39 (4), p. 789, 1912.

further that the molecular rotational energy in a substance can be resolved into a system of stationary waves with a finite number of frequencies and that the high frequency limit is obtained by putting the total number of modes of vibration equal to the number of degrees of freedom, and that the velocity of propagation for each mode of vibration is proportional to the square root of its energy. Taking Planck's equation for the energy of rotation of a single molecule of frequency ν, where by frequency is understood the number of rotations per second,

$$U_{r\nu} = \tfrac{1}{2}\left\{\frac{h\nu}{e^{h\nu/KT} - 1} + \tfrac{1}{2}h\nu\right\} \tag{2}$$

we have for the mean rotational energy for two degrees of freedom about two equivalent axes

$$U_r = \frac{3}{\nu_{\max}{}^3}\int_0^{\nu_{\max}}\left\{\frac{h\nu}{e^{h\nu/KT} - 1} + \tfrac{1}{2}h\nu\right\}\nu^2 d\nu. \tag{3}$$

Introducting the auxiliary variables

$$\xi = \frac{h\nu}{KT}, \quad x = \frac{h\nu_{\max}}{KT}, \quad \theta = \frac{h\nu_{\max}}{K}, \quad \theta_0 = \frac{h\nu_{\max\,0}}{K}, \tag{4}$$

the following equations are obtained which determine U_r as a function of T.

$$\left(\frac{U_r}{U_{r_0}}\right)^{\frac{1}{2}} = 1 + \frac{8}{x^4}\int_0^x \frac{\xi d\xi}{e^{\xi} - 1}, \tag{5}$$

$$\frac{T}{\theta_0} = \frac{1}{x}\left(\frac{U_r}{U_{r_0}}\right)^{\frac{1}{2}}, \tag{6}$$

where

$$U_{r_0} = \frac{3}{8}K\theta_0. \tag{7}$$

The right-hand member of (5) may be developed in the following power series which hold respectively for the larger and smaller values of x:

$$\left(\frac{U_r}{U_{r_0}}\right)^{\frac{1}{2}} = 1 + \frac{8\pi^4}{15}\frac{1}{x^4} - 8\sum_{n=1}^{n=\infty} e^{-nx}\left\{\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right\}, \tag{8}$$

$$\left(\frac{U_r}{U_{r_0}}\right)^{\frac{1}{2}} = \frac{8}{3}\frac{1}{x}\left\{1 + \frac{1}{20}x^2 - \frac{1}{1680}x^4 + \frac{1}{90720}x^6 - \cdots\right\}. \tag{9}$$

In the introduction of the quantum theory into the Weiss theory, it is supposed that the only change brought about is that in discussing the statistics of the orientations of the elementary magnets, the expression RT for the energy of thermal agitation used in the relation deduced by Langevin is to be replaced by the value U_r for the rotational energy.

Thus the Langevin expression for the intensity of magnetization of a paramagnetic gas

$$\frac{I_v}{I_{v_0}} = \frac{\cosh a}{\sinh a} - \frac{1}{a} \quad \text{where}^1 \quad a = \frac{\mu H}{RT} \tag{10}$$

is modified only by putting a equal to $\mu H/U_r$. In the above expression, I_{v_0} is the intensity of magnetization supposing no thermal agitation present and μ is the moment of a single rotating magnetic molecule.

The particular region in which we are interested in this work, namely, that immediately above the Curie point, has been called by Weiss the region of induced ferromagnetism and is characterized by the fact that the molecular field is brought into existence only by the action of an external field and is not so large that the external field may be neglected in comparison to it as is the case in the ferromagnetic region. Accordingly, we have, for the total field of equation (10)

$$H = H_e + NI_v, \tag{11}$$

where N is the molecular field coefficient which is considered constant for a given substance.

The spontaneous magnetization I_v which corresponds to an external field $H_e = 0$, is obtained by the well-known Weiss construction by obtaining the intersection of the curve of equation (10) and the straight line

$$\frac{I_v}{I_{v_0}} = \frac{U_r}{\mu N I_{v_0}} a, \tag{12}$$

which corresponds to the particular value of T chosen. The magnitude of the rotational energy U_{rc} at the Curie point is obtained by equating the slope of the curve at the origin with that of the straight line. Accordingly,

$$\frac{U_{rc}}{\mu N I_{v_0}} = \frac{1}{3}, \tag{13}$$

whence

$$U_{rc} = \frac{\mu N I_{v_0}}{3} = \frac{n \rho \mu^2 N}{3}, \tag{14}$$

---

[1] Before proceeding further it is necessary to define clearly certain of the terms entering into the discussion which are frequently confused by writers in this field.

I_v equals vol. intensity of magnetization, = magnetic moment/volume,
I_m equals mass intensity of magnetization, = magnetic moment/mass,
K equals vol. susceptibility, $= I_v/H_e$.
χ equals mass susceptibility, $= I_m/H_e$;
accordingly

$$I_v = \frac{M}{v} = \frac{\rho M}{m} = \rho I_m$$

and $k = \rho\chi$.

Where ρ equals density. In equation (11) it is the volume intensity which is meant.

where n is the number of rotating molecular magnets per gram and ρ the density of the substance.

The relation between the energy of rotation and the susceptibility is obtained as follows:

$$\chi = \frac{I_m}{H_e} = \frac{I_m}{H - H_m} = \frac{I_v}{\rho(H - NI_v)}, \tag{15}$$

$$\frac{1}{\chi} = \rho\left\{\frac{H}{I_v} - N\right\} \tag{16}$$

but from (10) for this particular region

$$\frac{H}{I_v} = \frac{3U_r}{I_{v_0}\mu} = \frac{3U_r}{n\rho\mu^2}. \tag{17}$$

Therefore

$$\frac{1}{\chi} = \frac{3}{n\mu^2}\{U_r - U_{rc}\}. \tag{18}$$

In the first approximation, namely, for equipartition, and also in the second approximation when, in the development according to positive powers of x, of the second member of equation (5) only the first powers are used, this expression goes over into Weiss's law for the susceptibility above the Curie point. When, however, the complete development is used, the relation between χ and T is as shown in Fig. 7.

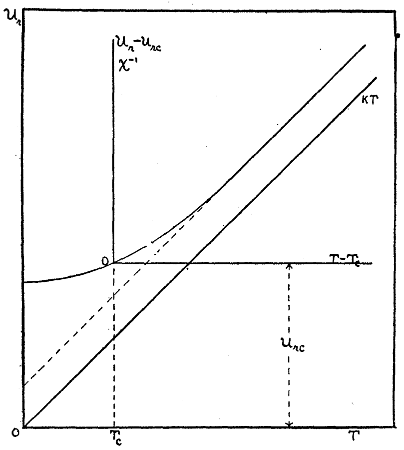

Fig. 7.

Application of Theory to Experimental Results.— Before the theory can be put to test it is necessary to determine the equation for the curve of Fig. 7. The problem algebraically consists in obtaining U_r as a function of T from equations (5) and (6) and substituting in equation (18). While it is impossible to write out this equation in analytical form, one may compute the theoretical curve by means of the power series (8) and (9). For simplicity write equation (18) in the form

$$\chi^{-1} = AU_r - B, \tag{19}$$

where $A = 3/n\mu^2$, and $B = N\rho$.

Put

$$\left(\frac{U_r}{U_{r_0}}\right)^{\frac{1}{2}} = 1 + \frac{8}{x^4}\int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} = f(x). \tag{20}$$

Then

$$\chi^{-1} = \alpha f^2()x + \beta, \qquad (21)$$

where $\alpha = AU_{r_0}$, $\beta = -B$.

$$T = \gamma \frac{f(x)}{x}, \qquad (22)$$

Whence

$$\frac{\chi^{-1} - \beta}{\alpha} = f^2(x) = n(y), \qquad (23)$$

$$\frac{T}{\gamma} = \frac{f(x)}{x} = y. \qquad (24)$$

Thus the experimental $\chi^{-1} - T$ curve is directly related to the experimental $\phi(y) - y$ curve by means of the three parameters α, β, and γ. From the developments of equations (8) and (9), the following table was computed.

TABLE V.

Calculation of Theoretical Curve.

x.	$f(x)$.	$f^2(x)$.	$\frac{f(x)}{x}$.
.250	10.702	114.5	42.81
.500	5.486	30.09	10.97
1.000	2.799	7.838	2.799
1.250	2.297	5.275	1.838
1.429	2.052	4.213	1.436
1.667	1.815	3.292	1.088
2.000	1.588	2.523	.794
2.500	1.378	1.897	.5508
3.000	1.252	1.566	.4172
3.200	1.216	1.478	.3800
3.333	1.1956	1.428	.3588
3.400	1.1856	1.406	.3488
3.600	1.1604	1.346	.3225
3.800	1.1388	1.297	.2998
4.000	1.1212	1.257	.2804
4.200	1.1056	1.221	.2632
5.000	1.0628	1.131	.2127
6.667	1.0238	1.049	.1535
10.000	1.0051	1.010	.1005

The y, $\phi(y)$ curve was then plotted, which is, in reality, the theoretical curve of Fig. 7. The direct method of obtaining the constants α, β, and γ, is by means of the slope of the asymptote and its intercept on the $\phi(y)$ axis, and this method was at first employed. A simpler method, sufficiently accurate for the purpose, is to determine γ by means of the point on the curve at which departure from the asymptote begins which then fixes the correspondence of T and y. Then, by getting corresponding values of χ^{-1} and $\phi(y)$ for two different values of T, two equations in α and β are obtained and their values computed therefrom.

When the calculations were carried out in this manner and applied to the results for nickel, it was found that, although the theoretical curve possesses the same general shape as the experimental one, the departure from the asymptote is not sufficiently rapid. An attempt was then made to see whether by the assumption of a larger zero point energy than is taken in Planck's equation, a better agreement with experimental results could be obtained. This was done by introducing in equation (2) the variable parameter λ as follows:

$$U_{r\nu} = \tfrac{1}{2}\left\{\frac{h\nu}{e^{h\nu/KT} - 1} + \frac{\lambda}{2}h\nu\right\}. \tag{25}$$

When this modified expression is used, and the analytical work carried through in a manner analogous to that employed by Keesom, the following modified developments result:

$$\left(\frac{U_r}{U_{r_0}}\right)^{\frac{1}{2}} = 1 + \frac{8\pi^4}{15\lambda x^4} - \frac{8}{\lambda}\sum_{n=1}^{n=\infty} e^{-nx}\left\{\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right\}, \tag{26}$$

$$\left(\frac{U_r}{U_{r_0}}\right)^{\frac{1}{2}} = 1 - \frac{1}{\lambda} + \frac{1}{\lambda}\frac{8}{3x}\left\{1 + \frac{1}{20}x^2 - \frac{1}{1680}x^4 + \frac{1}{90720}x^6 \cdots\right\}, \tag{27}$$

which were then used in connection with equations (5) and (6).

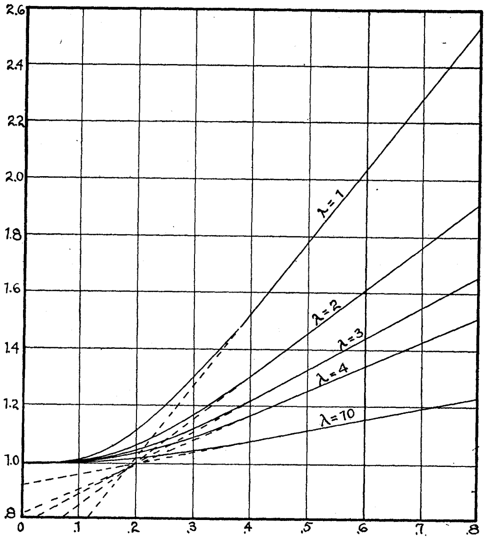

Fig. 8.

By assigning different values to λ the family of y, $\phi(y)$ curves shown in Fig. 8 was computed. These curves were then transformed so as to have the same asymptote with their points of departure from the asymptote made to coincide, and the family shown in Fig. 9 was computed. Taking λ equal to ten and fitting once more to the experimental curve for nickel, the curve shown dotted in Fig. 5 was obtained. It is to be observed that the agreement is still unsatisfactory. A better agreement would of course result if a still larger value of λ were used; but with the value employed, the theory is so badly distorted that it does not seem worth while. The experimental curve for cobalt shows no tendency to approach an asymptote below the melting point hence it is difficult to attempt to check it. However, selecting the region of the theoretical curve for which the curvature is greatest, to give the theory the best possible advantage, the dotted curve in Fig. 6 was obtained. The departures between the theoretical and experimental curves for beta iron are so great that no calculation was made.

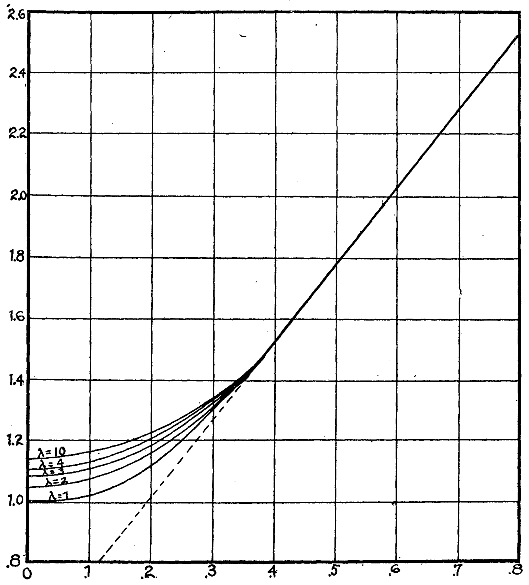

Fig. 9.

SUMMARY

1. The magnetic behavior of iron, nickel, and cobalt has been studied from the temperatures of their transformation points up through their melting points.

2. With the exception of nickel in limited regions, Curie's law is not obeyed.

3. In the regions immediately above the transformation points, for all three metals, the curve for the reciprocal of susceptibility is a smooth one with a marked upward concavity, instead of two intersecting straight lines as obtained by Weiss and Foëx.

4. Keesom's quantum theory of magnetism fits the experimental results in a qualitative way, but requires further modification.

5. The assumption of a larger zero point energy in Planck's equation is not sufficient to bring the theory into agreement with experimental facts.

Physical Laboratory,
University of Wisconsin,
December, 1916.