THE MAGNETIC PROPERTIES OF ISOLATED FERROMAGNETIC ATOMS

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(Received August 12, 1929)

Abstract

In order to obtain a better knowledge of the elementary atomic magnet, its behavior when surrounded by non-magnetic atoms rather than by other magnetic ones has been studied. For this purpose alloys of 90% and 95% platinum with the remainder cobalt and nickel, respectively, have been investigated. Only the cobalt alloys were found magnetic. The magnetic moment per cobalt atom being greater than for pure cobalt, the platinum may contribute to the magnetism. Variation of magnetization with temperature and the Curie points have been measured, the latter falling rapidly as the cobalt content decreased. Various hysteresis loops, showing the relation between the magnetization and applied magnetic force have also been obtained, the hysteresis being less for the 10% Co alloy, after annealing. In the hard-drawn state, however, the hysteresis and Curie points are considerably higher. The results are shown to be in agreement with Heisenberg's theory of ferromagnetism.

Introduction

Judging from the varied experimental results, the subject of ferromagnetism appears to be a most complicated one, and it has been very difficult to find a theory which will explain all the phenomena satisfactorily. The actual explanation cannot be as complicated as experiments suggest, because it must be closely bound with that of atomic structure, where there is little room left for any special mechanism to account for magnetism. The work of Barnett and of Einstein and de Haas points to the spinning electron as the elementary magnet. Weiss[1] has shown that Langevin's theory of paramagnetism may be extended to account for ferromagnetism by assuming the latter to be characterised by an "internal magnetic field" of very great magnitude. The recent theory of Heisenberg,[2] based on quantum mechanical considerations, although still very rough and incomplete, appears to point the way to the most satisfactory explanation of ferromagnetism. This theory explains the inner magnetic field of Weiss as due to resonance between the spins of the valence electrons of neighboring atoms, just as Heitler and London[3] introduced the idea of resonance to explain the formation of the H_2 molecule. Ferromagnetism thus means the orientation over a crystal of the spins of the electrons, the force of orientation being really

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[1] P. Weiss and G. Foëx "Le magnétisme" (1926).
[2] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928).
[3] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).
W. Heitler, Zeits. f. Physik **47**, 835 (1928).
F. London, Zeits. f. Physik **46**, 455 (1928).

Pauli's exclusion principle (or symmetry considerations of the eigenfunctions). The complete success of the theory seems to be limited only by the complication of the mathematics, due to the fact that we are dealing with a problem of many particles and hence of many dimensions. But Fowler and Kapitza[4] already have succeeded in applying it in a rough way to account for the phenomena of the Curie point-change in volume, specific heat, etc.

That ferromagnetism has appeared from experiments to be such a complicated subject is due mainly to the fact that what have generally been observed are statistical phenomena from which it is naturally very difficult to arrive at a knowledge of the elementary mechanism. In the present experiment, an effort was made to simplify conditions. In a specimen of, say, cobalt, each ferromagnetic cobalt atom is immediately surrounded by others which greatly modify its behavior through interaction. But the aim of this problem was to measure the magnetic properties of alloys of cobalt with a non-ferromagnetic element, the cobalt content being so small that most of the cobalt atoms would be surrounded by non-ferromagnetic atoms. In this isolated state, it was hoped to obtain a better idea of the behavior of the cobalt atoms.

According to the theory of Heisenberg, on the other hand, ferromagnetism is not due so much to the individual atoms as to the interaction between closely neighboring atoms. A single atom may have a magnetic moment, as Gerlach and Stern have shown, but it cannot exhibit the peculiarities of ferromagnetism, such as hysteresis. In view of this, one would expect the isolation or separation of the ferromagnetic atoms to result in reduction of hysteresis or even loss of ferromagnetism. This problem was, therefore, of interest in the light of Heisenberg's theory.

The Alloys

In the choice of suitable alloys, the first consideration was that the two constituents should be mutually soluble, forming solid solutions. Consultation of the International Critical Tables[5] and other sources limited the possibilities to certain alloys of Fe, Ni, or Co with Cu, Ag, Au, Cr, Mn, Pd, or Pt. Several of these combinations have already been investigated[6, 7, 8, 9, 10] and found non-magnetic even for large proportions of the ferromagnetic element. Hadfield,[11] for example, found the Fe-Mn series non-magnetic beyond 17% Mn, due, presumably, to a chemical combination between the iron and manganese. Mn and Cr were further to be avoided because they are so closely related to Fe in their electronic configurations, and Fe, as it, with its several phases, is more complex.

[4] R. H. Fowler and P. Kapitza, Proc. Roy. Soc. **A124,** 1 (1929).
[5] International Critical Tables, Vol. II, 400–455.
[6] B. V. Hill, Verh. d. D. P. Ges. **4,** 194 (1902); Phys. Rev. **24,** 321 (1907).
[7] G. Tammann, Zeits. f. phys. Chem. **65,** 73 (1909); Z. f. anorg. Chem. **52,** 25 (1907), etc.
[8] R. Sahmen, Zeits. f. anorg. Chem. **57,** 1 (1908).
[9] K. Lewkonja, Zeits. f. anorg. Chem. **59,** 293 (1908).
[10] R. Gans and A. Fonseca, Ann. d. Physik [4] **61,** 742 (1920).
[11] R. Hadfield, Proc. Roy. Soc. **A115,** 120 (1927).

The second chief consideration was to find alloys in which the concentration of Ni or Co could be made small without disappearance of ferromagnetism. This was generally impossible, as Heisenberg's theory predicts. Fortunately, it was found that Co-Pt and Ni-Pt wires of about the desired compositions were being made by the Bell Telephone Laboratories, and that at least some of these alloys were magnetic; they very kindly supplied alloys whose compositions by weight were the following:

10% Co—90% Pt
5% Co—95% Pt
10% Ni—90% Pt
5% Ni—95% Pt

The metals used in making them had been carefully purified to 99.9+%. These alloys were analysed and found not to vary from the above proportions by more than 0.05%. The crystal structure was believed to be that of platinum, i.e. face-centered cubic, and on measurement, the densities proved to be about the same as those calculated from the relative proportions of the two constituents and their repsective densities. Platinum has been found to form solid solutions with both cobalt and nickel, and no compounds are known.

To have the alloys in the form of wires was advantageous because of the greater homogeneity produced by the cold work of drawing. The wires were 1m long and 0.003 to 0.03 inches indiameter. They were tested in both the hard-drawn state and after a heat treatment which consisted of annealing them for three hours at 1000°C and then at lower temperatures.

Experimental Method

For each alloy, two sets of measurements were made. (1) The applied magnetic force, H, was kept fixed and the intensity of magnetization, I, measured at different temperatures up to the Curie point, or temperature above which the alloy is no longer ferromagnetic. (2) At a given temperature, hysteresis loops, showing the cyclic variation of I with H, and the value of I near saturation were obtained. The results for the cobalt and nickel alloys were compared and the effect of increasing the platinum content studied.

The ballistic method was employed for measuring the magnetization. Two identical copper rings with grooves were constructed, mean diameter = 3.58 cm. In the groove of one ring was wound the alloy wire, the ends being spot-welded together. The two rings were wound identically with a primary and secondary winding of enameled copper wire, the layers being insulated with satin ribbon. The rings were connected differentially, the secondaries being in series with a ballistic galvanometer, which, on calibration, gave a sensitivity of 48 maxwells per mm. The only effect on the galvanometer was that caused by the presence of the alloy, the total flux through the circuit being:

$$F = N_s A_w (B - H) = 4\pi N_s A_w I$$

where N_s is the number of secondary turns, A_w the cross-section of the alloy, B the magnetic induction, and I the intensity of magnetization, whose change can thus be measured. The primary current was supplied by storage cells and read on an ammeter. H was then given by:

$$H=0.4N_p i/d$$

where N_p is the number of primary turns, i the current in amperes, and d the mean diameter of a ring. By means of switches and resistances any variation, ΔH, could be produced.

The two rings were placed in a Dewar flask containing a temperature-controlling bath. The temperature of the alloy was measured by copper-

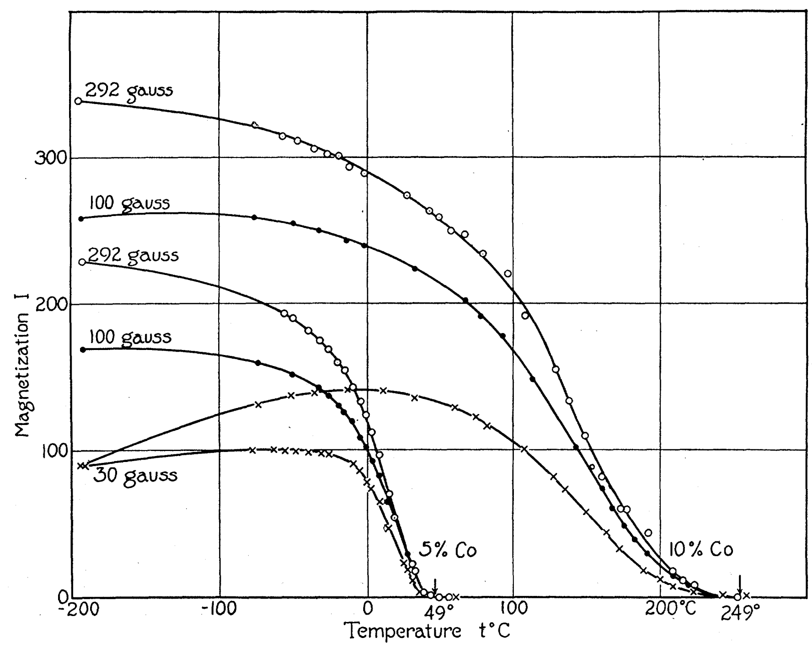

Fig. 1. Magnetization as a function of temperature.

constantan thermocouples, one set of junctions being soldered at various points around the ring of alloy and the other set kept in ice. The e.m.f.'s were measured by a potentiometer arrangement, the thermocouples being standardised at various fixed points covering the range over which they were used. For constant temperature baths, the following were used: liquid air, (about $-192°C$); a mixture of solid CO_2 and alcohol, (about $-78°C$); and boiling acetone, ($+56°C$). In measuring the variation of I with temperature, various non-conducting liquids were used for baths and the primary current allowed to warm them up at the rate of 1° per minute or less.

In order to measure the initial curve of magnetization for an alloy, the alloy was first demagnetized by heating it above its Curie point, where the magnetization is lost; above this point, any deflection of the galvanometer on reversing H was due only to inequality in the dimensions of the two rings and in their windings, and the small correction thus obtained was applied to all the readings.

Results and Discussion

Fig. 1 gives the variation of magnetization with temperature for the two cobalt alloys in the annealed state. The values of H used were 30,

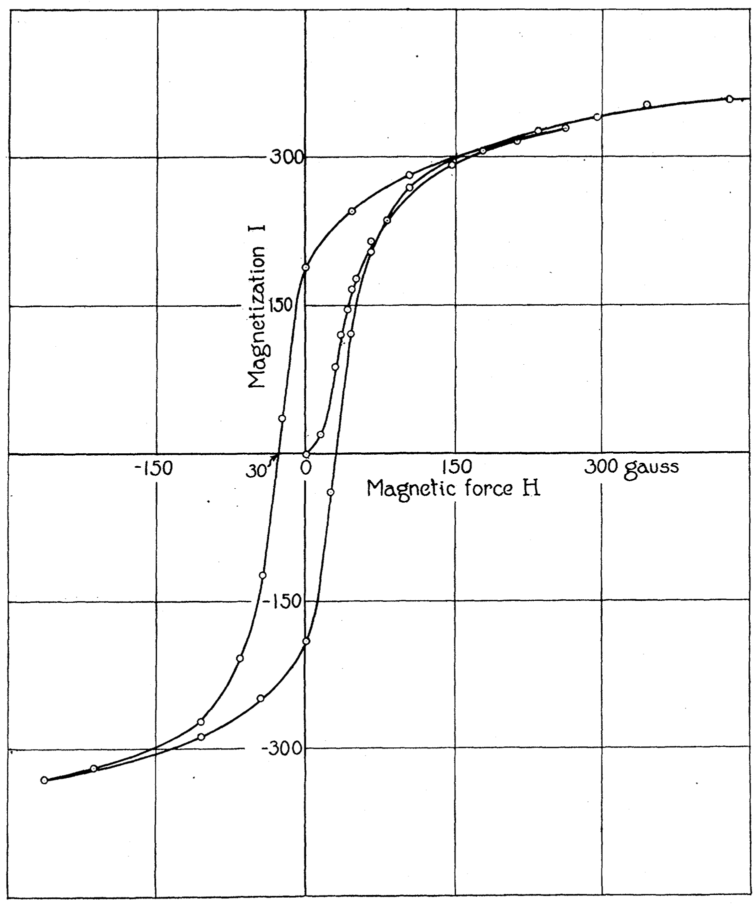

Fig. 2. Hysteresis loop for 10% Co-90% Pt alloy at −194°C.

100 and 292 gauss. As has often been observed in other cases, such as that of soft iron, with small values of H susceptibility at first increases with temperature and then rapidly falls to zero at the Curie point, while for larger values of H it decreases steadily and more gradually.

The Curie points are at 249°C (522°K) and 49°C (322°K) for the 10% Co and 5% Co alloys respectively. For pure cobalt the Curie point is 1115°C (1388°K). As the atomic percentage of platinum in the alloys was

73.1% and 85.2% respectively, the depression of the Curie point is not proportional to these percentages nor to the amount of platinum present by weight (Van't Hoff's formula), but the Curie point appears to drop more and more rapidly as the platinum content increases. This continuous depression of the Curie point has been observed for other series of alloys in which one component is ferromagnetic, e.g. the Ni-Cu series. These results agree with Heisenberg's theory of ferromagnetism, further isolation of the ferromagnetic atoms resulting in less interaction or resonance between them. This is equivalent to making the factor n of the Weiss[1] molecular field smaller and hence, the Curie point, which is proportional to n, lower.

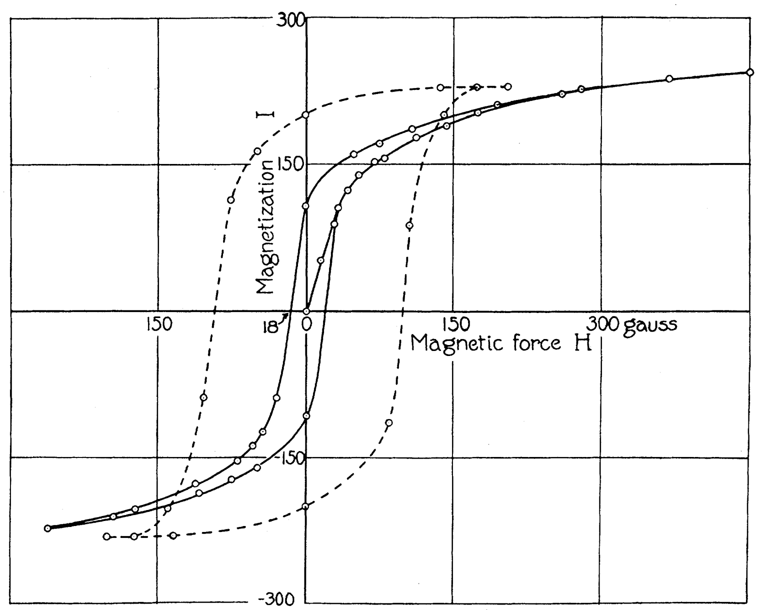

Fig. 3. Hysteresis loop for 5% Co −95% Pt alloy at −192°C.

The two nickel alloys showed no ferromagnetism, on the other hand, even down to liquid air temperatures, (80° K), although a value of I as small as 0.5 cgs units could have been measured. The question arises whether the Curie points are between 0° and 80° K, or whether the alloys are non-magnetic at all temperatures. As the Curie point for nickel is 358°C(631° K), the depression has been much more rapid and not at all proportionate to that in the cobalt series. Kamerlingh-Onnes, Hadfield and Woltjer[12] in their investigation of the Fe–Mn series found that although for all the magnetic alloys, the Curie point was at about 770°C, with 16% or more manganese, the alloys were non-magnetic even in liquid helium, due, perhaps, to the formation of a compound, Fe_5Mn. This may be the explanation in the present

[12] H. Kamerlingh Onnes, R. A. Hadfield and H. R. Woltjer, Proc. Roy. Soc. **A99**, 174 (1921).

case. However, even without compound formation sufficient separation of the ferromagnetic atoms should result in complete loss of ferromagnetism on the Heisenberg theory, so that the Curie point would probably reach absolute zero before the platinum content has become 100%.

Figs. 2 and 3 (full lines), give the curves of initial magnetization and typical hysteresis loops at liquid air temperatures for the two Co alloys after complete annealing. Although H was increased to 600 gauss a slight increase in I still continued. The maximum values attained are given in Table I.

TABLE I. *Maximum values of I and the magnetic moment per cobalt atom.*

	100% Co	10% Co	5% Co
I_{max}	1400	364	254
$\sigma_a \times 10^{20}$	1.56	1.96	2.48
		1 Bohr magneton $=0.92\times10^{-20}$	

The second row of Table I gives the magnetic moment per cobalt atom, σ_a, assuming the platinum atoms do not contribute to the magnetism. But as σ_a is considerably greater as the platinum content increases it appears likely that the platinum does contribute. Consider Heisenberg's interaction integral:

$$J_0=\tfrac{1}{2}\int\int \psi_k{}^{\kappa}\psi_k{}^{\lambda}\psi_l{}^{\kappa}\psi_l{}^{\lambda}\left\{\frac{2e^2}{r_{kl}}+\frac{2e^2}{r_{\kappa\lambda}}-\frac{e^2}{r_{\kappa k}}-\frac{e^2}{r_{\kappa l}}-\frac{e^2}{r_{\lambda k}}-\frac{e^2}{r_{\lambda l}}\right\}d\tau_k d\tau_l$$

where k, l refer to the two electrons and κ, λ to the two neighboring nuclei, Ψ is the unperturbed wave function for the given electron near the given nucleus, and $d\tau$ is an element of the configuration space of the electron. It is essential for ferromagnetism that J_0 be positive. Now Fowler and Kapitza[4] have pointed out that it is quite likely that J_0 is positive for platinum and hence, it would not be surprising for platinum atoms to be capable of ferromagnetism.

TABLE II. *Coercive force for various loops.*

t	H_{max}	H_c(10% Co)	H_c(5% Co)
$-192°$	262	30	18
$-\ 54°$	262	22	12
$-\ 69°$	140	21	12
$+\ 56°$	262	17	non-mag.

The hysteresis loops, while quite steep are otherwise normal. The hysteresis for the 5% Co alloy is, however, only about half that for the 10% Co alloy. Just as for the Curie points, this can be explained as due to the decrease in the Weiss factor, n, which Heisenberg's theory predicts. Table II gives values of the coercive force, H_c, given by various loops.

The effect of annealing was found very important. Annealing presumably produces a more uniform and regular distribution of the cobalt atoms through-out the platinum crystal lattice, while in the hard-drawn state, groups of cobalt atoms will be bunched together. As, on Heisenberg's theory, it is only the closely neighboring atoms that contribute to the magnetism, the effect of annealing should be similar to that of further isolating the magnetic atoms. This was found to be the case. The broken curve of Fig. 3 corresponds to the hysteresis loop for the 5% cobalt wire in the hard-drawn state, and it is seen to be much larger and more rectangular; H_c is 96. The other curves for the hard-drawn state are similarly larger, though H_c is here greatest for the 5% Co alloy. Annealing at temperatures as low as 350° C produced considerable effect. The effect of annealing on the Curie point was again in agreement with theory, the hard drawn 10% Co specimen losing its magnetism at 305° C as against 249° C for the annealed state. The Curie point of the 5% Co alloy was only slightly affected.

A temperature hysteresis was noted. Although the loss of magnetism on heating and its reappearance on cooling occurred at about identical temperatures with the annealed wires, the values of I at temperatures a little below the Curie points were considerably less for the cooling measurements.

In conclusion, it may be said that while the isolation of ferromagnetic atoms attempted in these alloys has not produced any unusual changes in the magnetic properties of these atoms, except a possible increase in the average atomic magnetic moment, yet the changes that are observed are all in agreement with the Heisenberg theory of ferromagnetism.

The writer wishes to thank the National Research Council for its support and the Bell Telephone Laboratories for so kindly supplying the wires used. It also gives the writer great pleasure to acknowledge his indebtedness to Professor L. W. McKeehan for suggesting the problem, and to Professor R. A. Millikan for the facilities of the Norman Bridge Laboratory.