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SOME MAGNETIC PROPERTIES OF PLATINUM-RICH Pt-Fe ALLOYS

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Résumé. — On présente les résultats des mesures de la susceptibilité magnétique et de l'aimantation spontanée des alliages platine-fer ayant la structure cubique à faces centrées et une composition voisine de Pt_3Fe et également des alliages contenant moins de fer. Au voisinage de la surstructure Pt_3Fe il semble que les alliages sont antiferromagnétiques quand ils sont ordonnés et ferromagnétiques quand ils sont désordonnés. Les alliages les plus dilués sont ferromagnétiques jusqu'à 2 at. % de fer.

Abstract. — Measurements of magnetic susceptibility and spontaneous magnetization on face centred cubic platinum-iron alloys having compositions around Pt_3Fe and also on alloys with lower iron contents, are reported. In the Pt_3Fe superlattice region the alloys appear to be antiferromagnetic when ordered and ferromagnetic when disordered. The more dilute alloys are ferromagnetic, even down to 2 at. % of iron.

The existence of superlattices in platinum-rich solid solution alloys containing chromium, manganese or iron has been known for some time. In each case, the face-centred cubic solid solution based on platinum extends from 0 % to well above 25 % of the solute. The superlattices all exist over a range of composition, with maximum ordering at the 25 % composition, and are of the AuCu_3 type. They are stable up to temperatures of the order of 700 °C and above, and are easily formed.

Ferromagnetism has been previously detected in the platinum-rich solid solutions, by Friedrich and Kussman (1935) for the platinum-chromium system, by Auwärter and Kussman (1950) for platinum-manganese, and Kussman and von Rittberg (1950) for platinum-iron. In the two systems platinum-chromium and platinum-manganese the strongest ferromagnetic effects were reported to occur near the composition of maximum superlattice. For platinum-iron, however, the 25 % alloy was found not to be ferromagnetic under the conditions used by Kussman and von Rittberg: the ferromagnetic properties developed on both sides of this composition.

In the present work, the magnetic susceptibility of various platinum-iron alloys near the Pt_3Fe composition has been measured as a function of temperature. It has been found that in general the Curie-Weiss Law is obeyed at high temperatures, extrapolating towards a paramagnetic Curie point θ_p , which depends on composition. The observations are typified by the results shown in fig. 1, which refer to an annealed alloy containing 26.3 atomic percent of iron. In this case θ_p is about -90 °K. On cooling this alloy below room temperature, deviations from the Curie-Weiss Law begin at about 200 °K. The susceptibility rises to

a distinct maximum at 105 °K, and then falls at lower temperatures. At about 50 °K another increase in susceptibility begins.

In most cases, susceptibilities were measured in an

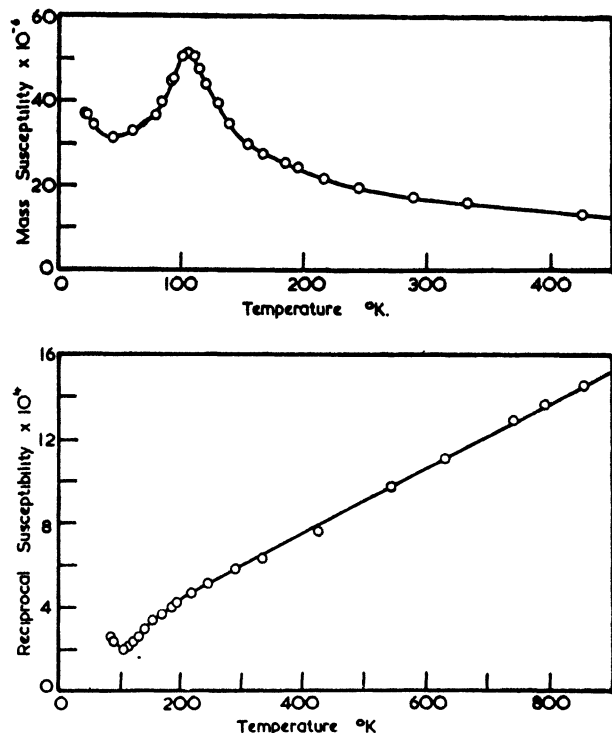


FIG. 1. — Susceptibility of annealed 26.3 % PtFe alloy.

applied field of 8.2 kilo-oersteds. In the alloy to which fig. 1 refers, measurements were also made in a range of field strengths between 2.5 and 10.8 kilo-oersteds at temperatures of 20°, 80°, 200° and 290 °K. No significant variation of the sus-

ceptibility with field was detected here, implying that no ferromagnetism was present. All the measurements were repeatable, and no time-dependent effects were discovered.

The presence of the superlattice in this non-ferromagnetic specimen has been confirmed by X-ray examination, and diffraction observations made at 80 °K showed that no major phase transformation was associated with traversing the peak in the susceptibility-temperature curve.

All these observations seem to suggest the existence of antiferromagnetism in the ordered state of alloys near to the 25 % composition.

The effect of composition variations is shown in fig. 2. The lowest value of θ_p was about

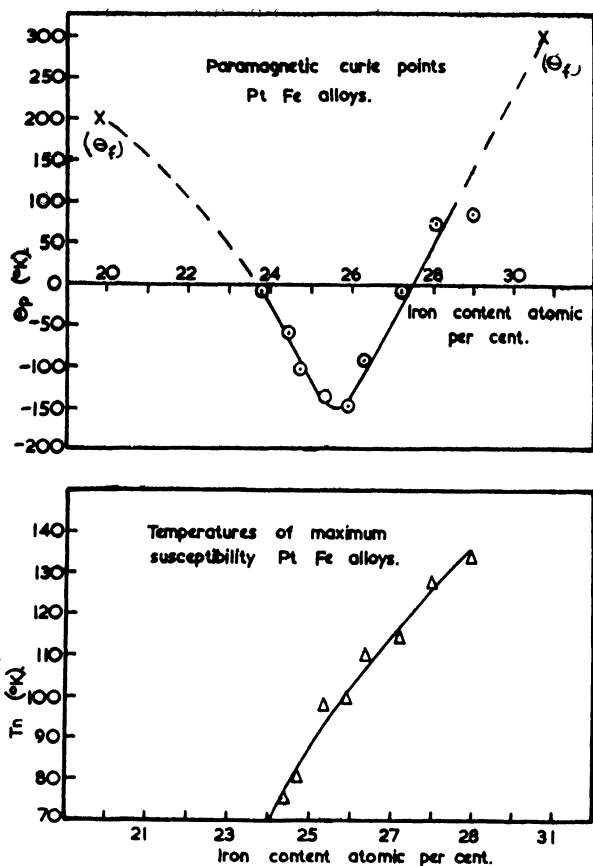


FIG. 2. — Variation of θ_p and T_n with composition for annealed PtFe alloys.

— 150 °K, at a composition of about 25.5 atomic percent of iron. It was below 0 °K between 23.7 % and 27.2 %, otherwise having positive values. The temperature T_n of the susceptibility maximum also changes with composition, being below 80 °K at 24.5 % and above 130 °K at 29.0 % of iron. The shape of the susceptibility peak depends on the iron content, being rather obtuse when it occurs at the lower temperatures

and becoming very acute at about 27 % of iron and above.

In some alloys possessing low but positive values of θ_p , a dependence of susceptibility on applied field was detected at the lower temperatures. This appeared to have the characteristics of the development of a weak ferromagnetism superimposed on the paramagnetic properties also present at the higher temperatures. The magnetization, estimated from the variation of the apparent susceptibility with field, changed with temperature after the general manner of a normal ferromagnetic. In the 28.0 % alloy, the specific magnetization (extrapolated to zero temperature) was rather less than 1.0×10^{-2} e. m. u./gm, and the ferromagnetic Curie point θ_f of this component was about 230 °K. In this same alloy θ_p was + 85 °K and T_n just below 130 °K. At the somewhat higher iron content of 30.7 %, the alloy appeared to have all the properties of a normal ferromagnetic: its magnetization at the absolute zero corresponded to a mean moment of 0.07 Bohr magnetons per atom, and its Curie point θ_f was 300 °K.

At compositions with lower iron contents than 24 %, quite strong ferromagnetism develops rapidly. In the 19.8 % alloy the mean moment per atom at zero temperature was 0.28 and at 13.4 % it was 0.65 Bohr magnetons. Ferromagnetism is still present at only 2 % of iron.

It was found that in those alloys in the centre of the composition region studied, which showed no ferromagnetism in the annealed state, the application of cold work caused them to become quite strongly ferromagnetic, even at room temperature. In the 26.3 % alloy, the mean moment per atom of material powdered by means of a file was 1.22 Bohr magnetons. X-ray examination of this same powder showed that its structure was still face-centred cubic. The lattice parameter was apparently the same as for the undeformed material, but no superlattice reflexions were observed. The production of ferromagnetism cannot possibly have arisen primarily from an undetected precipitation of iron from solution, for if the magnetization were attributed wholly to the iron present, the iron atoms would each have a moment of about 4.6 Bohr magnetons. This is more than twice the value normally observed in metallic iron. Annealing removed the ferromagnetism and restored the superlattice reflexions. It is tentatively suggested that the primary effect of the cold work was to destroy the superlattice, and that the disordered state is ferromagnetic.

Another interesting and surprising feature of the ferromagnetic alloys is the strong magnetization of the alloys with the smallest iron contents. In the 13.4 % alloy, if all of the magnetic moment resided on the iron atoms, they would each have a moment of 4.8 Bohr magnetons. Also, in such an

alloy, the mean separation of the iron atoms is very large indeed, compared with the usual interatomic distances in other ferromagnetic iron alloys in which iron is the solvent.

Further work on this and related problems is at present in progress.

REFERENCES

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DISCUSSION

Mr. Wohlfarth. — The result that very small amounts of iron causes ferromagnetism to appear in these dilute alloys may mean that the platinum itself becomes the carrier of ferromagnetism, in agreement both with results for palladium alloys and also with my ideas on these alloys, based on the collective electron treatment (*J. Phys. Chem. Solids*, 1956, **1**, 35). There is also an old idea that the number of effective carriers in platinum is smaller than that in palladium. On the other

hand, small amounts of iron in gold (Kaufmann) also causes ferromagnetism to appear, and here the explanation is presumably different. The question remains open, but is one of great interest.

Mr. Crangle. — While it is true that the magnetic moment per iron atom when iron is dissolved in different solvents differs, this does not prevent the iron from being the carrier of the moment. Different states of ionisation of the iron are presumably possible, depending on the solvent.

M. Voigt (Remarque). — Dans les alliages Pt-Cr, on trouve du ferromagnétisme, mais on ne le trouve pas dans les alliages Pd-Cr.

Mr. Kikuchi. — In the solid solution region of the dilute Fe alloy, the Curie point is expected to vanish at a certain finite concentration of Fe. (A theoretical analysis is to be published by Sato, Arrott and Kikuchi.)

Mr. Crangle. — The measured Curie point is proportional to the Fe concentration, and passes through 0 °K at 0 % Fe. There is no indication of the Curie point vanishing down to 2 atomic % of Fe.