

The Magnetic Properties of Platinum Metals and Alloys

A SURVEY OF RECENT RESEARCH

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Well-marked magnetic properties are associated always with electrons in incomplete inner electron shells which maintain a comparatively localised and atomic character in the solid state – unlike the delocalised conduction electrons which become a property of the solid as a whole. There is not, however, an absolutely clear-cut division between localised and non-localised situations. The best example of the well-localised situation is provided by the incomplete *f*-electron shells of the rare earth metals. In gadolinium the 7 *f*-electrons per atom play no part in bonding and *f*-electrons on neighbouring atoms in the metal are only “aware of one another” because of indirect coupling through the three conduction electrons per atom which can, as it were, tell one atom of the orientation of the magnetic moment provided by the *f*-electrons on another atom.

The 3*d* electron shells of the first transition group metals (especially manganese, iron, cobalt and nickel) are not as well localised as the rare earth *f*-electrons, and in the pure metals strong direct interactions between *d*-electrons on neighbouring atoms are certainly present. (We still do not know whether these direct interactions or indirect ones through the conduction electrons are dominant in providing the ferromagnetism of iron, cobalt and nickel.) The *d*-electrons become somewhat more localised on passing along a transition series (Ti→Ni) but appreciably less localised on going from the first to the second to the third transition

series (Co→Rh→Ir), and strong *magnetic* interactions are absent in osmium, iridium and platinum because the 5*d* electrons on neighbouring atoms are behaving more like conduction electrons than like localised ones. Palladium, at the end of the second transition series, is very nearly a magnetically ordered material, and small amounts of iron in solid solution produce a ferromagnetic moment which is not all provided by the iron atoms.

Even stronger effects are produced when small amounts of iron are added to those palladium-rhodium alloys (~5 per cent rhodium) where the work of F. E. Hoare and others at the University of Leeds has shown that the conditions required for ferromagnetism are very nearly satisfied.

A large amount of work has been carried out recently on dilute alloys of transition metals of the 3*d* series dissolved in palladium or platinum, much of it at the Bell Telephone Laboratories. The results have been compared with the magnetic behaviour of solutions of iron in the earlier members of the 4*d* series, where iron does not always carry a magnetic moment. In niobium where the electronic density of states is high dissolved iron atoms have no moment; but the high density of states in platinum and palladium does not prevent the appearance of a moment on the iron atoms, presumably because of the more localised character of the *d*-electrons of the solvent.

If manganese, iron or cobalt is dissolved in a non-transition metal (for example gold) the *d*-electrons have no neighbouring *d*-elec-

trons to interact with and become more localised – that is, more like the *f*-electrons or rare earth metals – and there are interesting resemblances between *lanthanum-gadolinium** alloys and *gold-iron* or *copper-manganese* alloys, since in all three the only magnetic interactions are via the conduction electrons. From this point of view platinum, iridium and rhodium can perhaps be regarded as simple “non-magnetic” solvents for iron, but palladium certainly gives a different and more complicated situation. Recent work by the present author has revealed striking effects in the low temperature electrical resistance of dilute solutions of iron in palladium, platinum, rhodium and iridium. These seem to be related to, but much stronger than, the well-known anomalies in electrical resistance shown by the above mentioned *gold-iron* and *copper-manganese* alloys.

In more concentrated alloys of the iron group metals neighbouring atom interactions become important, and striking effects can sometimes be produced by transitions from disordered structures to ordered structures. FeAl and Au₃Mn provide examples of this, but for metallurgical reasons, such as size factors, most extensive solid solutions where ordering is possible are in alloys with platinum metals. A striking example is the Pt₃Fe alloy, which if perfectly ordered (no Fe-Fe nearest neighbours) is antiferromagnetic; but a few extra iron atoms that occupy platinum sites convert much of the neighbouring material to a ferromagnetic state (1).

Iron-Rhodium Alloys

A number of papers presented to the Eighth Conference on Magnetism and Magnetic Materials held recently in Pittsburgh dealt with various aspects of the magnetic properties of the platinum metals and their alloys which can be discussed in relation to the points made above.

*This notation indicates a dilute solid solution of gadolinium in lanthanum.

The striking change with temperature in magnetic properties in iron-rhodium alloys containing equal atomic percentages of each element has been known for some time, and a short review of the data available up to about a year ago was given in this journal in January last year (2). This ordered CsCl type alloy changes from antiferromagnetic to ferromagnetic at $\sim 360^\circ\text{K}$ in zero external field, but at $\sim 220^\circ\text{K}$ in a field of 120,000 gauss.

Now Flippen and Darnell of du Pont (3) have discussed the thermodynamics of this field dependence; while Shirane, Chen and Flinn of Westinghouse, together with Nathans of Brookhaven (4) have published the results of Mossbauer studies of the magnetic field seen by the *nucleus* of an iron atom and the differences for iron atoms in “right” positions and “wrong” positions.

Kouvel and his co-workers at the Schenectady laboratory of General Electric who carried out transformation studies on the iron-rhodium alloy, have now moved on to investigate the possibility of an analogous behaviour being found in its isomorph MnRh (5).

There is a martensitic transformation (with hysteresis) from a high temperature ordered CsCl structure to a low temperature CuAu structure. The high temperature form is paramagnetic (it would probably become antiferromagnetic at low temperatures) and the low temperature form is *strongly* antiferromagnetic. The change therefore produces a change in density and resistance, but these are not sharp since there seems to be a rather extensive range between the start and end of the martensite transformation. In this connection a survey of the behaviour of the related phases FeRh, MnIr, MnNi and the effects of substitutions into these of other transition metals would probably be of interest.

Platinum Alloys

Alloys of platinum with small amounts of manganese, iron, cobalt and nickel were

described by Bozorth, Davis and Wernick of Bell Laboratories to the International Conference on Magnetism in 1961 and were compared with similar palladium-based alloys (6).

For the platinum alloys effects are much weaker (the highest Curie temperature for a 1 per cent alloy (Co or Fe) is $\sim 17^\circ\text{K}$ as compared with 80°K for Pd-Co 1 per cent and the size of the magnetic moment produced on platinum atoms is very much less than that produced on palladium atoms. It is clear that even if the *d*-electrons of iron can be regarded as localised when it is dissolved in platinum (like the *f*-electrons of gadolinium when dissolved in lanthanum) the strength of the interaction between them (the indirect interaction via the conduction electrons) is very much stronger than in non-transition solvents because the conduction electrons in platinum have a lot of *d*-character themselves.

In another paper to the Pittsburgh Conference Pickart and Nathans (7) have reported neutron diffraction studies on manganese-platinum and chromium-platinum alloys. Both have the Cu_3Au structure and there seems to be some magnetic moment on the platinum atoms, but in Pt_3Cr this is in the opposite direction to the tenfold larger moment on the chromium atoms.

Iron-Palladium and Gadolinium-Palladium Alloys

Iron-palladium alloys with small amounts of iron have also been studied by neutron diffraction by Cable and his colleagues at Oak Ridge (8). The magnetic moment on the iron atoms has been found to be equivalent to 3.0 electron spins (as compared with 2.22 in pure iron). There is a moment of 0.15 units on the palladium atoms in the 3 per cent iron alloy. This has been calculated assuming that all palladium atoms have similar moments. There is other evidence to suggest, however, that for very dilute alloys down to 1 per cent iron only palladium

atoms next to an iron atom have a moment and that it is ~ 0.5 units.

Gadolinium-palladium alloys with small amounts of gadolinium have been studied extensively by workers at the Bell Laboratories, using the techniques of electron paramagnetic resonance. The magnetic field for this resonance is significantly different from that for gadolinium in alloys with non-transition metals, so that although the magnetic properties are dominated by the 7 localised *f*-electrons of gadolinium the nearly magnetic character of palladium does modify matters slightly, although less strongly than in palladium-iron. This has now been shown (9) by adding hydrogen to palladium containing gadolinium and thereby filling up with extra electrons the *d*-electron states of the palladium. The effect is to make the gadolinium behave as it does in non-metallic situations or in solution in simple metals. The same effect is produced, incidentally, by adding silver to palladium containing gadolinium. (With the metals osmium and ruthenium gadolinium forms weakly ferromagnetic intermetallic compounds GdOs_2 and GdRu_2 , but the similarity in properties to GdAl_2 suggests that the transition metal character of the osmium and ruthenium is less important than that of palladium in the above alloys).

References

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