Electronic Structure and Properties of Palladium and its Alloys

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At a Conference held in April at the University of Leeds, organised by Professor F. E. Hoare and Professor J. S. Dugdale, a number of papers were presented and discussed on the subject of the electronic structure and properties of palladium, platinum and their alloys. The greater part of proceedings dealt with palladium, and in this article the author summarises and reviews the discussion.

Palladium is not ferromagnetic, not antiferromagnetic and not superconducting, but no one could call it a normal metal. If we exclude manganese and plutonium, there is no metal that exerts so powerful a fascination over anyone who has ever been concerned with its nature and properties; and since no one therefore can be impartial with respect to various theories of these it must be emphasised that this report on the Conference is a personal view.

After the pioneer work of Mott in the 1930s, palladium took up the role of the archetypical transition metal, that is one in which a narrow *d*-band containing some empty states was overlapped by a broad free-electron like *s*-band which dominated the conductivity. Since it is not ferromagnetic it was felt to be simpler than nickel, which it otherwise seemed to resemble as closely as or more closely than the Periodic Table would lead us to expect; and although this also meant that magnetisation evidence for the number of empty *d*-states was lacking, there was much indirect evidence (especially from alloys) to support the view that this number was close to the 0.6 per atom found for nickel. Discussions of magnetic properties were based on the high density of *d*-band states at the Fermi energy (indicated by the large value of the linear term in the low temperature specific heat), while the electrical properties were believed to be explicable in terms of *s*-like current carriers being scattered predominantly to *d*-like states.

Much of this picture has recently been called into doubt. The de Haas-van Alphen data of Vuillemin and Priestly seem to require a number close to 0.36 for the *s*-electrons (and hence for the *d*-holes), galvanomagnetic data make a very large difference in *s*-electron and *d*-hole effective masses unlikely, and the very recent theories of persistent spin fluctuations of Doniach, Schrieffer and their co-workers imply that these make the traditional interpretation of the low temperature specific heat very uncertain. This last point should not be regarded as purely hypothetical, for experimental studies of the effects of magnetic-moment-bearing impurities by susceptibility, neutron scattering, and paramagnetic resonance techniques have agreed in indicating that exchange interaction effects in the *d*-band of palladium can by no means be regarded as a small perturbation, and hence low-lying excitations of a non single-particle type must be considered.

The Conference had as its aim an examination of the new situation and as its achievement a reconciliation of much of the traditional view with the new theories and results. It seemed as if the final doubts of those who hesitated to believe in 'paramagnons' (the name given to the persistent spin fluctuations) crumbled before the elegant experimental and theoretical work on their effects as scatterers of conduction electrons presented by Dr A. I. Schindler (U.S. Naval Research Laboratory, Washington and Imperial College) and Dr M. J. Rice (Imperial College).

Energy Band Structures

Since it is now possible for one theoretician to make calculations of energy band structures for metals that others will believe, the Conference began with a survey by Dr W. M. Lomer (AERE) of the calculations that have been made for palladium and platinum. He emphasised the large maximum in the density of states near the top of the *d*-band found in these calculations, the role of spin-orbit coupling which removes certain degeneracies between the different branches of the *d*-band, and the possibility that peculiar features in the Fermi surface might follow from the closeness in energy of certain points in the Brillouin zone to the Fermi surface.

Dr G. Leman (Orsay and Lille) presented details of his calculations using tight-binding methods with special reference to their significance for the magnetic susceptibility and its maximum as a function of temperature; and Dr O. K. Anderson (Copenhagen) gave details of his and Professor Mackintosh's relativistic Augmented Plane Wave calculation with special reference to the form of the three portions of the Fermi surface – one *s*-electron surface, one open *d*-hole surface (heavy holes) and one closed *d*-hole surface (light holes). In this last calculation an electronic specific heat was calculated which requires an enhancement factor (of a type to be discussed later) of 1.7 to give agreement with the experimental value of 9.4T millijoules/mole.deg.

Fermi Surface Studies

This last theoretical contribution followed a survey by Dr Priestley (Bristol) of the current status of experimental information about the Fermi surfaces of palladium and platinum, including his own de Haas-van Alphen studies, galvanomagnetic work by Alexeevski and recent low temperature de Haas-van Alphen work at the Argonne Laboratory in which the open *d*-band holes of palladium (which contribute most of the specific heat) have been seen. Models of the Fermi surfaces were shown.

Magnetic Measurements

A wide range of magnetic measurements on palladium and platinum alloys with 3*d* transition metals and rare earths was surveyed by Dr J. Crangle (Sheffield), who emphasised the part played by the possible co-existence of both ferro- and antiferromagnetic interactions in solid solutions and ordered compounds. Results for **Pd**-Mn do not seem to follow the pattern of ferromagnetism at quite small concentrations found for **Pd**-Fe and **Pd**-Co. A contribution from Miss M. MacDougall (University of Leeds) presented analyses of data for very dilute **Pd**-Fe (down to 0.01 per cent Fe), and indicated that Curie temperatures obtained from a treatment of low field magnetisation values are in better agreement with those from resistivity results than those previously reported. Magnetostriction measurements on both para- and ferromagnetic materials were shown by Dr E. Fawcett (Bell) to yield the volume dependence of the susceptibility or magnetisation.

Magnetic properties on the atomic scale can be examined by neutron scattering, and Dr G. G. Low (AERE) explained the technique and presented some results for **Pd**-Fe and **Pd**-Co. The striking feature of these is that the 'giant' moment associated with a solute atom is contributed to by about 200 neighbouring palladium atoms on which a small magnetisation is induced. Interest was expressed in the effects that would be produced on this magnetisation by additions of rhodium to the palladium. The use of nuclear properties of alloys in providing information about charge distributions (from Mössbauer isomer shifts) and local susceptibilities (from nuclear magnetic resonance) was shown by Dr H. Montgomery (Argonne) and Dr C. Froidevaux (Orsay).

Some of the new theoretical aspects were then presented. Dr S. Doniach (Imperial College) introduced the ideas of wave-vector and energy dependent susceptibilities and explained how the long range effects in palladium lead one to expect spin fluctuations of long lifetime. These can be responsible for real scattering effects (of neutrons, as discussed later by Dr R. Lowde (AERE) for nickel above its Curie temperature, and electrons) and for renormalisation effects which are seen in enhanced specific heat effective masses. (A great deal of discussion took place at various times during the Conference of the magnitude of this enhancement; the theoretical and experimental consensus being that a factor of much more than two is unlikely for pure palladium, although data of Dr C. A. Mackliet (NRL) for **Pd**-Ni alloys are strong evidence for significant enhancement. There were also a number of discussions of how far changes in specific heat on alloying should be ascribed to changes in this factor and how far to changes in band structure).

Dr J. R. Schrieffer (University of Pennsylvania) considered a number of aspects of spin fluctuation theory, including the role of the specific character of the band structure (Fermi surface multiplicity reduces the calculated mass enhancement) and the opposition provided by spin coupling effects to the establishment of superconductivity.

Thermal and Transport Properties

Specific heat data play a large part in discussions of both experimental and theoretical results, and Professor E. P. Wohlfarth (Imperial College) indicated the various ways in which the traditional interpretations of $\gamma T + \beta T^3$ form may require modification because of the partly localised-partly itinerant character of the *d*-electrons in palladium and the types of spin ordering that can be set up in alloys. He also reminded us that anomalous temperature dependence can be found for the γ of good old-fashioned Bloch electrons if the density of states varies very rapidly with energy.

The final session was devoted to transport properties. The writer looked at the history of our view of them and concluded that the frame of the traditional picture could be kept although the objects inside it had changed their form and number, and scattering by paramagnons rather than individual *d*-electrons was reponsible for the T^2 term at low temperatures.

Dr D. Greig (University of Leeds) showed thermopower data for alloys that not only fitted the old frame but even the much-abused rigid band model.

Paramagnon scattering in electrical resistivity was the subject of theoretical contributions by Dr M. J. Rice (Imperial College) and Dr P. Lederer (Orsay) who, using different models, arrived at remarkable agreement with the results found by Dr Schindler. These results showed a very large and convincing increase in the T^2 term as nickel was added to palladium, with a consequent increase in exchange interaction effects.

Differential Thermal Analysis in Platinum Equipment

Differential thermal analysis of volatile materials in contact with thermocouple junctions has hitherto proved impossible, but work by A. D. Russell at the Building Research Station (*J. Sci. Instrum.*, 1967, **44**, (5), 399) has now extended this technique to such samples by encapsulating them in a small platinum tube which, with a platinum wire welded to one end, forms one limb of the thermocouple, a 10 per cent rhodium-platinum wire forming the other limb. The reference junction containing an inert material is constructed similarly. Both junctions are protected by a platinum shield, and the alumina tubes carrying the thermocouple leads are sheathed in platinum. The apparatus has shown fast response and accurate results with calcium fluoride, which melts about 1413°C, and with volatile systems involving dicalcium silicate.