

tronium in some simple gases while no effect was found when the electric field was applied in polyatomic gases. On the other hand, a decrease was observed with increasing electric field for the gas SF_6 alone, but this fact remained unexplained. However, it is doubtful at present that a connection can exist between this result obtained in gas with our results obtained in solids.

It is interesting to note that the investigated polymers which display the electric effect are typical nonpolar

polymers, i.e., structures in which there are no permanent dipole moments, while the materials where the positronium formation is unaffected by the field are typical polar polymers.

ACKNOWLEDGMENT

We wish to express our thanks to Dr. Mario Pegoraro of the Istituto di Chimica Industriale of this Politecnico for useful discussions on the properties of polymeric materials.

Magnetic Coupling in Pd-Dilute Iron Group Alloys

E. O. WOLLAN

Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received October 28, 1960; revised manuscript received March 10, 1961)

The magnetic properties of palladium and its alloys with iron group elements are discussed in terms of the splitting of the d orbitals. The paramagnetic properties of pure palladium are accounted for on the basis that the holes in the d shell are associated with the nonoverlapping e orbitals, whereas the ferromagnetic coupling in the face-centered $3d$ elements and their alloys is associated primarily with holes in the overlapping t orbitals. On this basis and on the basis of a change in the splitting when palladium is alloyed with $3d$ metals, it is possible to account for the paramagnetic and ferromagnetic properties of the Pd-dilute iron group alloys. Because of the larger amount of available data, attention is given primarily to the Pd-Fe system.

IN a recent paper¹ dealing with magnetic coupling in the $3d$ metals it was suggested without elaboration that the absence of magnetic ordering in palladium in contrast to nickel might be associated with a difference in the orbital location of the holes in the d shells.

It is the purpose here to bring recent experimental evidence to bear on this point and on the palladium problem in general.

On the previously suggested basis the ferromagnetic coupling in the face-centered $3d$ metals is to be associated with electron sharing among the t orbitals which have strong overlaps between nearest neighbor atoms and to which the holes (~ 0.6 per atom) in the d shell are ascribed. The e orbitals in the face-centered $3d$ metals have negligible overlaps between neighboring atoms and hence unpaired electrons in these orbitals should play no direct role in magnetic coupling.

Palladium which has about 0.65 holes in the d shell remains paramagnetic down to 0°K and hence the d orbital overlaps pertinent to magnetic coupling must be of a different character than in the case of pure nickel. It was suggested that in pure palladium the orbital splitting might be reversed over that in nickel, and the holes in the d shell would then be located in the e orbitals. The negligible overlap of these orbitals with those of neighboring atoms would then account for the absence of ferromagnetic coupling in pure pal-

ladium. That this might well be the case is suggested by the observation² that hydrogen dissolved in palladium in the β phase goes into the octahedral sites which are most intimately associated with the e orbitals of the surrounding palladium atoms. It is, of course, true that the octahedral holes are the largest in the fcc structure, but for a hydrogen atom which essentially gives up its electron to the surrounding palladium atoms, it is conceivable that the location of the holes in the intimately associated e orbitals would play the more important role in determining the rather unique properties of palladium with regard to hydrogen uptake and proton diffusion in the lattice. This is an essential point on which new evidence will be brought to bear.

Let us now consider first some measurements by Burger, Vogt, and Wucher³ on Pd-dilute iron alloys with and without hydrogenation. It was observed that a Pd-Fe alloy having 7 atomic percent iron had a maximum hydrogen uptake $\text{H}/\text{Pd}=0.44$ as against 0.65 for pure palladium. This suggested to the authors that each of the iron atoms in the crystal had lost about $(0.65-0.44)/0.07 = (0.21/0.07) = 3$ electrons which went to fill holes in the d shell of the palladium atoms and hence the iron atoms would be present in the crystal with a spin of $\frac{5}{2}$. This deduction which holds equally

² J. E. Worsham, M. K. Wilkinson, and C. G. Shull, *J. Phys. Chem. Solids* **3**, 303 (1957).

³ Jean-Paul Burger, Eckhart Vogt, and Jules Wucher, *Compt. rend.* **249**, 1480 (1959).

¹ E. O. Wollan, *Phys. Rev.* **117**, 387 (1960).

well for the 3% and 5% alloys was suggested also by the paramagnetic susceptibility measurements of the hydrogenated systems which gave quite accurately a spin of $\frac{5}{2}$ for the iron atoms on the assumption that the total spin of the system was to be assigned to these atoms. It is also observed that the Pd-Fe alloys become ferromagnetic when the iron concentration exceeds about 1%.

The deduction that the small percent of solute atoms added to an alloy exist in a highly ionized state with regard to their d -shell occupation is certainly difficult to accept for a conducting metallic system. It also has the disadvantage in this and other cases that it leads to no reasonable explanation of the magnetic coupling properties of the system.

On the basis of the previous considerations regarding the splitting of the d levels in a metal into e orbitals and t orbitals and the respective occupation of these orbitals, it is possible now to consider the palladium systems in an entirely different light. In pure palladium all the holes in the d shell (0.65 per atom) are taken to be in the e orbitals and the purely paramagnetic properties of palladium are then ascribed to the non-overlapping character of these orbitals. A consistent picture of the ferromagnetic properties of the Pd-Fe group alloys can then be made on the assumption that small quantities of a $3d$ element such as iron have the effect of increasing the energy of the t band relative to the e band so that holes will be present in both bands. For the 7% iron alloy the quantity $(0.65 - 0.44) = 0.21$ should then be interpreted as holes in the t orbitals of the alloy system rather than assigning them to the iron atoms only. On this basis the moments of the constituents would be about $2.2 \mu_B$ for the iron atoms and $0.2 \mu_B$ for the palladium atoms in the 7% alloy, the number of holes in the t orbitals would be a function of the iron concentration, and the interactions between these overlapping, partially filled orbitals would give rise to the ferromagnetic coupling just as in the case of the pure $3d$ metals and their alloys.

Implicit in this interpretation is the assumption that the number of holes in the d shell of palladium remains essentially constant with composition, in contrast to the idea that electrons from the iron atoms progressively fill the d -shell holes in the palladium atoms as the iron concentration increases.

To directly prove this point it would, of course, be necessary to measure the moment of the palladium atoms as a function of alloy composition. In principle this can be done by neutron diffraction, but it does not appear feasible in the case of the very dilute Pd-Fe alloys. It has been found possible, however, to carry out such an experiment on the ordered Pd_3Fe alloy.⁴ The details of this experiment are being published elsewhere but we take here the data which bear on the

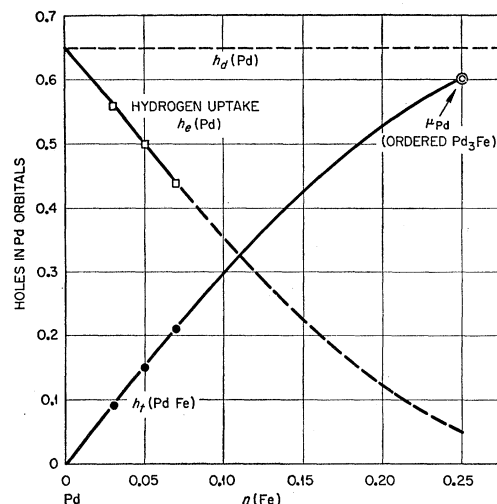


FIG. 1. Interpretation of orbital occupation as a function of composition in Pd-Fe alloy system. The quantities h_d , h_e , and h_t represent total holes in the d shell, and holes in the e orbitals and t orbitals, respectively.

point in question. In this experiment it was observed for the ferromagnetically ordered moment that $\mu_{\text{Fe}} \sim 2.6 \mu_B$ and $\mu_{\text{Pd}} \sim 0.6 \mu_B$. This moment value for the palladium atoms is plotted as the double circle in Fig. 1. It is consistent with the assumption that the number of holes in the d shell of palladium does not vary with alloy composition but rather that they are divided among the e orbitals and the t orbitals as indicated.

Let us now relate this t orbital occupation pattern to the ferromagnetic properties of the Pd-Fe system. According to the previous considerations the ferromagnetic coupling in the face-centered $3d$ metals is directly associated with interactions between the overlapping t orbitals. In the case of the Ni-Cu system in which the holes in the d shell are all in the t orbitals the strength of the coupling as measured by the Curie temperature is directly proportional to the average number of holes per atom (average atomic moment) in these orbitals,

$$T_c(\text{NiCu}) \sim 1000 h_t. \quad (1)$$

For systems containing iron and cobalt atoms in which there are unpaired electrons in the e orbitals as well as in the t orbitals the proportionality constant is also a function of composition. For the dilute alloy case under consideration this constitutes a rather minor correction and hence it is of interest to apply Eq. (1) without modification to the Pd-Fe system. The available Curie temperature data for this system^{3,5,6} are plotted as the open circles giving the curve of Fig. 2. The solid points in the figure represent T_c as determined by Eq. (1) with the values of h_t taken from the

⁴ E. O. Wollan, J. W. Cable, W. C. Koehler, and M. K. Wilkinson (to be published).

⁵ J. Crangle, Phil. Mag. **5**, 335 (1960).

⁶ M. Fallot, Ann. phys. **10**, 291 (1938).

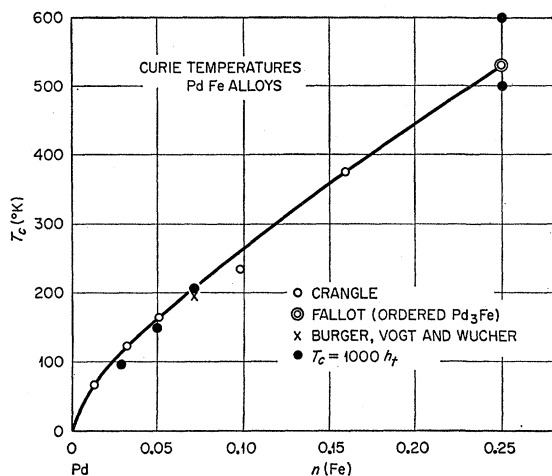


FIG. 2. Curie temperatures as measured and as interpreted in terms of occupation of t orbitals. The two values for Pd_3Fe are based on a possible difference in h_t for the ordered and disordered states of the alloy.

lower curve of Fig. 1. The agreement is seen to be very satisfactory, especially since the proportionality constant was determined for the Ni-Cu system which involves only $3d$ wave functions whereas for the present case both $4d$ and $3d$ properties are involved.

It is also of importance for an understanding of the properties of the palladium alloys to consider the saturation moment in the ferromagnetic state. In the Pd-Ni system for which it is generally assumed that the holes in the d shell remain essentially constant (~ 0.6 per atom) with composition, the saturation moment is very much less than this value for low nickel concentrations. The saturation magnetization per atom for this case as measured by Gerstenberg⁷ is shown by the lower curve of Fig. 3. It is evident from these and other similar data that not all the moments associated with the holes in the d shell of this alloy system become ordered in the ferromagnetic state. There is insufficient data to discuss this system in more detail but there are obvious inferences regarding it that will come from the consideration of the Pd-Fe system.

Ferromagnetic saturation data for this system as determined by Crangle⁶ are plotted together with our point for Pd_3Fe as the upper curve with the open circles in Fig. 3. Similar data obtained by Gerstenberg are plotted as crosses in the figure, but these data appear to have been less accurately determined at least at low iron concentrations. In any case it seems evident from these data that for low iron content the aligned moments in the Pd-Fe system are less than the total available moment.

On the basis that the magnetic ordering interactions are associated with the overlapping t orbitals, the moments associated with holes in these orbitals can be expected to be totally aligned in the ferromagnetic

state. Also from what we know of the behavior of the $3d$ face-centered alloys the two unpaired electrons in the e orbitals of the iron atoms are strongly Hund's-rule, coupled with the electron spins in the t orbitals and hence these two electrons must also be counted in the ordered moment. This is borne out by the total ordered moment and the iron atom moments in the Pd_3Fe system. As to the remaining moments which are taken here as occupying the e orbitals of the palladium atoms ($0.65 - h_t$) there is no *a priori* evidence as to how they might participate in the magnetic ordering. To investigate this point, the part of the total moment which must surely be included in the ordered state, i.e., $(h_t + 2n_{\text{Fe}})$ per atom, where n_{Fe} is the fractional iron atom content of the alloy, has been plotted as the solid points on the middle curve of Fig. 3. This curve coincides quite well with the crosses representing the saturation data as determined by Gerstenberg and hence on this basis it would be concluded that the moments associated with the unpaired spins in the e orbitals of the palladium atoms take no part in the ordered state of the system. As has been previously indicated, the results of Crangle appear to be the more reliable for the dilute alloys and on this basis one would conclude that there is indeed some ordering of the moments in the palladium e orbitals. The fact that only a small fraction of these electrons participate in the ordering suggests that the Hund's rule coupling in palladium is small. That this is the case for the $4d$ elements in general has been suggested by Van Vleck,⁸ and it is borne out by the nonmagnetic character of the $4d$ metals and many of their compounds.

There is some suggestion that the electrons in the e orbitals of the palladium atoms play a small role in the ferromagnetic coupling. It would be expected that the Hund's rule coupling, however small it might be, would depend on the probability of finding unpaired electrons simultaneously in the e orbitals and t orbitals of the same palladium atom. This probability would depend on the product $h_e \times h_t$ which should have its largest value in the middle of the range $n(\text{Fe}) = 0$ to 0.25 . As one sees from Fig. 3 the fractional ordering of electrons in the e orbitals appears to follow such a behavior.

Up to this point the magnetic coupling has been discussed in terms of a t band for the alloy as a whole in which the holes in the band have been taken as uniformly distributed over the alloy. That this is approximately true for the most concentrated sample (Pd_3Fe) is borne out by the individual fractional moment values of about $0.6 \mu_B$ for palladium and iron. One might expect, however, that some point would be reached in the dilution of an alloy of this type in which only those palladium atoms in the near vicinity of the added iron atoms would be influenced. In other words, the holes

⁷ D. Gerstenberg, Ann. Physik 2, 236 (1958).

⁸ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 313.

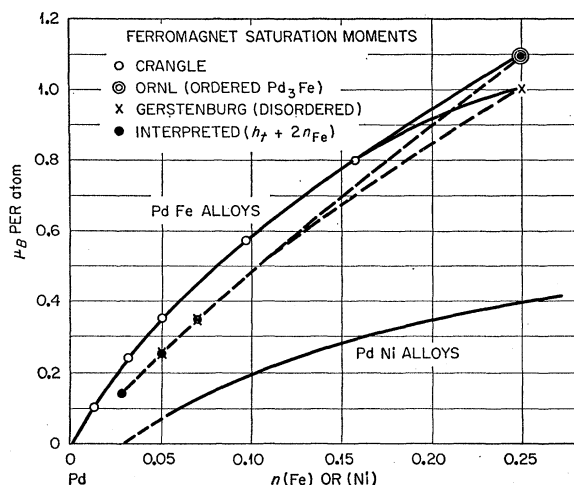


FIG. 3. Saturation moment data. The dashed line is interpreted as that part of the moment of the alloy not associated with holes in e orbitals of palladium.

in the t orbitals of palladium would fall off with some function of the distance from the iron atoms.

In this connection let us consider more critically the susceptibility measurements of Burger *et al.* on the hydrogenated Pd-Fe alloys with 1% to 7% iron atoms. In all cases these measurements gave very closely $5.9 \mu_B$ as the effective paramagnetic moment per iron atom in the alloy. Since this value is consistent with magnetic entities, each having a spin of $\frac{5}{2}$, it was logical for the authors to assume that each iron atom had given up three d electrons to the d orbitals of the palladium atoms. How then can the over-all picture as here presented which is consistent with so many other results on magnetic coupling in the transition elements be brought into line with these susceptibility measurements? One must conclude that the entity which has associated with it five coupled spins is not the iron atom itself but rather the iron atom and a group of surrounding palladium atom neighbors. In other words, the holes which decrease in number with distance from the iron atom are strongly spin coupled to the iron atom to which they are related. The paramagnetic

susceptibility data are thus of considerable significance to a better understanding of the nature of the magnetic coupling. It would thus be of interest to bring further experimental evidence to bear on this point. It is hoped that measurements of the field at the nucleus as a function of iron concentration by a Mössbauer experiment on these alloys will throw light on this problem.

Let us now consider the ferromagnetic properties of the hydrogenated alloys. It was observed by Burger *et al.* that the Pd-Fe (7%) alloy had a Curie temperature $T_c = 195^\circ\text{K}$ whereas when this alloy was hydrogenated the system remained ferromagnetic but with a lower Curie temperature $T_c = 92^\circ\text{K}$. Consider then the possibility that electrons from the iron atoms fill holes in the d shell of palladium and hence that the iron atoms exist in the alloy with a $3d^5$ configuration. In the hydrogenated alloy the holes in the d shell of the palladium atoms would then be completely filled and the d electrons would play no role in the magnetic coupling. Since there must be some long-range coupling in these dilute alloys, one would then be forced to conclude that this coupling takes place via the s electrons. One recognizes, however, that there are inconsistencies in such a line of argument.

Consider, on the other hand, the picture that has been developed with regard to the splitting of the d levels of palladium. On this picture, the hydrogenated system is only slightly modified over the nonhydrogenated system relative to its magnetic coupling properties. The hydrogenation of the alloy fills only the holes in the e orbitals which play a role only insofar as there is an intra-atomic Hund's rule coupling between the holes in the e orbitals and those in the t orbitals. This effect is related to the fraction of the e orbital holes which are ferromagnetically aligned with the t orbital holes in the ferromagnetic state of the nonhydrogenated system. The loss of this coupling and also the increase in lattice parameter in the hydrogenated alloys would then appear to be the most important factors in reducing the magnetic coupling which brings about the decrease in Curie temperature from 195° to 92°K in the 7% alloy.