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DISCUSSION

T. NAGAMIYA: You don't have the possibility that the low temperature form is cycloidal?

G. SHIRANE: The cycloidal spiral model does not explain the observed magnetic scattering in the low temperature phase, because it should give (00 l) satellites by the ordering of a perpendicular component.

R. J. ELLIOTT: The sine wave structure is stable in Er at high temperature, and this has been interpreted as arising because this arrangement has high entropy, and hence lower free energy at high temperature. The fact that this phase is stable at low temperature in Cr is surprising and would seem to be support for the Overhauser mechanism.

G. SHIRANE: In this connection, it may be interesting to see, as suggested by Dr. T. Kaplan, whether an additional ordering develops at lower temperature. The available powder data do not seem to indicate this.

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Magnetic Moment Distribution in Palladium and Iron Group Alloys

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The distribution of the magnetic electrons in the orbital of the individual atoms in alloys of palladium and nickel with iron and cobalt are discussed. These data suggest the change in orbital splitting which gives rise to ferromagnetism in dilute iron group-palladium alloys.

The magnetic moment distributions in face centered alloys of Fe and Co with Pd and Ni have been studied in an attempt to throw light on the magnetic coupling properties in such systems. The ferromagnetic coupling in face centered 3d metals has been previously discussed¹⁾ in terms of the splitting of the d -shell into e -orbitals and t -orbitals and the respective occupation and overlap properties of these orbitals. The proposed occupation of these orbitals for Fe, Co, and Ni is shown in Table I. The holes in the t -orbitals of

these metals $h_t \sim 0.6$ are taken as being primarily responsible for the magnetic coupling because of the strong overlaps of these orbitals. The absence of ferromagnetic coupling in pure Pd has been taken as evidence that the splitting in Pd is reversed over that in nickel and the holes are then associated with the essentially non-interacting e -orbitals.

The observation that alloys of palladium with very small quantities of the 3d metals Fe, Co, and Ni are ferromagnetic and that the Curie temperature increases with increased

iron group content suggests that alloying with these metals introduces holes in the t -orbitals of the alloy system and hence the ferromagnetic properties can be correlated with these holes as in the $3d$ metals themselves.

The alloy studies which are reported here have been undertaken in an attempt to throw light on this problem. Data obtained on a number of alloy systems are summarized in Table II. These data must as yet be considered as of a preliminary nature; work is in progress to improve them where possible. The data for FeNi_3 and FePd_3 were taken on ordered samples whereas the other results were derived from diffuse scattering measurements with in some cases rather large short range order effects. The FePd_3 results are based on measurements on an ordered as cast sample for which the absolute intensities

were determined from the nuclear difference scattering. Improved accuracy will be achieved when scheduled measurements on an ordered powdered sample are completed. All the alloys listed have been studied in this investigation except FeNi for which the previous results of Shull and Wilkinson are included here for completeness. Also FeNi_3 was measured by them and remeasured here.

The second column gives the magnetic moment per molecule as determined in magnetic induction measurements. The next two columns give the e -orbital occupation for Fe and Co as proposed in the upper part of Table I. The next column gives the average number of holes $\bar{h}_t$ per atom in the t -orbitals as deduced for these alloy systems. It is of interest that $\bar{h}_t$ lies in the rather narrow range 0.6 to 0.74 for these alloys. The measured individual moment values for Fe

Table I. In Face Centered Cubic Structures

	Fe	Co	Ni	Pd
e -orbitals	$\uparrow \uparrow$	$\uparrow \uparrow \downarrow$	$\uparrow \uparrow \downarrow \downarrow$	$\uparrow \uparrow \downarrow \downarrow$
t -orbitals	$\uparrow \uparrow \downarrow \downarrow$	$\uparrow \uparrow \downarrow \downarrow$	$\uparrow \uparrow \downarrow \downarrow$	$\uparrow \uparrow \downarrow \downarrow$
$\mu \sim$	2.6	1.6	0.6	0.6
s -electrons $\sim$	0.6	0.6	0.6	0.6

Table II. Magnetic Moment Data for Palladium and Iron Group Alloys

Alloy or element	$T_C^\circ\text{K}$	$\bar{\mu}$ per mol.	$\bar{h}_e$		$\bar{h}_e$ Pd or Ni	$\bar{h}_t$	μ		$\bar{h}_t$ Fe or Co
			Fe	Co			Fe or Co	Pd or Ni	
FePd	750	3.37	2		0	0.68	2.95	0.42	0.9
FePd ₃	540	4.40	2		0	0.60	3.0	0.47	1.0
FeNi	770	3.28	2		0	0.64	2.6	*	0.6
FeNi ₃	870	4.73	2		0	0.68	{2.97 2.75}	* 0.62 0.65	0.75
CoPd	970	2.35		1	0	0.65	2.0	0.35	1.0
CoPd ₃	600	3.40		1	0	0.60	2.0	0.45	1.0
CoNi	1110	2.47		1	0	0.74	1.8	0.65	0.8
CoNi ₃	900	3.85		1	0	0.71	1.9	0.65	0.9
Ni	632				0	0.60		0.60	
Pd	None				0.65	0		0.65	
							($\sim \pm 0.1$)		

Note: All moments reduced to saturation at $^\circ\text{K}$. Except for $\bar{\mu}$, all moments or holes are per atom values.

$\bar{h}_t$ = Moment per molecule minus $h_e(\text{Fe})=2$ or $h_e(\text{Co})=1$ divided by atoms per molecule.

*Early results of Shull and Wilkinson.

and Co and for Ni and Pd are shown in the next two columns. The last column shows the deduced values for $h_t(\text{Fe})$ and $h_t(\text{Co})$. One observes for these alloys that the h_t values for Fe or Co are larger than those for Ni and Pd and also that this asymmetry is more pronounced in the Pd alloys than in those containing Ni. This may arise from the different overlap properties of the t -orbitals in the alloys containing these two metals. The relative t -orbital overlaps for the FeNi and FePd alloys are represented qualitatively in Fig. 1, where the respective radial electron distributions are plotted against near neighbor separation distance. The larger asymmetry observed in the individual moment values for the Pd alloys as contrasted to the Ni alloys may be related to the greater asym-

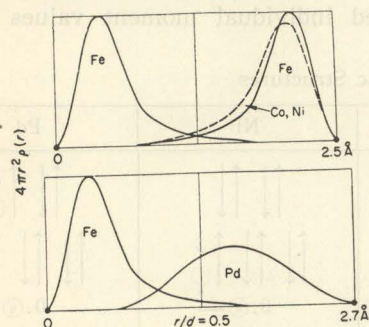


Fig. 1. Comparison of relative orbital overlaps between near neighbor atoms in iron group and in Fe-Pd alloys.

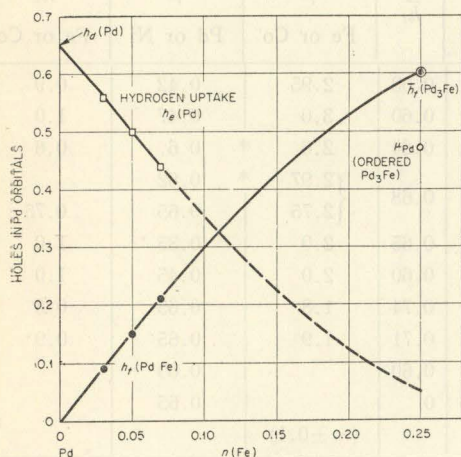


Fig. 2. Suggested orbital occupation for Fe-Pd alloys.

metry of the orbital overlaps in the Pd alloys.

The measurements here reported were undertaken in part with the objective of attempting to gain a better understanding of the magnetic properties of palladium and its alloys which are dilute in iron group constituents. It has been suggested²⁾ that in pure palladium the holes in the d -shell are in the nonoverlapping e -orbitals and that alloying with Fe, Co, or Ni modifies the splitting so that the d -shell holes tend to move into the t -orbitals. It has been shown by Burger, Vogt, and Wucher³⁾ that the hydrogen up-take in palladium alloys changes markedly with iron group metal content. In pure palladium this up-take corresponds to the 0.65 holes in the d -shell. The change of up-take with composition is shown in Fig. 2 for the Pd-Fe system. If it is assumed that the hydrogen up-take is a measure of the holes in the e -orbitals of palladium only, then the fall-off in the e -orbital occupation might be expected to be accompanied by a rise in the occupation of the t -orbitals of the alloy system, in a fashion shown by the lower curve of Fig. 2. The measurements on Pd₃Fe suggest a t -orbital occupation of 0.6 for the alloy and this point is seen to be in line with the trend of the lower curve.

If the holes in the overlapping t -orbitals are taken to be primarily responsible for the magnetic coupling then the t -orbital occupation as represented in Fig. 2 should follow closely the Curie temperature data for these alloys and indeed as previously shown this is actually the case for these alloys. The fact that h_t is smaller for the Pd atoms than for the Fe or Co atoms should be of significance primarily with regard to the relative strengths of the Pd-Pd exchange coupling as compared to that of the Pd-Fe or Fe-Fe type. This point may be of significance in relation to the lower Curie temperature for Pd₃Fe as compared to Ni₃Fe, the asymmetry in the t -orbital occupation for Ni and Fe being much less pronounced than for Pd and Fe.

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