Magnetic Coupling in the Ni–Pd Alloy System*

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The magnetic coupling properties of the Ni–Pd alloy system are considered in terms of a molecular-field solution based on a Heisenberg type of interaction for spin $\frac{1}{2}$. The unpaired electrons in Ni are assumed to be part of a band of mainly t_{2g} character in which the totality of interactions leads to an interatomic ferromagnetic coupling. The unpaired electrons in pure Pd are assumed to be part of a narrow, weakly interacting band with more nearly e_g symmetry. In the alloy, the Pd band structure becomes progressively more like that of Ni. The magnetic energy is then calculated in terms of the probability of finding unpaired electrons in the overlapping orbitals of the Ni and Pd atoms. The probability is determined from the average moment curve on the assumption of $3d^9$ and $3d^{10}$ states only. A fit to the data on the Curie temperature and average magnetic moment then gives the following relative values for the exchange constants (molecular-field coefficients); A for Ni–Ni, αA for Ni–Pd, and $\alpha^2 A$ for Pd–Pd, with $\alpha \cong 0.8$.

IN view of the apparent applicability[1] of a quasi-localized-moment model with a Heisenberg interaction between spins ($S=\frac{1}{2}$) in the case of Ni and Ni–Cu it seemed of interest to consider the, in some ways similar but yet very different, problem of Pd and the Ni–Pd alloys.

Palladium like nickel has generally been thought to have ~0.6 holes in the d band[2] but it differs from Ni in that it shows no tendency toward ferromagnetism; in fact there appears to be a rather weak antiferromagnetic coupling in the pure metal.[3] Yet, when small fractions of percents of Fe or Co and at most a few percent of Ni are alloyed with Pd the systems become ferromagnetic. In these alloys the palladium atoms contribute to the ferromagnetic moment but for the dilute alloys only a small fraction of the total available palladium moment contributes to the ferromagnetism of the system.[4,5] Proposals have been made that only those Pd atoms which are near neighbors of a $3d$ metal atom have their spins "polarized" but measurements by Low and Holden[6] have shown that the Pd moments in dilute Fe–Pd and Co–Pd alloys fall off very slowly with distance. These measurements bear on the problem of the basic nature of this so-called "polarization process" which undoubtedly arises from some type of magnetic coupling such as an s-d interaction, or an interatomic d-d interaction.

The unique property of these dilute alloys systems, namely, that only a fraction of the unpaired electrons associated with the holes in the Pd d band align ferromagnetically and that a large fraction are on the average oblivious to the over-all ferromagnetic coupling even at low temperatures suggested to the writer that there are essentially two types of unpaired electrons (two d bands) associated with the Pd atoms in these dilute alloys. This suggestion followed from some earlier considerations[7] regarding the d-shell properties of the iron group metals and alloys and the dependence of these properties on the splitting of the d shell into rather distinctly separated t_{2g} and e_g orbitals.

In the case of Ni all the holes were assumed to be in a band of t_{2g} symmetry which constituted the source of an interatomic d-d ferromagnetic exchange interaction.

More recently information on the symmetry properties of the unpaired electrons in Ni has been obtained by Mook[8] in his neutron-diffraction measurements of the magnetic form factor. Analysis of the data gave 81% t_{2g} and 19% e_g symmetry for the unpaired d electrons as against 60% t_{2g} and 40% e_g for spherical symmetry. These results thus show a strong preponderance of t_{2g} character for the unpaired electrons in Ni. The analysis of these data is based on the inclusion of a relatively large uniform negative polarization of what is referred to as "conduction electrons." This is included to give agreement with the magnetization data. Although the fit of the data on this basis is remarkably good, it must be recognized that what are termed conduction electrons, may indeed consist mostly of d electrons in the lower part of the band which can themselves have a complicated spacial dis-

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[1] E. O. Wollan, Phys. Rev. **148**, 517 (1966).

[2] The present considerations do not appear to be very sensitive to the exact value that one takes for the number of holes in the d band of nickel, and hence for simplicity the value of 0.6 has been used. Also, the number of holes in the d band of pure palladium is not of direct consequence to these considerations since we are concerned here with the holes in the d band of the Ni–Pd system which are effective in the ferromagnetic coupling. A constant factor applied to the average moment curve would have no effect on these considerations. Relative to some aspects of these qualifications, see J. J. Vuillimin and M. G. Priestly, Phys. Rev. Letters **14**, 307 (1965); G. Fischer, H. Herr, and A. J. P. Meyer, in Proceedings of the International Conference on Magnetism, Boston, 1967, J. Appl. Phys. **39**, 545 (1968).

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[4] E. O. Wollan, J. W. Cable, W. C. Koehler and M. K. Wilkinson, J. Phys. Soc. Japan **17**, 38 (1962).

[5] J. W. Cable, E. O. Wollan, and W. C. Koehler, J. Appl. Phys. **34**, 1189 (1963).

[6] G. G. Low and W. T. Holden, Proc. Phys. Soc. (London) **89**, 119 (1966).

[7] E. O. Wollan, Phys. Rev. **117**, 387 (1960).

[8] H. A. Mook, Phys. Rev. **148**, 495 (1966).

tribution of spin-up and spin-down electrons, which cannot be detected because of insufficient resolution in the data. What is then treated as the net unpaired spins at the top of the d band, may actually have some admixture of states lower in the band, and then other electrons with a somewhat different spacial distribution, should be included in the net unpaired spins near the top of the band. There may, of course, also be effects arising from hybridization of the d and s parts of the band. Although there is undoubtedly some uncertainty in the interpretation of the neutron form-factor data, it is, of course, true that the writer's original assumption, that all the unpaired spins at the top of the d band in Ni have t_{2g} symmetry, may be a considerable oversimplification. There are, however, reasons for believing that in the face-centered metals, the d band consists of two rather distinct parts, one which is primarily of t_{2g} character and is broadened by the near neighbor overlaps and the other a relatively narrow band of e_g character. With this qualification then, it will be assumed as previously that all the holes in the d shell of Ni are in what we shall now call the "t_{2g}" band. It will be assumed also that the magnetic coupling arises primarily from the over-all interactions within this band, and that it can be represented by a Heisenberg type of interatomic-exchange interaction between unpaired spins on neighboring (not necessarily near neighbors) atoms.

Now also, we shall assume, as previously, that the absence of ferromagnetic coupling in Pd is a result of the holes in the d shell being in the narrow, and hence weakly overlapping, orbitals of primarily e_g symmetry. A partially filled narrow "e_g" band in Pd is consistent with the observed high density of states at the Fermi level for this metal.

Let us then consider on this basis the case of the Ni–Pd alloy system. Adding Ni to Pd, could cause a small shift in the "e_g" band level of Pd to lower energies relative to the Fermi level and the predominantly t_{2g} character of the Ni band could impart some t_{2g} character to the unpaired electrons associated with the Pd atoms. The addition of more Ni would then progressively make Pd more like Ni and hence introduce a corresponding "t_{2g}" interatomic exchange coupling between Pd and Ni atoms as well as between Pd atoms themselves. For the dilute alloys there would naturally be some finite range associated with the effect on the Pd band of a small percentage of added Ni atoms. As the concentration is increased, a more homogeneous single-band character would develop and the Pd atoms would on the average, become magnetically more and more like the added Ni atoms, as far as the nature of their magnetic coupling properties is concerned. The strength of the ferromagnetic interatomic-exchange interaction associated with the Pd atoms would, however, not be expected to be the same as that for the Ni atoms because of the large difference in the radial extent of their $3d$ wave functions. We shall proceed then to evaluate the data on the Ni–Pd system on the basis of what might be termed a modified generalized Heisenberg treatment in which only $3d^9$ and $3d^{10}$ states are involved, and in which only those $3d^9$ states associated with unpaired electrons in "t_{2g}" orbitals contribute to the ferromagnetic coupling in the alloy. This picture is consistent with the observation that essentially a negligible addition of Fe, Co, or Ni to Pd gives rise to a ferromagnetically ordered state in spite of an apparent antiferromagnetic coupling between the atoms in pure Pd.

Let us then consider the average magnetic moment and the Curie-temperature data of Burger[9] and others[10,11] for the Ni–Pd system shown in Fig. 1 in terms of a Heisenberg interaction between spin $\frac{1}{2}$ states in the "t_{2g}" orbitals of the Ni and Pd atoms.

The shape of the average moment curve in Fig. 1 for the high Ni concentrations suggests that both the Ni and Pd atoms have close to $0.6\mu_B$ per atom of orderable moment in this region, although one could assume that the Ni moments increase as Pd is added to the system, and consequently that the Pd moment is always less than $0.6\mu_B$. Since the band properties of Ni appear to dominate the properties of the system, as seen by the rapid rise of $\bar{\mu}$ and T_C as Ni is added to Pd, it will be assumed that the holes in the d shell of Ni remain constant at $n=0.6$ per Ni atom over the whole composition range of the alloy. The holes in the "t_{2g}" orbitals of the Pd atoms would then increase with concentration of Ni, the average orderable moment being given by

$$\bar{\mu}=nx+p(1-x), \tag{1}$$

where p is taken as the probability of finding a hole in the "t_{2g}" orbitals of a Pd atom.

If now we let A be proportional to the average exchange energy for the Ni–Ni interaction and take αA for the Ni–Pd and $\alpha^2 A$ for the Pd–Pd interactions, we can express the free energy near T_C on the basis of a simple molecular field with a Heisenberg type of coupling between atoms with spin $\frac{1}{2}$ as

$$-F/A=n^2x^2M_1^2+2\alpha npx(1-x)M_1M_2+\alpha^2p^2(1-x)^2M_2^2 +T/A[1-nxM_1^2-p(1-x)M_2^2], \tag{2}$$

where x is the Ni composition variable, n and p have been defined above and $A(=1050°\text{K})$ is the coupling constant per spin $\frac{1}{2}$ for Ni which for convenience is measured in °K. The solution of Eq. (2) can then be written in the approximate form

$$T_C=A/\bar{\mu}[n^2x^2+2\alpha np(1-x)+\alpha^2p^2(1-x)^2], \tag{3}$$

[9] Jean-Paul Burger, thesis, University of Strasbourg, 1964 (unpublished).
[10] C. Sadran, Ann. Phys. (N.Y.) 371 (1932).
[11] V. Marian, Ann. Phys. (N.Y.) **7**, 459 (1937). Results of L. Néel included in this reference.

which agrees with the usual molecular-field solution when $(1+\alpha^2)\cong 2\alpha$, i.e., when α is near unity, which it will be observed to be in the present case.

To investigate the Ni–Pd interaction it is convenient to bring the effect of the Ni–Ni interaction to the left side of the equation, for which, then,

$$\bar{\mu}T_C/A - n^2x^2 = 2\alpha npx(1-x) + \alpha^2p^2(1-x)^2$$
$$= 2\alpha n(\bar{\mu}-nx)x + \alpha^2(\bar{\mu}-nx)^2. \quad (4)$$

The trend of $\bar{\mu}T_C/A$ is shown by the solid line in Fig. 2 and the term $[\bar{\mu}T_C/A - n^2x^2]$, in which T_C and $\bar{\mu}$ are taken from the solid curves through the data points in Fig. 1, is represented by the open circles on the lower dashed curve.

At $x=1$, $n=p=0.6$, and the derivative with respect to x of Eq. (4) gives

$$d/dx[(\bar{\mu}T_C/A) - n^2x^2]_{x=1.0} = 0.72\,\alpha,$$

from which one obtains the value of α and hence α^2. The light solid line for $d/dx[(\bar{\mu}T_C/A) - n^2x^2]$ gives $\alpha=0.775$ and $\alpha^2=0.6$. That these values are consistent with the Curie-temperature data over the whole composition range is evident from the agreement of the open circles and the dashed curve in Fig. 2. The open circles represent the left side of Eq. (4) with T_C and $\bar{\mu}$ taken from the solid curves through the data points of Fig. 1. The dashed curve corresponds to the right side of Eq. (4) determined with the above values of α and α^2 and the $\bar{\mu}$ data of Fig. 1. It is interesting to note also that the solid curve for $\bar{\mu}T_C/A$ appears to be linear over a large composition range ($x<0.5$) and it extrapolates

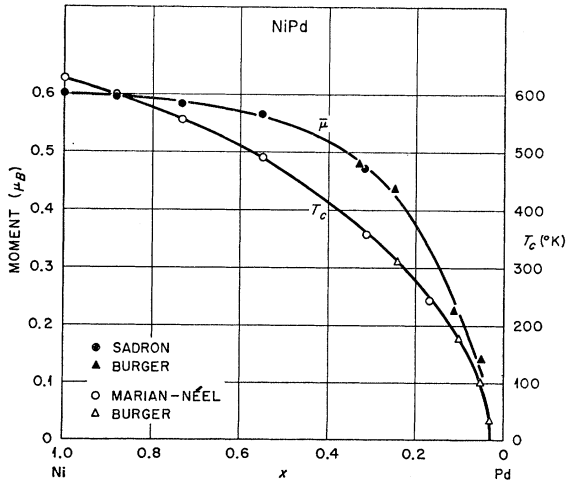

FIG. 1. Average magnetic moment and Curie-temperature data for the Ni–Pd alloy system. See Refs. 9–11.

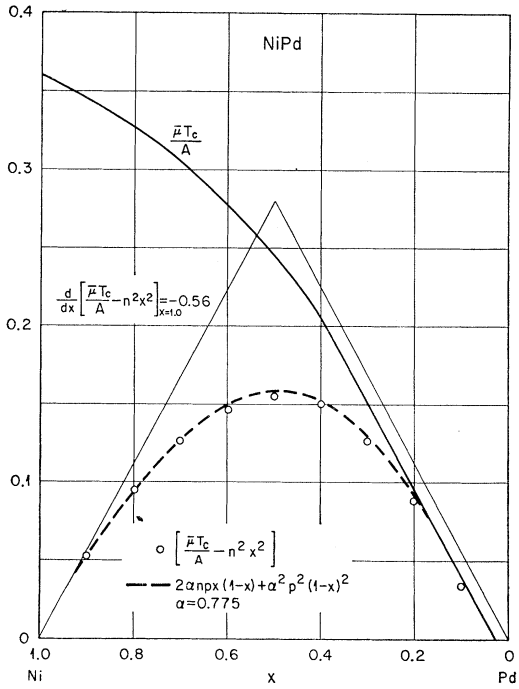

FIG. 2. Properties relating to the molecular-field solution for Ni–Pd. See text for further details.

to zero at $x\cong 0.03$, which suggests that for the Ni–Pd system one must establish a moment population in the "t_{2g}" orbitals of Pd before an effective ferromagnetic coupling can develop.

It is apparent that the Curie-temperature data are thus well fitted by the proposed model which includes a generalized Heisenberg type of exchange interaction, and it would seem of significance that they are fitted over the whole composition range with constant values of the average exchange integrals (molecular field constants) for the Ni–Ni, the Ni–Pd, and the Pd–Pd interactions. The decrease in the coupling for large Pd concentrations is associated with the decrease in the number of electrons which are effective in the exchange interaction.

On the present model then the polarization of the d shell of palladium by nickel corresponds to bringing the unpaired electrons in Pd into a relatively broad Ni-type t_{2g} band in which they then become effective in the ferromagnetic coupling. Under these conditions one finds not only a Ni–Pd but also a Pd–Pd exchange interaction and both of these interactions are quite comparable in magnitude to the Ni–Ni interaction when expressed in terms of the relative number of spin $\frac{1}{2}$ electrons in what is taken as a band of essentially t_{2g} symmetry.