MAGNETIC BEHAVIOR OF $Ni_{1-x}Pd_x$ ALLOYS

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ABSTRACT

The magnetization and the paramagnetic susceptibility of the $Ni_{1-x}Pdx$ alloys with composition ranging from 0 to 90 at % Pd are investigated. The composition dependence of the saturation magnetization, Ni and Pd localized moment are discussed in terms of the localized spin picture. The reciprocal susceptibility - temperature dependence of the alloys follow the Curie Wiess law. The paramagnetic Curie temperature and the effective paramagnetic moment behavior are interpreted in terms of the s-d interaction between the conduction electron and the localised moment.

INTRODUCTION

The paramagnetic behavior of pure palladium is drastically affected by the addition of the 3d transition metals[1-3]. The alloys with Cr and Mn exihibit antiferromagnetic tendencies [1]. Those with Fe [2] and Co[3] exihibit ferromagnetism throughout the concentration range down to solution as dilute as 0.1 at % iron or cobalt.

Mossbauer studies on $Ni_{1-x}Pd_x$ showed that the hyperfine field seen by ^{61}Ni nucleus increases by increasing Pd content from -76 KG for Ni to 173 KG for x = 0.9. The hyperfine field changes it's sign at x = 0.5 Such behavior is unusual, since in most of the ferromagnetic transition metal alloys the observed hyperfine field is always negative and is related to the core polarization and the bulk conduction polarization[4]. In Ni-Pd alloys a large positive contribution from Pd atoms on neighboring atoms leads to the positive hyperfine field [4].

Polarized neutron measurements on $Ni_{1-x}Pd_x$ alloys [5] indicated that magnetic moment of both Ni and Pd increases with increasing Pd content from ~$0.6\mu_B$, the value for the Ni-rich region isolated Pd atoms in a nickel environment have no moment but produce a positive enhanced Ni moment (spin lattice interaction)[6]. This moment enhancement is small and may be associated with a change in band structure on alloying[7]. In this respect pure nickel is considered to be a saturated ferromagnet i.e., it has no d holes in the majority spin band and has ~0.6 d holes in the minority spin band. It is difficult to explain the obtained results of the Ni magnetic moment in such model. A Ni atom must acquire additonal d holes, say 0.4 on it when it exihibit the moment of $1\mu_B$. This however means that the tight binding model with d atomic orbital only which is often used in discussion of pure metal as well as alloys loses its validity for the Ni-Pd system and that a more realistic model which take not only d states but olso s and p states into account may be required. Akai [8] investigated the full electronic structure of Ni-Pd alloys by means of the Green function method which is combined with the coherent potential approximation and the local spin denisty approximation. Akai's calculations indicated that the number of states contained in the d-band per spin is arround 4.4 in pure nickel and always smaller than 5 which is asumed in the simple minded picture. Some of d-electrons are lost into antibonding states laying above the top of the d band. This is the so called s-d hyperdization where a d-state of a given atom mixes with s and p states of surrounding atoms making the bonding and antibonding states. The d band states are mostly bonding ones. Since the antibonding states contain a portion of d states, five atomic d orbitals cannot be fully occupied even when the d-band states are fully occupied. According to Akai's calculations, the mixing of d-band of a given Ni atom with s and p states of surrounding atoms decreases by the increase of the number of states contained in the d-band per Ni site, and the nickel atoms tend to be more atomic. Akai's investigation of the $Ni_{1-x}Pd_x$ alloys as a prototypical localized system gives a reasonable interpretation for the unusual behaviour of the hyperfine field of nickel in this system. In the present work the magnetic behavior of the $Ni_{1-x}Pd_x$ alloys, in the ordered and paramagnetic regions, is ivestigated and the obtained results are discussed in terms of the localized spin picture.

EXPERIMENTAL

The alloys included in this study were $Ni_{1-x}Pd_x$ with x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1. The samples were prepared from Pd 99.99% purity and Ni 99.99% purity by high frequency melting in an argon atmosphere and heat treated at 900 C for 12 h. All the heat treated samples are examined at room temperature by x-ray diffraction and the lattice parameters of the alloys were determined. Magnetization measurements were carried out under vacuum in magnetic fields up to 13 kOe at temperatures down to 77 K. The moment per atom of alloy, was determined by extrapolation to T = 0 K. The paramagnetic Curie temperatures were determined from the reciprocal susceptibility - temperature measurements between room temperature and 1000°K except for Pd the temperature was between 77 and 600 K. The effective paramagnetic moments of the alloys were determined from the slopes of the reciprocal susceptibility - temperature dependence.

RESULTS AND DISCUSSION

X - ray analysis showed that the heat treated prepared $Ni_{1-x}Pd_x$ alloys form a continuous series of fcc solid solutions and were free from any other phases. The dependence of the lattice constants on palladium concentration (x) is presented in fig. 1. The increase of the lattice constants with (x) follows Vigard's law. The saturation magnetic moments μ_B of the of the Ni-Pd alloys are deduced from the extrapolations of the magnetizations to O°K. Fig. 1 showed the dependence of m of Pd content. The results indicate a decrease of the average moment μ with the increase of Pd concentration. μ decreases linearly by 0.11 per added Pd atom for $0<x<0.5$. μ falls more rapidly in the Pd - rich region and its extrapolation approaches zero at a concentration close to the reported concentration where ferromagnetism vanishes 0.98[9] or 0.97[10]. The dependence of the relative saturation magnetization M(T)K /

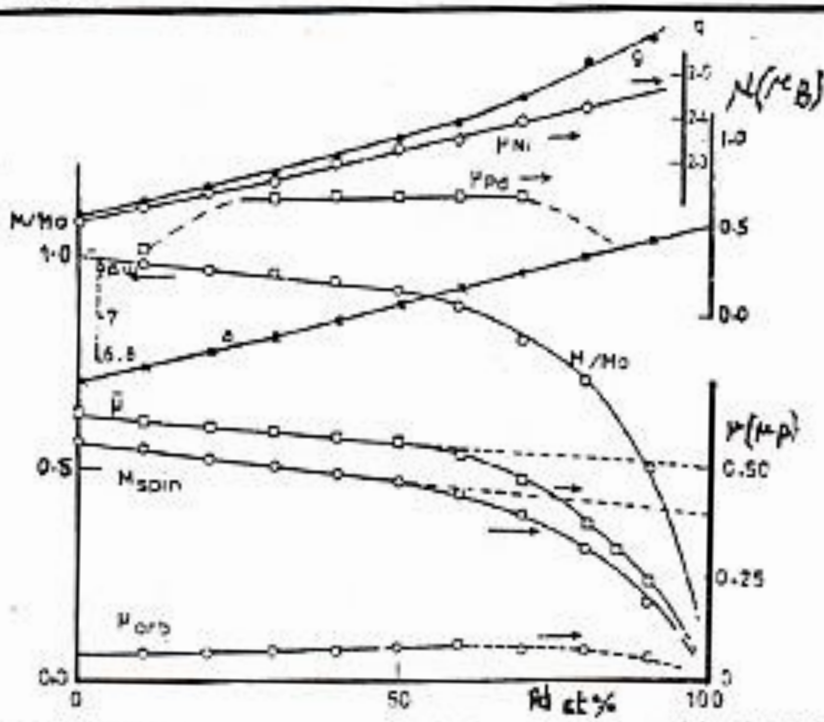

Fig. 1. Composition dependence of the lattice parameters (a), the saturation moment μ, localized moment of Ni (μ_{Ni}) and Pd (μ_{Pd}) in (μ_B, the g - factor, the spin (μ_{orb}) and orbital moment of the Ni_{1-x} and Pd_x alloys.

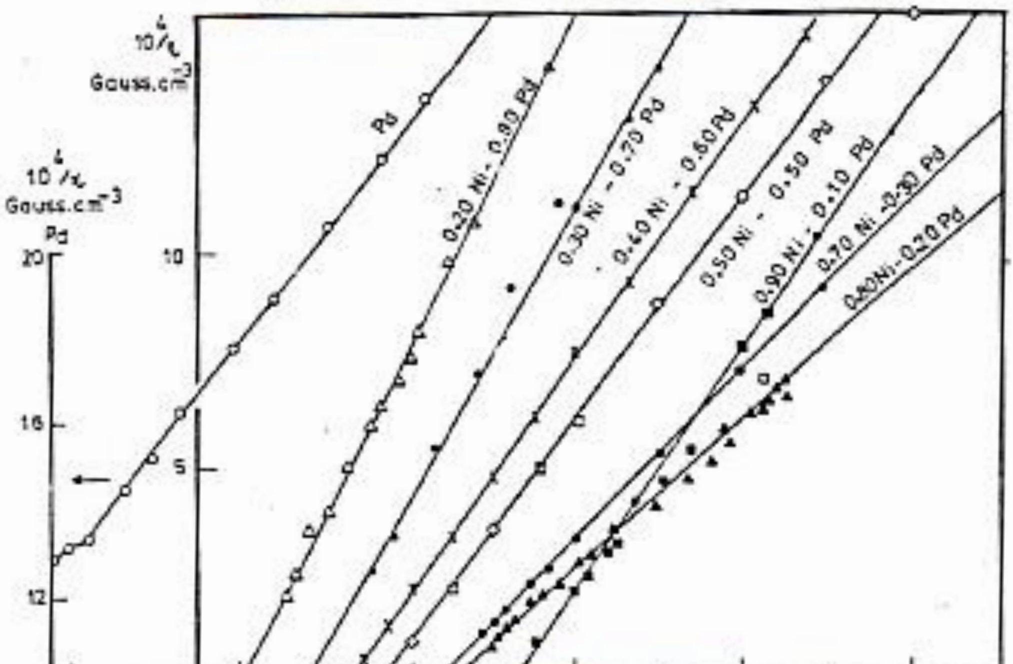

Fig. 2. The reciprocal susceptibility 1/χ (gauss. cm^{-3}) temperature dependence on the Pd content.

M(O)K on Pd content plotted in Fig. 1 confirms that ferromagnetism just vanishes at $x = 0.98$. The average saturation magnetic moments obtained from the magnetization measurements agree well with those obtained from the magnetization measurements of both Bragg and diffuse scaterring is smaller for the Ni-Pd alloys than that for pure Ni, for which a value of $-0.1\ \mu_B$ is reported [11]. Neglecting the conduction - electro polarization, the average moment per alloy can be written as

$$\mu = (1-x)\mu_{Ni} + x\,\mu_{Pd}.$$

In the range $0 < x < 0.5$ the individual Ni and Pd moment are given by $\mu_{Ni} = \mu + \Delta\mu$ and $\mu_{Pd} = \mu - (1-x)\Delta\mu$, where $\Delta\mu$ is the difference between the Ni moment and the Pd moment in the alloy. Using the values of $\Delta\mu$ reported in ref. [7], the values of the localized moment of Ni and Pd are determined . The variations of μ_{Ni} and μ_{pd} with the palladium content is presented in Fig. 1. μ_{Pd} increases with about $0.2\mu_B$/Pd atom in the range of x between 0.3 and 0.7. Extrapolation of μ - x dependence to the Ni-rich region indicates, as the extrapolation of the results of the neutron measurements [7], that the isolated Pd atoms in nickel environment has no moment but produce an enhanced Ni moment associated with the spin lattice interaction [6,7]. As Fig. 1 shows, the localized nickel moment (μ_{Ni}) increases with the increase of the Pd content to a maximum of about $1.2\mu_B$/Ni atom in the 90 at % Pd region. This increase of Ni magnetic moment accounted for by the localized-spin model[12,13] and Akai's electronic structure calculations of Ni-Pd alloys [8]. As observed in Fig. 1, The increase of Pd concentration (x) increases the lattice constant of the alloy. Such increase of the interatomic distance increases the number of localized states contained in the interatomic distance increases the number of localized states contained in the d-band per spin. So the mixing of nickel-d band with s and p states of surrounding atoms decreases i.e., the d-states of a nickel atom tend to be more localized[8]. According to Akai's calculation, the number of electrons for each spin direction $n^d_{majority}$ and $n^d_{minority}$ varies such that their sum is kept constant. Thus the increase of the majority d-electrons of Ni by the increase of (x) is accompanied by a decrease of the maniority d-electrons. In other words, the number of d-holes increases with (x) and the magnetic moment of nickel increases (Fig. 1).

The effective spectroscopic splitting g-factor for the studied Ni-Pd alloys was calculated according to Tsuya [14] and Wangsness [15]. The composition dependence of g-factor is given by

$$g = \mu\,[(\mu_{Ni}/g_{Ni})\,(1-x) + \mu_{Pd}/g_{Pd})\,x]$$

g_{Ni} and g_{Pd} are the splitting g-factor of Ni and Pd respectively. The spin wave resonance for $Ni_{1-x}Pd_x$ at 9300MHz [16] showed that the g-factor increases with the Pd content from 2.18 for pure Ni to 2.59 for the alloys with 90 at % Pd. The ferromagnetic resonance experiments carried at 35GHz [17] give values of 2.18 and 2.5 for Ni and Pd g-factor respectively. In this study, the vaules considered by Akai [8] is used (2.54 for Ni and 2.18 for Pd). The composition dependence of the g-factor of the alloys using the deduced moments of Ni and Pd are presented in Fig. 1. A linear dependence of g on Pd content is noticed up to x = 0.5. Above this concentration of Pd, g-x dependence is no longer linear. The rise of g-factor for x < 0.5 is related with decrease of the contribution of the spin moment (M_{spin}). M_{spin} of the $Ni_{1-x}Pd_x$ alloys determined by $M_{spin} = 2\mu/g$ are plotted in Fig. 1. M_{spin} varry linearly up to x = 0.5 according to the relation $M_{spin} = 0.563 - f\,(x)$, with $f = 0.17\mu_B$/added Pd atom. This leads to spin moment of Pd of $0.39\mu_B$. The linear M_{spin} (x) dependence implies that there is a true ferromagnetic state in this concentration region. Moreover, the proper orbital moment contribution, 0.12 μ_B in Pd is of the same order as in usual ferromagnets and the orbital contriution to the moment is certainly not negligible. Above x = 0.5, similar to μ, M_{spin} is no longer linear. This is understood by supposing that in dilute alloys the Pd moment varies with the environment and the polarization of the compensated carriers of Pd is increased to saturation only if half of the next neighbors are nickel[5].

The reciprocal susceptibility $1/\chi$ of Pd is plotted as a function of temperature T in Fig. 2. In agreement with Bozorth et al [3], below 90 K $1/\chi$ shows a nonlinear dependence on T, giving an evidence of antiferromagnetic behavior of Pd at low temperature. The paramagnetic moment of Pd calculated from the linear $1/\chi$ - T dependence is 1.8 μ_B. This value corresponds to $S = \frac{1}{2}$ putting $= 2[S(S+1)]^{(1/2)}$ It is observed from Fig. 2 that , for all the $Ni_{1-x}Pd_x$ alloys, $1/\chi$ - T variations satisfied the Curie Wiess law over the whole temperature range (from temperature up to 1000 K). The paramagnetic curie temperatures and the effective magnetic moments of the alloys are plotted in Fig. 3 as a function of the Pd concentration. Fig. 3 Shows also the change of reciprocal susceptibility at 600K ($1/\chi_{600}$) with (x). While a slight increase of $1/\chi_{600}$ is observed for $0.1 < x < 0.4$, an obvious increase is noticed in the Pd-rich region. Similar behavior was reported for Ag-Pd and H-Pd alloys [18]. The effective paramagnetic moment (μ_{eff}) decreases linearly with the increase of the Pd content following the relation.

$$\mu_{eff} = \mu_{eff\,(Ni)}\,(1-x) + \mu_{eff(Pd)}\,x$$

$\mu_{eff(Ni)}$ and $\mu_{eff(Pd)}$ are the effective moment of Ni and Pd respectively. The calculated and experimental values of μ_{eff} of the alloys agree well (Fig. 3). The paramaganetic Curie temperature θ_p is a measure of the magnetic interaction between the conduction electrons. The decrease of both θ_p and μ_{eff} with the increase of Pd concentration can be interpreted by considering the magnetic exchnage interaction between the 4d electrons of Pd and the localized 3d electrons of nickel. However, because of the large susceptibility and density of states in pure Pd, the exchnage integral required for the saturation of the Pd moment on a shell of atom surrounding a Ni atom is rather small [3]. The increase of the sd electrons contribution caused by the increase of the Pd atoms gradually decreases the moment of nickel as well as the paramagnetic Curie temperature. With $x < 0.9$, the moment of the alloy is expected to fall to the value of palladium.

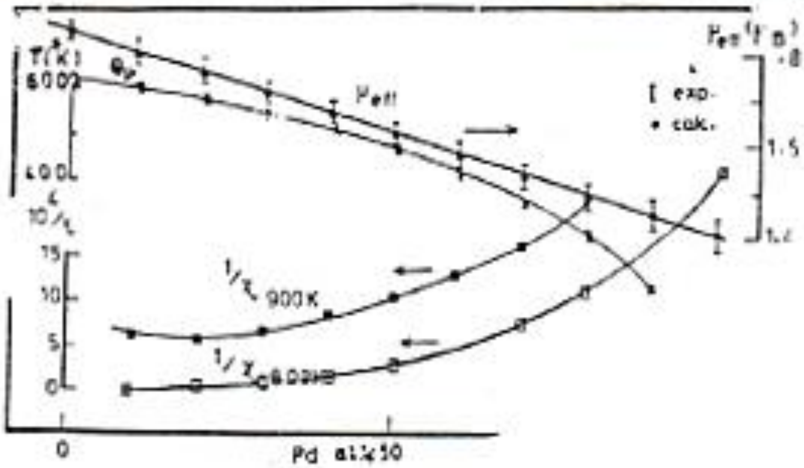

Fig. 3. The experimental and calculated effective magnetic moment μ_{eff} (μ_B), the reciprocal susceptibility $1/\chi$ at 600 and 900°K and the paramagnetic Curie temperature θ_p dependence on the Pd content x.

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