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Magnetic impurity effect in Pd-doped Ni₃Al

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Abstract. Isothermal magnetization curves of Ni_{77-x}Al₂₃Pd_x ($0 \leq x \leq 3$) intermetallic compound have been measured in the temperature range between 4.5 K and 110 K. The temperature dependence of spontaneous magnetization, $M_s(T)$, has been analysed according to the self-consistent renormalization theory of spin fluctuations. The qualitative agreement between the experimental result and the theoretical one is satisfactory. The value of Curie temperature, T_C as well as $M_s(0)$ does not vary significantly with the Ni concentration, though it varies remarkably in the Ni_{75+x}Al_{25-x} system. Pd impurity atoms occupy the Ni site and the Ni atoms expelled by the Pd atoms reside on the Al site. The expelled Ni atoms give the same magnetic effect as the excess Ni atoms in the off-stoichiometric binary compound. The values of T_C and $M_s(0)$ depend on the number of Ni atoms on the Al site, as well as on the Ni site, and the former is predominant.

1. Introduction

The intermetallic compound Ni₃Al forms in the L1₂ structure. Magnetic measurement indicates that small deviations from ideal stoichiometry have the strong effects on magnetic properties, with non-magnetic behaviour for slight Al enrichment. The critical concentration, x_c , for the transition from non-magnetic to ferromagnetic state is 74.5 at.%Ni. The magnetism of Ni₃Al compounds was analysed first using the Stoner theory. The Stoner theory represents the temperature dependence of spontaneous magnetization, M_s , as $M_s(T) = M_0 - \gamma T^2$ up $0.75T_C$ and the Ni concentration dependence of Curie temperature, T_C , as $T_C \propto (x - x_c)^{1/2}$ in Ni_xAl_{1-x} system (Edwards and Wolhfarth 1968). The experimental results in Ni₃Al compounds have been described by the Stoner theory (Robbins and Claus 1971, Dood and Chatel 1973, and Parthasarathi and Beck 1975). While, the self-consistent renormalization (SCR) theory of spin fluctuations (Moriya and Kawabata 1973) was applied to the experimental results of NMR study (Umamura and Masuda 1983) and magnetization measurements in Ni₃Al compound (Sasakura *et al* 1984). In the SCR theory the temperature dependence of spontaneous magnetization has the form $M_s(T)^2 = M_0^2 - \eta T^2$ at low temperatures and $M_s(T)^2 = \zeta(T_C^{4/3} - T^{4/3})$ over a fairly wide temperature range below T_C . It was concluded that the temperature dependence of spontaneous magnetization agrees with the prediction of the SCR theory rather than Stoner's form (Sasakura *et al* 1984). The magnetic properties of Ni_{75-x}Al₂₅Pd_x were experimentally examined from the viewpoint of the SCR theory, since Ni and Pd atoms are isoelectric and the interatomic exchange constant can be varied by alloying, keeping the other parameters constant (Sato 1975). The experimental results agree with the SCR theory rather than the Stoner model. The magnetic properties in the Ni-rich composition of the ternary and binary compounds attract our interest, since anomalies in the low-temperature specific heat were observed in the Ni-rich composition of Ni₃Al compound. The Ni atoms on the Al site, which have only

Ni nearest neighbours, make a cluster and behave as a nucleus of a 'giant magnetization cloud' (Robbins and Claus 1971, Dood and Chatel 1973 and Parthasarathi and Beck 1975). In this paper, the temperature dependence of $M_s(T)$ has been measured in $\text{Ni}_{77-x}\text{Al}_{23}\text{Pd}_x$ ($0 \leq x \leq 3$). The experimental results are analysed according to the SCR theory of spin fluctuations to confirm the predictions of the theory in the $\text{Ni}_{77-x}\text{Al}_{23}\text{Pd}_x$.

The anomalies in the specific heat were examined again by Stassis *et al* (1981) and no anomalous features could be found at low temperatures. They concluded that they could not find any evidence for the presence of magnetic inhomogeneities in Ni_3Al and that the magnetic moments of the excess Ni atoms on the Al sites are not significantly different from those on the Ni sites, and denied completely the existence of the magnetic cluster. We are interested in studying the role of Ni atoms on the Al site in the ferromagnetic structure. The Ni atoms on the Ni site are substituted by Pd atoms, with the number of Ni atoms on the Al site kept constant. Ni-concentration dependence of $M_s(0)$ and T_C is also investigated in the present study.

2. Experimental procedure

The raw materials used for alloying in the present investigation were 99.95 mass% Ni, 99.998 mass% Al and 99.98 mass% Pd. Alloy 'buttons' with the nominal composition $\text{Ni}_{77.0-x}\text{Al}_{23.0}\text{Pd}_x$ ($x = 0.4, 0.8, 1.8, 2.2$ and 3.0) (henceforth denoted as Pd-doped Ni_3Al) and $\text{Ni}_{75+x}\text{Al}_{25-x}$ ($x = 0.0, 1.5$ and 2.0) were prepared by arc-melting the raw materials four times to attain chemical homogeneity on a water-cooled copper hearth in an argon gas atmosphere at a pressure of approximately 93 kPa. As weight losses after the arc-melting were smaller than 0.1% for an ingot, the nominal composition was regarded as chemical composition. Since it was difficult to obtain a single crystal of Pd-doped Ni_3Al , we prepared a quasi-single crystal rod, instead of the single crystal, with a diameter of approximately 10 mm, containing a few grain boundaries by using the Bridgman technique. The quasi-single crystal rods were then homogenised in vacuum at 1323 K for 72 h and subsequently subjected to furnace cooling. Samples with a dimension of approximately $2.5 \times 2.5 \times 2.5 \text{ mm}^3$ for the magnetization measurement were cut from the quasi-single crystal rods.

There exists the possibility that $\text{Ni}_{77-x}\text{Al}_{23}\text{Pd}_x$ and $\text{Ni}_{75+x}\text{Al}_{25-x}$ include the γ phase. The appearance of the γ phase depends on the annealing temperature and time. The existence of the γ phase was ascertained in some samples by structure observation and the magnetization measurement. The latter method is more sensitive than the former. All the samples used in the present investigation were ascertained to be composed of the single phase.

Magnetization was measured by a SQUID magnetic flux-meter (Quantum Design) at temperatures from 4.5 to 110 K.

3. Experimental results

The magnetization measurements were carried out in the range of magnetic field strength between 0 and 4 MA m^{-1} . Figure 1 shows that the data fit nicely on straight lines in $M(T)^2$ versus H/M in $\text{Ni}_{75}\text{Al}_{25}$, which are commonly used in T_C (Arrot plots). The values for T_C in these ferromagnetic structures are obtained and shown in table 1. T_C of 75.0 at.%Ni is 43.5 K, which is slightly above 41.5 K in the stoichiometric composition. The Al content

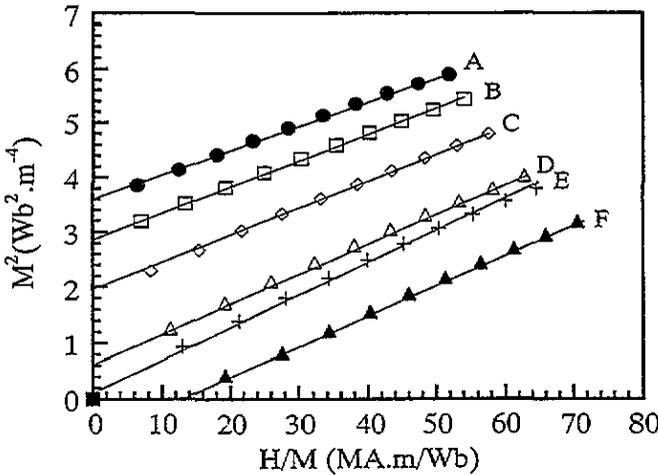


Figure 1. The Arrot plot of magnetization of Ni₃Al compound. A = 10 K, B = 20 K, C = 30 K, D = 40 K, E = 43.5 K and F = 50 K.

Table 1. Experimental values of spontaneous magnetization at $T = 0$ K, $M_s(0)$, the Curie Temperature, T_C , the coefficient of the T^2 term in M_s^2 versus T^2 plot, η , and the coefficient of the $T^{4/3}$ term in M_s^2 versus $T^{4/3}$, ζ , in the Ni₃Al and Pd-doped Ni₃Al compounds.

Ni ₃ Al and Pd-doped Ni ₃ Al samples	$M_s(0) \times 10^{-2}$ (Wb m ⁻²)	T_C (K)	$\eta \times 10^{-6}$ (Wb ² m ⁻⁴ K ⁻²)	$\zeta \times 10^{-5}$ (Wb ² m ⁻⁴ K ^{-4/3})
Ni _{75.0} Al _{25.0}	6.58	43.5	2.09	4.28
Ni _{76.5} Al _{23.5}	9.89	82.0	2.17	2.69
Ni _{77.0} Al _{23.0}	12.00	86.0	1.42	2.73
Ni _{76.6} Al _{23.0} Pd _{0.4}	11.31	82.0	1.74	4.06
Ni _{76.2} Al _{23.0} Pd _{0.8}	10.66	78.0	1.83	3.96
Ni _{75.2} Al _{23.0} Pd _{1.8}	11.17	78.0	2.15	4.04
Ni _{74.8} Al _{23.0} Pd _{2.2}	10.60	78.0	1.85	4.09
Ni _{74.0} Al _{23.0} Pd _{3.0}	9.78	71.0	2.33	3.39

would evaporate out during the crystal growth slightly less than 0.1 at.%. Small deviations from ideal stoichiometry would be realized in the present sample.

The experimental results of temperature dependence of $M_s(T)$ showed a good agreement with the SCR theory of spin fluctuation in Ni₃Al compounds; $M_s(T)$ has a temperature dependence in the form of $M_s(T)^2 = M_s(0)^2 - \eta T^2$ in low temperatures and $M_s(T)^2 = \zeta(T_C^{4/3} - T^{4/3})$ over a fairly wide temperature range below T_C (Sasakura *et al* 1984). Figure 2(a) shows the temperature dependence of $M_s(T)$ in the Ni_{77-x}Al₂₃Pd_x system, i.e. $M_s(T)^2$ versus T^2 . The spontaneous magnetization at 0 K is determined by the extrapolation of this linear relation. Figure 2(b) shows the relationship of $M_s(T)^2$ against $T^{4/3}$ below T_C . The values of $M_s(0)$, T_C , η and ζ are given in table 1.

Above T_C , the presence of superparamagnetic clusters is expected in the present samples as the previous investigation in Ni₃Al compounds (Robbins and Claus 1971). The cloud concentration and cloud moment in the Pd-doped Ni₃Al compounds have been obtained according to the modified Langevin function (Robbins and Claus 1971, Fang *et al* 1992). The cloud moment is very large, $(1 \pm 0.2) \times 10^3 \mu_B$ in the temperature range between T_C and 110 K, but the same order of magnitude as Ni₃Al obtained by the previous investigators (Robbins and Claus 1971). The cloud concentration near T_C is about 2×10^{-5} clusters/atom and it decreases rapidly at 90 K. The temperature dependence of the cloud concentration

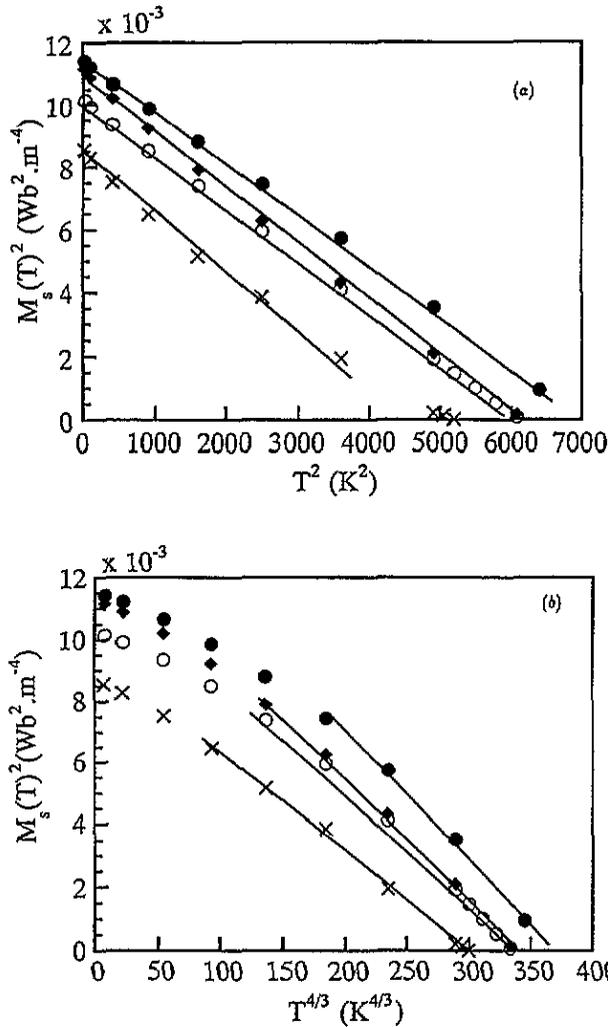


Figure 2. The temperature dependence of spontaneous magnetization, $M_s(0)$, in $\text{Ni}_{77-x}\text{Al}_{23}\text{Pd}_x$ (a): $M_s(T)^2 \propto T^2$, (b): $M_s(T)^2 \propto T^{4/3}$. $\text{Ni}_{76.6}\text{Al}_{23}\text{Pd}_{0.4}$ (●), $\text{Ni}_{76.2}\text{Al}_{23}\text{Pd}_{0.8}$ (○), $\text{Ni}_{75.2}\text{Al}_{23}\text{Pd}_{1.8}$ (◆) and $\text{Ni}_{74}\text{Al}_{23}\text{Pd}_3$ (×).

is similar to that of Robbins and Claus (1971). The experimental feature characterizing superparamagnetism is that the magnetization is a universal function of H/T (Cullity 1972). But the present measurements don't satisfy the experimental feature. A different, more subtle origin should be sought for the susceptibility above T_C .

Figure 3 shows the values of T_C and $M_s(0)$ in $\text{Ni}_{77-x}\text{Al}_{23}\text{Pd}_x$ ($0 \leq x \leq 3$). T_C as well as $M_s(0)$ shows a gentle increase with increasing Ni content even near 75 at.% Ni content. At 74 at.% Ni a ferromagnetic structure is admitted, though $\text{Ni}_{74}\text{Al}_{23}\text{Pd}_3$ compound shows paramagnetic. The values of T_C and $M_s(0)$ of $\text{Ni}_{74}\text{Al}_{23}\text{Pd}_3$ are comparable with those of $\text{Ni}_{76.5}\text{Al}_{23.5}$ (see table 1). Small changes of T_C and M_s in substitution of Ni element by Pd should be attributed to the isoelectric feature of Ni and Pd atoms.

The Ni-concentration dependence of T_C has been investigated by Kawabata (1983) within the frame work of the SCR theory taking account of the disorder effect. The experimental results, however, were explained by the Stoner theory as $T_C \propto (x - x_c)^{1/2}$ rather than the SCR theory (Sasakura *et al* 1984). So the present experimental results of Ni concentration dependence of T_C and $M_s(0)$ in the binary compounds are analysed according

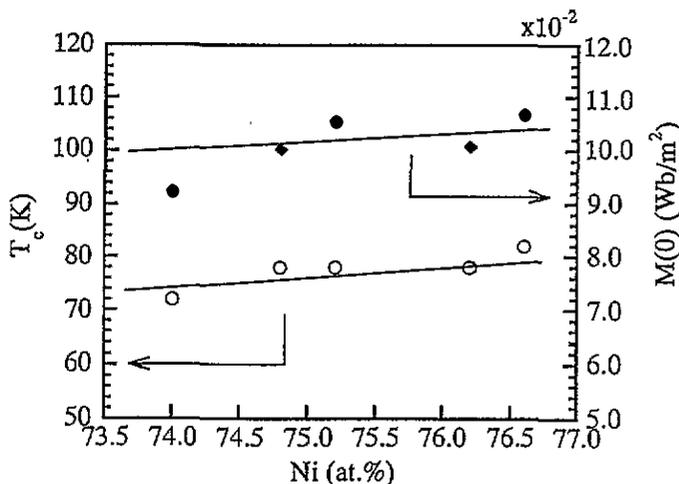


Figure 3. Ni concentration dependence of Curie temperature, T_C , (O), and spontaneous magnetization, $M_s(0)$, (◆), in $Ni_{77-x}Al_{23}Pd_x$ compounds.

to the Stoner theory, where spin fluctuation effects are not involved. $M_s(0)$ is the value of 0 K, where spin fluctuation effects are negligible. And they are shown in figures 4(a) and 4(b), comparing with the previous works. The relationship due to the Stoner theory agrees with the experimental results near the stoichiometry. But the values of $M_s(0)$ in the present study deviate from the relationship, $M_s(0) \propto (x - x_c)^{1/2}$ in 76.5 and 77 at.%Ni. The deviation shows that the relationship holds only for the compositions near stoichiometry.

4. Discussion

The excess Ni atoms that are found in the off-stoichiometric Ni₃Al samples have a ferromagnetic structure. The values of T_C and $M_s(0)$ increase rapidly with an increasing number of excess Ni atoms, as shown in figure 4. It can be assumed that the excess Ni atoms reside randomly on the Al sites and the Ni sites are fully occupied by the rest of the Ni atoms. Since the Ni atom on the Al site has only Ni atoms as its nearest neighbours, the host Ni atoms would carry the magnetic moment comparable to that in pure nickel (Robbins and Claus 1971, Dood and Chatel 1973, Parthasarathi and Beck 1975). This picture would be related closely to the formation of giant moments in Fe-doped Ni₃Al. However the magnetic moments of excess Ni atoms on the Al site are not significantly different from those on the Ni site (Felcher *et al* 1977). Although there is no difference in the magnetic moments between the two sites, the values of T_C and $M_s(0)$ vary remarkably with the number of Ni atoms on the Al site. The magnetic properties of $Ni_{77-x}Al_{23}Pd_x$ compounds have been studied in order to investigate the role of Ni atoms on the Al site in the ferromagnetic structure.

It is important to determine which site Pd atoms occupy, when we discuss the magnetic properties of Pd-doped Ni₃Al compound. The Pd atoms may substitute exclusively for Al atoms or exclusively for Ni atoms, or for both species. One of the present authors and his co-workers determined the substitution behaviour of Pd atoms in Ni₃Al compound by channelling enhanced microanalysis (ALCHEM) (Chiba *et al* 1991). They have concluded that Pd atoms have a strong tendency to occupy the Ni site. This tendency is established in the present sample of $Ni_{75.2}Al_{23}Pd_{1.8}$; more than 90% Pd atoms occupy the Ni site.

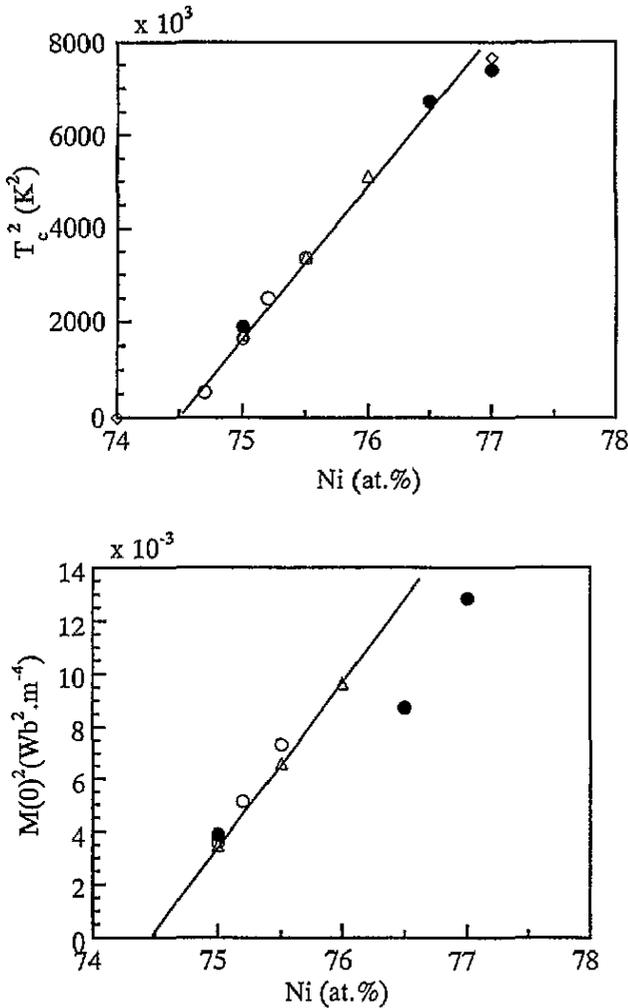


Figure 4. Ni-concentration dependence of Curie temperature, T_C and spontaneous magnetization, $M_s(0)$ in $\text{Ni}_{75+x}\text{Pd}_{25-x}$ compound, De Boer *et al* (Δ), Saskura *et al* (\circ), Yoshizawa *et al* (\diamond) and the present work (\bullet).

Ni atoms which are expelled by the Pd atoms occupy the Al site. The substituted Ni atoms occupy the same site as the excess Ni atoms in the off-stoichiometric sample. It would be reasonable to assume that the substituted Ni atoms reside randomly on the Al sites and that the Ni sites are completely occupied by the Pd atoms and the rest of the Ni atoms. If this assumption is made, there would be three kinds of atomic configurations in the Pd-doped Ni_3Al compounds: the $L1_2$ -type structure (I), one Pd atom occupying the Ni site (II), and one of the Al sites occupied by a Ni atom (III), as shown in figure 5. It is possible for the kind of atomic configurations to exist: for example, one Pd atom occupying the Al site in the $L1_2$ -type structure. But the number of these atomic configurations are so small that they are negligible in the present samples.

The relative composition of the three kinds of atomic configurations changes with the Pd content. The relative composition is expressed in values relative to the stoichiometric Ni_3Al composition as shown in table 2. N is 1% of the total number of unit cells per unit volume. In $\text{Ni}_{75.2}\text{Al}_{23.0}\text{Pd}_{1.8}$, for example, Pd atoms occupy the Ni site at random and 1.8 N atomic configurations of type II are formed. The expelled Ni atoms occupy Al sites randomly and

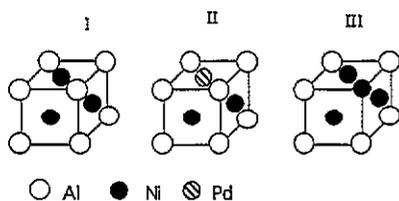


Figure 5. 3 types of atomic configurations in Pd doped Ni₃Al compounds.

form $2N$ atomic configurations of type III. The atomic configurations of type I decrease by $3.8N$ compared with the stoichiometry. The number of type III atomic configurations is $2N$ in all Pd-doped Ni₃Al samples.

Table 2. The relative composition of 3 types of atomic configurations in Ni₃Al and Pd-doped Ni₃Al compounds compared to the stoichiometric composition. N is one percent of total number of unit cells per unit volume.

Ni ₃ Al and Pd-doped Ni ₃ Al samples	Type I	Type II	Type III
Ni _{75.0} Al _{25.0}	0	0	0
Ni _{76.5} Al _{23.5}	-1.5 N	0	1.5 N
Ni _{77.0} Al _{23.0}	-2.0 N	0	2.0 N
Ni _{76.6} Al _{23.0} Pd _{0.4}	-2.2 N	0.4 N	2.0 N
Ni _{76.2} Al _{23.0} Pd _{0.8}	-2.8 N	0.8 N	2.0 N
Ni _{75.2} Al _{23.0} Pd _{1.8}	-3.8 N	1.8 N	2.0 N
Ni _{74.8} Al _{23.0} Pd _{2.2}	-4.2 N	2.2 N	2.0 N
Ni _{74.0} Al _{23.0} Pd _{3.0}	-5.0 N	3.0 N	2.0 N

Ni_{77-x}Al₂₃Pd_x compounds have nearly the same values in Curie temperature and spontaneous magnetization, admitting a small difference; the values of T_C and $M_s(0)$ increase slowly with increasing Ni content, but the rate of increase is much smaller than the binary compounds (see figures 3 and 4). The small change in T_C and $M_s(0)$ values in these Pd doped Ni₃Al may be attributed to the constant number of type III atomic configurations. We would like to assert that the type III atomic configuration has a relation with the values of T_C and $M_s(0)$ and that the density of the type III atomic configuration determines T_C and $M_s(0)$, since these values increase as the number of type III atomic configurations increases in the binary compounds, as shown in figure 4(b). The magnetic moment of the excess Ni atoms on the Al site is not significantly different from that of the Ni site (Felcher *et al* 1977). Not only do Ni atoms on the Al site, but Ni atoms on the Ni site, have the same magnetic moment in the type III atomic configuration, and even the Ni atoms in the vicinity of the type III atomic configuration would have nearly the same magnetic moment.

The experimental results of temperature dependence of $M_s(T)$ are consistent with the results of the SCR theory, as shown in figure 2(a) and (b). According to the SCR theory, T_C is represented as a function of the inverse susceptibility enhancement factor, $(1 - \alpha)$, as it is given by Moriya and Kawabata (1973).

$$T_C \propto [(\alpha - 1)/\Gamma_1]^{3/4} \quad (1)$$

where Γ_1 is a parameter depending on the band structure. In the Ni_{75-x}Al₂₅Pd_x system, since Ni and Pd are isoelectric, the factor $(\alpha - 1)$ can be varied by alloying, keeping Γ_1

nearly constant. The experimental results showed that the factor $(\alpha - 1)$ is a linear function of x (Sato 1975). T_C is a simple function of Ni content and it is given by

$$T_C = K(x - x_c)^{3/4}. \quad (2)$$

In the present Pd-doped Ni₃Al system, the same relation can be expected between T_C and x . But the present experimental results are different from those of the Ni_{75-x}Al₂₅Pd_x system; T_C is nearly constant in Ni concentrations between 76.2 and 74.8 at.% in the present experiment. The Ni_{75-x}Al₂₅Pd_x system includes no type III atomic configurations. Only type I (or type II) atomic configurations decrease (or increase) with increasing Pd content and the factor $(\alpha - 1)$ depends on the number of type I atomic configuration. In the present Ni_{77-x}Al₂₃Pd_x system, however, type III atomic configurations exist and play an important role in the origin of T_C ; the factor $(\alpha - 1)$ depends on the number of type III atomic configurations as well as that of type I atomic configurations and the former is predominant. The decrease of the number of type I atomic configurations is reflected in the small decrease of T_C with increasing the number of Pd atoms in the present ternary system, as shown in figure 3. We could not assert that T_C has a simple relationship with the number of type I atomic configurations, N_I , in the present Pd-doped Ni₃Al system; we could not decide from the experimental results which relation explains better the behaviour of T_C , $T_C \propto (N_I - N_c)^{1/2}$ or $T_C \propto (N_I - N_c)^{3/4}$, where N_c is the critical number of type I atomic configurations. We have no confirmation that the occupation probability of Pd atoms on the Ni site is independent of its concentration, though almost all the Pd atoms occupy the Ni site. There may be another metallurgical reason why the solute atoms are not distributed randomly in the host, so that clusters of atoms are important whatever the solute concentrations. The same may be said of the relation between $M_s(0)$ and N_I . The latter reason would be one factor of the deviation from the simple relationship between $M_s(0)$ and x , as shown in figure 4(b).

A detailed study, including the influence of plastic deformation on $M_s(T)$ and T_C in the Ni_{77-x}Al₂₃Pd_x system, is currently in progress.

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