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The magnetic properties of $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ single crystal compounds were studied by the measurements of magnetization, susceptibility and electrical resistivity. It was found that the Curie temperature takes a maximum at about $x=0.1$, while the magnetic moment decreases monotonically with increasing x and the compounds with $x \geq 0.8$ show the Pauli paramagnetism. The anisotropy constant K_1 was found to decrease rapidly with increasing x and becomes almost zero near $x=0.3$. The exchange interactions in Fe_2P are briefly discussed on the basis of the concentration dependence of T_c of this system.

§1. Introduction

As a series of the systematic research of M_2P compounds systems, we studied for the first time the magnetic properties of Fe_2P single crystal.¹⁾ Subsequently, we have extended our study to the compounds of $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ system for the purpose of elucidating the effect of substituting Ni for Fe in Fe_2P on the magnetic properties. The compounds of $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ system has a hexagonal structure with the space group $\text{P}\bar{6}2m(D_{3h}^3)$ in the whole range of the composition. In this structure, there are two metal atom sites: the tetrahedral site M_I and the pyramidal site M_{II} surrounded by four P atoms and five P atoms, respectively. The Mössbauer experiment²⁾ of $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ system has revealed that Ni atoms occupy M_I site preferentially in the range $0 \leq x < 0.3$, but M_{II} site for $x > 0.7$.

Fruchart *et al.*³⁾ have measured magnetizations of the $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ compounds on the polycrystals. They have shown that Ni_2P is a Pauli paramagnet of $\chi_g = 3.2 \times 10^{-6}$ emu/g, and the Curie temperature T_c takes a maximum of 342 K at $x=0.08$ and decreases below 100 K at $x=0.5$. But no saturation magnetizations have been measured by them. Until now, there has been no further study on the magnetic properties of this system.

This paper is concerned with the magnetic properties on the single crystals of the system $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$, which have been studied from

the measurements of magnetization, susceptibility and electrical resistivity.

§2. Experimental

The compounds $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ were made at an interval of $x=0.1$ by solid-vapor reaction. The stoichiometric mixtures of the elements, 99.99% in purity, were sealed in an evacuated quartz tube, then heated slowly up to 900°C in three days, kept at that temperature for two weeks and cooled in the furnace. The product was ground into powder, again sealed in a quartz tube in an argon atmosphere, melted at 1400~1450°C for about 30 minutes and rapidly cooled in water. The compound thus prepared was checked by X-ray diffraction and confirmed to have a single phase. The single crystals were grown by thermal annealing of the ingots just below the melting point. For the measurements of magnetization and susceptibility, a portion of the single crystal ingots was shaped into spheres of 2~3 mm in diameter by a two-pipe lapidary method. For the measurements of electrical resistivity, rectangular parallelepiped specimens of $1 \times 1 \times 7$ mm³ having the c axis parallel to the longest dimension were prepared by cutting the ingots.

Magnetization was measured in the range from 4.2 K to 250 K within an error of 1% with a Foner type vibrating-sample magnetometer in applied fields up to 50 kOe. Paramagnetic susceptibility was measured in the range from 77 K to 800 K within an error of

1% with a magnetic balance. Electrical resistance was measured by a standard four-probe method in the range from 77 K to 700 K with current reversal. The current leads and potential probes were spot-welded on the specimens with manganin wires of 0.2 mm in diameter.

§3. Results

Figure 1 shows, as an example, the magnetization curves along the direction parallel and perpendicular to the c axis at 4.2 K for Fe_2P and $(\text{Fe}_{0.8}\text{Ni}_{0.2})_2\text{P}$ compounds. The easy direction of magnetization was the c axis and no magnetocrystalline anisotropy in the basal plane was observed for all the compounds. The spontaneous magnetization σ_s was determined by extrapolating the linear part of the c axis magnetization back to zero field. The temperature dependence of σ_s is shown in Fig. 2 for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ compounds. The transition from ferromagnetic to paramagnetic at T_c for all the compounds shows a second order transition except for Fe_2P , where the transition at T_c is of the first order accompanying by the deformation of the lattice.

Figure 3 shows the inverse susceptibility χ_g^{-1} vs temperature curves for the compounds. Here, no correction for the temperature independent susceptibility was made except for the compound with $x=0.7$, for which the χ_g in Fig. 3 is the estimated value by subtraction of the χ_g for Ni_2P from the measured one. The χ_g for the compounds in the range of $0 \leq x \leq 0.7$ well obeys the Curie-Weiss law

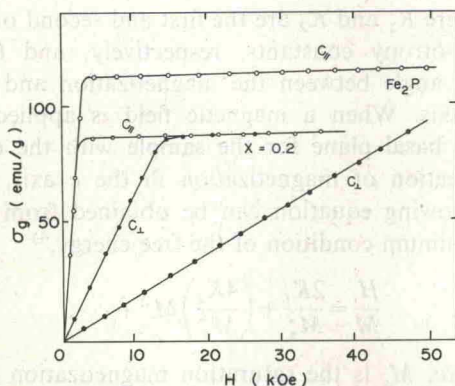


Fig. 1. Magnetization curves along the direction parallel and perpendicular to the c axis at 4.2 K for $x=0$ and $x=0.2$ in $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$.

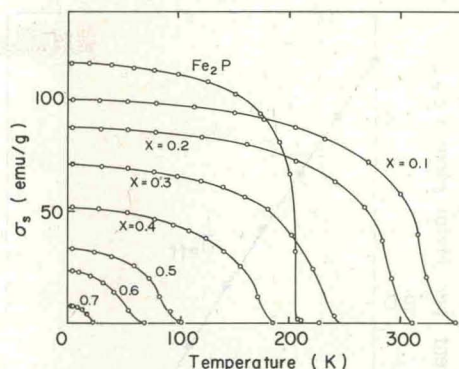


Fig. 2. Spontaneous magnetization per gram σ_s plotted against temperature for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$.

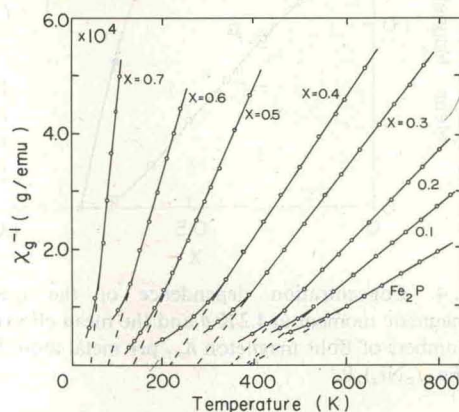


Fig. 3. Inverse susceptibility per gram χ_g^{-1} plotted against temperature for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$.

except in the vicinity of T_c . The compounds with $x \geq 0.8$ show the Pauli paramagnetism and the value of χ_g was 3.2×10^{-6} (emu/g) independent of x .

Figure 4 shows the concentration dependence of the magnetic moment $\bar{\mu}$ at 4.2 K and the effective numbers of Bohr magneton \bar{n}_{eff} per metal atom. Both $\bar{\mu}$ and \bar{n}_{eff} decrease monotonically with increasing x and become zero at about $x=0.7$. The ferromagnetic Curie temperature T_c and the paramagnetic Curie temperature θ_p are plotted against the concentration of Ni in Fig. 5. The value of θ_p decreases monotonically with increasing x . On the other hand, the curve of T_c takes a maximum at about $x=0.1$ in agreement with the result reported by Fruchart *et al.*³⁾

Figure 6 shows the temperature dependence of the electrical resistivity along the c axis for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ compounds. In the figure, the data of Ni_2P are those obtained by employ-

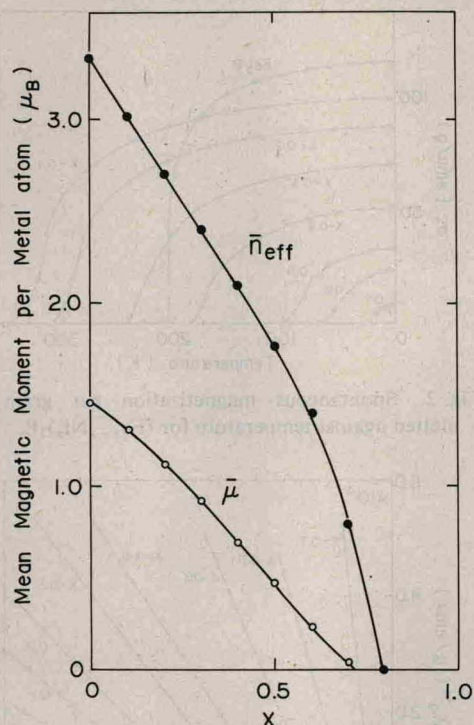


Fig. 4. Concentration dependence of the mean magnetic moment at 4.2 K $\bar{\mu}$ and the mean effective numbers of Bohr magneton \bar{n}_{eff} per metal atom for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$.

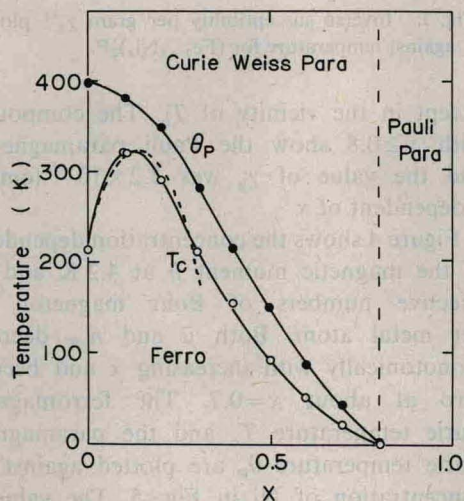


Fig. 5. The ferromagnetic and paramagnetic Curie temperatures, T_c and θ_p , respectively, plotted against composition for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$.

ing the polycrystal specimen since no single crystal was available. The resistivities of Fe rich compounds increase with increasing temperature at low temperatures which might be

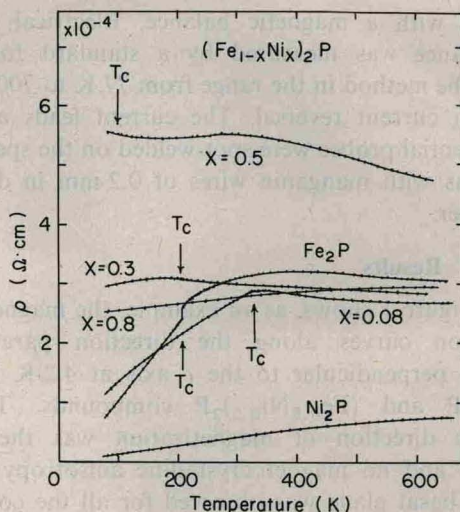


Fig. 6. Temperature dependence of the electrical resistivity along the c axis for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$.

associated with spin disorder, but decrease with increasing temperature at higher temperatures in paramagnetic state. On the other hand, the resistivities of the compounds with $x \geq 0.8$ increase with increasing temperature at all temperature ranges. These results might be attributable to the hole in the narrow d electron band. It may be noted that the jump of the resistivity due to the first order transition observed in Fe_2P disappears already by substituting only 8% of Fe by Ni.

§4. Discussion

For the hexagonal crystal in ferromagnetic state, the magnetocrystalline anisotropy is conventionally expressed by

$$E = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots, \quad (1)$$

where K_1 and K_2 are the first and second order anisotropy constants, respectively, and θ is the angle between the magnetization and the c axis. When a magnetic field is applied in the basal plane for the sample with the easy direction of magnetization in the c axis, the following equation can be obtained from the minimum condition of the free energy,⁴⁾

$$\frac{H}{M} = \frac{2K_1}{M_s^2} + \left(\frac{4K_2}{M_s^4} \right) M^2 + \dots \quad (2)$$

Here, M_s is the saturation magnetization and M is the magnetization along the direction perpendicular to the c axis at the effective field H . Since M is proportional to H as

seen in Fig. 1 for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ compounds, we know that K_2 is negligibly small. The concentration dependence of K_1 at 4.2 K is shown in Fig. 7 for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ compounds. The value of K_1 decreases rapidly with increasing x and becomes almost zero for the compounds near $x=0.3$. Since Ni atoms substitute preferentially for Fe atoms on M_I site in the range $x < 0.3$, it might be deduced that the magnetic anisotropy is due to the crystal field anisotropy of the Fe atoms on M_I site rather than those on M_{II} site. Furthermore, if the magnetic anisotropy comes from the crystal field effects, K_1 should be proportional to the third power of the magnetization.⁵⁾ The temperature dependence of K_1 in Fig. 8, however, appears to be represented by the fifth power function of the spontaneous magnetization in low temperatures. This suggests that the anisotropy may originate in not only the crystal field effects, but also the other mechanisms, such as the anisotropy of exchange interactions or the magnetoelastic interactions.

Accepting that only Fe atom contributes to the magnetic moment in the compound, we can estimate the magnetic moments per iron atom in the ferromagnetic and paramagnetic states, μ_f and μ_p , respectively. In Fig. 9, the estimated values of μ_f and μ_p are plotted against x . The value of μ_p decreases monotonically with increasing x , but that of μ_f slightly changes in the range $0 \leq x < 0.3$ and decreases with increasing x for $x > 0.3$. This means that substitution of Ni atom for Fe atom on M_I site produces little change

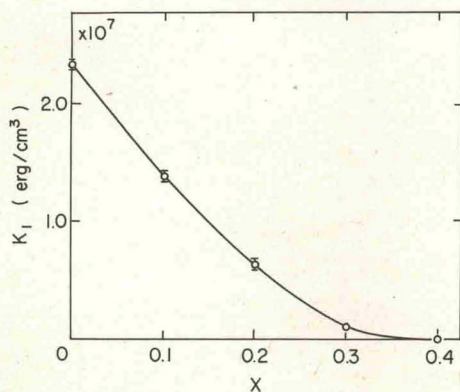


Fig. 7. Anisotropy constant at 4.2 K as a function of composition for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$.

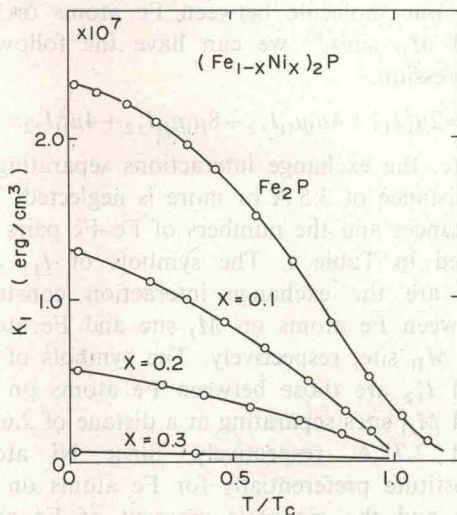


Fig. 8. Temperature dependence of the anisotropy constant K_1 for $x=0.0, 0.1, 0.2$ and 0.3 in $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$.

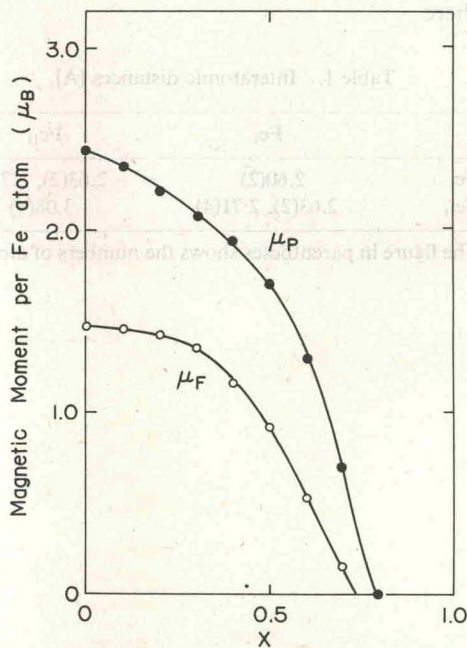


Fig. 9. Concentration dependence of the magnetic moments per Fe atom in the ferromagnetic and paramagnetic states μ_f and μ_p , respectively.

in μ_f and the decrease of μ_f is due to substitution of Ni atom for Fe atom on M_{II} site.

Finally, we will briefly describe the exchange interaction in Fe_2P by using the concentration dependence of the Curie temperature of $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ system. If the Curie temperature is given by the sum of the exchange energy

per one molecule between Fe atoms on M_I and M_{II} sites,⁶⁾ we can have the following expression,

$$T_c = 2\mu_I^2 I_{11} + 4\mu_I \mu_{II} I_{12} + 8\mu_I \mu_{II} I'_{12} + 4\mu_{II}^2 I_{22}. \quad (3)$$

Here, the exchange interactions separating at a distance of 3.5 Å or more is neglected. The distances and the numbers of Fe-Fe pairs are listed in Table I. The symbols of I_{11} and I_{22} are the exchange interaction constants between Fe atoms on M_I site and Fe atoms on M_{II} site, respectively. The symbols of I_{12} and I'_{12} are those between Fe atoms on M_I and M_{II} sites separating at a distance of 2.63 Å and 2.71 Å, respectively. Since Ni atoms substitute preferentially for Fe atoms on M_I site and the magnetic moment of Fe atom slightly changes for the compounds with $x < 0.3$, T_c is expressed as follows,

$$T_c = 2(1-x)^2 T_{11} + 4(1-x) T_{12} + 4 T_{22}, \quad (4)$$

where

Table I. Interatomic distances [Å].

	Fe _I	Fe _{II}
Fe _I	2.60(2)	2.63(2), 2.71(4)
Fe _{II}	2.63(2), 2.71(4)	3.08(4)

The figure in parentheses shows the numbers of atoms.

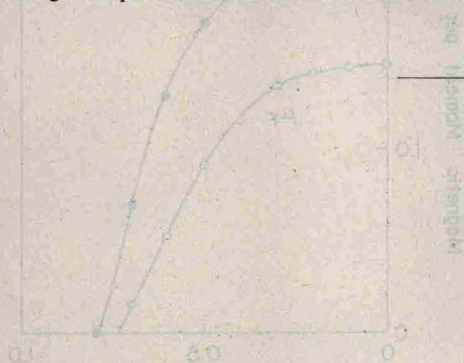


Fig. 9. Concentration dependence of the magnetic moment per Fe atom in the ferromagnetic and antiferromagnetic phases.

Finally, we will briefly describe the exchange interaction in Fe₂ by using the concentration dependence of the Curie temperature of Fe₂(1-x)Ni_{2x} system. If the Curie temperature is given by the sum of the exchange energy

$$T_{11} = \mu_I^2 I_{11}, \quad T_{12} = \mu_I \mu_{II} I_{12} + 2\mu_I \mu_{II} I'_{12},$$

and

$$T_{22} = \mu_{II}^2 I_{22}. \quad (5)$$

From the concentration dependence of T_c in Fig. 6, we obtained the values of $T_{11} = -1950$ k, $T_{12} = 1660$ k and $T_{22} = -630$ k. The dotted line of T_c in Fig. 5 is the calculated curve and is in fairly good agreement with the experimental curve within $x < 0.3$. It might be concluded that the exchange interaction between the first nearest neighbor Fe atoms is strongly antiferromagnetic and the exchange interaction between the 3rd neighbor atoms is weakly antiferromagnetic, but the 2nd neighbor exchange interaction is strongly ferromagnetic.

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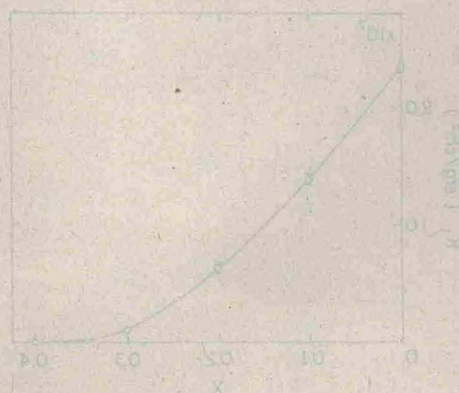


Fig. 7. Curie temperature T_c as a function of composition in Fe₂(1-x)Ni_{2x}.