G. T. DUBOVKA et al.: Some Peculiarities of the T-P-C Diagram

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# Some Peculiarities of the T-P-C Diagram of the System $Fe_{65}(Ni_{1-x}Mn_x)_{35}$

# By

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The form of the T-P-C diagram of the  $\operatorname{Fe}_{65}(\operatorname{Ni}_{1-x}\operatorname{Mn}_x)_{35}$  system is specified. The alloy with x = 0.171 is found to deviate from the linear Curie point dependence on pressure. The interrelation between the magnetic T-C diagram peculiarities and the anomalies of the thermal expansion coefficient and the isotherm of the magnetic susceptibility in the paramagnetic range is investigated.

Уточнен вид фазовой T-P-C диаграммы системы  $\operatorname{Fe}_{65}(\operatorname{Ni}_{1-x}\operatorname{Mn}_x)_{35}$ . У сплава с x = 0,171 обнаружено отклонение зависимости точки Кюри от давления от линейной. Исследована взаимосвязь между особенностями магнитной T-C диаграммы и аномалиями к.л.р. и изотермы магнитной восприимчивости в парамагнитной области.

## 1. Introduction

One of the reasons which recently caused an increasing interest in investigations of ternary alloys on Fe–Ni invar base is the possibility to study anomalies of physical properties by varying the ratio of alloying elements. These anomalies always appear simultaneously in binary invars: low magnitude of the Curie points  $T_{\rm C}$  and spontaneous magnetization at 0 °K, anomalies of P-V-T relations (including thermal expansion), decreasing stability of the  $\gamma$ -phase to  $\gamma \rightarrow \alpha$  transformation, etc.

The Fe-Ni-Mn system gives the opportunity to study the transition from alloys being ferromagnetically ordered at low temperature (Ni-rich alloys) to those being ordered antiferromagnetically (Mn-rich alloys) [1].

In the present work the T-P-C phase diagram of the Fe-Ni-Mn system was specified for  $\operatorname{Fe}_{65}(\operatorname{Ni}_{1-x}\operatorname{Mn}_x)_{35}$ , the relation of the peculiarities of the diagram with anomalies of linear expansion and magnetic susceptibility in the paramagnetic region was investigated.

#### 2. Experimental

The alloys were prepared from electrolytic Ni, Mn, and Fe carbonyl by melting in argon atmosphere in an induction furnace. The melts were subjected to homogeneous annealing at 1100 °C for 6 h and subsequent quenching in water. The susceptibility  $\chi$  was measured by the Faraday-Sucksmith method with an accuracy of  $0.1 \times 10^{-4}$  e.m.u./g. Alloys No. 1, 2, 3, 8, 9 (Table 1) were investigated at hydrostatic pressures up to 20 kbar. The pressure was measured by a manganin wire gauge with an accuracy of  $\pm 100$  bar, the temperature by a chromel-alumel thermocouple with an accuracy of  $\pm 1$  deg. Alloys No. 4 and 5 were investigated using AgCl as the pressure transmitting medium. In these

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No.	content (wt%)			$T_{\rm C}$	$T_{\rm N}$	$-\mathrm{d}T_{\mathrm{C,N}}/\mathrm{d}P$
	Mn	Ni	x	(°K)	(°K)	(deg kbar <sup>-1</sup> )
1	0	35	0.000	467	1.	$4.4\pm0.1$
2	1.5	33.5	0.043	402		$5.0\pm0.1$
3	3.0	32	0.086	353	-100	$4.8 \pm 0.15$
4	4.5	30.5	0.129	228	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	$4.2\pm0.4$
5	6	29	0.171	190		$3.7\pm0.3$
6	8	27	0.229	90	1. 25.22	1
7	24	11	0.686	Are and the second	253	100 m 100 m 100 m
8	29	6	0.829		341	$0.6\pm0.2$
9	35	0	1.000	-	442	$0.9\pm0.1$

Table 1

cases the pressure up to 25 kbar was measured with an accuracy of  $\pm 1$  kbar. The Curie points  $T_{\rm C}$  were determined by the differential transformer method [2] using the temperature dependence of the initial magnetic permeability with an accuracy of  $\pm 3$  deg. The Néel points  $T_{\rm N}$  were determined by controlling the position of the bend of the temperature dependence curve of electrical resistance with an accuracy of  $\pm 5$  deg. The fact that these bends in alloys No. 8 and 9 correspond to the Néel points was proved by means of neutron diffraction investigation.

#### 3. Results and Discussion

All the investigated alloys had a disordered f.c.c. structure. The obtained magnitudes of  $T_{\rm C}$ ,  $T_{\rm N}$  and initial values of  ${\rm d}T_{\rm C}/{\rm d}P$  and  ${\rm d}T_{\rm N}/{\rm d}P$  are given in Table 1 and Fig. 1. The T-C diagram at atmospheric pressure is in good agreement with data given in [1, 3]. The considerable disagreement of the values  $dT_{\rm c}/dP$  obtained in [3] with our data might possibly be due to great errors in the measurements [3] resulting from too small maximal pressure (3 to 5 kbar) used in the work.

For all the alloys studied under pressure except the alloy No. 5,  $T_{\rm C}$  and  $T_{\rm N}$ decrease linearly with increasing pressure. In the alloy No. 5, however, the marked divergence of the  $T_{\rm C}(P)$  dependence from the linear one is noticed (Fig. 2). It is worth pointing out that from all the alloys studied under pressure



Fig. 1. The phase diagram of magnetic transitions in the  $Fe_{65}(Ni_{1-x}Mn_{x})_{35}$  system at atmospheric pressure and dependences of  $dT_{\rm C}/dP$  and  $dT_N/dP$  on composition.  $O T_C$ ;  $O dT_C/dP$ ;  $\Box T_{\rm N}; \equiv {\rm d}T_{\rm N}/{\rm d}P$ 

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Fig. 3. The dependences of the linear expansion coefficient  $\alpha$  and magnetic susceptibility  $\chi$  at 573 °K on alloy composition

this specimen had the lowest  $T_{\rm C}$  and that for the alloy with similar composition (No. 4) investigated under the same (quasi-hydrostatic) conditions the  $T_{\rm C}(P)$  dependence deviates from the linear one only slightly and lies within the experimental error.

It is seen in Fig. 2 that the  $P(T_{\rm C})$  dependence for the alloy No. 5 is nearly parabolic in the investigated temperature range. The very dependence

$$\frac{\mathrm{d}T_{\mathrm{C}}}{\mathrm{d}P} = -\frac{A}{T_{\mathrm{C}}},$$

where A is the constant given by Wohlfarth's approximation [4] of a very weak itinerant ferromagnetism (in our case  $A \approx 700 \text{ deg}^2 \text{ kbar}^{-1}$ ). The fact that such an approximation may be used to describe the temperature dependence of magnetization of the system  $\text{Fe}_{65}(\text{Ni}_{1-x}\text{Mn}_x)_{35}$  for 0.15 < x < 0.3 was already illustrated in [5].

The results of measurements of the linear expansion coefficient  $\alpha$  at different temperatures and the isotherm of magnetic susceptibility  $\chi$  at 573 °K (in the paramagnetic range) are given in Fig. 3. It follows from Fig. 3 that on substituting Ni by manganese  $\alpha$  increases sharply near the composition Fe<sub>65</sub>Ni<sub>35</sub> and decreases more smoothly near Fe<sub>65</sub>Mn<sub>35</sub> at all temperatures. For  $\chi$  one can observe a sharp drop in the 0 < x < 0.3 range and a weak dependence on concentration at higher Mn contents. Thus it is seen from Fig. 3 that both the functional dependences  $\alpha(x)$  and  $\chi(x)$  are different in the regions  $x \leq 0.3$  and  $x \geq 0.3$  up to temperatures which are considerable higher than those of magnetic ordering of the investigated samples (the boundary between these regions is conventionally shown in Fig. 1 by a dashed line). All the investigated alloys had the same f.c.c. lattice at all temperatures, so the difference in the behaviour of the  $\alpha(x)$  and  $\chi(x)$  dependences in the mentioned regions may be due to the difference in the electron configuration in the paramagnetic state of the samples which are ferromagnetics ( $x \leq 0.3$ ) and antiferromagnetics ( $x \geq 0.3$ ) at low temperatures.

It is seen from Fig. 1 that a region of alloys paramagnetic down to temperatures close to 0 °K, may appear or extend with increasing pressure. Thus, for example, extrapolation gives  $T_{\rm C} = 0$  °K at P < 30 kbar (Fig. 2) for the alloy

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No. 5. Similar speculations are true for Fe–Ni–Mn antiferromagnetic alloys as well. The number of the s + d external electrons is considered as a criterion of a magnetic ordering to exist in alloys on the basis of d-metals in some papers [6, 7]. High pressure does not change this number in our Fe–Ni–Mn alloys, but may transform, for example, the state of alloy No. 5 from ferromagnetic at temperatures below 190 °K to paramagnetic at temperatures close to 0 °K. This fact seems to be unfavourable for the use of the number of external electrons as a criterion of magnetic ordering in alloys of d-metals.

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