Electronic Specific Heat of Disordered f.c.c. (Ni, Fe)_3 Mn

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(Received October 21, 1965)

Synopsis

The specific heats and the paramagnetic susceptibilities of disordered f.c.c. $(Fe, Ni)_3Mn$ alloy system have been measured at low temperatures. The alloys on the Fe-rich side show antiferromagnetic behavior with negative paramagnetic Curie temperatures, while those on the Ni-rich side show weakly ferromagnetic behavior. The specific heat *vs.* composition curve goes through a maximum near the composition where the paramagnetic Curie temperature changes its sign. This behavior of the specific heat is quite analogous to that observed by other workers in some f.c.c. alloy systems, *e.g.*, Fe-Ni, Mn-Fe or Mn-Cu. The electronic specific heat of an alloy with electron concentration (e/a) very close to 8, which corresponds to that of Fe, is much higher than that of b.c.c. Fe.

I. Introduction

The low temperature specific heat has frequently been used for the study of the band structure of metals and alloys, since it gives a direct information about the density of states of the electronic energy band. Especially for the 3d-transition metal alloys, Beck and his coworkers have made extensive measurements in connection with the problem of the occurrence of ferromagnetism.

As for b.c.c. binary alloys, Ti-V, V-Cr, V-Fe, Cr-Mn, Cr-Fe and Fe-Co[1], the electronic specific heat coefficient γ (which signifies the value of $\lim_{T\to 0} C/T$, where C is the specific heat and T the absolute temperature) was measured by these workers. After a survey of the results of their measurements, they found that the γ *vs.* electron concentration curve showed three well-separated regions of high density of states[1].

They also measured the γ values of f.c.c. binary alloys such as V-Ni, Mn-Ni, Mn-Fe, and Fe-Ni[2]. The derivation of the density of states in this case, however, was not so straightforward as in the cases of b.c.c. alloys, since it was considered that the extraordinarily high γ values observed in some of these alloy systems were not necessarily related to the high density of states but were most probably due to a peculiar situation that ferromagnetic and antiferromagnetic interactions are coexistent with each other in these alloys[3][4][5].

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* The **1217th** report of the Research Institute for Iron, Steel and Other Metals.

(1) C.H. Cheng, C.T. Wei and P.A. Beck, Phys. Rev., **120** (1960), 426.
(2) K.P. Gupta, C.H. Cheng and P.A. Beck, J. Phys. Chem. Solids, **25** (1964), 73.
(3) J.S. Kouvel and C.D. Graham, J. Phys. Chem. Solids, **11** (1959), 220.
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(5) J.S. Kouvel and R.H. Wilson, J. Appl. Phys., **32** (1961), 435.

Although the data by Beck *et al.* pointed to a pronounced character of this anomalous effect of Fe in alloys in which the electron concentration (e/a) is near 8, as can be seen from their data on Fe-Mn and Fe-Ni alloys, data were lacking just in this range because of the difficulty in obtaining the alloys of f.c.c. structure. In order to complement this gap the present measurements were made of the specific heat of the ternary alloy system $(Fe, Ni)_3$ Mn in which f.c.c. structure covers a wide range of composition[6][7].

II. Experimental procedure

Four alloy specimens were made by induction melting in vacuum, compositions being Fe60Ni15Mn25, Fe45Ni30Mn25, Fe30Ni45Mn25, and Fe15Ni60Mn25 in atomic percent, respectively. They were all annealed at 950°C for 15 hrs in argon atmosphere and then water-quenched. In this way f.c.c. $(Fe, Ni)_3$ Mn alloys were obtained. The results of the chemical analysis are given in Table 1.

Table 1. The results of the chemical analysis of the specimens.

Specimen No.	Charge at. %			Analysis at. %		
	Ni	Fe	Mn	Ni	Fe	Mn
1	15	60	25	14.96	61.03	24.01
2	30	45	25	29.62	45.92	24.46
3	45	30	25	44.99	30.58	24.43
4	60	15	25	60.46	15.33	24.21

The standard calorimetric techniques were used for the specific heat measurement. The calorimeter was calibrated by measuring the specific heat of Cu, and good agreements with the previous results were obtained. The thermometer, a 1/10-watt, 10 ohm Allen Bradley carbon resistor, was calibrated against the vapor pressure of liquid helium which was kept constant by a manostat. The "1958 ^{4}He Scale of Temperatures"[8] was used to convert helium vapor pressure into temperature. Paramagnetic susceptibilities of the alloys were also measured above room temperature with a pendulum magnetometer in order to correlate the specific heat data with magnetic properties.

III. Experimental results

The results of the specific heat measurement are shown in Fig. 1 in the form of C/T *vs.* T^2 curves. They were analyzed in terms of the following equation:

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(7) J.S. Kouvel, J. Phys. Chem. Solids, **16** (1960), 152.
(8) F.G. Brickwedde, Physica, **24** (1958), 128.

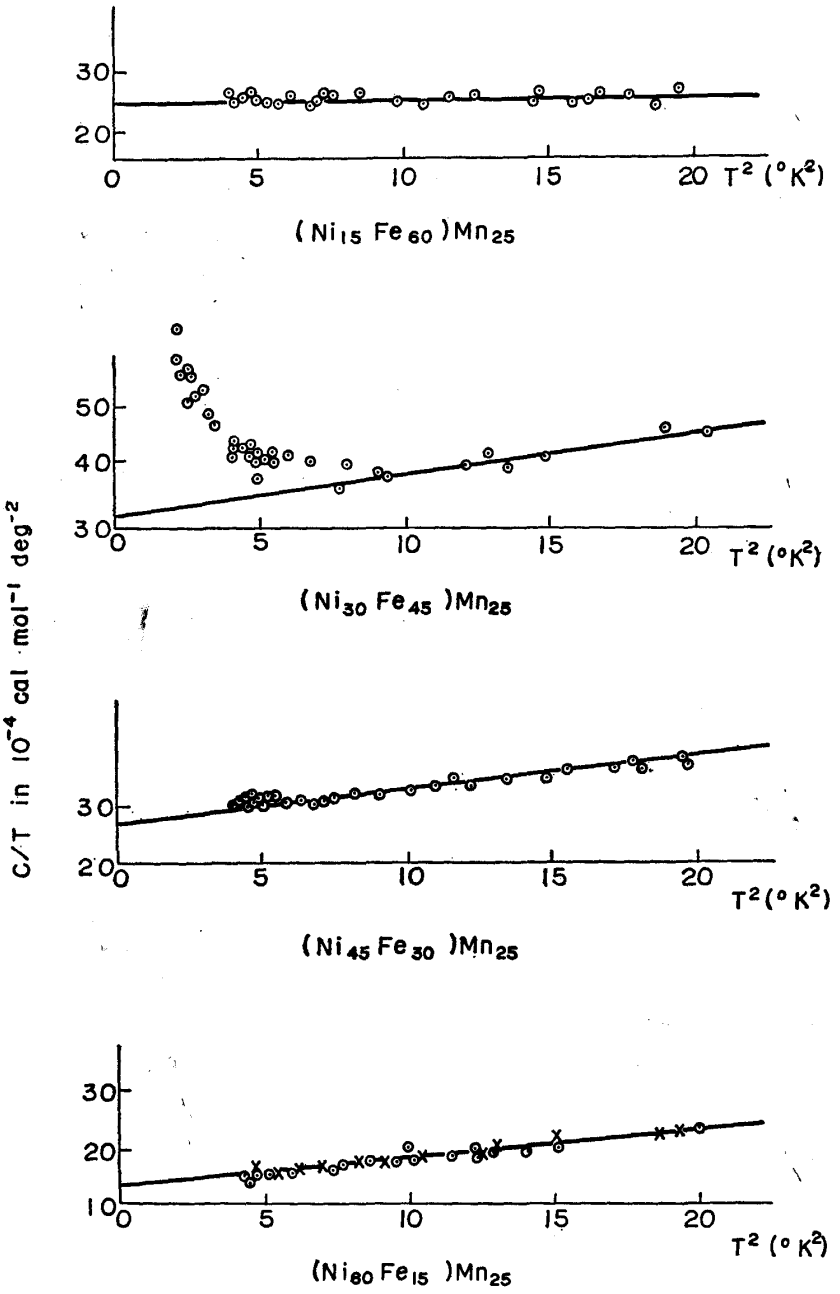

Fig. 1. C/T versus T^2 of the specimens.

$$\frac{C}{T} = \gamma + \beta T^2, \tag{1}$$

where β is related to the Debye temperature Θ_D by the formula $\beta = \frac{12}{5}\pi^4 R/\Theta_D{}^3$, where R is the gas constant.

For three alloys Ni15, 45 and 60, Eq. (1) is satisfied down to the lowest temperature measured, while, for the alloy Ni30, experimental points deviate from this at low temperatures. The measurements were extended to lower temperatures and a sharp increase in C/T was observed.

The result of the magnetic measurement is given in Fig. 2. $1/\chi$ *vs.* T (χ:

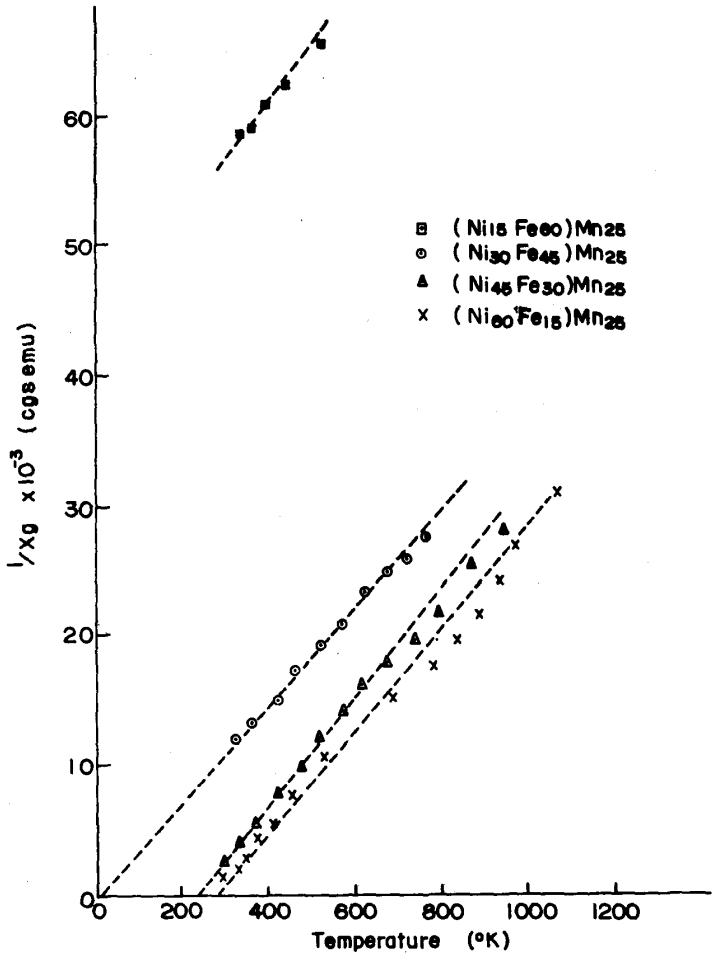

Fig. 2 $1/\chi$ versus T of the specimens.

susceptibility) curves are roughly straight lines and the paramagnetic Curie temperatures θ were obtained from the intersections of these lines with the temperature axis.

The values of θ, Θ_D and γ are listed in Table 2 and are plotted against composition in Figs. 2, 3 and 4, respectively.

Table 2. γ, Θ_D, and θ values of the specimens.

	$Ni_{15}Fe_{60}Mn_{25}$	$Ni_{30}Fe_{45}Mn_{25}$	$Ni_{45}Fe_{30}Mn_{25}$	$Ni_{60}Fe_{15}Mn_{25}$
e/a	8.06	8.35	8.65	8.97
γ 10^{-4} cal mol^{-1} deg^{-2}	25	31	28	14
Θ_D(°K)	359	177	222	224
θ(°K)	600±100	20	240	290

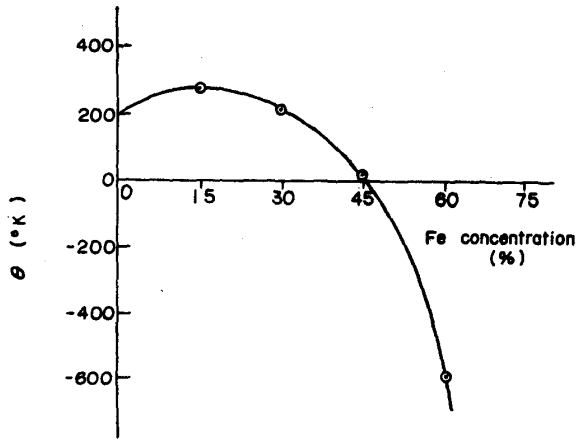

Fig. 3. θ versus composition curve.

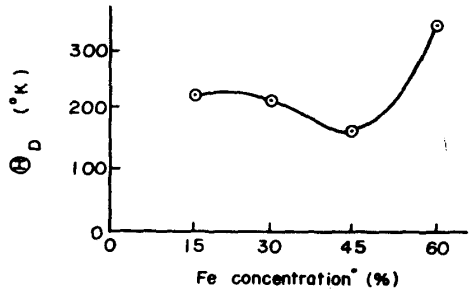

Fig. 4. Θ_D versus composition curve.

IV. Discussion

As seen in Fig. 5, γ value goes through a maximum for the disordered alloy system (Fe, Ni)$_3$ Mn. This behavior is similar to the data obtained by Beck *et al.* for Fe-Mn and Fe-Ni alloys, in which extraordinarily high γ values were obtained. Whereas the data of other workers are lacking in the electron concentration range of 7.9 to 8.6, where f.c.c. structure is unstable, the present

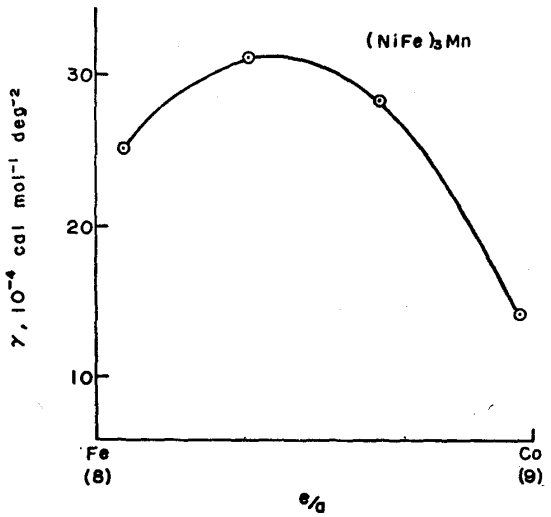

Fig. 5. γ versus e/a.

results cover this range completely.

According to Beck *et al.*, this anomalous effect is probably due to the situation that in these alloys there are a sufficient number of spins located in near zero field, because antiferromagnetic and ferromagnetic interactions are coexistent between magnetic atoms which are distributed in a random way. Also in the data by Zimmerman and Sato[6] on Cu-Mn system, high γ-values were obtained and interpreted on the basis of an analogous mechanism that the exchange interactions between randomly distributed Mn atoms become ferromagnetic or antiferromagnetic according to the distance between them[2]. The present result that the maximum γ value is found near the concentration where the paramagnetic Curie temperature is zero seems to support their interpretation. If this is the case, γ values obtained in the present work are by no means considered to reflect the high density of states of the electronic energy band.

In the present authors' opinion, however, it is difficult to conclude that the true γ which is directly connected with the density of states does not have any anomalous behavior but has low values over the concentration range studied. In order to eliminate the magnetic effect in question it is necessary to have either a calculation which will give a quantitative prediction of the effect, or experimental data on alloys which are free from the effect; Beck *et al.* considered that the behavior of Ni-V alloy system reflected the shape of the true electronic energy band. But Ni-V system is not appropriate for this type of discussion, since it is generally believed that the electrons from V enters the d-band of Ni[9], thus increasing the electron concentration instead of decreasing it, so that e/a value of this system should be considered to be greater than 10. In order to settle this problem, further studies are required.

Acknowledgements

The authors would like to thank Messrs. K. Noto and Y. Sato for valuable experimental assistance. A part of the expenditure of this study has been defrayed from the Scientific Research Funds of the Ministry of Education.

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