Specific Heats of Fe-Ni (fcc) Alloys at High Temperature

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Synopsis

Specific heats at constant pressure, C_p, of Fe-Ni (fcc) alloys have been measured a temperatures 300∼1000 K. For alloys containing more than 50%Ni, the C_p-T curve shows a sharp λ-type peak at ferromagnetic Curie temperature. For the alloys less in concentration of nickel, however, only a dull peak is observed. The C_p-T curve is analyzed using the values of thermal expansion coefficient and of compressibility measured on the same conditions, separating the magnetic contribution from total specific heats.

I. Introduction

Many studies of thermal expansion coefficients in Fe-Ni (fcc) alloys have been carried out since the discovery of 'Invar properties' by Guillaume(1). It has been found, for example, that the thermal expansion coefficients of Fe-Ni alloys in the Invar range show no sharp peak around Curie temperature, T_c, quite different from those of nickel-rich alloys. These features have been interpreted by Kachi and Asano(2) as being caused by the "microscopic fluctuation of concentration" in the Invar alloys.

On the other hand, Dumas has pointed out that the specific heat curve of the alloys shows a sharp peak at T_c, similar to that of pure nickel(3). Such a difference of temperature dependence between thermal expansion coefficient and specific heat is unreasonable in view of thermodynamics. No systematic investigations on specific heat at high temperatures have been developed for Fe-Ni (fcc) alloys of less than 50%Ni since Dumas' study, although those alloys with more than 50%Ni have been studied by Kaya and Nakayama(4). In the present study, specific heats at high temperatures have been measured for Fe-Ni alloys throughout the whole range of fcc phase so that the magnetic contribution to the specific heats may be evaluated.

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* The **1588th** report of the Research Institute for Iron, Steel and Other Metals. Reported originally in Japanese in the J. Japan Inst. Metals, **36** (1972), 1100.

(1) C.E. Guillaume, C.R. Acad. Sci. Paris, **125** (1897), 235.

(2) S. Kachi and H. Asano, J. Phys. Soc. Japan, **27** (1969), 536.

(3) J.S. Marsh, *The Alloys of Iron and Nickel*, McGraw-Hill (1938), 129, 126.

(4) S. Kaya and M. Nakayama, Z. Phys., **112** (1939), 420.

II. Specimens and experimental methods

The specimens are prepared from the same ingots as those used in our previous experiments on thermal expansion coefficients and elastic moduli of the Fe-Ni alloys(5),(6). The ingots are forged and lathe-processed into round bars $30\phi\times30$ mm. Each bar is provided with three holes, $5\phi\times20$ mm at the center, and $3\phi\times20$ mm each 8 mm apart from the center on both sides, containing a heater, an ordinary thermocouple, and a differential thermocouple, respectively. These bars, 10 kinds in all, are annealed at 1000°C for 25 hours and cooled in the furnace. Compositions determined by chemical analysis and densities of the specimens are shown in Table 1.

Specific heats at a constant pressure are measured during heating at a rate of 1~2°C/min by means of standard apparatus of Agune Co.(7)

Table 1. Composition (determined by chemical analysis) and density of Fe-Ni alloy specimens used.

Specimen No.	Ni-content		Density ρ (g/cm^3)
	(wt%)	(at%)	
P- 1	99.98	99.98	8.904
P- 2	89.9	89.4	8.757
P- 3	78.6	77.7	8.600
P- 4	70.1	69.0	8.476
P- 5	59.9	58.7	8.334
P- 6	50.4	49.2	8.205
P- 7	45.9	44.7	8.165
P- 8	40.1	38.9	8.142
P- 9	34.9	33.8	8.138
P-10	30.2	29.2	8.165

III. Results and analysis

1. Specific heat at constant pressure

Specific heats at a constant pressure, C_p, at temperatures, T, between 300~1000 K are illustrated in Fig. 1 (a)~(j). The C_p-T curves for pure nickel and 89.4 at%Ni-Fe alloy show a conspicuous λ-type peak at the Curie temperature, T_c, while the curves for the alloys with 77.7 at% and 69.0 at%Ni have two peaks, one at a higher temperature corresponding to T_c and another at a lower temperature due to Ni_3Fe ordering. The peak of C_p-T curve becomes suddenly lower for the alloys with less than 44.7 at%Ni. These results are different from Dumas' data(8). It is to be noted, however, that T_c can fairly be identified by the peak of C_p-T curve, different from the case of the temperature dependence of thermal

(5) Y. Tanji and Y. Shirakawa, Sci. Rep. RITU, **A 22** (1970/71), 135.
(6) Y. Tanji, Y. Shirakawa and H. Moriya, Sci. Rep. RITU, **A 22** (1970/71), 84.
(7) S. Nagasaki and A. Maesono, Metal Phys., **11** (1965), 182 (in Japanese).

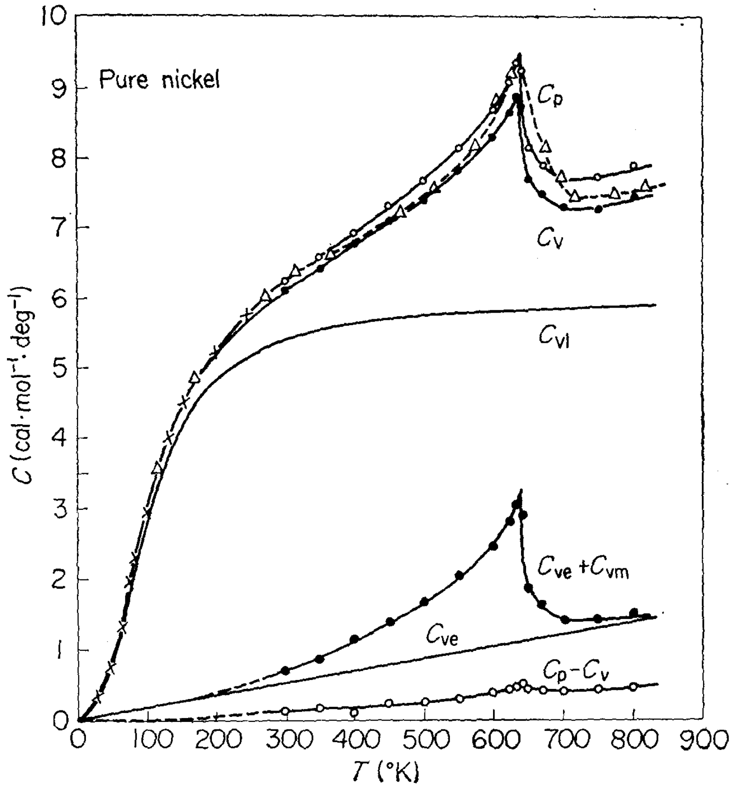

Fig. 1(a). Specific heats of pure nickel. C_p is observed specific heat at constant pressure; C_v, C_{vl}, C_{ve} and C_{vn} are total, lattice, electronic and magnetic specific heats at constant volume, respectively.
---△---: the values of C_p measured by Sykes and Wilkinson(8)
---×---: those values of C_p measured by Eucken and Werth(9)

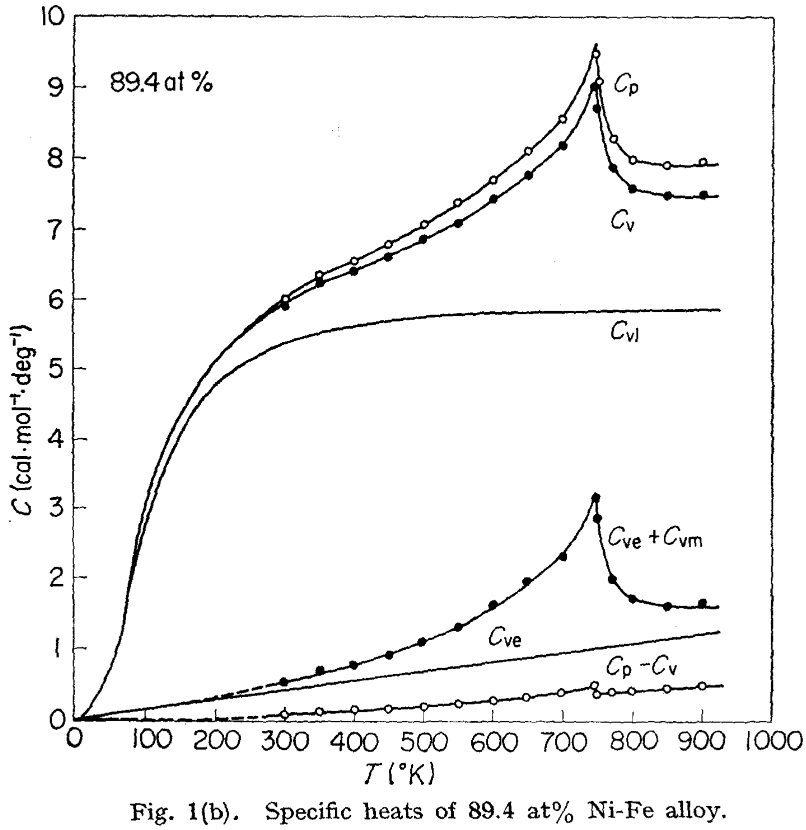

Fig. 1(b). Specific heats of 89.4 at% Ni-Fe alloy.

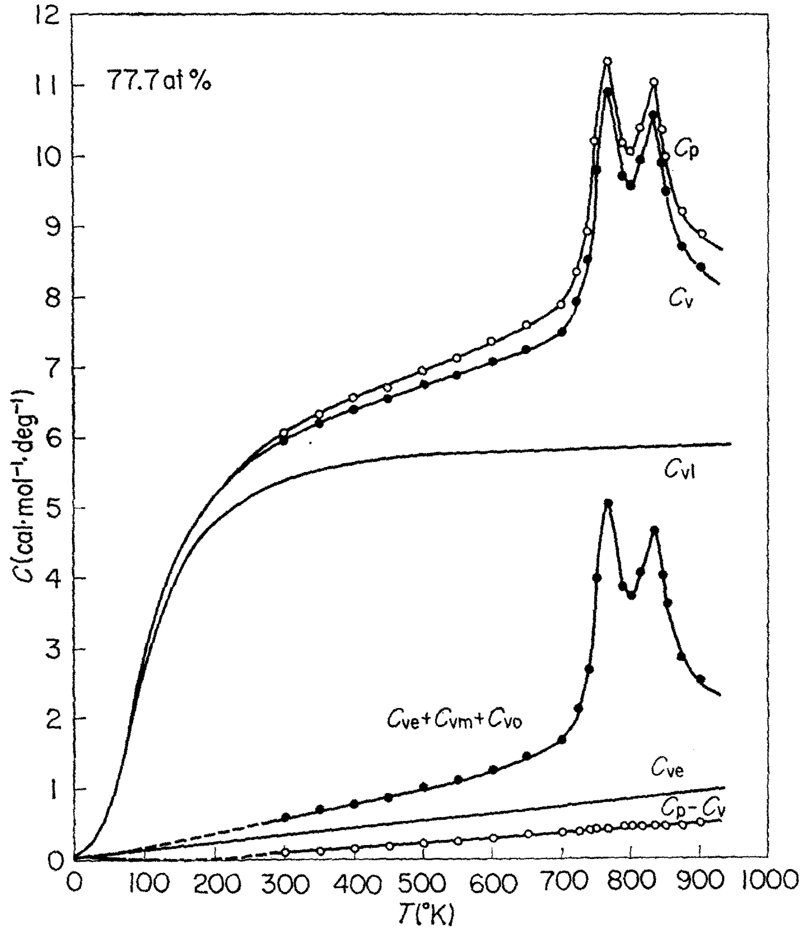

Fig. 1(c). Specific heats of 77.7 at% Ni-Fe alloy. C_{Vo} is the specific heat at constant volume due to superlattice formation.

expansion coefficients[5]. In Fig. 1 (a)~(j), C_p-T solid curves in the region below room temperature are obtained by theoretical analysis, as explained later. For pure nickel, the experimental values determined by Sykes and Wilkinson[8] and by Eucken and Werth[9] are also shown in the same figure.

2. Specific heat at constant volume

As well known, the value of specific heat at a constant volume, C_V, can be obtained from the experimental value of C_p by subtracting the contribution of thermal expansion, as

$$C_V = C_p - \frac{\alpha^2 V}{3\kappa} \cdot T, \qquad (1)$$

where α, V and κ are linear thermal expansion coefficient, specific volume and compressibility, respectively. The values of α and κ were those determined by the present authors using the specimens prepared from the ingots identical with

(8) C. Sykes and H. Wilkinson, Proc. Phys. Soc. (London), **50** (1938), 834.
(9) A. Eucken und H. Werth, Z. anorg. allgem. Chemie, **188** (1930), 152.

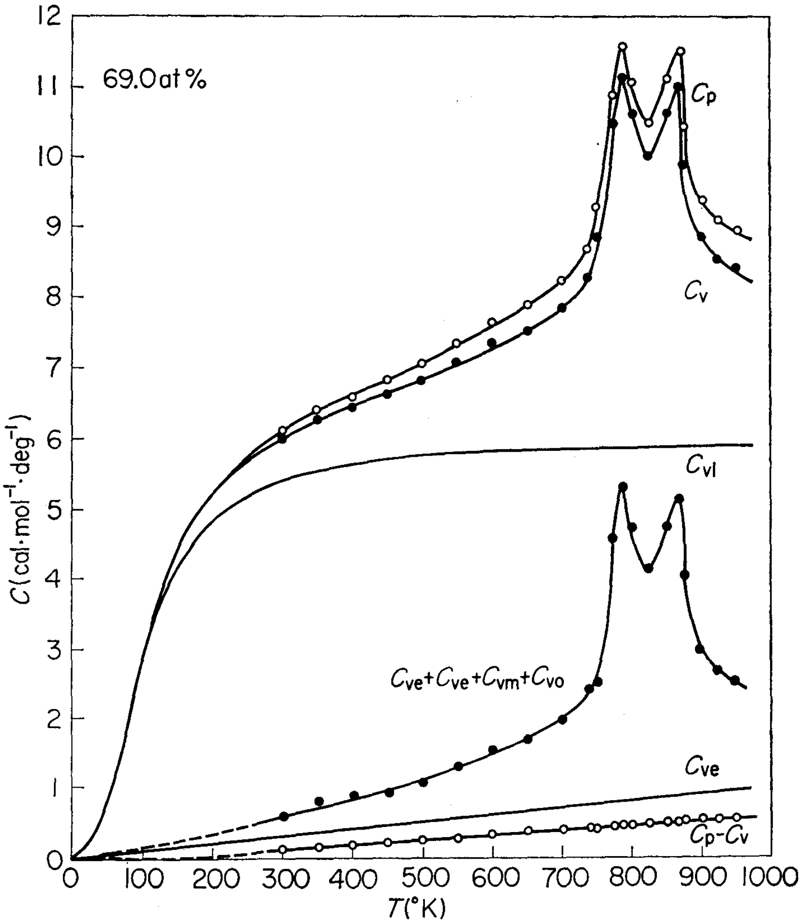

Fig. 1(d). Specific heats of 69.0 at% Ni-Fe alloy.

those in the present work. Thus the values of $(C_P - C_V)$ and then C_V can be calculated, as shown in Fig. 1 (a)$\sim$(j) together with the values of C_P.

As can be surmised from Eq. (1), the $(C_P - C_V)$–T curve should reasonably reflect the trends of both α–T and κ^{-1}–T curves, but experimentally it only matches the α-T curve, forming a small peak at T_c in pure nickel or alloys with a high concentration of Ni. In the Invar range, 45$\sim$30%Ni-Fe, α is so small that the curves of $C_P - C_V$ almost follow the base line. Probably C_V of Fe-Ni (*fcc*) alloys is composed of four terms, as

$$C_V = C_{Vl} + C_{Ve} + C_{Vm} + C_{Vo}\,, \tag{2}$$

where C_{Vl}, C_{Ve}, C_{Vm} and C_{Vo} represent the contributions, respectively, of lattice vibration, conduction electron, magnetic ordering and atomic ordering formation. Estimation of the temperature dependence of these contributions was made as described below.

(i) Contribution of lattice vibration and conduction electron

The values of C_{Vl} are calculated in terms of Debye approximation for

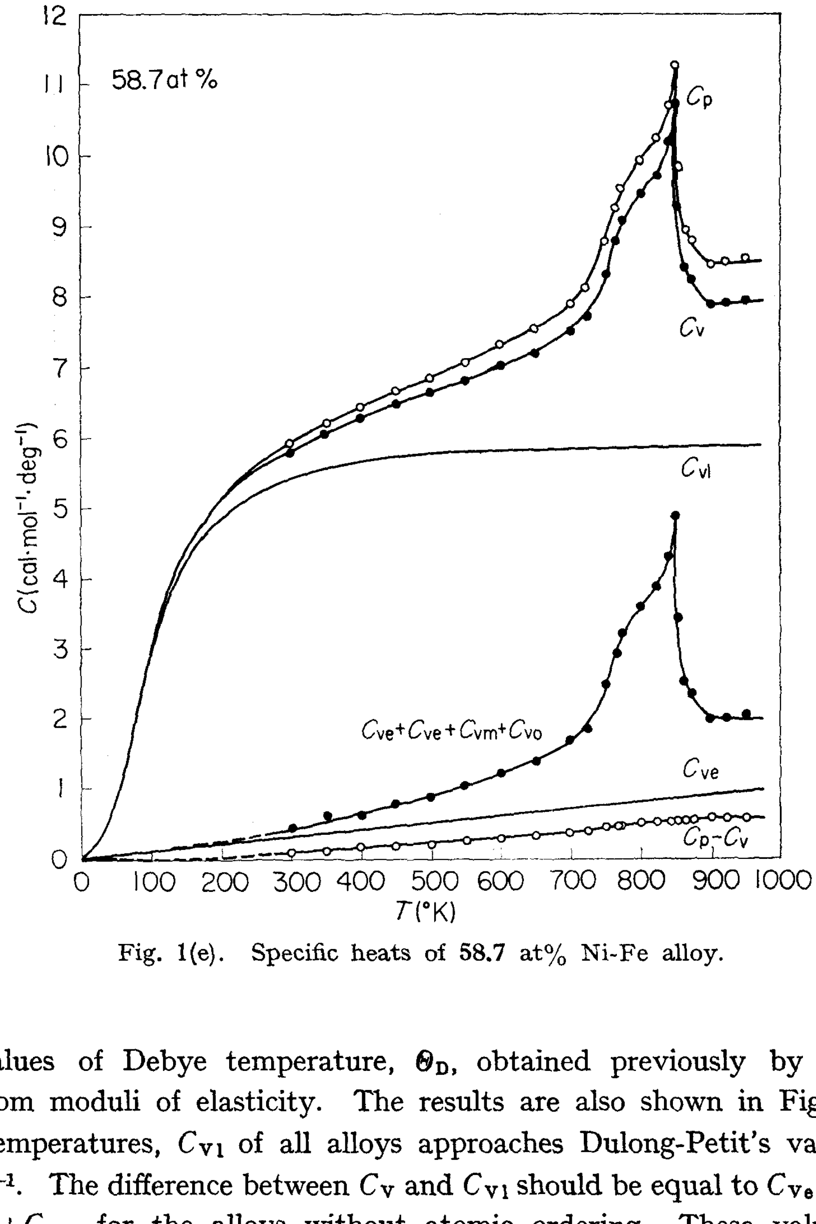

Fig. 1(e). Specific heats of 58.7 at% Ni-Fe alloy.

various values of Debye temperature, Θ_D, obtained previously by the present authors from moduli of elasticity. The results are also shown in Fig. 1 (a)~(j). At high temperatures, C_{Vl} of all alloys approaches Dulong-Petit's value, 5.9 cal. $mol^{-1} \cdot deg^{-1}$. The difference between C_V and C_{Vl} should be equal to $C_{Ve}+C_{Vm}+C_{Vo}$, or to $C_{Ve}+C_{Vm}$ for the alloys without atomic ordering. These values are also shown in Fig. 1 (a)~(j).

Theoretical calculations of C_{Ve} for 3d-transition metals and alloys are made by Wohlfarth(10), Wilson(11) and Shimizu *et al.*(12) However, detailed analysis of C_{Ve} of Fe-Ni alloys is difficult because the theoretical values are sensitively dependent on the shape of 3d band. In the present study the so-called linear relation of $C_{Ve}=\gamma T$ is assumed to hold up to high temperatures, and the values of γ at low temperatures obtained by Gupta *et al.*(13) (see Table 2) are used for estimating the value of C_{Ve} at high temperatures. The results are presented also in Fig. 1

(10) E.P. Wohlfarth, Proc. Roy. Soc., **A195** (1949), 434.
(11) A.H. Wilson, *Theory of Metals*, 2nd Ed, Cambridge at Univ. Press, (1953), 147.
(12) M. Shimizu, T. Takahashi and A. Katsuki, J. Phys. Soc. Japan, **17** (1962), 1720.
(13) K.P. Gupta, C.H. Cheng and P.A. Beck, J. Phys. Chem. Solid, **25** (1963), 73.

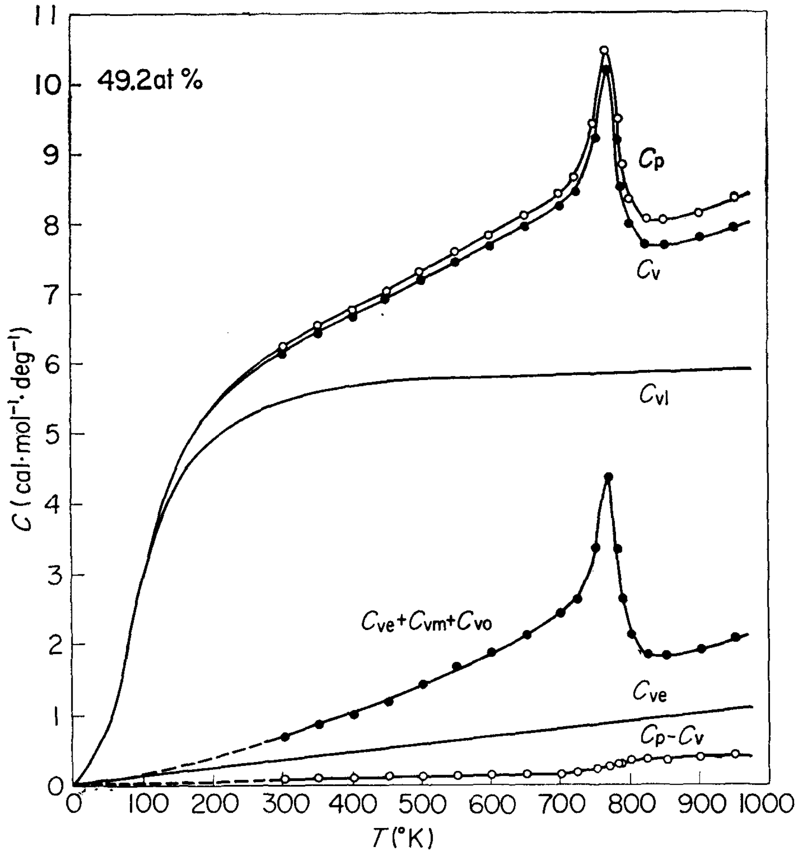

Fig. 1(f). Specific heats of 49.2 at% Ni-Fe alloy.

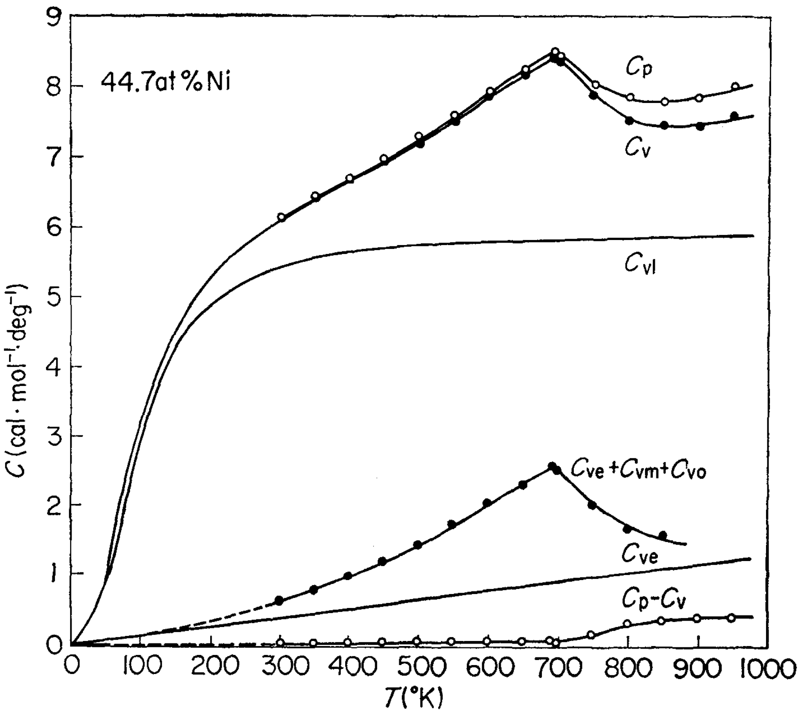

Fig. 1(g). Specific heats of 44.7 at% Ni-Fe alloy.

Table 2. Magnetic internal energy U and entropy Σ of pure nickel and Fe-Ni (fcc) alloys, together with parameters S, T_c and γ used in the analysis of specific-heat curves.

Ni (at%)	S	T_c (K)	U (cal·mol·$^{-1}$deg^{-1})	Σ (cal·mol·$^{-1}$deg^{-1})	$\gamma\times10^4$ (cal·mol·$^{-1}$deg^{-2})
Pure Ni[14]	0.30	630	420	0.81±0.003	12.5
Pure Ni	0.303	635	412	0.76	17.4*
89.4	0.415	745	465	0.76	14.3*
77.7	0.545	835	—	—	10.5*
69.0	0.645	865	—	—	10.1*
58.7	0.760	850	—	—	10.1*
49.2	0.870	775	—	—	11.4*
44.7	0.905	700	—	—	13.1*
38.9	0.920	595	289	0.71	17.7*
33.8	0.875	490	237	0.63	21.9*
29.2	0.500	300	176	0.68	33.3*

* measured by K.P. Gupta *et al.*[13]

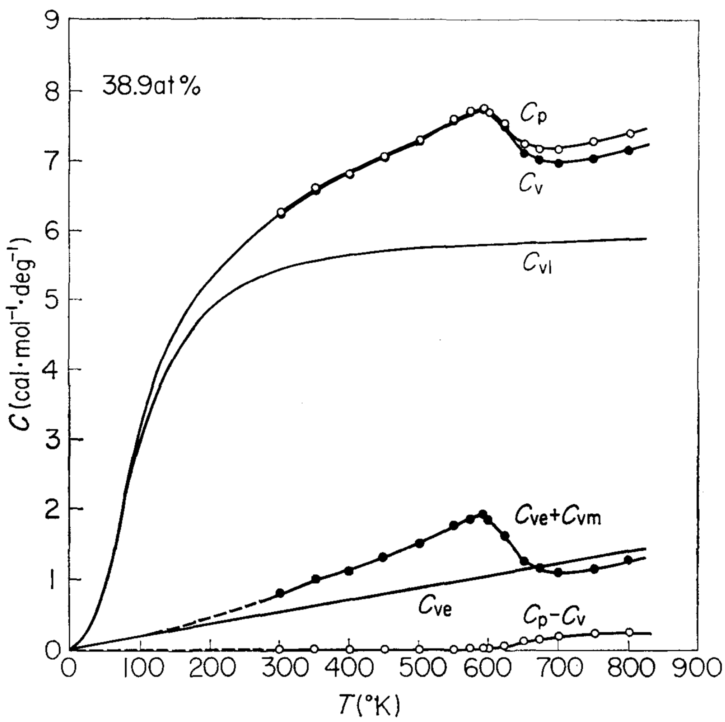

Fig. 1(h). Specific heats of 38.9 at% Ni-Fe alloy.

(a) ~ (j).

It must be noted that the values of γ, relating to the Fermi levels, may be different between ferromagnetic and paramagnetic states. Further discussion regarding the density of states at the Fermi energy is difficult, since C_{Ve} may not be separated with physical significance from C_{Vm} in the itinerant electron model. In the present study, C_{Vm} is discussed on the basis of the localized electron model.

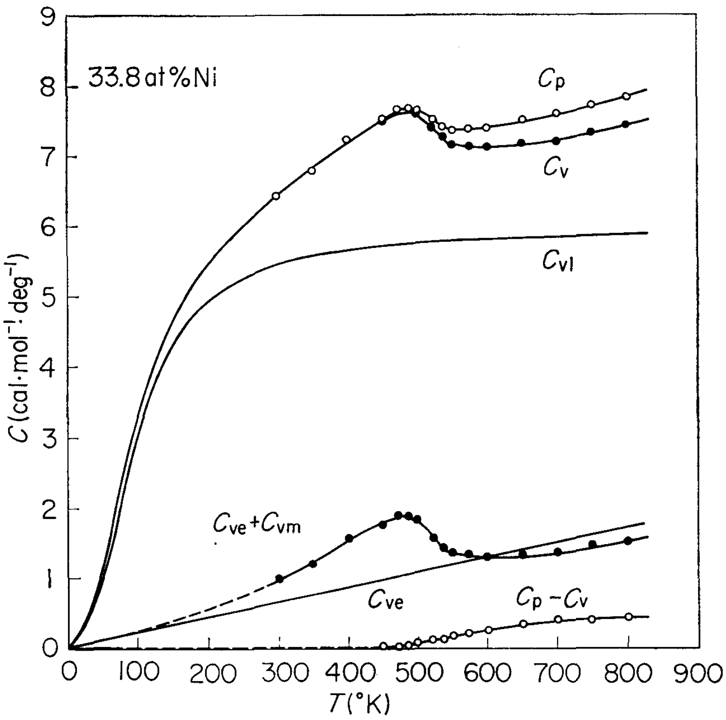

Fig. 1(i). Specific heats of 33.8 at% Ni-Fe alloy.

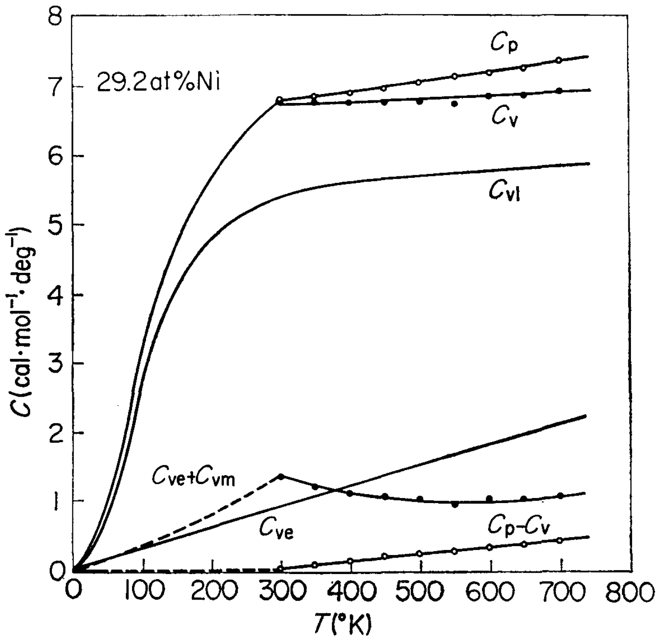

Fig. 1(j). Specific heats of 29.2 at% Ni-Fe alloy.

(ii) Contribution of magnetic ordering

It is difficult to separate the magnetic contribution, C_{Vm}, from the experimental values of C_V, if the contribution of atomic ordering C_{V_0}, co-exists. For pure nickel, 89.4, 38.9, 33.8 and 29.2 at%Ni-Fe alloys, on the other hand, C_{Vm} could be evaluat-

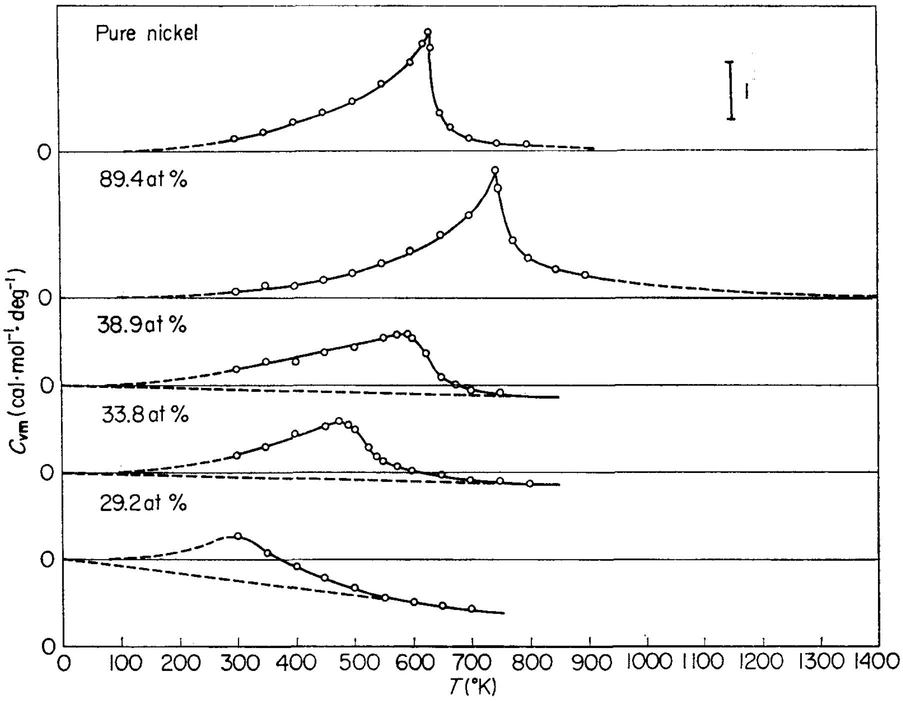

Fig. 2. C_{Vm}-I curves for Fe-Ni (*fcc*) alloy.

ed by subtracting C_{Ve} (calculated with $C_{Ve}=\gamma T$) from $C_{Ve}+C_{Vm}$. The values of C_{Vm} thus obtained are shown by C_{Vm}-T curves in Fig. 2. In the temperature range above T_c, C_{Vm} must gradually approach zero with disappearance of short-range magnetic ordering. As seen in Fig. 2, the C_{Vm}-T curves for pure nickel and the 89.4at%Mi-Fe alloy can be extrapolated smoothly for C_{Vm} to become zero, while in the 38.9, 33.8 and 29.2at%Ni-Fe alloys, the extrapolation results in straight lines with negative slopes shown by dotted lines in Fig. 2. This may be due to a deviation from the relation $C_{Ve}=\gamma T$ for these alloys. The electronic specific heat at high temperatures may be expressed as $C_{Ve}=(\gamma+\gamma_0)T$, where $\gamma_0(<0)$ is the gradient of straight lines mentioned above.

From the C_{Vm}-T curves thus determined, magnetic internal energy $U=\int_0^\infty C_{Vm}\cdot dT$ and entropy $\Sigma=\int_0^\infty C_{Vm}/T\cdot dT$ are obtained. For Fe-rich alloys, these formulae are corrected as $U=\int_0^\infty (C_{Vm}-\gamma_0 T)\cdot dT$ and $\Sigma=\int_0^\infty (C_{Vm}-\gamma_0 T)/T\cdot dT$, respectively. The results are tabulated in Table 2 together with other parameters referred to later on. The values of U of pure nickel obtained by Hofmann *et al.*[14], also shown in the table, are in good agreement with the present result.

IV. Discussion

On the basis of a localized electron model, U is equivalent to the magnetic ordering energy at 0K and can be given as

(14) J.A. Hofmann, A. Paskin, K.J. Tauer and R.J. Weiss, J. Phys. Chem. Solid, **1** (1956), 45.

$$U = NZS^2 \cdot J, \tag{3}$$

where N is the number of atoms in a crystal, Z the number of nearest neighbour atoms, S the spin quantum number and J the magnetic exchange integral. If S in Eq. (3) is assumed to be equal to a half of the number of Bohr magnetons per atom (see Table 2), J can be determined from U. In another way, J can be evaluated from the value of T_c (see also Table 2) in the following relation based on Weiss' molecular field theory

$$J = \frac{3kT_c}{2ZS(S+1)} \,. \tag{4}$$

Other reliable methods for estimating the values of J are the small angle scattering of neutron[15], the spin-wave resonance[16],[17], the inelastic neutron scattering[18] and the temperature dependence of saturation magnetization at low temperatures[17],[19]. The values of J obtained by these methods are compared with those from Eqs. (3) and (4) by the following procedures. In pure nickel, the values of J are 16.2 meV and 17.3 meV from Eqs. (3) and (4), respectively, while they are 50~60 meV[13] from the spin-wave resonance and the temperature dependence of saturation magnetization at low temperatures. The latter is about 4 times greater than the former. Such discrepancy is probably due to the exceedingly simplified model for Eqs. (3) and (4). If the values of J for Fe-Ni alloys are normalized to the value for pure nickel, that is, J/J_{Ni} is plotted as a function of alloy composition, the various methods produce similar results, as shown in Fig. 3. Strictly speaking, Eq. (3) is in better agreement with other methods than Eq. (4).

On Weiss' molecular field theory, the height of the hump of specific heat at T_c, is given by

$$\Delta C_p = \frac{5}{2} \cdot \frac{(2S+1)^2-1}{(2S+1)^2+1} \cdot R, \tag{5}$$

where R is the gas constant. The calculated values are plotted in Fig. 4 together with the experimental values of ΔC_p. In the range of 60~100%Ni, these values agree with each other. With a decrease in Ni content toward 50%, ΔC_p increases almost linearly, but turns to decrease with further decrease in Ni content. At about 45%Ni-Fe the measured values show a precipitous fall, revealing a conspicuous difference from the calculated values. These results, with a possible relation to the Invar problem, may be explained in terms of the broadening of T_c on account of the "fluctuation of concentration" that more reasonable interpretation can be given, however, on the basis of the itinerant electron model.

(15) M. Hatherly, K. Hirakawa, R.D. Lowde, J.F. Mallets, M.S. Stringfellow and B.H. Torrie, Proc. Phys. Soc., **84** (1964), 55.
(16) G.I. Rusov, Soviet Physics-Solid State, **9** (1967), 146.
(17) T. Maeda, H. Yamauchi and H. Watanabe, To be published in J. Phys. Soc. Japan.
(18) F. Menzinger, G. Cagliot, G. Shirane and R. Nathans, J. Appl. Phys., **39** (1968), 455.
(19) B.E. Argyle and S.H. Charap, J. Appl. Phys., **35** (1964) ,802.

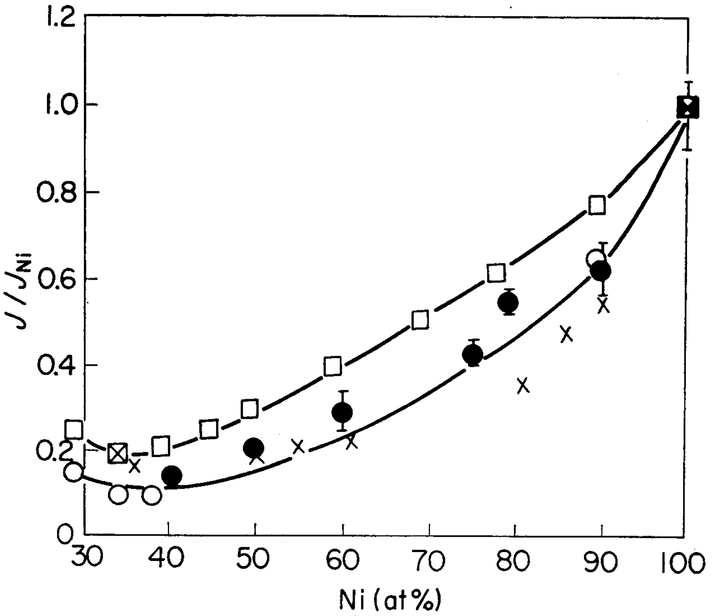

Fig. 3. Magnetic exchange parameter, J/J_{Ni}, for Fe-Ni (*fcc*) alloys.
○ by specific heat (Eq. (3)) ● by neutron scattering[16]
□ by Curie temperature (Eq. (4)) × by spin wave resonance and $T^{3/2}$ law.[17]

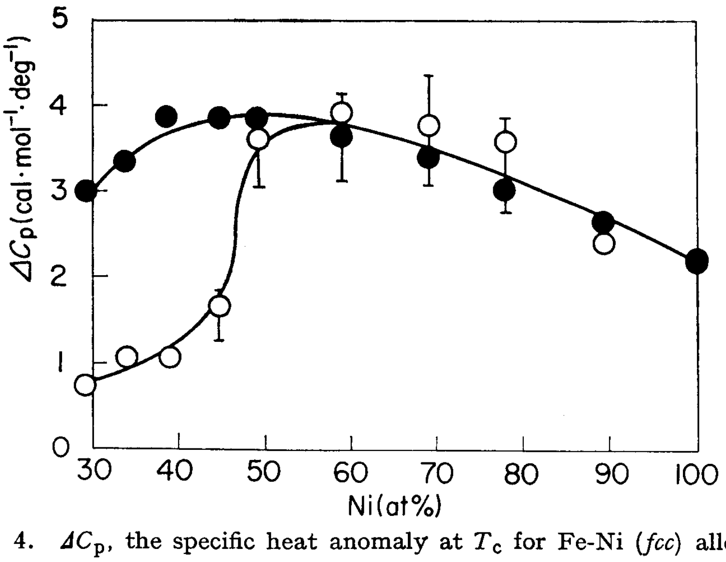

Fig. 4. ΔC_p, the specific heat anomaly at T_c for Fe-Ni (*fcc*) alloys.
○ Experimental ● by Weiss theory

Summary

In Fe-Ni (*fcc*) alloys (30～100%Ni), the values of specific heat at a constant pressure, C_p, have been measured in the range from room temperature to 1000 K. The results are summarized as follows:

(1) The C_p-T curves for 50～100%Ni-Fe alloys show a sharp λ-type peak at

the Curie temperature, T_c. With a decrease in concentration of Ni from 50%, the height of the peak at T_c lowers and shows a sudden fall at 45%Ni-Fe. In either case, however, T_c can be identified well with the peak of C_p.

(2) In 50~100%Ni-Fe alloys, the measured values of ΔC_p, the specific heat anomaly at T_c, agree well with those calculated on Weiss' molecular field theory. In 30~45%Ni-Fe alloys, however, the measured values become far apart from the calculated values.

(3) With the measured values of α and κ (compressibility) for the specimens prepared under identical conditions, the C_p-T curves are analyzed so that the magnetic contribution to the specific heat may be determined.

(4) Values of magnetic exchange integral, J, obtained from specific heat curves show a composition dependence similar to those obtained from the spin-wave resonance and other experiments.

Acknowledgements

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