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The Specific Heat of Copper Alloys Containing Small Amounts of Iron*

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Synopsis

The specific heat of copper alloys containing small amounts of iron (0.3 to 3.5 at.% of iron) was measured under various heat treatment conditions at liquid helium temperatures. The excess specific heat of copper-iron alloys in solid solution was observed and it would be due to a magnetic origin. It is tried to explain the specific heat by the Marshall-Klein theory based on *s-d* interactions and the Ising model. The specific heat of copper alloys containing γ-iron precipitates involves a temperature independent contribution from the superparamagnetic character of γ-iron precipitates.

I. Introduction

The density of states of b.c.c. alloy system consisting of transition elements were extensively studied by Beck and his coworkers(1) by means of the specific heat measurements. They also investigated the specific heat 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 these f.c.c. systems, however, was not so simple as in the case of b.c.c. alloys, since it was considered that the anomalously high γ value was not necessarily related to the high density of state but it was probably due to a peculiar situation that the ferromagnetic and antiferromagnetic interactions are coexistent in these alloys. Here γ denotes the value of $\lim_{T\to 0} C/T$ where C means the specific heat and T the absolute temperature. Inasmuch as their data exhibited a striking character of this anomalous effect in alloys in which the electron concentration (e/a) is near 8, we carried out the specific heat measurements with respect to a specific alloy system of $(\mathrm{Fe}_x\mathrm{Ni}_{7-x})\mathrm{Mn}$,(3) in which f.c.c. structure covers a wide range of composition. The behavior of the specific heat in this system is quite analogous to those observed by other workers on several f.c.c. binary alloys.

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* The **1350**th 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) H. Watanabe, K. Ehara, T. Fukuroi, Y. Muto and H. Yamamoto, Sci. Rep. RITU, **A17** (1965), 300.

The value of the alloy with the electron concentration close to 8, which corresponds to that of iron, appears to be much higher than that of b.c.c. iron. It is difficult to know whether the measured γ value is the one which is directly correlated to the density of states at the Fermi level, or not.

According to the established phase diagram of copper-iron alloy system,⁽⁴⁾ the solubility limit of iron into copper is about 4.0 at.% at 1094°C and becomes extremely small below 400°C. So it is known that a supersaturated solid solution can be obtained by rapid quenching from high temperatures. By subsequent annealing at elevated temperature between 600 ~ 700°C, the constituent in excess of the solubility limit precipitates out of the matrix. In the present case, iron precipitates coherently with the copper matrix as γ-iron in the form of small particles.⁽⁵⁾ The initial purpose of this study was to obtain the electronic density of states of γ-iron by measuring the specific heat in such a system. Unfortunately the authors failed in this, as is described later on, whereas some data were obtained for the alloys in the high concentration-solid solution range as well as those containing precipitates.

II. Experimental procedures

Four alloy specimens and a pure copper one were prepared. The purities of copper and iron was 99.998% and 99.98%, respectively. All alloy specimens were prepared by induction melting at 1350°C for an hour under a vacuum of 10^{-5} mm Hg. After these specimens were solution annealed at 1060°C for an hour in vacuum, they were quenched into cold water. Since the specific heat measurements on alloys in solid solution were desired, the specimens were solution annealed at

Table 1. Iron concentrations and heat treatments of alloy specimens.

Specimen	Charged Fe concentration at. %	Analyzed Fe concentration wt. %	Heat-treatment	Annealing temperature °C	Annealing time
Cu-Fe (A)	0.30	not analyzed	solid solution	1060°	24 hrs.
Cu-Fe (B)	0.60	0.59	solid solution	1060°	24 hrs.
			precipitation	600°	24 hrs.
Cu-Fe (C)	2.50	2.38	solid solution	1060°	24 hrs.
			precipitation	600°	5 min.
			precipitation	600°	75 min.
Cu-Fe (D)	3.50	2.73	solid solution	1060°	24 hrs.
			precipitation	600°	75 min.

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(4) M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, (1958).

(5) S.C. Abrahams, L. Guttman and J.S. Kasper, Phys. Rev., **127** (1962), 2052.

1060°C for 24 hours as shown in Table 1 and then quenched. After finishing the specific heat measurements of specimens in solid solution, specimens were annealed at 600°C for various periods as described in Table 1, in order to produce γ-iron precipitates. The pure copper specimen was also induction-melted and annealed at 600°C for 24 hours. All specimens used were about 1 mole in weight. In Table 1 are also given the charged concentrations and the analyzed ones determined by means of X-ray fluorescent spectroscopy on alloy specimens.

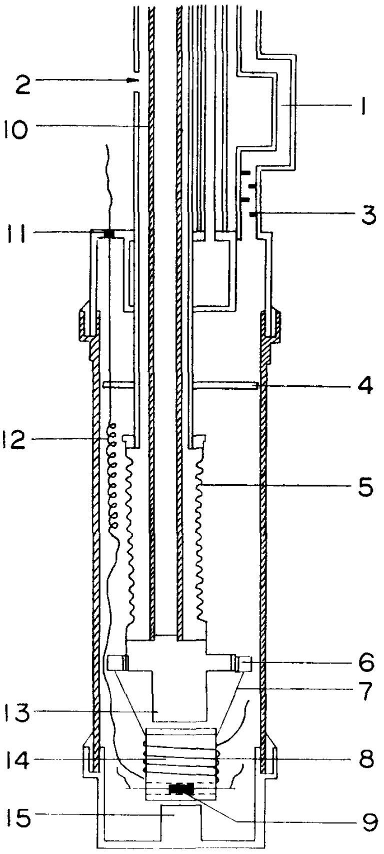

Fig. 1. Cut-off construction of calorimeter.
(1) Radiation trap, (2) Hole, (3) Copper plates radiation shield, (4) Copper plate for radiation shield, (5) Phosphor bronze bellows, (6) Copper ring, (7) Silk threads, (8) Heater, (9) Carbon resistor thermometer, (10) Thin walled Cu-Ni tube hanged from the screw assembly at the top of cryostat, (11) Kovar seal, (12) Nb-wire, (13) Upper copper heat sink, (14) Specimen, and (15) Lower copper heat sink.

Specific heat measurements were made in a calorimeter illustrated in Fig. 1. The specimen (14), which carries a thermometer (9) and a heater (8) was suspended from a copper ring (6) by three silk threads (7). Allen Bradley's carbon resistor, 1/10-watt and 10 ohm, was used as the thermometer and a constantan wire, 0.08 mm in diameter, of about 100 ohm was wound around the specimen as the heater. In order to achieve good thermal contact between the specimen and the thermometer (or the heater), the Apiezon N grease was used. Superconducting niobium wires, 0.075 mm in diameter, were used as the electrical leads (12) both to the thermometer and to the heater in the calorimeter in order to avoid Joule's heat. All lead wires were led out through Kovar seals (11) out of the calorimeter can. In order to shield radiation from higher temperature portions of the system, the high vacuum pumping line (1) was bent just above the calorimeter can as shown in Fig. 1. Furthermore, a number of copper plates were provided in the pumping tube (3) and in the calorimeter (4) for the same purpose.

The temperature of the specimen was controlled by means of a mechanical heat switch. This switch, which makes use of thermal contact of the specimen with the upper and lower heat sinks, can be operated through the phosphor-bronze bellows (5) from outside as is evident from Fig. 1. The bellows can be moved vertically by about 8 mm by means of the thin walled Cu-Ni tube (10) connected to the screw assembly at the top of the cryostat. When the bellows are lowered, the specimen first rests on the lower copper heat sink (15). Upon further lowering of bellows, the upper heat sink (13) presses the specimen against the lower sink. In order to obtain good thermal contact, the contact surfaces of both heat sinks were indium plated. Liquid helium was introduced into the interior of the bellows through a hole (2) in order to promote cooling efficiency. Thus, the specimen was cooled down to 1.1°K. At the lowest temperature, we can make the specimen free from both heat sinks by raising the bellows by means of the screw assembly. Then specific heat measurements could be started. This system enabled us to measure the specific heat from 1.3°K to about 5°K.

The standard method of specific heat measurements was adopted. The

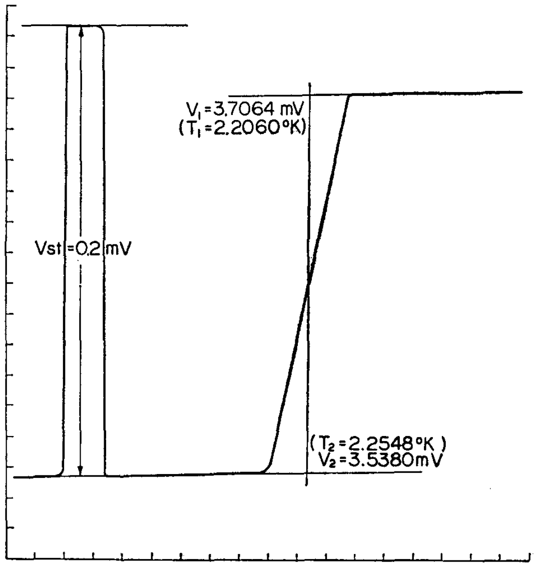

Fig. 2. A recorder trace of a typical heating curve.

potential difference across the carbon thermometer, but that amount, which have been subtracted by a definite voltage with the aid of a potentiometer, was displayed on a recorder as a function of time elapsed. A typical heating curve is reproduced in Fig. 2. The temperature increase in each run was adjusted about 0.05°K. The accuracy of temperature reading for every run could be attained as high as 0.003°K. Heating time duration ranging from 20 to 30 seconds was measured by a frequency counter. The wattage of current in the heater was measured by a separate potentiometer. The resulting accuracy of specific heat measurements is estimated as about 2%.

After completion of every set of measurements, the carbon resistance thermometer was calibrated against the helium vapour pressure. A small amount of helium exchange gas was introduced into the calorimeter can in order to facilitate a thermal equilibrium between the thermometer and the outer liquid helium bath. The "1958 ^{4}He Scale of Temperature"(6) was used to convert vapour pressures into temperature scale. Throughout this experiment, the resistance temperature relationship could be fitted to the next expression,(7)

$$(\log R/T)^{1/2} = A + B \log R + C (\log R)^2 , \tag{1}$$

where R is the resistance of the thermometer, T the absolute temperature. The parameters A, B and C were determined by the least squares method in every run. The processes of temperature and specific heat data were all carried out by the NEAC 2230 electronic computer at Tohoku University.

III. Experimental results

The specific heat, C, of metals and alloys at low temperatures is, in general, expressed in terms of the following equation,

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

where γ is the electronic specific heat coefficient which is proportional to the density of states at the Fermi level and β is related to the Debye temperature, Θ_D, by the next relationship,

$$\beta = \frac{12}{5} \pi^4 R/\Theta_D{}^3 , \tag{3}$$

where R is the gas constant.

In Fig. 3, C/T of the pure copper specimen is plotted as a function of T^2. Thus we get the γ value of copper as 0.70 mJ/°K^2 mole and the Debye temperature is 322° K. These results are in good agreement with results of previous measurements

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(6) P.G. Brickwedde, H. van Dijk, M. Durieux, J.R. Clement and J.K. Logan, J. Res. National Bureau of Standards, **64A** (1960), 1.

(7) S.S. Shinozaki and A. Arrott, Phys. Rev., **152** (1966). 611.

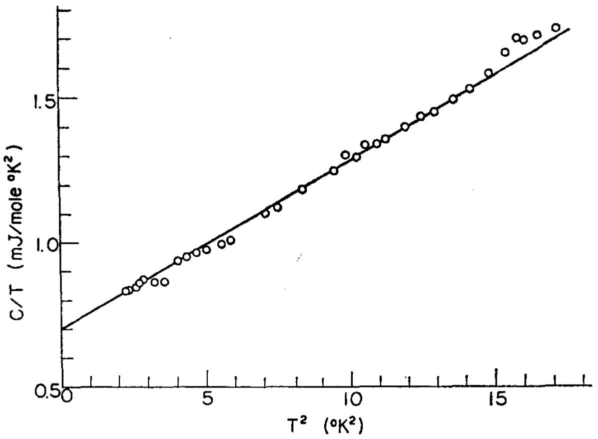

Fig. 3. Specific heat of pure copper.

Table 2. The electronic specific heat coefficient and the Debye temperature of pure copper.

Authors	γ(mJ/mole°K²)	Θ_D (°K)
Present authors	0.700	322
Esterman (8)	0.753	315
Corak et al. (9)	0.688	344
Franck et al. (10)	0.681	327
Isaacs et al (11)	0.698	342
Satoh et al. (12)	0.680	320

by Esterman et al.,(8) Corak et al.,(9) Franck et al.,(10) Isaacs et al.(11) and Satoh et al.(12) as seen in Table 2.

In Fig., 4, C/T of the solid solution alloy Cu-Fe (A) is displayed as a function of T^2. It is rather hard to get a linear relationship. If the straight line is drawn through the measured points at higher temperatures as seen in Fig. 4, the γ and Θ_D values are obtained as displayed in Table 3. The value of Θ_D is near that of pure copper, while the γ value becomes extraordinarily high compared to that of copper alloy containing the same concentration of zinc.(11) Moreover, the deviation in the lower temperature portion from the linear change cannot be accounted for in terms of eq. (2). It seems that such a deviation and high γ value would imply the existence of a contribution to the specific heat from paramagnetic impurities as will be discussed in the next section.

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(8) I. Esterman, S.A. Friedberg and J.E. Goldman, Phys. Rev., **87** (1952), 582.

(9) W.S. Corak, M.P. Garfunkel, C.B. Satterthwaite and A. Wexler, Phys. Rev., **98** (1955), 1699.

(10) J.P. Franck, F.D. Manchester and D.L. Martin, Proc. Roy. Soc., **263** (1961), 494.

(11) L.L. Isaacs and T.B. Massalski, Phys. Rev., **138A** (1965), 134.

(12) T. Satoh and T. Ohtsuka, J. Phys. Soc. Japan, **23** (1967), 9.

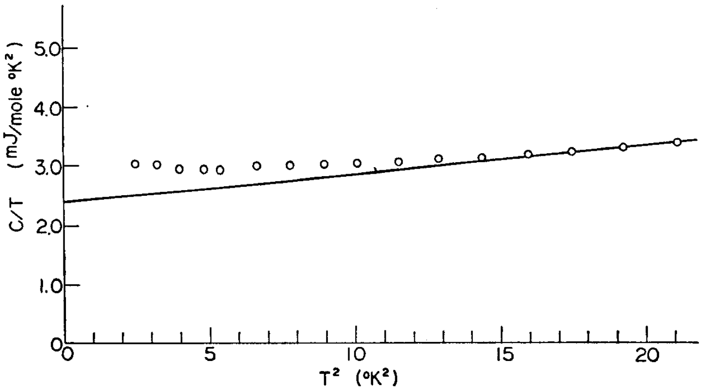

Fig. 4. Specific heat of the specimen Cu-Fe (A) in solid solution.

Table 3, Θ_D, γ, and A values of copper-iron alloys.

Specimens		Θ_D (°K)	γ(mJ/°K²mole)	A(mJ/°Kmole)
Cu-Fe (A)	solid solution	348	2.40	
Cu-Fe (B)	solid solution	494	4.01	
	precip. 24hr.	358	1.19	2.10
Cu-Fe (C)	solid solution	610	4.11	
	precip. 5min.	600	2.56	1.50
	precip. 75min.	317	1.26	2.54
Cu-Fe (D)	(solid solution)	427	3.75	0.80
	precip. 75min.	359	1.57	2.99

In Figs. 5, 6 and 7 are shown the C/T versus T^2 curves for the alloys Cu-Fe(B), Cu-Fe(C) and Cu-Fe(D), respectively. In solid solutions, the specific heat of Cu-Fe (B) and Cu-Fe (C), is expressed by eq. (2). For the Cu-Fe (D), however, there appears small deviation from eq. (2) even in a state of solid solution. This might be ascribed that, for such a concentrated alloy, a perfect solid solution would not be achieved but a small amount of precipitate would appear in conformity with the usual phase diagram.(4) In Table 3 are shown the values of γ and Θ_D for these solid solution alloys.

The Debye temperatures of these solid solution alloys, however, are extraordinarily higher than that of pure copper or those of alloys containing iron precipitates, which are also listed in Table 3. It can hardly be believed that such high Debye temperatures should have resulted from the contamination of a small amount of iron. Furthermore, the experimental values of γ are plotted as a function of iron concentration in Fig. 8. In it are also included the results by Franck et al.(10) which have been analyzed by us in terms of eq. (2). The γ value increases linearly with iron content up to 0.6 at. % of iron and then saturates to a constant value. This constant value, about 4.0 mJ/mole°K², for Cu-Fe alloys (B), (C) and (D) is only a

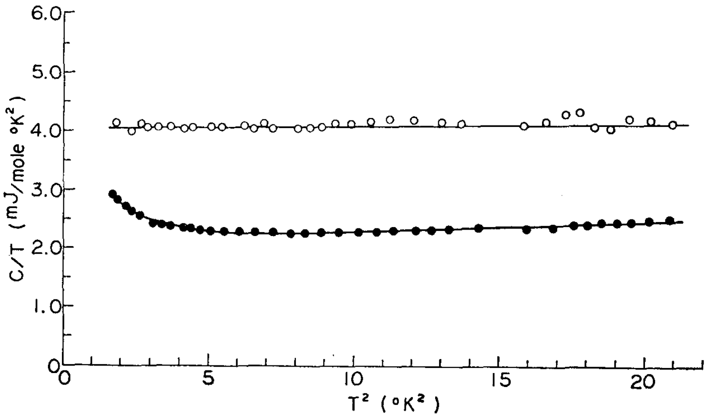

Fig. 5. Specific heat of the specimen Cu-Fe (B). Table 1 is to be referred to about the heat treatments of specimens.
○ Solid Solution • Precipitation (24 hrs.)

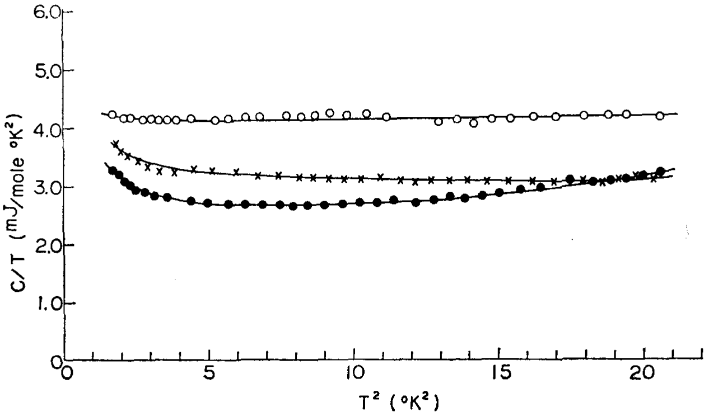

Fig. 6. Specific heat of the specimen Cu-Fe (C). Table 1 is to be referred to about the heat treatments of the specimen.
○ Solid Solution × Precipitation (5 min.)
• Precipitation (75 min.)

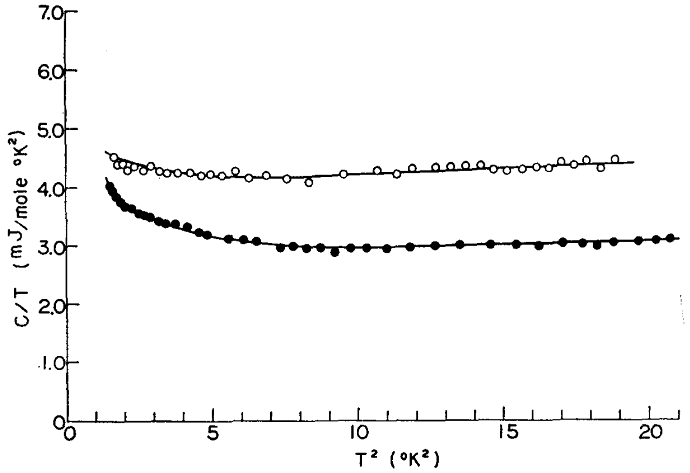

Fig. 7. Specific heat of the specimen Cu-Fe (D). Table 1 is to be referred to about the heat treatments of the specimen.
○ Solid Solution • Precipitaton (75 min.)

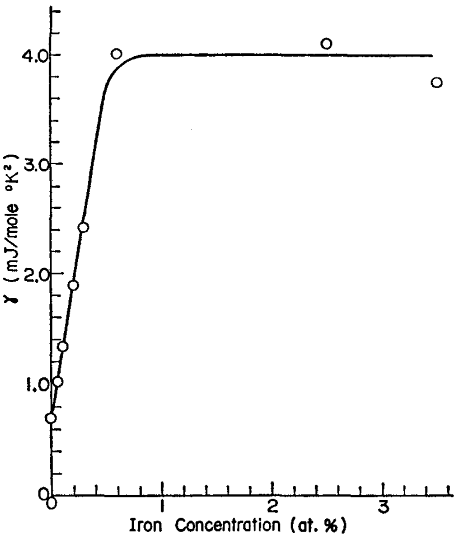

Fig. 8. γ value as a function of Fe concentration. Points for low concentrations are due to Franck et al.(10)

little less than the γ value of b.c.c. Fe, viz. 4.8 mJ/mole °K² and it is much larger than the γ value of pure copper, viz. 0.7 mJ/mole°K².

On the other hand, a marked deviation from eq. (2) can be seen in the specific heat of all alloys with γ-iron precipitates. It is often reported that small particles like such precipitates give an extraneous contribution to the specific heat(13) which is independent of temperature. The feature referred to above is already known as a superparamagnetic behavior. If this is the case, eq. (2) should be replaced by the following expression,

$$C = A + \gamma T + \beta T^3 . \qquad (4)$$

By taking a suitable value for A in the C versus T relation, $(C\text{-}A)/T$ versus T^2 curve

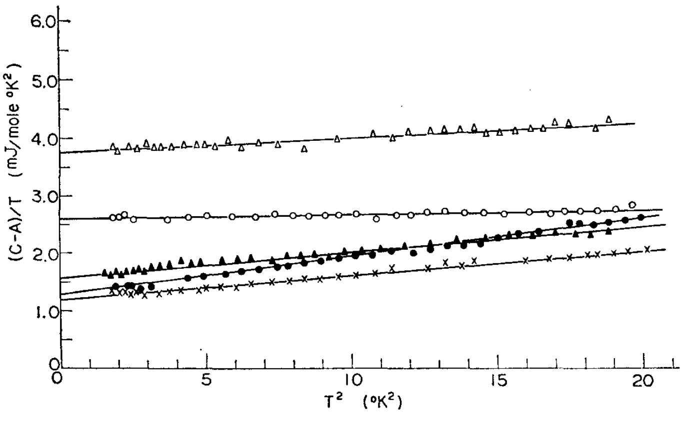

Fig. 9. $(C-A)/T$ versus T^2 curve for the specimen Cu-Fe (B), (C) and (D) with precipitates.

△ Cu-Fe(D) solid solution ▲ Cu-Fe(D) precipitation (75 min.)
○ Cu-Fe(C) precipitation (5 min.) ● Cu-Fe(C) precipitation (75 min.)
× Cu-Fe(B) precipitation (24 hrs.)

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(13) K. Schröder and C.H. Cheng, J. Appl. Phys., **31** (1960), 2134.

would become a straight line as is apparent from Fig. 9. Thus, eq. (4) gives a good fit to the experimental results for the alloys with γ-iron precipitates. The Debye temperatures derived from eq. (4) for these alloys are close to that of pure copper as visualized in Table 3. Therefore, it seems that the above analysis is not unreasonable. The values of Θ_D, γ and A for all alloys studied are summarized in Table 3.

IV. Discussions

(1) The specific heat of solid solution alloys

In the previous section we have treated the experimental data on alloys in the solid solution range with the formula (2); this is equivalent to assuming that the γ value derived from this procedure is the one associated to the electronic density of states. What we have obtained, however, is an anomalously rapid increase of γ value and also of the Debye temperature with increase of iron concentration, which cannot be considered to be real for the following reason. γ values in dilute copper alloys containing small amounts of non-magnetic metal, e.g. zinc, make only small change with zinc content, i.e. 0.0072 mJ/°K^2 mole per at. % of zinc.(11) Similarly, the Debye temperature decreases, instead of increasing by 1.0°K per at. % of zinc according to the specific heat measurements.(11) On the other hand, Zimmerman and Hoare(14) measured the specific heat of copper rich side of copper-maganese alloys and found that γ values, as analyzed with the formula (2), were anomalously high and roughly independent of manganese concentration between 0.5 and 10 at. % of manganese. They concluded that these γ values were not the electronic specific heat coefficient which is proportional to the electronic density of states but are due to an extraneous magnetic contribution to the specific heat.

In view of the above considerations, it is very doubtful that the γ and Θ_D values for the specimens in solid solution listed in Table 3 are real values. Rather it is more natural to assume that changes of both the electronic specific heat coefficient and the Debye temperature for copper alloys containing small amounts of impurities from those values of pure copper are very small, if any.

As is frequently done in analyzing the specific heat data of dilute alloys containing paramagnetic impurities, the specific heat of pure copper, C_{Cu}, is subtracted from that of every copper-iron alloy, C_{Cu-Fe}. In Fig. 10 is shown the value of ΔC $(=C_{Cu-Fe}-C_{Cu})$ as a function of temperature, together with that of more concentrated specimens, Cu-Fe(C) and (D), is nearly the same as that of the specimen Cu-Fe (B), they are not included in Fig. 10 in order to avoid confusion. Since the data for the copper alloy containing 0.086 at .% of iron by du Chatenier and de Nobel(15) is also quite close to that of the copper alloy containing 0.1 at.% of iron, it is not comprised in Fig. 10 either.

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(14) J.E. Zimmerman and F.H. Hoare, J. Phys. Chem. Solids, **17** (1960), 52.

(15) F.J. du Chatenier and J. de Nobel, Physica, **32** (1966), 1097.

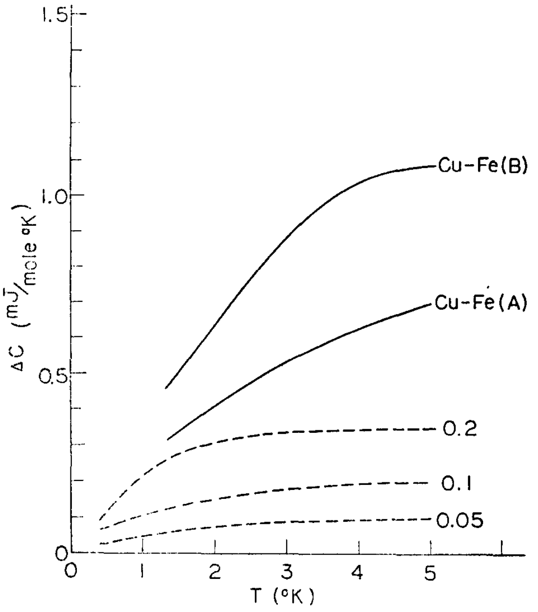

Fig. 10. ΔC as a function of temperature. Solid curves are obtained from the present study while the dashed curves from the study by Franck et al.[10]

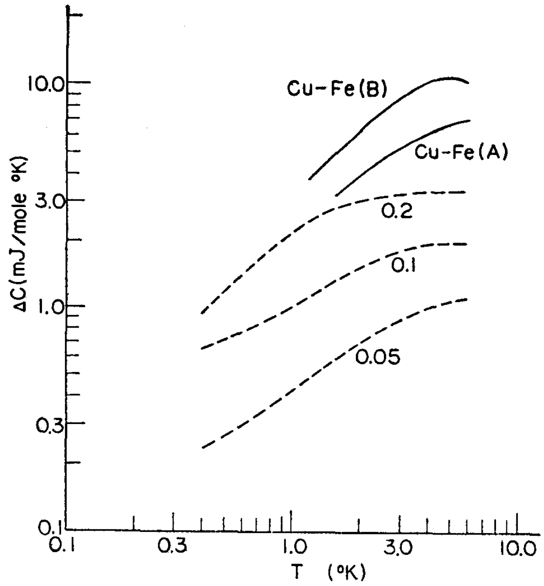

Fig. 11. log ΔC versus log T curve for several copper-iron alloys. Numbers on the curves represent the concentration of iron for Franck et al'.s data.

As is obvious from Fig. 10, the value of ΔC increases linearly with temperature at low temperatures but varies sublinearly at higher temperatures. In order to clarify the temperature dependence of ΔC, log ΔC is plotted as a function of log T in Fig. 11. Linearity in T is seen below about 4°K and 3°K for the specimen Cu-Fe(B) and (A), respectively, while linearity is only held well below 1°K for the copper alloy containing 0.2 at.% of iron. Such linearity was reported by Zimmerman and Hoare(14) for the copper-manganese alloy system. Their result, however, shows that the proportionality constant, $\Delta C/T$, is independent of the magnanese concentration. A similar result was reported on the silver-manganese alloy system,(16) in which case the excess specific heat is proportional to temperatures below 2°K but is independent of manganese concentrations (0.29 to 1.0 at.% of manganese). Unfortunately, it cannot be determined in the copper-iron alloy system whether the proportionality constant, $\Delta C/T$, depends on iron content or not, since our measurements are only confined to above 1.2°K. As mentioned above, however, the values of ΔC for specimens Cu-Fe(B), (C) and (D) are almost the same. Therefore, $\Delta C/T$ for the copper alloy in solid solution containing more than 0.6 at. % of iron is independent of iron concentration at liquid helium temperatures. It is noticeable that ΔC for copper alloys containing less than 0.1 at.% of iron is nearly proporitional to $T^{1/2}$ as seen in Fig. 11.

In order to evaluate the excess entropy, $\Delta C/T$ is plotted as a function of

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(16) J. de Nobel and F.J. du Chatenier, Physica, **25** (1959), 969.

temperature for the same alloys in Fig. 12. This figure will also be used in order to compare the experimental results with theory.

Many studies,(17) which have been carried out with monovalent and divalent metals containing small amounts of paramagnetic impurities revealed an anomalous specific heat of magnetic origin at liquid helium temperatures, in addition to the fact that the alloys exhibit a low temperature electric resistance minimum and an antiferromagnetic behavior. In these alloys, atoms of paramagnetic impurities have localized magnetic moments and consequently the origin of such anomalies may be ascribed to an exchange interaction between spins of conduction electrons and impurity atoms, i.e. to the so-called *s-d* interaction. A copper alloy doped with a very small amount of iron exhibits a resistance minimum which has well been accounted for by Kondo's theory.(18) Recent measurements of magnetic susceptibility of very dilute iron alloy in copper by Hurd(19) have indicated the existence of the localized moments, though the concentration of his specimens was less than 220 ppm. As the concentration of iron in our specimens is rather larger, i.e. 0.3 to 3.5 at.%, it is naturally expected that our specimens also have localized magnetic moments.

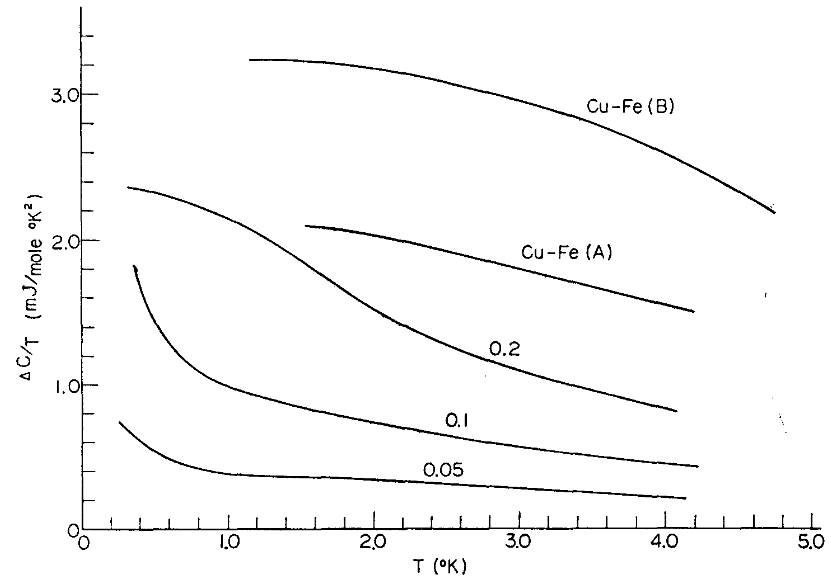

Fig. 12. ($\Delta C/T$) versus T curves for several copper-iron alloys. Numbers on the curves represent the concentration of iron for Franck et al.'s data.

Among several theories regarding the specific heat of metals with dilute

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(17) For reviews, see G.J. van den Berg, *Progress in Low Temperature Physics* (ed. C.J. Gorter, North-Holland Publishing Co. Amsterdam) IV (1964) 194 and G.J. van den Berg, *Low Temperature Physics LT9* (ed. J.G. Daunt et al. Plenum Press, New York) Part B (1965), 955.

(18) J. Kondo, Prog. Theor. Phys., **32** (1964), 37.

(19) C.M. Hurd, J. Phys. Chem. Solids, **28** (1967), 1345.

magnetic impurities,(20-22) the theory by Marshall and Klein seems to be the most appropriate to account for the results of present investigation. Marshall(20) developed a theory in order to interpret the specific heat data of copper-manganese alloy measured by Zimmerman and Hoare.(14) Starting from the Ruderman-Kittel-Kasuya-Yosida Hamiltonian, he ascribed the anomalous specific heat to the Schottky anomaly associated with the Zeeman splitting of the localized spins. In order that the anomaly should be linear with temperature at low temperatures as observed in copper-manganese system, the Ising model for the localized spins has to be assumed.

Furthermore, Klein(21,23) extended the Marshall theory by investigating in detail the probability distribution of the internal field surrounding an impurity atom caused from the other spins. The final expression(23) of Klein's theory is as follows,

$$\Delta C = \frac{N_0 \, c \, k_B}{2\,(2\pi)^{1/2}} f(\sigma \beta)\,, \tag{5}$$

where c is the concentration of solute atoms, N_0 the Avogadro number, $\beta = 1/k_B T$, where k_B the Boltzmann constant, and

$$\sigma\,(T=0) \approx 7.8 J S^2 c\,. \tag{6}$$

The function $f(\sigma\beta)$ is given by eq. (4.4) of Klein's paper.(23) J is an interaction energy which was obtained by Yosida(24) and S the magnitude of the impurity spin. For $\sigma\beta \gg 1$, the next expression results

$$\lim_{T\to 0} \Delta C = \left[N_0 k_B T/2\,(2\pi)^{1/2}\right] 0.25\,(c/\sigma)\,. \tag{7}$$

Since σ is proportional to c in eq. (6), it is known from eq. (7) that the specific heat at very low temperatures, $\Delta C_{T\to 0}$, is independent of the solute concentration and varies linearly with temperature. Equation (7) predicts that $\Delta C_{T\to 0}$ is inversely proportional to the strength of the interaction, JS^2. If the specific heat data at very low temperatures are available, the value of JS^2 should be estimated from the intercept of $\Delta C/T$ at 0°K. Hence the single parameter necessary to determine the detailed behavior of the system is obtained. Equation (5) enables us to obtain the specific heat for a particular solute concentration and temperature, once the value of JS^2 is obtained from the experimental results of $\Delta C/T$ at 0°K.

Klein studied the probability function of the copper-iron alloy system(23,25) and ascertained the fact that the excess specific heat of this alloy system is proportional to the concentration at liquid helium temperatures. In Fig. 13, we have

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(20) W. Marshall, Phys. Rev., **118** (1960), 1519.
(21) M.W. Klein and R. Brout, Phys. Rev., **132** (1963), 2412.
(22) J. Kondo, Proc. Theor. Phys., **33** (1965), 575.
(23) M.W. Klein, Phys. Rev., **136** (1964), A1156.
(24) K. Yosida, Phys. Rev., **106** (1957), 893.
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given the specific heat of specimens of various compositions at several temperatures as a function of iron concentration. It is seen from the figure that Klein's prediction holds well up to 0.6 at.% of iron at about 4°K, but does not hold at lower temperatures. Klein(25) calculated the excess specific heat of the copper alloy containing 0.2 at.% of iron, by using the specific heat data down to 0.4°K by Franck et al.(10) and obtained a good agreement between theory and experiment. As seen in Figs. 10, 11 and 12, the behavior of our specimen, Cu-Fe(A), follows a similar trend to the copper alloy with 0.2 at.% of iron. Therefore, it is qualitatively in accord with Klein's result, while no quantitative agreement is obtained. The specific heat of these two alloys containing 0.2 and 0.3 at.% of iron, however, might be the same at 0°K. The behavior of the specific heat at temperatures near 0°K of the copper alloy containing more than 0.6 at.% of iron is still unknown from the present results in the temperature range studied.

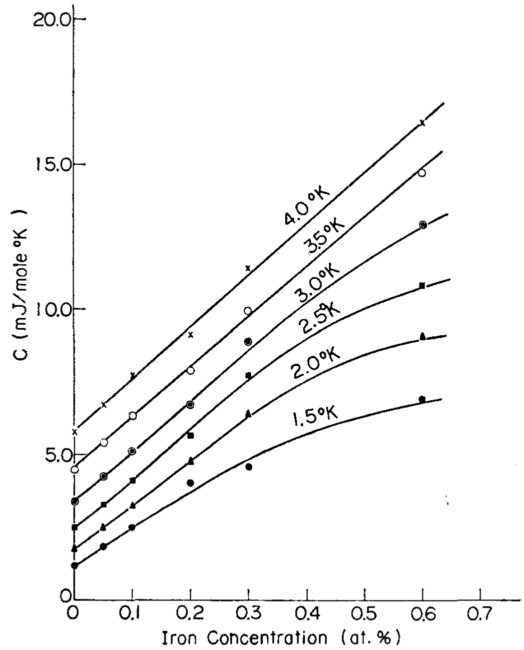

Fig. 13. Specific heat as a function of iron concentration at several temperatures. Points corresponding to iron concentrations 0.3 and 0.6 are those for specimens A and B, respectively, and other points are due to Franck et al.(10)

Kondo(22) published an alternative explanatation on such anomalous specific heat basing also on an *s-d* interaction. The interaction results from a process in which the first electron excites a localized spin and the second one deexcites the same spin as a consequence of the dynamical character of the *s-d* interaction. This interaction between conduction electrons is quite large at the Fermi surface and the thermal mass of the conduction electrons becomes several times larger than the free electron mass. Such a large thermal mass seems to account for the anomalous specific heat which is linear in temperature. This theory also brings out the dependence on concentration in the copper-iron alloy system, when the internal field is assumed to be independent of concentration.

At present we have no experimental evidence which can distinguish between Klein's and Kondo's theories. As regards $\Delta C/T$ versus T curves in Fig. 12, the result by Klein is qualitatively similar to our data, while that by Kondo cannot account for the temperature dependence at rather higher temperatures because his calculation is only done at very low temperatures.

In order to know the magnitude of localized spin, entropy from the excess specific heat, S, is estimated in Fig. 12. Equation (7) is assumed to be valid at very low temperatures and a suitable extrapolation is done to rather higher temperatures. Entropy and spin values for the specimens Cu-Fe (A) and (B) are displayed in Table 4. As our measurements are confined only to liquid helium temperature range, the estimated value would be uncertain to some extent. Nevertheless, it would be confirmed that the spin value of iron in dilute alloys is close to 1/2. This result is also in agreement with those of Franck et al.⁽¹⁰⁾ and du Chatenier et al.⁽¹⁵⁾ from their specific heat studies. But it is clearly different from the spin value, 3/2, deduced from the magnetic measurements by Hurd.⁽¹⁹⁾

Table 4. Entropy and spin values for specimens, Cu-Fe (A) and (B).

Specimen	Entropy (J/mole°K)	Spin value
Cu-Fe (A)	5.46	0.46
Cu-Fe (B)	4.42	0.35

(2) The specific heat ascribable to precipitated atoms

As are illustrated in Figs. 5, 6 and 7, the specific heat of copper alloys with γ-iron precipitates is always smaller than that of the alloys containing iron in solid solutions. Such a phenomenon is due to the fact that the iron concentrations in solid solutions decrease as a result of precipitation and, in addition to that the specific heat of the precipitates is probably smaller than that in solid solution. Therefore, as seen for the specimen Cu-Fe (C) in Fig. 6, the alloy which was annealed for a longer period at 600°C and brought forth more precipitates showed smaller value of the specific heat. Quite similar results were reported on dilute cobalt alloys in copper by R. Tournier et al.⁽²⁶⁾

As seen in Fig. 8, eq. (4) holds well for the copper-iron alloys with precipitates. Table 3 indicates that Θ_D and γ values remain almost constant for lengthy annealing. Because of the occurrence of the temperature independent term in specific heat, i.e. A in eq. (4), and because of the existence of the magnetic specific heat owing to the s-d interactions; there is no way to separate the electronic specific heat of γ-iron, which is directly related to the density of states, from the observed value of specific heat against our expectation.

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(26) R. Tournier, J.J. Veyssie' and L. Weil, J. Phys. Radium, **23** (1962), 672.

On the other hand, the temperature independent term, A, in eq. (4) would give some information with respect to the state of precipitate itself. Appearance of such a term in the low temperature specific heat has been observed in Fe-Ti,⁽¹³⁾ Fe-V,⁽²⁷⁾ Ni-Cu,⁽²⁷⁾ and Cu-Co⁽²⁶⁾ alloys. In these alloy systems, superparamagnetic clusters survive down to liquid helium temperatures. Their paramagnetic moments contribute to the specific heat at low temperatures. The contribution referred to above was given by Livingston and Bean⁽²⁸⁾ as follows,

$$C_{superparamag.} = NR\left(\frac{2\,\mu_B H}{kT}\right)^2 \frac{e^{2\mu_B H/kT}}{(1-e^{2\mu_B H/kT})^2}\,, \tag{8}$$

where μ_B is the Bohr magneton and other letters have conventional meanings. In the case of $T \gg 2\mu_B H/k$, which is well fulfilled in the temperature range studied, this value approximates to NR, i.e. becomes independent of temperature.

Then we can put

$$C_{superparamag.} = A = NR\,, \tag{9}$$

where N is the total number of superparamagnetic particles. When Z is the total number of atoms in a precipitate and c is the concentration, we get

$$c = N\,Z\,. \tag{10}$$

In the present case, provided that nearly all iron atoms precipitate in copper matrix, we have

$$A = R\,c/Z\,. \tag{11}$$

In accordance with the investigation of the neutron diffraction by Abrahams et al.⁽⁵⁾ and of the Mössbauer effect by Gonser et al.⁽²⁹⁾ iron atoms would precipitate in the copper matrix as γ-iron through annealing at high temperature below the solution temperature. This γ-iron particle behaves antiferromagnetically below 8°K.⁽⁵⁾ According to Néel,⁽³⁰⁾ when the size of antiferromagnetic substance becomes quite small, the influence of its surface can hardly be neglected. Since the numbers of the magnetic ions on two sub-lattices are different, the spontaneous magnetization will appear. Above a blocking temperature, however, superparamagnetism will appear due to a thermal agitation. If this idea be acceptable, γ-iron precipitates in copper matrix behaves superparamagnetically and will give rise to a temperature independent specific heat.

By using eq. (11) and the observed value of A, the value of Z can be obtained. When the shape of γ-iron precipitates is assumed to be sphere, their mean diameter, d, is calculated by the next expression

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(27) K. Schroder, J. Appl. Phys., **32** (1961), 880.

(28) J.D. Livingston and C.P. Bean, J. Appl. Phys., **32** (1961), 1964.

(29) U. Gonser, R.W. Grant, A.H. Muir and H. Wiedersich, Acta Metallurgica, **14** (1966), 259.

(30) L. Néel, C.R. Acad. Sci. (Paris), **252** (1961), 4075; ibid., **253** (1961), 203.

$$\frac{4}{3}\left(\frac{d}{2}\right)^3 = \frac{Z}{4} a^3 , \tag{12}$$

in which a means the lattice constant of f.c.c. iron precipitates and its value was given as 3.588 Å by Abraham et al.⁽⁵⁾ Thus estimated values of Z and d are listed in Table 5. The value of d is about 8 to 15Å. Mima and Saji⁽³¹⁾ have recently observed the size of γ-iron particle by using a transmission electron microscopy and obtained that the value of d is about 50 Å to 430Å for the copper alloy with γ-iron precipitates after various heat treatments at 650°C. So our values of d are smaller than their values.

Table 5. The value of Z and d for three specimens with γ-Fe precipitates by holding at 600°C.

Specimen	Precipitation hours	Z	d(Å)
Cu-Fe (B)	24 hrs.	23.7	8.1
Cu-Fe (C)	5 min.	138.3	14.5
	75 min.	81.7	12.1
Cu-Fe (D)	75 min.	96.0	12.7

Summary

The specific heat of copper alloys containing 0.3, 0.6, 2.5 and 3.5 at. % of iron has been measured at liquid helium temperatures. In order to obtain solid solutions, specimens were annealed for 24 hours at 1060°C and quenched into cold water. In order to get γ-iron precipitates, specimens were annealed at 600°C for the durations as listed in Table 1. The excess specific heat is observed for the copper-iron alloys in solid solutions. The data can be accounted for by the Marshall-Klein theory based on the idea that the excess component is due to s-d interaction. The spin value of iron atom is estimated to be 1/2 from the evaluation of excess entropy. The specific heat of copper alloys with γ-iron precipitates includes the temperature independent component. The interpretation of this component may be accomplished by considering it as due to some kind of superparamagnetism. Because of antiferromagnetism of γ-iron precipitates below 8°K and by resorting to Néel's theory, we ascribe this component to a superparamagnetic behavior of the precipitates. It is, however, impossible to get the value of electronic specific heat coefficient of γ-iron by such a procedure.

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(31) G. Mima and S. Saji, J. Japan Inst. Metals, **31** (1967), 761 (in Japanese).

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