

HIGH TEMPERATURE SPECIFIC HEAT AND MAGNETIC SUSCEPTIBILITY OF IRON-SILICON ALLOYS

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ABSTRACT. Specific heat and magnetic susceptibility of iron-rich iron-silicon alloys containing 2.37, 4.05, 6.44 and 8.56 at.% Si have been studied up to 1650 and about 1870 °K respectively. Silicon influences the physical properties of pure iron quite considerably. With increasing amount of silicon the magnetic energy of the alloys decreases. The alloy with 6.44 at.% Si is one of the most important alloy in the Fe-Si system both for theoretical and practical considerations. The observed specific heat of this alloy has been separated into its lattice, electronic and magnetic parts. From the knowledge of the magnetic contribution the value of magnetic energy, spin quantum number, magnetic entropy and exchange integral have been evaluated. In the specific heat vs temperature curves of the alloys with 6.44 and 8.56 at.% Si anomalies are found between 750 and 800 °K. With the help of the measurements of magnetic susceptibility it has been shown how Curie constant, para-magnetic Curie temperature and effective paramagnetic moment of iron change due to the presence of silicon.

INTRODUCTION

Besides the phase transformation of second-order at the Cuire temperature pure iron possesses transformation of the first-order at 910 and 1390°C. The b.c.c. α -iron transforms into f.c.c. γ -iron at 910°C which again suffers phase change at 1390°C of the first-order. Iron above 1390°C is known as b.c.c. δ -iron. Silicon reduces the γ -loop of binary iron-silicon alloys. The alloys containing more than 2 wt. %Si do not possess γ -loop and they suffer phase change of second-order at ferromagnetic Cuire temperature. Because of this characteristic of iron-silicon alloys it is interesting to study their physical properties at high temperatures. Little is known about the specific heat both at low and high temperatures and magnetic susceptibility in the liquid state of iron-silicon alloys.

To study especially these two properties at high temperatures the following four alloys have been selected. Their chemical analysis is given in the following table.

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TABLE 1
Analysis of the Fe-Si alloys

- a) Alloy containing 2.37 at.% Si (other elements in wt.%):
0.003 C, < 0.001 Mn, 0.001 P, 0.003 S, 0.001 Al, 0.002 N₂, 0.001 O₂, < 5.10⁻⁵ B, rest Fe.
- b) Alloy containing 4.05 at.% Si (other elements in wt.%):
0.008 C, 0.02 Mn, 0.006 P, 0.006 S, 0.003 Al, 0.001 N₂, 0.004 O₂, rest Fe.
- c) Alloy containing 6.44 at.% Si (other elements in wt.%):
0.012 C, 0.07 Mn, 0.016 P, 0.014 S, rest Fe.
- d) Alloy containing 8.56 at.% Si (other elements in wt.%):
0.007 C, < 0.002 Mn, 0.002 P, < 0.003 S, < 0.002 Al, < 0.002 N₂, < 0.002 O₂,
< 5.10⁻⁵ B, rest Fe.

EXPERIMENTAL CONSIDERATION

Before measurements the specimens were annealed at about 1200°C in the presence of pure argon gas for several hours and then they were cooled down to room temperature slowly. This was done to homogenize the specimens.

The specific heat of the alloys containing 2.37, 6.44 and 8.56 at. % Si was measured using the adiabatic calorimeter constructed by Braun (1964) which enables the continuous measurement of this quantity *vs* temperature. The average weight of the specimens were nearly 130g and they were cylinders of 60 mm length and 20 mm diameter. The measurements followed at constant pressure in argon atmosphere and a few *Pt—Pt/Rh* thermocouples were used for the measurements of temperature. The error in the observed values amounts to only $\pm 2\%$. Braun (1964) reports how this calorimeter functions at high temperatures.

Magnetic susceptibility as a function of temperature of all the four alloys was measured using the balance developed by Kohlhaas (1965). This balance is automatic compensated and it enables the relative measurement of susceptibility. For the absolute values of susceptibility at different temperatures the calibration was done using an iron specimen whose susceptibility was determined by Kohlhaas and Lange (1964). The specimens were small cylinders weighing about 250mg. Here again the temperatures were determined with the aid of a *Pt—Pt/Rh* thermocouple. Kohlhaas (1965) describes fully the method of measurement with this balance.

RESULTS AND DISCUSSIONS

A. Specific heat

The observed specific heat ($C_{p,T}$) *vs* temperature (T) of the Fe-Si alloys compared to that of pure Fe is shown in fig. 1.* A small variation from the standard

* The ($C_{p,T}-T$)-curve of the alloy with 6.44 at.% Si here differs a little from that reported by Kohlhaas and Pandey (1966). Its reason lies evidently in different duration of annealing the specimens.

lambda shapes of the specific heat curves of a ferromagnetic material is obvious in cases of the alloys with 6.44 and 8.56 at. % Si between 750 and 800°K. A further anomalous was observed in these cases between 1375 and 1450°K. These

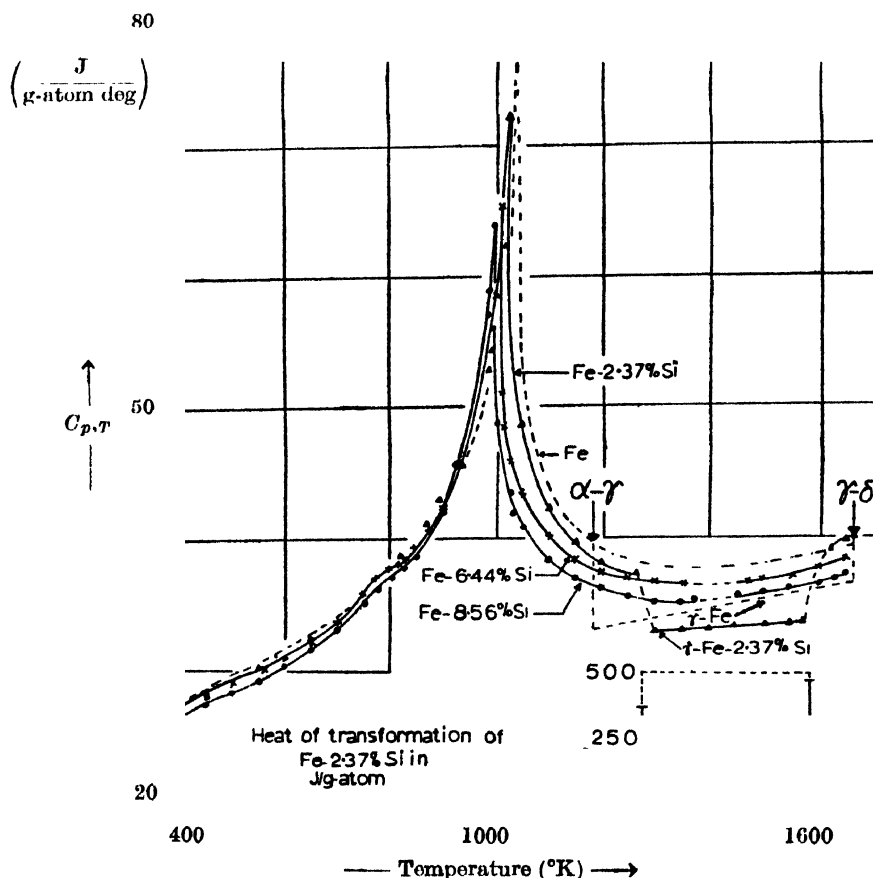


Fig. 1. Specific Heat of Fe-Si alloys containing 2.37, 6.44, 8.56 at. % Si. Fe-curve according to Braun (1964).

anomalies cannot be explained on the basis of the various phase diagrams of Fe-Si alloys. Different investigations are required for an explanation of these anomalies which is not the aim of this paper. Also van Kempen, Kohlhaas and Lange (1966) report that they find an anomalie in the curves of saturation magnetostriction of a single crystal of an Fe-Si alloy with about 8.5 at. % Si at 850°K. An anomalie in the measurements of magneto-caloric effect of an Fe-Si alloy containing 6.44 at. % Si is found by Hirschler and Rucker (1966) at about 970°K. The anomalies in the $(C_{p,T}-T)$ -curves of the alloys with 6.44 and 8.56 at. % Si between 1375 and 1450°K are shown in fig. 1 using broken lines. The phase change of first-order in the alloy with 2.37 at. % Si takes place at 1273 ($\alpha-\alpha+\gamma$), 1297($\alpha+\gamma-\gamma$), 1583($\gamma-\gamma+\delta$) and 1601°K($\gamma+\delta-\delta$). These results agree quite

well with those obtained with the help of measurements of magnetic susceptibility of this alloy. The heat of transformation for this alloy at 1290 and 1588°K amounts to 368 and 472 J/g-atom respectively. According to Braun (1964) for iron this amounts to 910 and 850 J/g-atom at A_3 and A_4 points respectively. It is interesting to observe in fig. 1 that the $(C_{p,T}-T)$ -curves of the alloys fall monotonously with increasing amount of silicon above their respective Curie points. The alloy containing 2.37 at.% Si is an exception to this observation in γ -range. A theoretical explanation of this fact will be given later in this paper.

1. Separation of $(C_{p,T}-T)$ -curve of a ferromagnetic material

The $(C_{p,T}-T)$ -curve of a ferromagnetic material can be separated into its three main components: lattice, electronic and magnetic. Besides these three components to the observed specific heat there may be a further contribution due to anharmonic vibration of atoms. Regarding this contribution there are different opinions (see Forman, 1962; Keller *et al*, 1962 and Wallace, 1963) and a final clarity of this problem is as yet unknown. Anyway the contribution owing to the anharmonic vibration may be regarded as belonging to the (C_p-C_v) -correction of the lattice part. The method of separation of $(C_{p,T}-T)$ -curve of a ferromagnetic material is explained in short in following lines.

a) lattice contribution $C_{p,D}$

The contribution to the observed specific heat of a metallic element at constant volume due to the thermal vibration of lattice is given to sufficient accuracy by the equation

$$C_{v,D} = f_D(\theta_D/T), \quad (1)$$

where θ_D is the Debye temperature, f_D is the Debye function and T is the absolute temperature. Usually it is assumed that θ_D is independent of temperature but actually it varies slightly with it. It may, however, be considered as a constant in order to estimate at all the lattice contribution to the measured specific heat. Measurements of specific heat are done at a constant pressure and not at a constant volume. Consequently the correction for lattice expansion in eq. (1) is necessary. This may be done using the equation

$$C_{p,D} = C_{v,D}(1 + \beta GT), \quad (2)$$

where β is the coefficient of volume expansion and G is the Grüneisen constant. Even Grüneisen constant is thought to be temperature independent. Blackmann (1955) doubts it, whereas Hofmann, Paskin, Tauer and Weiss (1956) consider it as a constant to simplify the separation of the observed specific heat into its lattice part. Such a simplification may be justified at least in the case of a ferromagnetic material where the knowledge of the magnetic specific heat is more important.

b) *Electronic contribution C_{el}*

According to Todd (1950) the electronic specific heat is given on the basis of free-electron model by the equation

$$C_{el} = \gamma T \left[1 - \frac{3\pi^2}{10} \left(\frac{T}{T_0} \right)^2 \right], \quad \dots \quad (3)$$

where γ is the electronic specific heat coefficient and T_0 is the temperature of degeneracy. Degeneracy temperature for metals is usually of the order of 10^4 °K and as such the second term on the right hand side of the eq.(3) may be neglected. Under this condition the electronic specific heat is given approximately by the relation

$$C_{el} = \gamma T. \quad (4)$$

γ is determined with the help of the measurements of specific heat at low temperatures.

c) *Magnetic contribution C_m*

The total specific heat of a ferromagnetic material can be written as

$$C_{p,T} = C_{p,D} + C_{el} + C_m. \quad (5)$$

After the contributions to the observed specific heat due to lattice and electronic parts are estimated the magnetic part is at once known. The anomaly of specific heat in a ferromagnetic material is due to the magnetic contribution. It can be defined as the thermal energy required to break the exchange coupling between the elementary magnets.

2. *Estimation of $C_{p,D}$, C_{el} and C_m of the Fe-Si alloy containing 6.44 at. % silicon*

For the separation of $(C_{p,T}-T)$ -curve the values of the Debye temperature θ_D , the Grüneisen constant G , the coefficient of volume expansion β (which may be taken as three times the value of the coefficient of linear expansion) and the electronic specific heat coefficient γ must be known as accurately as possible. Pandey (1967) describes in detail how the values of G and β for this alloy have been determined. The values of θ_D and γ have been obtained graphically using the values given by Gupta, Cheng and Beck (1964) for a large number of Fe-Si alloys. The results are given in table 2. The values of β at different temperatures have been obtained with the aid of the X-ray measurements of lattice parameters (see Pandey, 1967).

TABLE 2

Values of the Debye temperature θ_D , the electronic specific heat coefficient γ and the Grüneisen constant G for an Fe-Si alloy containing 6.44 at. % Si

Constant	Unit	Value
θ_D	°K	426
γ	J/g-atom deg ²	5.2×10^{-3}
G	—	2.2

The results of the separation of the observed specific heat are shown in fig. 2. In this figure the $(C_{p,T}-T)$ -curve has been interpolated from room temperature

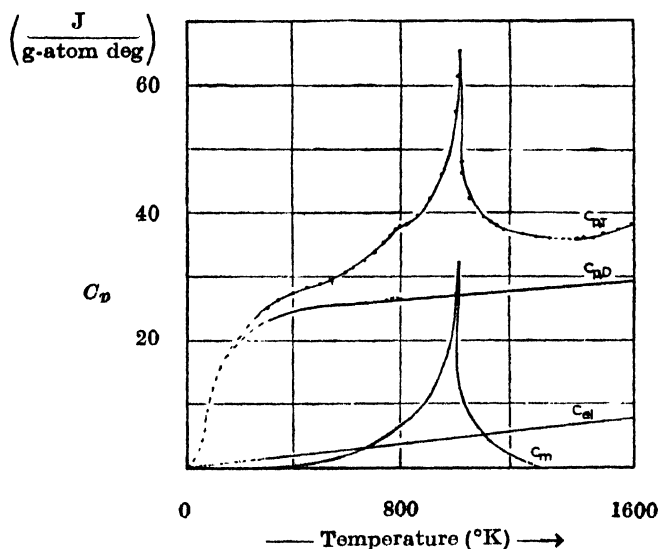


Fig. 2. Different parts of observed Specific Heat of Fe- 6.44% Si. alloy.

to absolute zero (broken and dotted line) using the equation (see Roberts, 1949)

$$C_{v,D} = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_D} \right)^3, \quad \dots (6)$$

where R is the gas constant. Near about $T \cong \frac{\theta_D}{15}$ is $C_{v,D} \cong C_{p,D}$ and therefore the $(C_p - C_v)$ -correction is unnecessary. Between $\theta_D/15$ and 250°K too this correction has not been done because the values of the coefficient of linear expansion are not known in this low temperature region. In the range of interpolation the

magnetic contribution to the total specific heat has not been considered since it can be assumed that this is negligible below room temperature.

In fig. 2 the anomalous in $(C_{p,T}-T)$ -curve between 750 and 800°K is shown using dots in the lattice part of the specific heat since this belongs most probably to the $(C_{p,D}-T)$ -curve. Theoretically its belonging either to the electronic or to the magnetic part cannot be explained. In fig. 3 it can be seen that above the Curie temperature (736°C) the (C_m-T) -curve of this alloy lies below that of pure iron. According to Gupta *et al* (1964) the values of γ for Fe-Si alloys

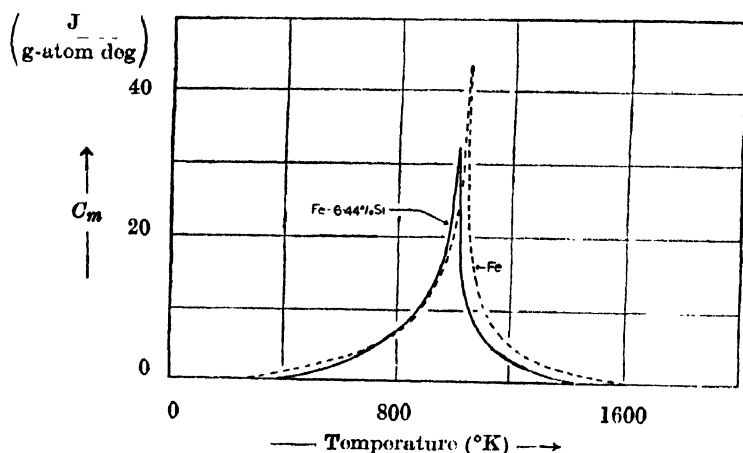


Fig. 3. Magnetic part of observed Specific Heat of Fe- 6.44 % Si alloy. Fe-curve according to Braun (1964).

containing up to 7.8 at. % Si increase whereas the values of θ_D decrease. This means that with increasing amount of silicon $C_{v,D}$ as well as C_{el} for Fe-Si alloys (till approximately 8 at. % Si) will increase slowly. It can be shown theoretically (see Pandey, 1967) that the magnetic energy of all the four alloys decreases with increasing amount of silicon. The magnetic energy $E_m = \int_0^\infty C_m dT$. Most probably the decrease of magnetic energy with increasing amount of silicon is responsible for the monotonous sinking down of the $(C_{p,T}-T)$ -curves.

3. General considerations of the (C_m-T) -curve of the alloy with 6.44 at. % Si

The magnetic specific heat leads to the addition of knowledge of a few but very important characteristic physical quantities. These are magnetic energy, magnetic entropy, spin quantum number and exchange integral.

Magnetic energy can be defined as the energy which is required to bring the spin system from the state of order at $T \ll T_c$ to the state of disorder at $T \gg T_c$ (Curie point). It is given by the equation

$$E_m = \int_0^\infty C_m dT, \quad (7)$$

which is equal to the area enclosed in (C_m-T) -curve. The value of E_m for this alloy is obtained graphically and it amounts to 6160 ± 430 J/g-atom whereas it is 8095 ± 500 J/g-atom for Fe according to Hofmann and coworkers (1956). This means that the value of the magnetic energy for Fe-Si alloy with 6.44 at. % Si is approximately 25% less than that of pure iron. This result is in good agreement with those obtained theoretically on the basis of molecular field theory and Heisenberg model (see Pandey, 1967). There is, however, a discrepancy in the quantitative results. This disagreement is shown in the following table.

TABLE 3
Values of magnetic energy E_m of the Fe-Si alloy containing 6.44 at % Si

Method	E_m in J/g-atom
Molecular field theory	6040
Heisenberg approximation	9306
(C_m-T) -curve of the observed specific heat	6160 ± 430

A similar disagreement in the quantitative values of E_m using different methods is found also for iron.

According to Heisenberg model there is a relationship between the magnetic energy E_m and the spin quantum number s which can be written as

$$\frac{E_m}{N_0 k T_c} = \frac{3s}{2(s+1)}, \quad (8)$$

where N_0 is the number of magnetic atoms, k is the Boltzmann constant and T_c is the Curie temperature in °K. From the above equation the value of s for this alloy comes out to be 1.08. This result agrees well with that obtained from the measurement of saturation magnetization (see Pandey, 1967).

Magnetic entropy S is equal to the change in entropy during the process of order to disorder of the spin system and it is to be formulated as

$$S = \int_0^T \frac{C_m}{T} dT. \quad \dots (9)$$

The value of S obtained graphically from the (C_m-T) -curve amounts to 8.32 ± 0.5 J/g-atom deg. The theoretical value of S is given by the equation

$$S_{th} = N_0 k \ln (2s+1). \quad \dots (10)$$

It amounts to 8.94 J/g-atom deg. A small disagreement in the experimental and theoretical values of S is reported even for Fe and Ni by Hofmann and coworkers (1956).

The exchange integral J is given by the relation

$$J = \frac{E}{N_0 z s^2} \quad \dots (11)$$

where z is the number of nearest neighbours. From the above equation the value of J follows to be $(0.72 \pm 0.05) \times 10^{-2}$ eV. This value is smaller than the one using the formula given by Rushbrooke and Wood (1958). It amounts to 1.13×10^{-2} eV. A discrepancy between the values of J obtained on the basis of experimental result and theoretical relations is also reported for Fe and Ni by Hofmann *et al* (1956). Its reason lies in the difference of the values of magnetic energy obtained by different methods.

B. Magnetic Susceptibility

The inverse specific magnetic susceptibility ($1/\chi$) vs temperature (T) of the Fe-Si alloys is shown in fig. 4. It is evident from this figure that the value of $1/\chi$ increases along with the increase of the amount of silicon in the alloys both in

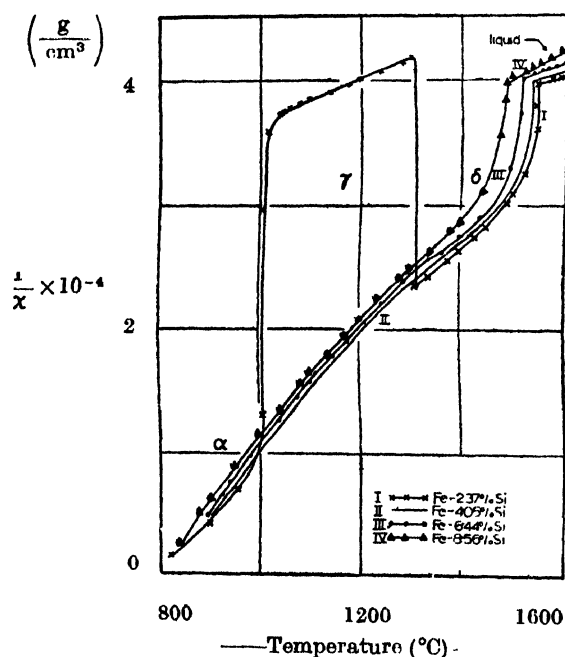


Fig. 4 Inverse Magnetic Susceptibility of Fe-Si alloys.

solid and liquid states. The only exception is to be observed in the case of the alloy containing 2.37 at.% Si between 995 and 1325°C. In this temperature range this alloy possesses f.c.c. γ -phase. An abrupt increase and decrease in the value of $1/\chi$ takes place at the beginning and at the end of the phase changes respectively. This characteristic behaviour of the observed magnetic susceptibility

serves as an important method to determine the boundaries of phase transformation of first-order. The phase transformation of first-order takes place in the Fe-Si alloy with 2.37 at. % Si at 995 ($\alpha-\alpha+\gamma$), 1020($\alpha+\gamma-\gamma$), 1300 ($\gamma-\gamma+\delta$) and 1325°C ($\gamma+\delta-\delta$). This result agrees well with that reported in the previous section. In pure Fe the phase change of first-order takes place at 910 and 1390°C. The alloy with 4.05 at.% Si suffers no phase transformation of first-order. This result is in agreement with the phase diagram of Fe-Si alloys according to Fischer (1966). It is also evident from fig. 4. that in the liquid state the $(1/\chi-T)$ -curve of the alloys becomes steeper as the content of silicon increases.

For all the four alloys the values of the Curie constant C , the paramagnetic Curie point θ_p and the number of paramagnetic moments μ_{eff} in Bohr magnetons have been estimated. C and θ_p are determined with the aid of the conventional inverse magnetic susceptibility *vs* temperature plot both in solid and liquid states of the alloys. For the purpose of comparison the method suggested by Danielian (1962) which is strongly recommended by Koch and Arrot (1962) has also been applied. According to this method one needs to plot $(\chi T)^{-1}$ *vs* T^{-1} . The extrapolation of this curve at $T^{-1} = 0$ gives the reciprocal value of the Curie constant. This method has the advantage that one need not assume the validity of the Curie-Weiss law

$$\chi = \frac{C}{T - \theta_p} \quad (12)$$

This law is a consequence of the molecular field model which is a first-order approximation of the localized magnetic moment model. Based on this model the exact expression for the magnetic susceptibility χ is given by (see Danielian, 1962)

$$\chi^{-1} = \frac{T}{C} \left(1 + \sum_{j=1}^{\infty} \frac{\alpha_j}{T_j} \right), \quad \dots \quad (13)$$

where the coefficients α_j are functions of the crystal structure, the magnetic moment at each lattice site and the interactions between the moments. When $\alpha_j = 0$ for $j > 1$ this equation reduces to eq. (12) with $\alpha_1 = -\theta_p$. The quantitative values of C of the alloys obtained with the two methods differ about 4% with each other.

The values of μ_{eff} per Fe-atom of an Fe-Si alloy can be obtained according to Aarås and Miller (1960) using the equation

$$\mu_{eff} = [3kCN_A^{-1}(A_{Fe} + x A_{Si}/100-x)]^{1/2} \mu_B^{-1}, \quad \dots \quad (14)$$

where k is the Boltzmann constant, C the Curie constant, μ_B the Bohr magneton, x the at. % Si in the alloy, N_A the Avogadro number and A_{Fe} and A_{Si} are the atomic weights of iron and silicon respectively.

The values of the above mentioned constants for the Fe-Si alloys are shown in fig. 5('a' and 'b'). One can obviously conclude the following facts from these figures :

a) the values of the Curie constant C and the number of paramagnetic moments μ_{eff} are much smaller in solid state (α -region) than those in liquid state

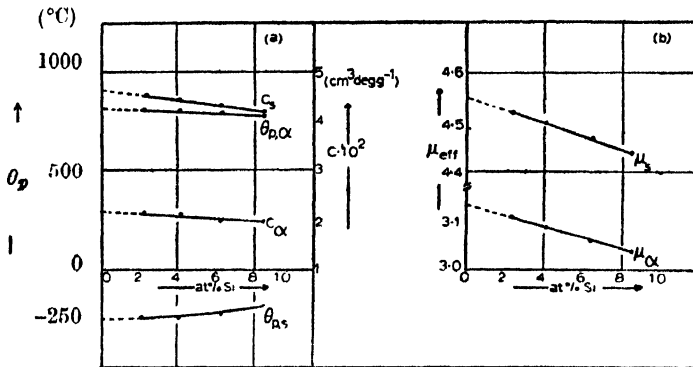


Fig. 5. Curie temperature, θ_p , curie constant, C , and effective number of Bohr magneton, μ_{eff} , of Fe-Si alloys in α -range and liquid state.

b) the paramagnetic Curie temperature θ_p changes its sign in molten state.

Undoubtedly the origin of ferromagnetism in Fe, Co and Ni lies in the 3d-electrons of these elements. Besides that the influence of conduction electrons can be quite considerable so far as the magnetic behaviour of transition metals is concerned. Arjas and Miller (1960) report that this problem has been studied by Vonsovskii and according to them the exchange interaction between the ($s-d$)-electrons should contribute to a temperature independent term of paramagnetic susceptibility. The theoretical consideration based on the measurements of paramagnetic susceptibility of all the four Fe-Si alloys show that in the range of high temperatures the Curie-Weiss law is fulfilled quite satisfactorily. The theoretical analysis of the measurements of magnetic susceptibility of various Fe-Si alloys by Arajs and Miller (1960), Rocker and Kohlhaas (1966) and Übelacker (1966) lead to the same result. One can, therefore, conclude that the contribution to the observed susceptibility due to the exchange interaction between s and d electrons in the cases of Fe-Si alloys is negligibly small.

According to Volkov and Pshenichkin (quoted by Dubinin *et al*, 1962) the exchange integral can change considerably when ferromagnetic alloys are in liquid state. It can, therefore, cause the changes in the values of the Curie constant C and the paramagnetic Curie temperature θ_p . Such a change in the values of C and θ_p has already been reported in this paper. In the molten state the Curie-Weiss law applicable to the four Fe-Si alloys can be written as

$$\frac{C}{T + \theta_p}, \quad \dots (15)$$

which is valid for antiferromagnetic materials. Since the sign of θ_p is negative for the alloys in the molten state one can conclude that these alloys in the liquid state might possess an antiferromagnetic character. Besides that the alloy containing 2.37 at. % Si might also be antiferromagnetic in the f.c.c. γ -range. The probable antiferromagnetic character of these alloys are even more pronounced when $(\chi T)^{-1}$ vs T^{-1} is plotted. According to Danielian (1962) the value of $(\chi T)^{-1}$ increases with increasing value of T^{-1} for a f.c.c. antiferromagnetic material whereas it decreases in the case of a f.c.c. ferromagnetic material.

In fig. 6 the Danielian-plot of the γ -phase of the alloy with 2.37 at.% Si is shown (curve I). It can be clearly seen that $(\chi T)^{-1}$ increases with the increase

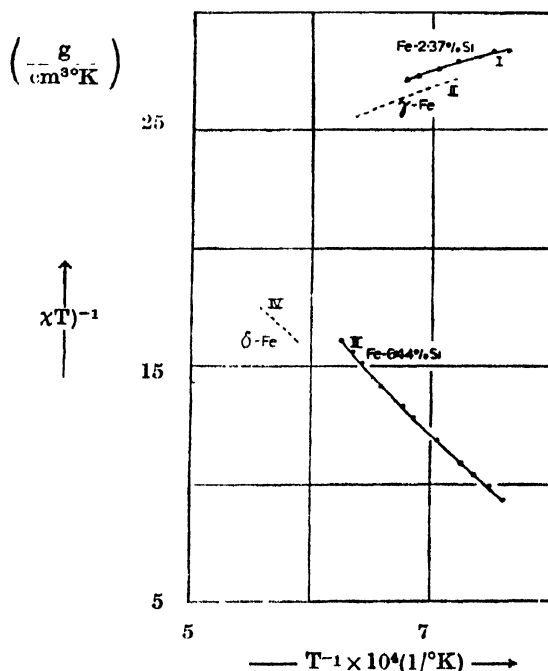


Fig. 6. Danielian plot for Fe and Fe-Si alloys.

of T^{-1} . This fact again hints to the antiferromagnetic nature of this alloy in γ -range. The curve II of this figure shows a similar result in case of γ -Fe whose susceptibility has been measured by Kohlhaas (1965). He too reports about the antiferromagnetic nature of γ -Fe.

The curves III and IV should serve as examples of the application of Danielian plot for a b.c.c. crystal. Both these curves represent evidently the typical behaviour to be expected from ferromagnetic materials in the region of paramagnetism. It may be mentioned here that Danielian (1962) reports only about the f.c.c. antiferromagnetic and ferromagnetic crystals. But on the basis of fig. 6 it may be assumed that his theoretical considerations are not so limited and they can well be applied to b.c.c. crystals.

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