

ANALYSIS OF MAGNETIC ANOMALY IN BCC IRON

JAROSLAV KUČERA

*Institute of Physical Metallurgy, Czechosl. Acad. Sci., Brno**

The depression of the homodiffusion coefficient of iron upon magnetic ordering is analyzed with the use of the Heisenberg model and Kirkwood's method. Data of LAI D. Y. F. and BORG R. J. (Trans. AIME 233 (1865), 1975) and HETTICH G., MEHRER H. and MAIER K. (Scripta Met. 11 (1977), 795) extended to the temperature range $511 \div 1200$ °C have been used in this analysis. The computer fit of an analytic form, derived for the excess activation enthalpy ΔH_p , to the experimental data enabled us to calculate the values of exchange integral $J_0 = (345.3 \pm 3.6) k$ and of the paramagnetic temperature $T_p = (1207 \pm 15)$ K. The activation enthalpy of homodiffusion in a completely ordered ferromagnetic α -Fe is higher by the value $\Delta H_p = (56.41 \pm 0.59)$ kJ/mol than the value corresponding to a paramagnetic state. The expression for ΔH_p , the experimental values of J_0 and T_p and the Zener's theory of the frequency factor D_0 have been used to develop an equation giving the temperature variation of the homodiffusion coefficient in BCC iron for both, above and below the Curie temperature. A treatment analogous to the Bragg-Williams description of order-disorder in alloys was used to demonstrate that the long-range order parameter in ferromagnets is identical to the spontaneous magnetization \mathcal{S} . The quotient of $\Delta H_p(T)/\Delta H_p(0)$ may be well used as a short-range order characteristic.

1. INTRODUCTION

Many experimental results [1, 2, 3, 4, e.g.] show that the magnetic order in ferromagnets and the other quantities connected with it do not change during the transition from the paramagnetic to the ferromagnetic state at a given temperature suddenly but gradually, in a temperature interval called the Curie-zone [5]. In homogeneous primary solid solutions the width of the Curie-zone increases with the increasing solute concentration as demonstrated in the Cu-Ni system [6] e.g. The transition from the ferromagnetic state to the paramagnetic zone results in some expressive anomalies that have been reported for high temperature yielding [3], creep (see [1-9] in [3]) and for diffusion ([2, 4] and [16-25] in [3]).

The diffusion anomaly is characterized by the following features:

- i) The diffusion coefficients in ferromagnetic metals below the Curie temperature are considerably lower than would be expected from extrapolating the Arrhenius plot in paramagnetic region [7].
- ii) The activation enthalpy of diffusion in the ferromagnetic region H_f is higher than that one in the paramagnetic region H_p and the variation of $H(T)$ from H_f to H_p is a continuous one. The frequency factors possess very close values, however it may be shown that $(D_0)_f > (D_0)_p$, as a rule.

*) Žižkova 22, 616 62 Brno, Czechoslovakia.

iii) The effective activation enthalpy defined by

$$(1) \quad H_{\text{ef}} = -R \, d(\ln D)/d(1/T)$$

is noted for a sharp peak at the Curie temperature.

The analysis of diffusion anomaly in ferromagnets has been reported by GIRIFALCO [8], LEE RUCH et al. [9] and by HETTICH et al. [4]. GIRIFALCO has shown that the anomaly and the observed difference in H_p and H_f can be explained by using the excess activation enthalpy $\Delta H_p(T)$ associated with a local demagnetization arising from the vacancy formation and migration. Applying the exchange integral value $J_0 = 232k - k$ is the Boltzmann constant – Girifalco was able to show that the excess activation enthalpy in BCC-Fe $\Delta H_p(0) = 9.65$ kJ/mol, when the fully paramagnetic state is compared to the ferromagnetic one at very low temperatures. This value is in a good agreement with the data $\Delta H_p(0) = 11.7$ kJ/mol (Fe \rightarrow α -Fe) and 11.3 kJ/mol (Co \rightarrow α -Fe) given in [7], p. 554. However, it differs in order from the value $\Delta H_p(0) = 55.0$ kJ/mol claimed in paper [4]. Relating the activation enthalpy to the relative spontaneous magnetization $\mathcal{S}(T)$, Girifalco obtained the variation of actual activation enthalpy given by the equation

$$(2) \quad H(T) = H_p + \Delta H_p(T),$$

and the effective activation enthalpy $H_{\text{ef}}(1)$ in the temperature range $0 \text{ K} \div \Theta$; Θ is the Curie ferromagnetic temperature [5] (p. 157). It may be mentioned that the results obtained in [10] at temperature $T > \Theta$ are not involved in Girifalco's analysis.

LEE RUCH et al. [9] have based their analysis on the similarity between atomic and ferromagnetic ordering using the Bragg-Williams theory of order-disorder alloys [11]. They have found that the actual activation enthalpy of Fe diffusion in Fe-7.64 at. % Si [12] and in Fe [10] can be expressed in the form $H(T) = H_p(1 + \alpha \mathcal{S}^2)$, where α is an experimental constant. For the data [12] the value of α has been determined by the authors to be 0.112 and 0.102 for pure Fe data, respectively. The maximum value of the excess activation enthalpy evaluated in [9] is $\Delta H_{p(\text{Fe-Si})}(0) = 27.5$ kJ/mol and $\Delta H_{p\text{Fe}}(0) = 30.69$ kJ/mol. In the LEE RUCH's et al. paper, similarly to [8], the $D(T)$ values extended to a small region near the Curie temperature are not analyzed.

HETTICH et al. [4] investigated the diffusion anomaly in α -Fe exploiting the $D(T)$ values of [10, 13, 14] and their own values measured in the temperature interval $511 \div 744$ °C. For the temperature dependence of homodiffusion coefficient in α -Fe they have proposed the relation

$$(3) \quad D(T) = 1.0 \exp \left\{ -\frac{234.5(1 + 0.23\mathcal{S}^2)}{RT} \right\} \quad [\text{cm}^2/\text{s}, \text{kJ/mol}],$$

with $\Delta H_p(0) = 54.0$ kJ/mol. In developing the eq. (3) HETTICH et al. did not take into consideration the Zener's theory of D_0 . With respect to this theory they have

obtained the relation

$$(4) \quad D(T) = 0.98 \exp \left\{ -\frac{239.7}{RT} \right\} \exp \left\{ -\frac{4.34\mathcal{L}^2 + 5.74(\mu(T) - \mu_p)}{RT} \right\},$$

where $\mu(T)$ denotes the shear modulus, μ_p is the same modulus for a fictitious, disordered low temperature state. The $D(T)$ values corresponding to the temperature $T > \Theta$ are not analyzed in paper [4], either.

In the present paper, an equation (11) for the excess activation enthalpy in BCC-iron is developed by using the Heisenberg model [15] and the Kirkwood's method [16]. This equation may be applied to the analysis of the diffusion data at both the temperatures $T < \Theta$ and $T > \Theta$. With the use of eq. (11) the actual (2) and effective (1) activation enthalpies can be calculated. The computer fit of eq. (11) to the experimental data gives an opportunity to calculate the values of exchange intergral J_0 and paramagnetic temperature T_p . At this temperature the depression of the diffusion coefficient starts to be non-detectable. On the basis of the present analysis both the experimental values [2] and [4] of $D(T)$ are described by an only equation (19) that is applicable at all temperatures in α and δ -Fe.

2. EXCESS ACTIVATION ENTHALPY

The energy of interaction of the next nearest atoms bearing spins \mathbf{S}_i and \mathbf{S}_j [15] contains a term

$$(5) \quad U = -2J_0 \mathbf{S}_i \cdot \mathbf{S}_j$$

that is responsible for an increase of the atom-atom binding energy in a ferromagnetic system. This increase may be evaluated by different methods [16] based on the solution of a partition function which has, in the absence of an applied field, the form

$$(6) \quad f(T) = \sum_{\langle \mathbf{S}_i \rangle} \exp \left\{ \frac{2J_0}{kT} \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \right\}.$$

With this relation the Helmholtz function is given by

$$(6.1) \quad E'' - kT \ln W = -kT \ln f(T),$$

where $W = N!/(N_+! N_-!)$; N_+ are the spins oriented to the "north", N_- to the "south"; E'' is the increase of the free energy of the system due to the spin-spin interaction. This energy may be used as a measure of the excess binding energy E' so that $E' = -E''$. Expanding the exponential $f(T)$ KIRKWOOD [22] obtained

$$(6.2) \quad E' = kT \ln \left[1 + \frac{\langle y \rangle}{1!} + \frac{\langle y^2 \rangle}{2!} + \frac{\langle y^3 \rangle}{3!} + \dots \right]$$

with

$$\langle y^n \rangle = \frac{1}{W} \sum_{\langle S_i \rangle} y^n \quad \text{and} \quad y = \frac{2J_0}{kT} \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j.$$

The laborious calculating of the individual values of $\langle y^n \rangle$ has been done by different authors [23]. In the present paper D. TER HAAR's [24] solution for a simple cubic lattice and for $n \leq 4$ is used. It results, after a simple arithmetic operation, into the equation (7).

$$(7) \quad E' = \frac{Nz}{2} 2J_0 \left\{ \mathcal{S}^2 + 0.5 \left(\frac{2J_0}{kT} \right) (1 - \mathcal{S}^2)^2 + \frac{2}{3} \left(\frac{2J_0}{kT} \right)^2 (1 - \mathcal{S}^2)^2 \mathcal{S}^2 + \right. \\ \left. + \frac{1}{22} \left(\frac{2J_0}{kT} \right)^3 (1 - \mathcal{S}^2)^2 [(3z - 9)(1 - \mathcal{S}^2)^2 + 2(1 - 3\mathcal{S}^2)^2] + \dots \right\} = \\ = \frac{Nz}{2} 2J_0 A'(T),$$

where z is the coordination number, \mathcal{S} is the relative spontaneous magnetization plotted in fig. 3.

Interpreting (5) with the spin moment $S = 1$ in the classical form we see that $A' = \overline{\cos \varphi}$, which is the mean value of the cosine of the angle between two neighbour spins. Furthermore it is clear from (7) that the product $2J_0 A'(T)$ gives the excess interaction energy per a pair of spins.

On forming one mole of vacancies $\frac{1}{2}Nz$ atom-atom contacts are broken [8]. This means that (7) gives an excess magnetic activation enthalpy of vacancy formation ΔH_F . On forming one mole of activated complexes an excess activation enthalpy of vacancy migration ΔH_M is needed. Let us suppose that the quotient $\Delta H_F / \Delta H_M \doteq \doteq H_{pF} / H_{pM} \doteq H_{fF} / H_{fM}$, where H_{pF} , H_{pM} , H_{fF} , H_{fM} are the activation enthalpies of vacancy formation and migration in a completely paramagnetic or ferromagnetic state, respectively. For the actual enthalpy (2) this assumption gives the equation

$$(8) \quad H(T) = H_p + \Delta H_F + \Delta H_M = H_p + E' \frac{H_{fF} + H_{fM}}{H_{fF}} = H_p + \Delta H'_p(T),$$

where $\Delta H'_p(T)$ is the excess activation enthalpy due to the spin-spin interaction in a ferromagnet. Introducing a substitution $B = 2J_0/k\theta$, we get

$$(9) \quad \Delta H'_p(T) = \frac{H_{fF} + H_{fM}}{H_{fM}} \frac{Nz}{2} k\theta B A'(T).$$

Experimental results ([2] e.g.) show that at and after a paramagnetic temperature T_p the magnetic contribution to the activation enthalpy of diffusion is not measur-

able. This may be respected in such a way that A' in (7) is replaced by

$$(10) \quad A(T) = \mathcal{S}^2 + 0.5B \left[\frac{\Theta}{T} - \frac{\Theta}{T_p} \right] (1 - \mathcal{S}^2)^2 + \frac{2}{3} B^2 \left(\frac{\Theta}{T} \right)^2 \mathcal{S}^2 (1 - \mathcal{S}^2)^2 + \\ + \frac{1}{12} B^3 \left[\left(\frac{\Theta}{T} \right)^3 - \left(\frac{\Theta}{T_p} \right)^3 \right] (1 - \mathcal{S}^2)^2 [(3z - 9)(1 - \mathcal{S}^2)^2 + 2(1 - 3\mathcal{S}^2)^2 + \dots].$$

This transformation which makes $A = 0$ at $\mathcal{S} = 0$ and $T \geq T_p$, relates the calculation of ΔH_p to a certain paramagnetic energy level corresponding to the temperature T_p . The way of introducing the parameter Θ/T_p into (10) has been chosen on the basis of the best fit of the theory to the experimental data. It may be noted that the eq. (10) is a semi-empirical one, in fact. By the use of (10) in the form $A(T) = A'(T) - A'(T_p)$ or with the term $[(\Theta/T)^n - (\Theta/T_p)^n]$ in all the series terms, the fit of the theoretical values to the experimental data was much more less satisfactory in comparison with [10].

3. EXPERIMENTAL DATA ANALYSIS

Very good sets of experimental data describing the influence of magnetic ordering on diffusion in BCC-iron have been published by LAI and BORG [2] and by HETTICH et al. [4]. The data of [2] relate to the temperature interval 700° to 1500 °C in α -Fe, δ -Fe and in the α -stabilized Fe-1.8 at. % V alloy, which may be considered a satisfactory substitute for pure BCC-iron, with respect to homodiffusion in iron. HETTICH's et al. diffusion experiments have been performed at the temperature 511° to 744 °C. Both the data sets complete well in that sense that they yield very close characteristics D_{op} and H_p and, moreover, they represent a rather continuous function of temperature $D(T)$ (see fig. 4) that can be compared with the theory.

With the use of NIHOUL's experimental values [17] for $H_{FF} = 1.5$ eV and $H_{FM} = 1.1$ eV we get from (9) and (10) for the excess activation enthalpy in BCC-iron the equation

$$(11) \quad \Delta H_p(T) = 85.187B A(T) \quad [\text{kJ/mol}].$$

To get the corresponding experimental values of $\Delta H_p(T)$ we write, with respect to the Zener's theory of D_0 [7] (p. 485), the temperature dependence of homodiffusion coefficient in BCC-iron on the form

$$(12) \quad D(T) = D_{op} \exp \left\{ \frac{0.35 \Delta H_p(T)}{RT_m} \right\} \exp \left\{ - \frac{H_p + \Delta H_p(T)}{RT} \right\},$$

where T_m is the melting point of Fe. From eq. (12) the values of $\Delta H_p(T)$ can be calculated if the characteristics D_{op} and H_p are known. For calculating the values of $\Delta H_p(T)$ that are presented in fig. 1, the relations $D_p(T) = 1.39 \exp \{-236.6/RT\}$ [2] and $D_p(T) = 0.99 \exp \{-235.9/RT\}$ [4] were used.

The paramagnetic temperature T_p included in the term $A(T)$ (10) can be estimated from the diffusion measurements only approximately ($T_p \approx 1180$ K, [2]) and the exchange integral (see eq. (9) term B) in α -Fe may be found in the interval $J_0 = 100k \div \div 343k$ [5] (pp. 175, 176). That is why the values of B and Θ/T_p have been calculated as fitting parameters in least squares fitting process of (11) to the experimental values of $\Delta H_p(T)$, see fig. 1. In this computing procedure the OPTIPACK system [18] has been used.

Quite similarly to (11) an equation can be developed on the basis of the Fowler-Guggenheim's quasi-chemical method [16], p. 303. In the case of BCC-iron it reads

$$(13) \quad \Delta H_p(T) = 85 \cdot 187B \left\{ 1 - \frac{2(1 - \mathcal{F}^2)}{1 + \sqrt{\left\{ 1 + (1 - \mathcal{F}^2) \left[-1 + \exp 4B \left(\frac{\Theta}{T} - \frac{\Theta}{T_p} \right) \right] \right\}}} \right\}.$$

The results of least squares fits of (11) and (13) to the various combinations of experimental data [2, 4] are shown in table 1.

Table 1

The values of exchange integral J_0/k , paramagnetic temperature T_p and excess activation enthalpy $\Delta H_p(0)$ in BCC-iron.

J_0/k [K]	T_p [K]	$H_p(0)$ [kJ/mol]	Data	Method
353.8 ± 2.6	1193.0 4.7	57.80 0.43	[2]	Kirkwood's
242.7 6.0	1227 50	55.98 0.99	[4]	
345.3 3.6	1207 15	56.41 0.59	[2, 4]	
446 15	1221 17	72.8 2.5	[2]	Fowler- -Guggenheim's
372 11	1449 98	60.8 1.8	[4]	
390.5 8.3	1301 31	63.8 1.3	[2, 4]	

It is visible in table 1 that the Kirkwood's method results in a better fit and that, moreover, the values of exchange integral J_0 and paramagnetic temperature T_p obtained by this method seem to be more realistic if compared with other authors [5, pp. 174, 175], [2] and [19]. A comparison of the theory (eq. (11)) with experimental data [2, 4] is given in fig. 1.

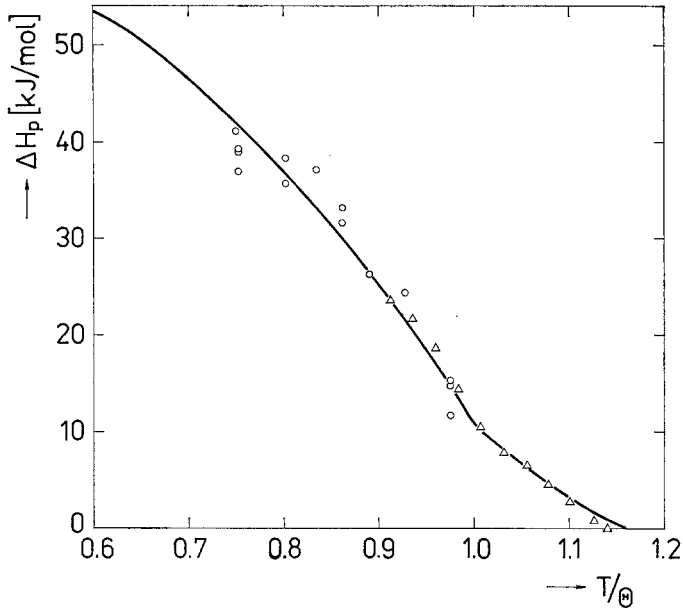


Fig. 1. Variation of excess activation enthalpy $\Delta H_p(T)$ in BCC-iron. θ — Curie ferromagnetic temperature; $\Delta\Delta\Delta$ experimental data [2]; $\circ\circ\circ$ experimental data [4]; ——— present theory.

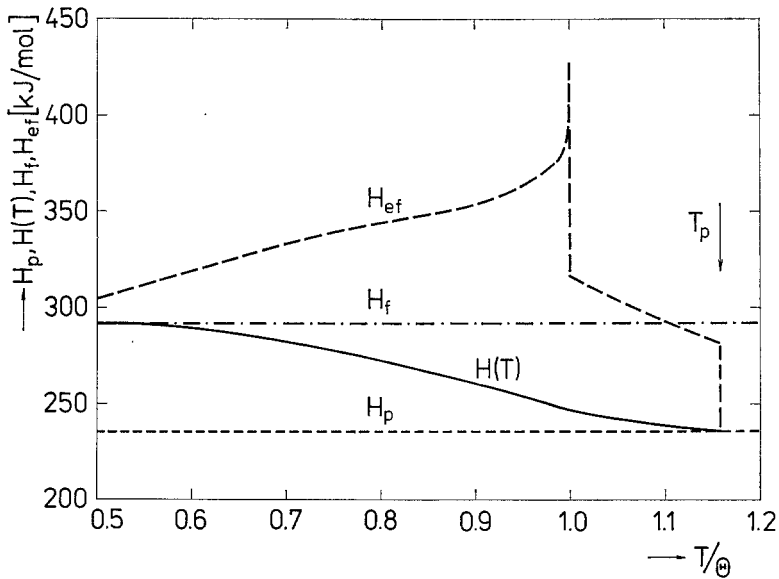


Fig. 2. Variation of activation enthalpy in BCC-iron. — — — — H_p — for completely paramagnetic state, T_p is the paramagnetic temperature; ——— $H(T)$ — actual activation enthalpy; - · - · - H_f — for completely ferromagnetic state; — — — H_{ef} — for effective activation enthalpy.

4. ACTIVATION ENTHALPIES OF HOMODIFFUSION IN BCC-IRON

On the basis of experimental data [2, 4] and their analysis, the activation enthalpies of homodiffusion in BCC-iron can be evaluated. The paramagnetic enthalpy H_p is obtained from the experimental data with the use of the standard Arrhenius plot. The ferromagnetic enthalpy is given as the sum $H_f = H_p + H_p(0)$, the actual one $H(T)$ is given by (2) and (11). The effective activation enthalpy, as measured from the slope of a $\ln D$ vs. $1/T$ plot (see eq. (1)) differs considerably from the actual activation enthalpy. Below the Curie point Θ it is defined (see (12)) by

$$(14) \quad H_{ef} = H_p + \Delta H_p(T) - \frac{T d(\Delta H_p(T))}{\Theta d(T/\Theta)} (1 - 0.35T/T_m).$$

Table 2

The values of activation enthalpies in BCC-iron.

References	[2]	[9] + data [10]	[4]	Present work + data [2, 4]
H_p [kJ/mol]	236.5 ±4.2	281.5	236.4	236.5 4.2
H_f [kJ/mol]	—	312.2	289.6	292.9 4.8

Some values of H_p , H_f are given in tab. 2, the variations of actual and effective enthalpy are presented in fig. 2.

5. COMMENTS ON PARAMETERS OF MAGNETIC ORDER IN BCC-IRON

The long-range order parameter in a magnetic domain containing N atoms may be defined by

$$(15) \quad \mathcal{S} = \frac{N^+ - N^-}{N},$$

where N^+ are the spins oriented to the “north”, N^- to the “south”; $N^+ + N^- = N$. It is possible to show, quite analogically to the Bragg-Williams long-range order theory in alloys [20], that

$$(16) \quad \mathcal{S} = \operatorname{tgh} \left(\frac{\varphi_0 \mathcal{S}}{2kT} \right),$$

where φ_0 is the energy change of the system if one spin changes its orientation from the position + to -. On the other hand it is possible to show (20, pp. 455–468),

that with $S = \frac{1}{2}$ the relative spontaneous magnetization

$$(17) \quad M_{sr} = \operatorname{tgh} \left(\frac{\varphi_0 M_{sr}}{2kT} \right).$$

Furthermore it can be supposed that $M_{sr} \doteq (N^+ - N^-)/N$ [5], p. 173. From this latter relation and from the formal conformity of (16) and (17) it may be concluded that the long-range order parameter \mathcal{S} in ferromagnetics with $S = \frac{1}{2}$ is identical to the relative spontaneous magnetization. For the other spin values it is expedient to introduce the relation $\mathcal{S} = M_{sr}$ per definitione.

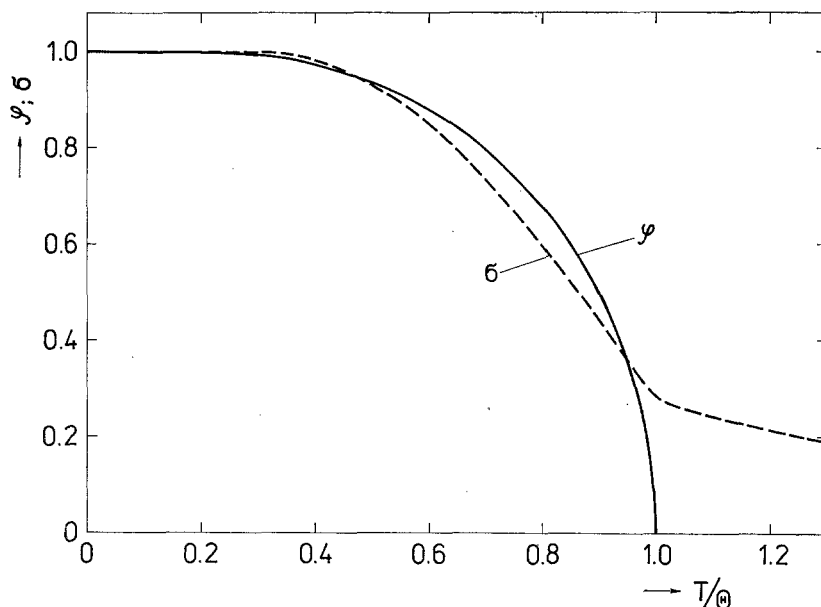


Fig. 3. Long-range order \mathcal{S} and short-range order σ parameters in BCC-iron with $S = 1$ and $J_0 = 205k$. — \mathcal{S} ; - - - σ .

It was shown in eq. (7) that the term $A'(T) = \overline{\cos \varphi}$ can be interpreted as a mean value of the cosine of the angle between two nearest neighbour spins. This quantity may be well used as a characteristic of the short-range order in ferromagnets so that the short-range order parameter in BCC structure is defined by the relation

$$(18) \quad \sigma = \mathcal{S}^2 + 0.5 \frac{2J_0}{kT} (1 - \mathcal{S}^2)^2 + \frac{2}{3} \left(\frac{2J_0}{kT} \right)^2 \mathcal{S}^2 (1 - \mathcal{S}^2)^2 + \\ + \frac{1}{12} \left(\frac{2J_0}{kT} \right)^3 (1 - \mathcal{S}^2)^2 [15(1 - \mathcal{S}^2)^2 + 2(1 - 3\mathcal{S}^2)^2] + \dots$$

The parameter σ is, besides \mathcal{S} and T , a function of J_0 . The variation of σ , together with \mathcal{S} , is given in fig. 3. The values of \mathcal{S} were calculated with $S = 1$, the values of σ with $J_0 = 205k$ [5], p. 174 f. It should be mentioned that this value of J_0 approximately corresponds to the centre of the interval $100k + 343k$ reported for J_0 in [5]. With $J_0 = 345.3k$ (this work) we get at $T \geq \Theta$ (e.g.) the values of about $2 \times$ higher than those given in fig. 3.

SUMMARY

The diffusion data [2, 4] obtained in BCC-iron have been analyzed by using the Heisenberg model and Kirkwood's (or Fowler-Guggenheim's resp.) method of solving the equation of partition function (6). This treatment enabled us to develop an equation (11; 10) for excess activation enthalpy which is induced by the magnetic order in BCC-iron. The optimum fit of the theory to experimental data has been found by means of the Kirkwood's method and with the spin moment $S = 1$ in \mathcal{S} and $\Delta H_p(T)$ calculations. The choice of the mode of introducing the paramagnetic temperature T_p into the relation (10) has been done on the basis of the least squares fit as well. On the basis of the optimization process the values of the exchange integral and paramagnetic temperature T_p have been found. The value $J_0 = (345.3 \pm \pm 3.6)k$ is in a very good agreement with $J_0 = (343 \pm 50)k$, calculated from the experimental value of the exchange energy constant [21]. It must be mentioned that the paramagnetic temperature $T_p = (1207 \pm 15)K$ evaluated in the fitting process is a fictitious one in the case of pure iron, however, it has a real sense in α -Fe stabilized by a small amount of V, or other elements, respectively. Its value agrees well with the temperature $T_p \doteq 1180K$ found in paper [2]. Furthermore, it is worth noticing that the deviation of reciprocal of the susceptibility in a Fe-2.5 at. % V alloy from the Curie-Weiss law can be observed at about 1200 K [19].

The actual and effective enthalpies have been calculated from eqs. (8), (9), (10), (11) and (14). The results are presented in fig. 2. The variation of H_{ef} displays, as expected, a sharp maximum at the Curie point due to the fact that $d\mathcal{S}/dT \rightarrow \infty$ at this temperature. The discontinuity at the temperature $T/\Theta = 1.157$ is caused by the fact that $\Delta H_p = 0$ at all the temperatures $T \geq T_p$.

A more detailed investigation of the short-range order parameter defined by (18) shows that it possesses a local maximum in the temperature interval $0 \div 0.5T/\Theta$. The amplitude of this maximum increases with the increasing value of J_0 (see eq. (18)). The position of this maximum in the mentioned temperature interval depends on the value of J_0 as well. In the given case with $J_0 = 205k$ the maximum of σ occurs at the temperature $(T/\Theta)_m = 0.25$ and its amplitude is $a_m = 100.3\%$ of $\sigma(0)$. With the value of $J_0 = 345.3k$ (present work) it can be shown that $(T/\Theta)_m = 0.40$ and $a_m = 104.7\%$ of $\sigma(0)$. From this analysis and from the fig. 2 it is clear that the activation enthalpy values calculated from $\log D$ vs. $1/T$ plots in BCC-iron do not corres-

pond to the actual activation enthalpies unless data below $T = 0.5\Theta$ or above $T = 1.16\Theta$ are available. In particular, if the data in a ferromagnetic state above 0.5Θ are available, it may be recommended to treat them in a procedure given in [4, 9] or in this paper, resp.

Comparing experimental values $D(T)$ [2, 4] to the present theory it has been found that the homodiffusion in α and δ -Fe can be described by the equation

$$(19) \quad D = 1.77 \exp \{0.0233 \Delta H_p(T)\} \exp \left\{ -\frac{236.5 + \Delta H_p(T)}{RT} \right\} [\text{cm}^2/\text{s}, \text{kJ/mol}].$$

From this relation we get for the completely paramagnetic state

$$(20) \quad D_p = \sqrt{(D_{p1} D_{p2})} = 1.77 \exp \left\{ -\frac{236.5}{RT} \right\},$$

where D_{p1} is given by [2] and D_{p2} by [4].

In a completely ferromagnetic state ($\Delta H_p(0) = 56.41 \text{ kJ/mol}$) the equation

$$(21) \quad D_f = 6.59 \exp \left\{ -\frac{292.9}{RT} \right\}$$

is valid. The coincidence of the experimental data $D(T)$ with the calculated values from eq. (19) is displayed in fig. 4.

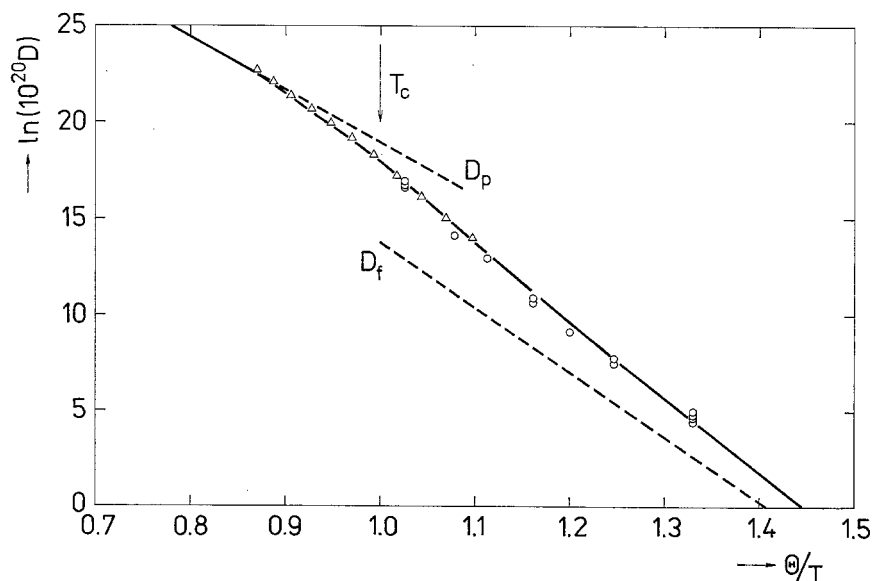


Fig. 4. Arrhenius plot of homodiffusion in para- and ferromagnetic α -Fe. $\Delta\Delta\Delta$ experimental data [2]; $\circ\circ\circ$ experimental data [4]; ——— present theory.

Added in proof:

In calculating the numerical constant in eq. (11) the BEN-ABRAHAM'S [25] value of $\bar{\varepsilon} = H_{FM}/H_{FF} = 0.61$, which is valid for any BCC metal, may be used. This results in

$$(11a) \quad \Delta H_p(T) = 91.375 \times B \times A(T) \quad [\text{kJ/mol}] .$$

Relation (10) used in the present paper and giving the value of $A(T)$ is exactly valid for a simple cubic or square lattice [16]. This fact is respected by the term $(3z - 9)$ in the 4th member of the series (10). The extension of (10) to BCC lattice may be executed with the use of KRIVOGLAZ and SMIRNOV results [26] by replacing the term $(3z - 9)$ by $3(y_1 - z)/z$, $y_1 = 96$ ([26], p. 157). Respecting this substitution and eq. (11a) we get from the least squares fit:

$$J_0 = k(315.4 \pm 2.9), \quad T_p = (1169 \pm 9) \text{ K}, \quad \Delta H_p(0) = (55.19 \pm 0.62) \text{ kJ/mol}$$

and

$$H_t = (291.7 \pm 4.8) \text{ kJ/mol} .$$

It may be concluded from these results that the respective activation energies agree in the frame of standard deviations with the previous ones. The most influenced parameter is the exchange integral J_0 , the value of which is decreased by cca 9%.

The author wishes to express his thanks to RNDr. K. OBRTLÍK (ÚFM ČSAV Brno) for information concerning the applicability of [26] results in the present work.

Received 24. 8. 1978.

References

- [1] BOZORTH R. M., *Ferromagnetism*, V. Nostrand C., Princeton (New Jersey) 1951.
- [2] LAI D. Y. F., BORG R. J., *Trans. AIME* 233 (1965), 1975.
- [3] IMMARIGEON J. P. A., JONAS J. J., *The Deformation of Armco Iron and Silicon Steel in the Vicinity of the Curie Temperature*, McGill U., Montreal 1973.
- [4] HETTICH G., MEHRER H., MAIER K., *Scripta Met.* 11 (1977), 795.
- [5] KNELLER E., *Ferromagnetismus*, Springer Ver., Berlin 1962.
- [6] KUSSMANN A., SCHULZE A., *Phys. Z. S* 38 (1937), 42; acc. to [5].
- [7] ADDA Y., PHILIBERT J., *La diffusion dans les solides*, P.U.F. (1966), p. 552.
- [8] GIRIFALCO L. A., *J. Phys. Chem. Solids* 23 (1962), 1171.
- [9] LEE RUCH et al., *J. Phys. Chem. Solids* 37 (1976), 649.
- [10] BORG R. J., BIRCHENALL C. E., *Trans. AIME* 218 (1960), 980.
- [11] BRAGG W. L., WILLIAMS E. J., *Proc. Roy. Soc. (London) A* 145 (1934), 699.
- [12] MIRANI H. V. M. et al., *Phys. Stat. Sol. (a)* 29 (1975), 115.
- [13] BUFFINGTON F. S. et al., *Acta Met.* 9 (1961), 434.
- [14] WALTER C. M., PETERSON N. L., *Phys. Rev.* 178 (1968), 922.
- [15] KITTEL CH., *Introduction to the Solid State Physics (IV. ed.)*, J. Wiley and Sons Inc., New York 1971, p. 532.

- [16] EYRING H. et al., *Statistical Mechanics and Dynamics*, J. Wiley and Sons Inc., New York 1964, p. 308.
- [17] SEGER Y. et al. (eds.), *Vacancies and Interstitials in Metals*, Proc. Int. Conf. Jülich, September 1968, p. 865, North-Holland P. C., Amsterdam 1970.
- [18] KUČERA JAN et al., OPTIPACK-Research Report VZ 314/411, ÚFM ČSAV Brno 1976.
- [19] BERKOWITZ A. E., KNELLER E. (eds.), *Magnetism and Metallurgy*, Vol. 1, A. P., New York—London 1969, p. 297.
- [20] DEKKER A. J., *Solid State Physics*, P. - H. Inc. (1959), p. 111.
- [21] RADO G. T., WEERTMANN J. K., *J. Phys. Chem. Solids* *11* (1959), 315.
- [22] KIRKWOOD J., *J. Chem. Phys.* *6* (1938), 70; acc. to [16].
- [23] GUGGENHEIM E. A., *Mixtures*, Oxford C. P. 1952.
- [24] TER HAAR D., *Elements of Statistical Mechanics*, Rinehart, New York 1954, p. 274; acc. to [16].
- [25] BEN-ABRAHAM S. I., RABINOVITCH A., PELLEG J., *Phys. stat. sol. (b)* *84* (1977), 435.
- [26] KRIVOGLAZ M. A., SMIRNOV A. A., *Těorija uporjadočivajuščichsja splavov*, Iz. fiz. mat. lit., Moskva 1958, p. 153.