Thermal properties of iron in solid solutions of silicon in iron near the Curie point

V. E. Zinov'ev, Sh. Sh. Abel'skii, M. I. Sandakova, E. G. Dik, L. N. Petrova, and P. V. Gel'd

Ural Polytechnic Institute

(Submitted July 20, 1973)
Zh. Eksp. Teor. Fiz. **66**, 354–360 (January 1974)

We investigated the diffusivity and specific heat of pure iron, and also of solid solutions of silicon in iron in the range 900–1500°K. We found that the diffusivity of iron at $-2.5 \leq \log|(T-T_c)/T_c| \leqslant -1$ is characterized by the critical exponents $\gamma(T>T_c)=0.17 \pm 0.04$ and $\gamma(T<T_c)=0.16 \pm 0.04$, while the thermal conductivity has a minimum in the region of T_c. It is established that the increase of the silicon impurity concentration in the iron leads to a certain growth of the total thermal conductivity and to a change in the character of its anomaly near T_c. It is shown within the framework of the model of disordered spins that the electronic component of the thermal conductivity above $T/T_c = 0.7$ can be calculated in accordance with the Wiedemann–Franz law, but at low temperature it is necessary to take into account the change in the Lorentz number.

1. At the present time, the question of the character of the behavior of the temperature conductivity and thermal conductivity of substances at critical points remains open [1]. This question is also unclear for a classical ferromagnet as iron, in spite of the fact that the investigation of its thermal properties has been the subject of many studies (see, e.g., [2-10]). Nor has the influence of impurities on these properties been investigated. In this connection, a study was made of the influence of silicon on the thermal properties of its alloys with iron, silicon being convenient because it increases the resistance sharply, at least at low temperatures, but produces hardly any change in the lattice parameters and does not introduce an additional magnetic moment into the matrix at low concentrations.

Comprehensive investigations of the thermal diffusivity, of the heat capacity, and of the resistivity$^{1)}$ were carried out using pure iron from the Johnson and Matthay firm ($\rho(298°K)/\rho(4.2°K) = 128$) and its alloys with silicon containing 0.80, 1.77, 3.00, 5.79, 11.15, 18.11, and 25 at.%. The alloy preparation procedure was described earlier [10]. The samples for the investigations of the diffusivity and the heat capacity were plane-parallel plates ~0.2 mm thick with area ~8×8 mm.

The diffusivity a was investigated by the method of plane temperature waves [11], improved by using a more sensitive infrared photoreceiver, a low-noise preamplifier, and a phase detector [12]. In addition, measurements of the temperature wave amplitude oscillations (simultaneously with the phase shift) have made it possible to determine the heat capacity C_p of the same sample by the method described in [13]. The measurements were performed in a vacuum of 1×10^{-6} mm Hg at 32 Hz for the heat capacity and 168.8 Hz for the diffusivity. The adopted measures have made it possible to attain a resolution of 0.2% in the diffusivity measurements at a total error of 2.5–3% and a resolution 1% in the measurements of the specific heat at 3.5% error.

2. The results of the investigations of the diffusivity of pure iron (with allowance for the small correction for the thermal expansion) are shown in Fig. 1. We see that the character of the anomaly of a(T) near T_c is a mirror reflection of the anomaly of $C_p(t)$ (see, e.g., [14]), the latter being connected with the splitting of the maximum and of the discontinuity of C_p. The figure shows also the dependence of log a on log ϵ ($\epsilon = (T-T_c)/T_c$), under the assumption that T_c corresponds to the minimum of a(T). In the range $(-3 \text{ to } -2.5) \leq \log|\epsilon| \leq -1$, it can be represented in the form $a(T) = \Lambda|\epsilon|^{\gamma}$, where $\gamma = 0.16$ at $T < T_c$ and $\gamma = 0.17$ at $T > T_c$, with Λ = const. The error in the determination of γ, due to the scatter of the points and the uncertainty in the regular part of a, is approximately 20–30%. We note that the obtained exponents differ greatly from the value 0.53 observed for a number of liquids [1].

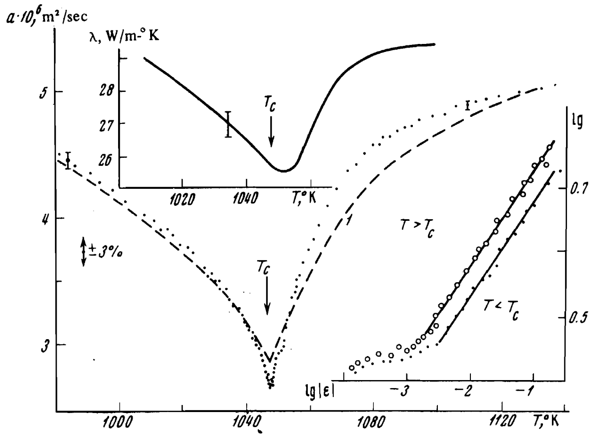

FIG. 1. Temperature diffusivity a and thermal conductivity λ of iron in the region of the Curie point. Curve 1—data of [8].

Figure 2 shows the results of investigations of the diffusivity of Fe-Si alloys. The main feature of the obtained data is the fact that the values of a in the region of T_c constitute an extremal function of the concentration of Si—there is a strong increase of a up to 5 at.%, which gives way to a gently sloping decrease, with the area above the minima decreasing [9]. We note that the a(T) curves reflect also the α-β transitions and the superstructure orderings, which conform approximately, just as the Curie points, to the phase diagram [15]. In addition, it is seen from Fig. 2 that above 1400°K and below 1000°K the value of a remains practically constant at low silicon concentrations (<3%) and decreases monotonically only at high silicon contents.

Figure 3 shows the results of investigations of the specific heat (C_p) of pure iron, and also of the alloys Fe + 0.80 and Fe + 1.77 at.% Si. The figure shows also the published data [6,7,16,17]. The results confirm the tendency towards decreasing C_p at maximum, and also of the area under the $C_p(T)$ curves with increasing silicon content. The figure shows also plots of $C_p(T)$ in a semilogarithmic scale, from which it follows that

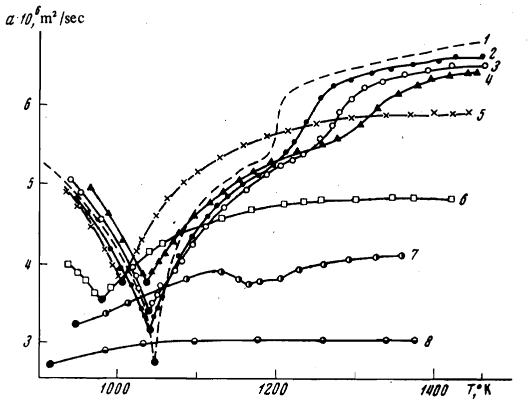

FIG. 2. Diffusivity of solid solutions of Si in Fe at high temperatures. Curves 1–8—values for Fe alloys with 0.0, 0.80, 1.77, 3.00, 5.79, 11.15, 18.11, and 25.0 at.% Si, respectively. The dark large symbols distinguish the diffusivity values at the minimum.

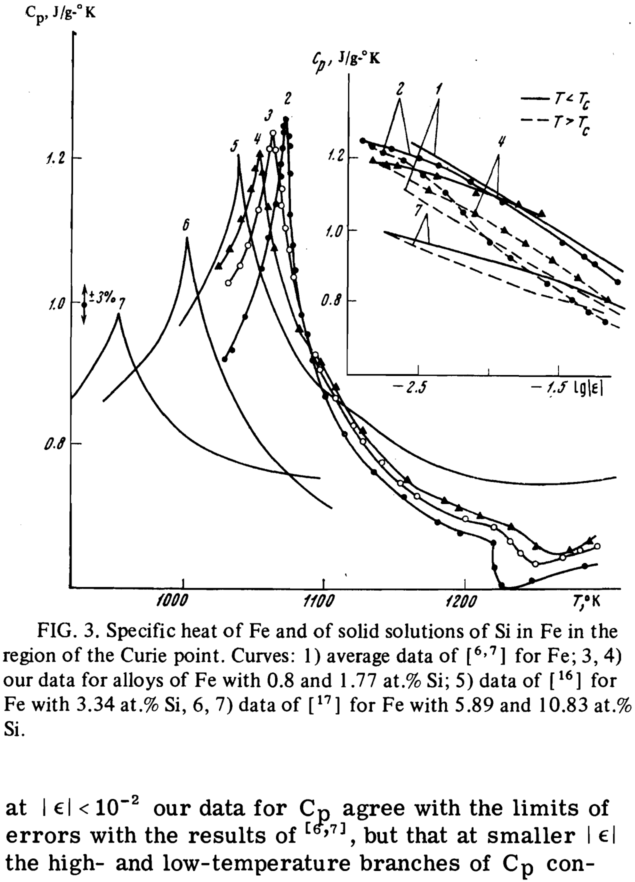

FIG. 3. Specific heat of Fe and of solid solutions of Si in Fe in the region of the Curie point. Curves: 1) average data of [6,7] for Fe; 3, 4) our data for alloys of Fe with 0.8 and 1.77 at.% Si; 5) data of [16] for Fe with 3.34 at.% Si, 6, 7) data of [17] for Fe with 5.89 and 10.83 at.% Si.

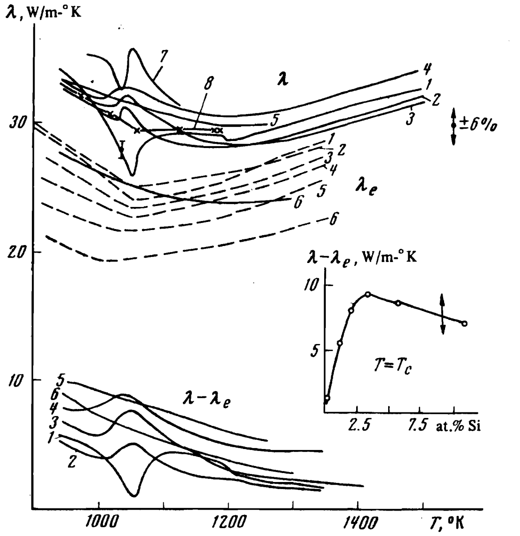

FIG. 4. Total thermal conductivity λ, its electronic component λ_e, and its "lattice" component $\lambda-\lambda_e$ in solid solutions of Si and Fe at high temperatures. Curves 1–6) Fe and 0.0, 0.80, 1.77, 3.00, 5.79, and 11.15 at.% Si, respectively; 7) data of [5]; 8) data of [2]. The insert shows $\lambda-\lambda_e$ at $T = T_c$ as a function of the silicon content.

at $|\epsilon| < 10^{-2}$ our data for C_p agree with the limits of errors with the results of [6,7], but that at smaller $|\epsilon|$ the high- and low-temperature branches of C_p converge. Our data are then described more readily by a power-law relation of the type $C_p = A|\epsilon|^{-\alpha} + B$, with $\alpha = \alpha' = 0.08$ with an error of 50–80%. Comparison of Figs. 2 and 3 shows that the specific heat depends much less on the impurity content than the diffusivity.

3. Using the data obtained for the diffusivity and the specific heat, and also for the density [15], we calculated the thermal conductivity λ of iron and of solid solutions of silicon in iron. The results are shown in Fig. 4, from which it is seen that the function λ(T) has in the region of T_c a well pronounced minimum for pure iron, shown in detail in Fig. 1. We note that the depth of this minimum greatly exceeds the total error in the determination of λ. It follows also from this figure that the addition of up to 3 at.% Si leads near T_c to an increase of the total thermal conductivity and to a change in the anomaly, namely, a maximum appears alongside the minimum. In this case λ changes little at the ends of the temperature interval, and its decrease begins only starting with 6 at.% Si. The same figure shows the data of [2,5], with the data of [5] having an anomaly of the same type, but even more strongly pronounced, as well as data on iron with silicon impurities.

4. To explain the nature of the described anomalies it is necessary to distinguish between the contributions made to the thermal conductivity and to separate from the total thermal conductivity the electronic component λ_e of the thermal conductivity. According to [18], λ_e can be represented in the form

$$\lambda_e = k_B^2 T (L_{11}L_{00} - L_{10}L_{01})/L_{00}, \tag{1}$$

where

$$L_{ij} = L_{ij}^{+} + L_{ij}^{-}, \quad L_{ij}^{\pm} = \frac{1}{6\pi^2 m}\int_{-\infty}^{\infty} k_{\pm}^{3}\tau_{\pm}\varepsilon_{\pm}^{i+j} f_1(\varepsilon_{\pm})\,d\varepsilon_{\pm},$$
$$j_1(\varepsilon) = e^{\varepsilon}/(e^{\varepsilon}+1)^2, \quad \varepsilon_{\pm} = (\varepsilon_{k\pm} - \varepsilon_F)/k_B T, \tag{2}$$

e and m are the charge and mass of the electron, $\epsilon_{k\pm}$ is the energy of electrons with quasimomentum k and with spin directed parallel and antiparallel to the magnetization, ϵ_F is the Fermi energy, k_B is the Boltzmann constant, and $\tau_{\pm}$ is the relaxation time. Unlike in [18], where only the mechanism of the scattering of electrons by spin inhomogeneities is taken into account, let us consider the thermal conductivity in the presence of two other scattering mechanisms, phonon and impurity. In addition, it is possible to calculate more accurately the integrals (2) without some of the simplifications used in [18]. Similar calculations of the electric conductivity [10], with account taken of the essentially inelastic character of the spin scattering mechanism, have led to a noticeable deviation from the Matthiessen rule at $T < T_c$.

Calculating the integrals of (2) 2), we obtain for the Lorentz number the expression

$$L = L_0\left(1 + \frac{I_1}{I_0}\right), \quad L_0 = \frac{\pi^2}{3}\frac{k_B^2}{e^2},$$
$$I_1 = \frac{1}{\pi^2}\frac{(a_\mu - e^{-x})\ln^3 a_\mu}{(a_\mu - 1)^2}, \quad I_0 = \frac{e^{-x}-1}{a_\mu - 1} + \frac{(a_\mu - e^{-x})\ln a_\mu}{(a_\mu - 1)^2}, \tag{3}$$

where L_0 is the standard Lorentz number, $x = H_0/k_BT$, $H = sg\mu_BH_e$, s is the spin (which we assumed to be 1/2), g is the Landé factor, μ_B is the Bohr magneton, and H_e is the Weiss molecular field. The expression for the function a_μ (μ is the relative magnetization) is given in [10]. We note that formula (3) is valid only within the framework of the molecular-field theory at $T > T_D$ (T_D is the Debye temperature). We note in addition that $a_\mu(-x) = 1/a_\mu(x)$, thereby ensuring satisfaction of the Onsager relations.

The estimates of L by means of formula (3), using the necessary data (in analogy with [10]), show that the Wiedemann-Franz law is satisfied at $T \geq T_C$, i.e., $L = L_0$. In the ferromagnetic region on the other hand, a deviation from this law appears, with $|L-L_0|/L_0| = \Delta L$ increasing monotonically with decreasing temperature reaching 12% for pure iron at $T/T_C = 0.3$. It is clear therefore that the separation of the electronic and lattice thermal conductivities on the basis of the standard Wiedemann-Franz law (see, e.g., [2]), may be one of the causes of the incorrect physical results. In view of the results, it becomes likewise unnecessary to use the unjustified methods of separating λ_e [20].

Allowance for the impurity scattering does not lead to a noticeable change of L near and above T_C, and since ρ changes weakly in this case with changing composition [10], the small dependence of λ on the Si content becomes understandable (see Fig. 4). Calculation shows that when the temperature is lowered the deviation ΔL becomes smaller than for pure iron.

We note also that the thermal-conductivity anomaly connected with the critical scattering of electrons by short-range spin fluctuations appears to have the same character as the corresponding anomalies in the electric conductivity [3)], and that the observed minimum of $\lambda(T)$ cannot be due to this scattering. It is possibly due to strong phonon-electron scattering near T_C, as indicated by the growth of $\lambda - \lambda_e$ following introduction of impurities (see Fig. 4) that attenuate this scattering. In addition, it is not excluded that the character of the anomaly of $\lambda(T)$ is influenced by the conditions under which the experiment is performed, inasmuch as the obtained values were measured at relatively high frequencies, i.e., under nonstationary conditions.

We note in conclusion that in view of the distinct relation between the electron and phonon scattering mechanisms in iron, which leads to a damping of one of the mechanisms by the other, the introduction of impurities does not affect the kinetic properties in not-too-accurate experiments on either the electric conductivity [10] or the thermal conductivity. This leads to a fact that seems paradoxical to us, namely, Armco iron of rather indefinite composition is successfully used by a number of investigators (see [2-4]) as a thermal-conductivity standard.

[1)] The data on the resistivity were reported earlier [10].

[2)] The integrals have been calculated in [19].

[3)] This has been demonstrated in [21] for antiferromagnetic metals.

[1] E. H. Stanley, Introduction to Phase Transitions and Critical Phenomena, Oxford, 1971.

[2] W. Fulkerson, J. R. Moore, and O. L. McElroy, J. Appl. Phys. 37, 2639 (1968).

[3] B. N. Oleĭnik, Teplofiz. Vys. Temp. 2, 109 (1964).

[4] H. R. Shanks, A. H. Klein, and G. C. Danielson, J. Appl. Phys. 38, 2885 (1967).

[5] F. Richter, R. Kohlhaas, Arch. Eisenhüttenwes. 36, 827 (1965).

[6] M. Braun and R. Kohlhaas, Phys. Stat. Sol. 12, 429 (1965).

[7] Ya. A. Kraftmakher and T. Yu. Romashina, Fiz. Tverd. Tela 7, 2532 (1965) [Sov. Phys.-Solid State 7, 2040 (1966)].

[8] V. E. Zinov'ev, R. P. Krentsis, and P. V. Gel'd, Fiz. Met. Metalloved. 26, 743 (1968).

[9] R. P. Krentsis, V. E. Zinov'ev, L. P. Andreeva, and P. V. Gel'd, Fiz. Met. Metalloved. 29, 118 (1970).

[10] V. E. Zinov'ev, Sh. Sh. Abel'skii, M. I. Sandakova, L. N. Petrova, and P. V. Gel'd, Zh. Eksp. Teor. Fiz. 63, 2221 (1972) [Sov. Phys.-JETP 36, 1174 (1973)].

[11] V. E. Zinov'ev, R. P. Krentsis, and P. V. Tel'd, Teplofiz. Vys. Temp. 6, 927 (1968).

[12] L. P. Gel'd and V. E. Zinov'ev, Teplofiz. Vys. Temp. 10, 656 (1972).

[13] V. E. Zinov'ev, I. G. Korshunov, and P. V. Gel'd, Fiz. Tverd. Tela 13, 3459 (1971) [Sov. Phys.-Solid State 13, 2924 (1972)].

[14] M. A. Mikulinskiĭ, Usp. Fiz. Nauk 110, 213 (1973) [Sov. Phys.-Usp. 16, 361 (1973)].

[15] P. V. Gel'd and F. A. Sidorenko, Silitsidy perekhodnykh metallov chetvertogo perioda (Silicides of Group IV Transition Metals), Metallurgizdat, 1971.

[16] U. Gonska, W. Kierspe, and R. Kohlhaas, Zs. für Naturforsch. 23a, 783 (1968).

[17] W. Pepperhoff and H. H. Ettwig. Zs. Angew. Phys. 22, 496 (1967).

[18] T. Kasuya, Progr. Theor. Phys. 22, 227 (1959).

[19] Sh. Sh. Abel'skiĭ and Yu. P. Irkhin, Fiz. Tverd. Tela 13, 241 (1971) [Sov. Phys.-Solid State 13, 189 (1971)].

[20] M. G. Bäcklund, J. Phys. Chem. Sol. 20, 1 (1961).

[21] Y. Suezaki and H. Mori, Progr. Theor. Phys. 41, 1177 (1969).

Translated by J. G. Adashko
36