MATTHIESSEN RULE AND HIGH-TEMPERATURE ELECTRICAL RESISTIVITY OF SOLID SOLUTIONS OF SILICON IN IRON

V. E. ZINOV'EV, Sh. Sh. ABEL'SKIĬ, M. I. SANDAKOVA, L. N. PETROVA and P. V. GEL'D

Urals Polytechnic Institute

The results are given of an investigation of the electrical resistivity of pure iron and of solid solutions of silicon in iron in the temperature range 300–1300° K. A theoretical calculation is made of the resistivity on the basis of the disordered spin model. It is shown that, in this case, the Matthiessen rule is not obeyed and the usual division of the scattering mechanisms is incorrect. The results of the calculation are in good agreement with the experimentally obtained temperature and concentration dependences.

ALTHOUGH the electrical resistivity of iron and solid solutions based on it have been investigated by many workers,[1-5] the influence of impurities has not been studied sufficiently and the question of the contributions of various electron scattering mechanisms at high temperatures still remains open. Usually, the anomalous behavior of the resistivity of ferromagnets[2-5] is treated either on the basis of the Mott s-d model[6] or on the basis of the disordered spin model.[7,8] The contributions of the various scattering mechanisms are usually described by the Matthiessen rule:

$$\rho = \rho_i + \rho_{ph} + \rho_s, \tag{1}$$

where ρ_i, ρ_{ph}, and ρ_s are, respectively, the impurity (residual), phonon, and magnetic components of the resistivity. However, the scattering of electrons is a complex process and one mechanism can affect the others so that their contributions may not be additive.

We obtained information on the behavior of the electrical resistivity under the influence of changes in the temperature and composition by recording the temperature dependences (300–1300° K) of the resistivity of pure iron and of solid solutions of silicon in iron containing 0.80, 1.77, 3.00, and 5.79 at.% Si. These particular solutions were investigated because silicon did not contribute an additional magnetic moment to the iron matrix but increased very considerably the resistivity without altering significantly the lattice parameters.

Our sample of well-annealed iron (average grain size about 2 mm) was supplied by the firm of Johnson Matthey. It contained less than 0.03 wt.% of impurities and the ratio of the resistance at 298° K to the residual value was 128. The solid solutions were prepared from iron of the V-3 grade (containing about 0.01% of impurities) and silicon single crystals (>99.999% Si). A mixture of ground components was first formed into briquettes and then sintered in a hydrogen atmosphere. It was finally fused in an induction vacuum furnace. Chemical and spectroscopic analyses indicated that the total concentration of impurities in our solid solutions did not exceed 0.025%. Forged ingots were cut into samples of about 4 mm² cross section and 30 mm long. These samples were annealed in vacuum for 5 h at

1400° K and then slowly cooled with the furnace to room temperature. The electrical resistivity was measured in vacuum (~ 10^{-5} mm Hg) under quasistatic conditions. The rate of heating did not exceed 1 deg/min and the resistivity was determined by the standard potentiometric method with the aid of thin welded potential contacts. The error in the determination of the resistivity was about 0.5% due to the geometrical factors and about 0.1% due to all the other factors. The temperature was determined to within 0.3%.

The temperature dependences of the resistivity of pure iron and solid solutions of silicon in iron are plotted in Fig. 1. The same figure includes the data[1] for pure iron supplied by Johnson Matthey, which are in good agreement with our results. Examination of Fig. 1 shows that the polytherm of the solution containing 0.80% Si intersects near T_c the polytherm of pure iron and above T_c the resistivity of this solution is considerably less than that of the pure metal. Moreover, we can
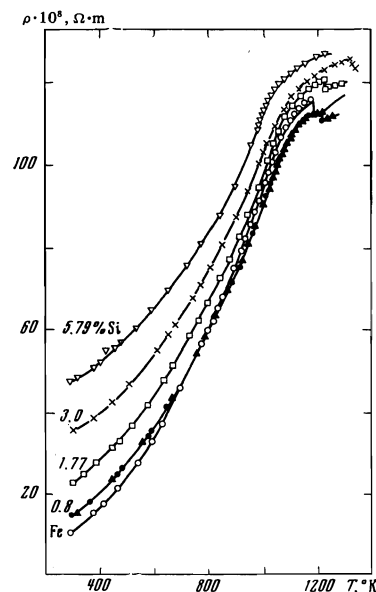

FIG. 1. Temperature dependences of the electrical resistivity of pure iron and of solid solutions of silicon in iron. The curve for the solution with 0.80% Si represents the data obtained for two samples.

see that the difference between the resistivity of the solution and that of pure iron decreases considerably with increasing temperature. This observation shows clearly that the Mott s-d model[6] is inapplicable to our results (according to this model the additional resistivity can only increase with temperature[2,3]). It is pointed out in[2,3] that the disordered spin model describes quite satisfactorily the behavior of the resistivity of ferromagnets.

This model was developed by Kasuya[7] and by de Gennes and Friedel,[8] but they did not establish the explicit form of the temperature dependence $\rho(T)$ and they ignored the influence of the impurities as well as the fact that the relaxation time $\tau_{s\pm}$ relating to the scattering of the carriers by spin inhomogeneities is a power function of the carrier energy. Bearing in mind these points, the Kasuya formula[7] for the resistivity, obtained in the molecular field approximation, can be written in the form

$$\frac{1}{\rho} = \frac{e^2}{6\pi^2 m} \left[\int_{-\infty}^{+\infty} k^3 \tau_+ f_1(\varepsilon) \, d\varepsilon + \int_{-\infty}^{+\infty} k^3 \tau_- f_1(\varepsilon) \, d\varepsilon \right]. \qquad (2)$$

Here,

$$f_1(\varepsilon) = e^{\varepsilon}/(e^{\varepsilon}+1)^2, \qquad \varepsilon_\pm = \frac{\varepsilon_{k\pm} - \varepsilon_F}{k_B T},$$

$$\frac{1}{\tau_\pm} = \frac{1}{\tau_i} + \frac{1}{\tau_{ph}} + \frac{1}{\tau_{s\,c}} = C_i + C_{ph} + C_s \left[W + V_\pm \frac{e^{\varepsilon}_\pm + 1}{e^{\varepsilon}_\pm{}^{\pm x} + 1} \right],$$

$$W = \overline{\sigma}^2 - \bar{\sigma}^2, \qquad V_\pm = \overline{(s \pm \sigma)(s \mp \sigma + 1)},$$

$$x = \frac{H_0}{k_B T} = \frac{3s}{s+1} \frac{T_c}{T} \mu; \qquad (3)$$

e and m are the charge and mass of an electron; $\varepsilon_{k\pm}$ is the energy of electrons with a quasimomentum k and a spin directed parallel and antiparallel to the magnetization; ε_F is the Fermi energy; τ_i and τ_{ph} are the relaxation times for the scattering by impurities and phonons; C_i, C_{ph}, and C_s are the power functions of the electron energy; $\bar{\sigma} = \mu s$ is the average value of the projection of a spin s at a site; μ is the relative magnetization; k_B is the Boltzmann constant; H_0 is the molecular field.

Using all these relationships and performing the standard calculations, we obtain the following expression for the resistivity at $T \le T_c$:

$$\rho = \left[\rho_i + \rho_{ph} + \rho_s \left(1 - \frac{s\mu + 1}{s+1} \mu \right) \right] F_1 \bigg/ \left(1 - F_2 \frac{\ln a}{a-1} \right); \qquad (4)$$

$$F_1 = [1 + \gamma_{ph} T + \gamma_s s^2 (1 - \mu^2)] F^{-1},$$
$$F_2 = \gamma_s s (1 - \mu) F^{-1},$$
$$F = 1 + \gamma_{ph} T + \gamma_s [s^2 (1 - \mu^2) + s(1 - \mu)];$$
$$\gamma_{ph} = \frac{\rho_{ph}(T_c)}{\rho_i(T_c)}, \qquad \gamma_s = \frac{\rho_s(T_c)}{\rho_i s(s+1)}, \qquad a = F e^{-x} + F_2. \qquad (5)$$

Thus, in order to include the various contributions to the electrical resistivity at $T \le T_c$ we must use an expression which differs considerably from the Matthiessen rule. We note that Eq. (4) reduces to Eq. (1) at $T > T_c$ if $\mu = 0$ but $\rho_s(T < T_c) > \rho_s(T > T_c)$. It follows from Eqs. (4) and (5) that the electron scattering mechanisms are interrelated both in pure ferromagnets and in ferromagnets with impurities so that the mutual influence of these mechanisms cannot be ignored. This is why near T_c the resistivity of an alloy differs little

from the resistivity of a pure metal: the introduction of impurities not only affects strongly the magnetic component which is due to the scattering of electrons by disordered spins but also reduces it somewhat due to screening. The damping effect of these two mechanisms is responsible for some fall in the total resistivity of the Fe + 0.80% Si solution compared with pure iron.

The possibility of a correlation between the temperature dependences of ρ, ΔH, $\partial\rho/\partial T$, and C_p has been pointed out in[3,9,10]. In view of this, we investigated the temperature dependence of the enthalpy of the Fe + 0.80% Si solution by the method of mixtures in a calorimeter[11] (the error was 0.8% between 600 and 700°K). We found that, within the limits of the experimental error, our results agreed with the tabulated standard values of the enthalpy of pure iron,[12] which indicated that the electrical resistivity and magnetic energy were correlated.

Figure 2 shows the polytherms of the derivative of the electrical resistivity with respect to temperature, plotted for pure iron and its solutions on the basis of the results given in Fig. 1. Within the estimated 10% error the temperature coefficient of pure iron is in agreement with the results of Kraftmakher and Romashina.[13] It is clearly evident from Fig. 2 that the amplitudes of the maxima and the areas under them decrease rapidly with increasing concentration of silicon in the solid solution. Similar behavior was also observed in studies of the specific heat[14] so that the analogy between $\partial\rho/\partial T$ and C_p is quite justified. It follows from the results in Fig. 2 that above 1200°K the values of $\partial\rho/\partial T$ are approximately equal for all the solutions, which shows that the influence of impurities affects ρ_s more strongly than it does ρ_{ph}.

If we use the results plotted in Figs. 1 and 2 and the published data[10] on the relative spontaneous magnetization (assuming that it is a universal function of T/T_c for all our solutions) and assume that s = 1/2 for iron, we can calculate the temperature dependences of the electrical resistivity of iron and its solutions with the aid of Eq. (4). Figure 3 shows the results of such calculations of the contribution due to the impurities ($\Delta\rho = \rho_{sol} - \rho_{Fe}$), which is usually identified with the impurity resistivity if the Matthiessen rule is valid.[2-5] However, it follows from Fig. 3 that the influence of
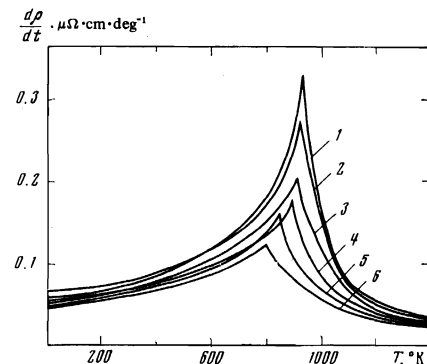

FIG. 2. Polytherms of the temperature coefficients of the electrical resistivity of iron and of solid solutions of silicon in iron. Curves 1-6 represent the results obtained for solid solutions with 0.0, 0.80, 1.77, 3.00, 5.79, and 7.20 at.% Si.
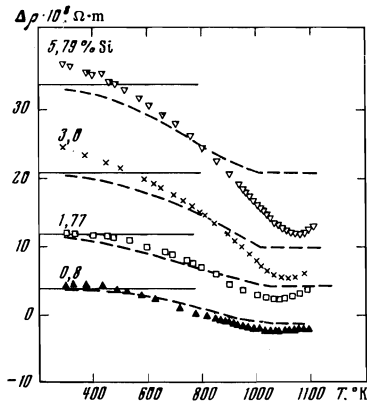
FIG. 3. Temperature dependences of the difference between the electrical resistivity of a solid solution and that of pure iron. The dashed curves are the results of calculations based on Eq. (4); the continuous horixontal lines represent the residual resistance of the solid solutions (extrapolated using the data given in [5]).

other mechanisms on the value of $\Delta\rho$ is quite considerable. It is clear from Fig. 3 that, within the limits of the approximations employed, the calculated values explain reasonably the observed behavior of the electrical resistivity. The experimental values of the additional high-temperature resistivity decrease in comparison with the residual resistivity, reaching a minimum near and above T_c. The value of $\Delta\rho$ near T_c is much smaller than that given by calculations based on Eq. (4).

We shall conclude our discussion by pointing out that the simple model employed here ignores some factors, particularly a possible perturbation of the electron and phonon spectra by impurities and contributions due to fluctuations in the long- and short-range order near the Curie point.[15] Possible changes in the relations be-

tween these contributions may complicate considerably the behavior of the transport properties of impure ferromagnets.

[1] S. Arajs and R. V. Colvin, Phys. Status Solidi 6, 797 (1964).

[2] F. C. Schwerer and L. J. Cuddy, Phys. Rev. B2, 1575 (1970).

[3] B. R. Coles, Advan. Phys. 7, 40 (1958).

[4] N. G. Backlund, J. Phys. Chem. Solids 20, 1 (1961).

[5] F. C. Schwerer, J. W. Conroy, and S. Arajs, J. Phys. Chem. Solids 30, 1513 (1969).

[6] N. F. Mott, Advan. Phys. 13, 325 (1964).

[7] T. Kasuya, Progr. Theor. Phys. 16, 58 (1956).

[8] P. G. de Gennes and J. Friedel, J. Phys. Chem. Solids 4, 71 (1958).

[9] V. M. Nabutovskiĭ and A. Z. Patashinskiĭ, Fiz. Tverd. Tela 10, 3121 (1968) [Sov. Phys.-Solid State 10, 2462 (1969)].

[10] K. P. Belov, Matnitnye prevrashcheniya, Fizmatgiz, M., 1959 (Magnetic Transitions, Consultants Bureau, New York, 1961).

[11] N. N. Serebrennikov and P. V. Gel'd, Tr. Uralsk. Politekh. Inst. No. 49 (1956).

[12] B. M. Mogutnov and I. A. Tomilin, Izv. Akad. Nauk SSSR, Metally No. 4, 28 (1967).

[13] Ya. A. Kraftmakher and T. Yu. Romashina, Fiz. Tverd. Tela 9, 1851 (1967) [Sov. Phys.-Solid State 9, 1459 (1967)].

[14] W. Peperhoff and H. H. Ettwig, Z. Angew. Phys. 22, 496 (1967).

[15] S. Takada, Progr. Theor. Phys. 46, 15 (1971).

Translated by A. Tybulewicz
243