Electrical Resistivity of High-Purity Iron at 4.2 K

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The electrical resistivity of single crystal iron specimens with different orientations and purities and of polycrystalline iron specimens with different purities has been measured at 4.2 K as a function of the measuring current density up to 7 A/mm² and the applied longitudinal magnetic field up to 1 kOe. The electrical resistivity at 4.2 K without the applied field, $\rho_{H=0}$ (4.2 K), strongly depends on the measuring current density, especially in the low current density region and for high purity specimens. In an applied longitudinal magnetic field of 700 to 800 Oe the electrical resistivity of pure single and poly-crystal specimens takes a minimum value, $\rho_{\min}$ (4.2 K), which is independent of the measuring current density and can be measured with high accuracy, regardless of specimen purity and of the orientation of single crystal specimen. The longitudinal magnetoresistivity curves of high-purity single crystal iron specimens are closely related to the magnetization curves characteristic of the longitudinal axis of each specimen.

The modified residual resistivity ratio RRR_H based on $\rho_{\min}$ (4.2 K) can be used as an appropriate measure of purity for iron. The origin of the resistivity increase with increasing the current density without applied fields and the resistivity decrease under the low longitudinal magnetic fields is discussed in terms of the electron scattering by the internal magnetic field within each magnetic domain.

(Received July 26, 1975)

I. Introduction

Electrical resistivity measurements at 4.2K can be very useful for characterizing the purity of metals and studying behaviour of lattice defects in metals. The residual resistivity ratio, $RRR = \rho(298K)/\rho(4.2K)$, where $\rho(298K)$ and $\rho(4.2K)$ are the electrical resistivity at 298K and 4.2K respectively, has been used as a measure of purity of metals. This is based on the assumption that the total resistivity at 4.2K of a well-annealed metal, $\rho(4.2K)$, can be approximated to be equal to the resistivity due to scattering by impurities, ρ_{impurity} . In the case of iron, however, there is another important contribution to $\rho(4.2K)$; a magnetoresistive term ρ_{mag} due to ferromagnetism⁽¹⁾⁽²⁾. For example, the resistivity $\rho(4.2K)$ of iron without applied magnetic field is influenced by the current-induced magnetic field, the earth magnetic field and the demagnetization procedure^{(3)~(7)}. With increasing purity of iron specimen the contribution to $\rho(4.2K)$ from ρ_{mag} becomes large because of the decrease in ρ_{impurity} .

Therefore $\rho(4.2K)$ can no longer be directly related to ρ_{impurity} . In this regard it has been proposed that the resistivity obtained by extrapolating the high-field magnetoresistivity data back to zero magnetic induction $B=0$ ($\rho_{B=0}$) or the minimum value in resistivity measured as a function of the applied longitudinal magnetic field ($\rho_{\min}$) should be used for estimation of the residual resistivity ratio (designated by $RRR_{B=0} \{ = \rho(298K)/\rho_{B=0}(4.2K) \}$ and $RRR_H \{ = \rho(298K)/\rho_{\min}(4.2K) \}$ respectively)⁽⁸⁾⁽⁹⁾. The resistivity increase with increasing the measuring current without applied fields and the resistivity decrease under low applied longitudinal magnetic fields have been attributed to the electron scattering by the internal magnetic field of ~ 22 kG within each magnetic domain⁽¹⁾ or the scattering by domain walls⁽⁴⁾⁽¹⁰⁾, but the situation has not been fully clarified up to the present^{(5)(7)(11)~(16)}.

In the present study, the effects of the following factors on the resistivity of iron at 4.2K are investigated: (a) the measuring current density, (b) the applied longitudinal magnetic field ($H < 1$ kOe), (c) the specimen purity, (d) the presence of grain boundaries and (e) the crystal orientation. The optimum condition for electrical resistivity measurement at 4.2K for high-purity iron and the origin of the resistivity change with the applied current density and longitudinal magnetic field are discussed.

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II. Experimental Procedure

Commercial grade electrolytic iron and Johnson Matthey pure iron were used as starting materials in this experiment and purified by anion exchange separation, floating-zone melting and hydrogen treatment. The procedure of purification and the preparation of specimens will be described in detail in a separate paper⁽¹⁷⁾. Polycrystalline specimens are 0.5 mm in diameter and 160 to 180 mm in length. Iron single crystals, 0.7 mm in diameter and 150 to 180 mm in length, were grown by the strain-anneal method in a furnace with a steep temperature gradient and then purified by the hydrogen treatment. The orientations of longitudinal axes of single crystal wire specimens are shown in the inserted stereographic triangles of the figures that follow.

The electrical resistivity measurements were made by a standard four-probe potentiometric method with a sensitivity of $\pm 2 \times 10^{-8}$ V. A cryostat was set in a solenoid at the center of a wooden frame Helmholtz coil 1.5 m in diameter set in the direction of the earth magnetic field. The longitudinal magnetic fields up to 1 kOe were applied by a solenoid (50 cm in length by 11 cm in diameter, 63 G/A). The earth magnetic field was compensated to less than 2.5×10^{-3} Oe by the Helmholtz coil. The demagnetizing factor of specimens is of the order of 10^{-5} and the demagnetizing field is negligible. The grain-size effect⁽⁹⁾ on resistivity $\rho_{\min}$ was negligible because the grain boundary resistivity was measured to be in the order of $10^{-12} \Omega \cdot \text{cm}^2$.

In this paper the value of $\text{RRR}_H \{ = \rho(298\text{K})/\rho_{\min}(4.2\text{K}) \}$ is used to describe the purity of a specimen and to distinguish specimens having different purities.

III. Experimental Results and Discussion

1. Dependence of electrical resistivity at 4.2K on the measuring current density without applied magnetic fields

Figure 1 shows the dependence of the electrical resistivity at 4.2K for polycrystalline specimens with different purities on the measuring current density. The results for single crystal specimens with different orientations and purities are shown

Fig. 1 Electrical resistivity at 4.2K and RRR_H of polycrystalline iron specimens with different purities (indicated by RRR_H) as a function of measuring current density without the application of magnetic field.

in Figs. 2 and 3. The resistivity in zero applied field was measured after the longitudinal magnetic field was applied up to 750 Oe and then reduced to zero Oe in the compensated earth magnetic field in order to demonstrate the effect of the current-induced transverse magnetic field. It is seen that the electrical resistivity of iron at 4.2K without the applied magnetic field, $\rho(4.2\text{K})$, strongly depends on the measuring current density, especially in the low current density region and for high-purity specimens. Therefore RRR_H is also remarkably dependent upon the measuring current density as shown on the right ordinate in Fig. 1. For example, RRR_H varied from 500 to 170 with the increasing current density for a high-purity specimen having RRR_H of 2500. The purity of iron cannot be compared by the usual RRR which has generally been used as an indication of purity without specifying conditions of the resistivity measurement. The dependence of the electrical resistivity on the measuring current density for single and polycrystalline specimens with nearly same purity is shown in Figs. 3 and 4. It is seen that the resistivity

Fig. 2 Electrical resistivity at 4.2K of single crystal iron specimens with three different axes as a function of measuring current density without the application of magnetic field. Orientations of longitudinal axes of single crystal wire specimens are shown in the inserted stereographic triangle by corresponding symbols.

Fig. 3 Current dependence of electrical resistivity without the application of magnetic field for single crystal iron specimens with two different axes and a polycrystalline iron specimen with nearly the same RRR_H (the upper three curves with the upper abscissa) and longitudinal magnetoresistivity for the two single crystal specimens at a few kinds of measuring current densities at 4.2K.

for single crystal specimens is larger than that for a polycrystalline specimen.

The origin of the resistivity increase with increasing applied current has been explained by either the scattering due to the internal magnetic field within each magnetic domain⁽¹⁾ or the

Fig. 4 Current dependence of electrical resistivity without the application of magnetic field (the upper two curves with the upper abscissa) and longitudinal magnetoresistivity at 4.2K for a single crystal iron specimen and a polycrystalline iron specimen.

domain wall scattering⁽⁴⁾ as well as the interpretation of the origin of the low-field magnetoresistance effect described later. The current-induced magnetic field is calculated to be 20 Oe for current density of 0.8 A/mm² at the surface of a specimen 0.5 mm in diameter where the field is strongest. Since the specimen is magnetized in the direction perpendicular to the current by the field, the domain wall density is not thought to be higher than the initial density before applying the current. The resistivity, however, increases with current density as shown above. Furthermore, the structure of magnetic domains is more complicated owing to grain boundaries in polycrystalline specimens⁽¹⁸⁾ than in single crystal specimens, so that the domain wall density of polycrystal iron is thought to be higher than that of single crystal iron. As shown in Figs. 3 and 4, however, the resistivity of a polycrystal specimen is smaller than that of single crystal specimens. On the contrary, since the current-induced magnetic field increases the volume of magnetic domains which have magnetization perpendicular to the current and the volume in a single crystal specimen is thought to be easier to increase than in a polycrystalline specimen with complex structure of magnetic domains, the present experimental results could be explained mainly by the scattering due to the internal magnetic field.

From the above results it is evident that the resistivity without applied fields at 4.2K is dependent upon the condition of resistivity measurements and includes magnetoresistive contribution due to the current-induced magnetic field. In the next section the longitudinal magnetoresistance effect will be described. The effect was investigated in order to determine the most suitable condition of resistivity measurement under which the magnetoresistive contribution due to the current-induced magnetic field is excluded and a reproducible resistivity value can be obtained with high accuracy.

2. Longitudinal magnetoresistivity at 4.2K

Figure 5 shows a result of the longitudinal magnetoresistivity $\rho(4.2K)$ for different measuring current densities on a polycrystalline iron specimen with the applied longitudinal magnetic field $H(Oe)$ indicated by the lower abscissa on the same scale for each curve, together with the dependence of the resistivity on the measuring current density in zero applied field (the uppermost curve with the upper abscissa). Figure 6 shows a comparison of the longitudinal magnetoresistivity curves obtained for less pure polycrystalline specimens and high-purity polycrystalline specimens. For the less pure specimens the resistivity decreased slowly and reached ρ_{min} , while for the high-purity specimens it decreased rapidly and reached ρ_{min} with a little further change. It is seen that the influence of the current-

Fig. 5 Current dependence of electrical resistivity without the application of magnetic field (the uppermost curve with the upper abscissa) and longitudinal magnetoresistivity at 4.2K for a polycrystalline iron specimen.

Fig. 6 Electrical resistivity of polycrystalline iron specimens with different purities at 4.2K as a function of applied longitudinal magnetic field. Upper four curves and lower two curves were measured at 0.5 A/mm² and 1.0 A/mm², respectively.

induced magnetic field on the resistivity is almost excluded by the application of low longitudinal magnetic fields of less than 20 Oe. In an applied field of 700 to 800 Oe the resistivity reached a minimum value, which is independent of the measuring current density.

Figures 3, 4, 7 and 8 show the longitudinal magnetoresistivity at 4.2K for different measuring current densities for single crystal iron specimens of different orientations and purities together with the current dependence of the resistivity in zero applied field. It is seen that the longitudinal magnetoresistivity curves of single crystal specimens closely correspond to the magnetization curves⁽¹⁹⁾ characteristic of each crystal orientation. The resistivity rapidly decreased by the application of magnetic fields of less than 20 Oe, then slowly decreased and reached a minimum value at the applied field of 400 Oe and 500 Oe in single crystal specimens having axes oriented near $[111]$ and $[011]$, respectively (Figs. 7 and 4). In a single crystal specimen with an axis oriented near $[001]$ the resistivity decreased more rapidly and reached ρ_{min} with a little further change (Fig. 8).

Fig. 7 Current dependence of electrical resistivity without the application of magnetic field (the uppermost curve with the upper abscissa) and longitudinal magnetoresistivity at 4.2K for a single crystal iron specimen.

Fig. 8 Current dependence of electrical resistivity without the application of magnetic field (the uppermost curve with the upper abscissa) and longitudinal magnetoresistivity at 4.2K for a single crystal iron specimen.

In both single and poly-crystal specimens the value of $\rho_{\min}$ was measured with an accuracy of $5 \times 10^{-11} \Omega \cdot \text{cm}$ in an applied longitudinal magnetic field of 700 to 800 Oe regardless of the measuring current density, the specimen purity and the orientation of longitudinal axis of single crystal. The value is not influenced by the demagnetization procedure and the earth magnetic field⁽⁶⁾. Consequently, this reproducible value can be used as a reliable resistivity value with high accuracy and less magnetoresistive

contribution.

The origin of the resistivity decrease with the application of low longitudinal fields has been explained by either the scattering due to the internal magnetic field within each magnetic domain or the domain-wall scattering. As mentioned above, the initial rapid decrease in magnetoresistivity is considered to correspond to the irreversible magnetization range, where irreversible domain wall displacements take place. Supposing that domain wall has high resistivity, domain walls parallel to the current are thought to contribute little to the total resistivity but the contribution of domain walls perpendicular to the current comes into question, because conduction electrons may pass through the inner part of magnetic domain which has lower resistivity rather than domain walls parallel to the current. When the low longitudinal fields are applied, domain walls parallel to the current will be swept out but there may be little possibility of a rapid and considerable decrease in the density of domain walls perpendicular to the current. On the contrary, since the low longitudinal fields reduce the volume of magnetic domains which have the magnetization perpendicular to the current, the scattering due to the internal magnetic field perpendicular to the current decreases.

Furthermore, in the case of a specimen with an axis oriented near $[\bar{1}11]$ as shown in Fig. 7, the resistivity considerably decreased in the region corresponding to the rotation magnetization range, where there is no change in the domain boundary density but a change in the direction of magnetization within domains. The result suggests that scattering by the internal field within each domain is very effective. On the basis of this result, the amount of the initial resistivity decrease obtained in the present experiment can be understood because a specimen is initially magnetized transversely by the current-induced field without the application of magnetic field and then longitudinally magnetized in the applied fields.

From the above discussion, the scattering by the internal magnetic field within each domain is thought to be the principal origin of the low-field negative magnetoresistance effect rather than the scattering by domain-walls.

3. Comparison of three kinds of residual resistivity ratios: RRR_H , $RRR_{B=0}$ and RRR

From the results described above, it becomes evident that the usual residual resistivity ratio RRR is not suitable for describing the purity of iron and the modified residual resistivity ratio RRR_H obtained by using the value of $\rho_{\min}$ can be used as an appropriate index of purity for iron.

The other modified residual resistivity ratio $RRR_{B=0}$ obtained by using the value of $\rho_{B=0}$ has the following weak points: It is difficult to extrapolate the high-field magnetoresistivity data to $B=0$ and hence the value of $\rho_{B=0}$ accompanies considerable errors as pointed out also by Araj et al.⁽⁹⁾ The relation between the high-field magnetoresistivity and impurity has not been fully understood as Wagenblast et al.⁽²⁰⁾ have given some data that the high-field magnetoresistivity is dependent on the state of carbon in iron present (for example, as solute carbon, as metastable carbides, or as cementite Fe_3C).

On the other hand, the value of $\rho_{\min}$ cannot be considered to be essentially equal to ρ_{impurity} because $\rho_{\min}$ is not the resistivity corresponding to $\rho_{\text{mag}}=0$ but contains "normal" magnetoresistivity; consequently it should be noted that RRR_H cannot be used as a measure of purity when the purity of iron is much improved in the future and ρ_{impurity} becomes smaller than the "normal" magnetoresistivity. In the present situation, however, the value of $\rho_{\min}$ is the value that can be measured with a high degree of accuracy and contains the least magnetoresistive contribution.

Values of the modified $RRR_H = \{\rho(298K)/\rho_{\min}(4.2K)\}$ calculated from values of resistivity $\rho_{\min}$ at 4.2K with $H=750$ Oe are compared with the usual $RRR (I=0.5A/mm^2)$ for iron specimens of different purities as shown in Fig. 9. For $RRR < 100$ there is no difference between RRR and RRR_H , but for $RRR > 100$ the difference becomes larger with increasing purity and it is seen that the usual RRR may be saturated for $RRR > 500$. Therefore it becomes evident that RRR_H can be used as a more appropriate measure to reveal a distinct difference in purity of iron. In addition the values of RRR_H obtained for

Fig. 9 Relation between $RRR (I=0.5 A/mm^2)$ and $RRR_H (H=750 Oe)$ of iron specimens with different purities.

some high-purity irons used in the present experiment are found to reach the order of 10^3 comparable to the values of RRR for high-purity nonferromagnetic metals. It is interesting to revalue the purification effect of various refining methods for iron by RRR_H . In a separate paper⁽¹⁷⁾ the results of such experiments will be reported.

IV. Conclusions

(1) The electrical resistivity of pure iron at 4.2K without the application of magnetic field, $\rho_{H=0}(4.2K)$, strongly depends on the measuring current density, especially in the low current density region and for high-purity specimens.

(2) In an applied longitudinal magnetic field of 700 to 800 Oe the electrical resistivity of pure single and poly-crystal iron specimens takes a minimum value, $\rho_{\min}(4.2K)$, which is independent of the measuring current density and can be measured with an accuracy of $5 \times 10^{-11} \Omega \cdot cm$, regardless of the specimen purity and the crystal orientation. The longitu-

dinal magnetoresistivity curves of high-purity single crystal iron specimens closely correspond to the magnetization curves characteristic of the longitudinal axis of each specimen.

(3) The modified residual resistivity ratio $RRR_H = \rho(298K)/\rho_{\min}(4.2K)$ can be used as an appropriate measure of purity of iron and $\rho_{\min}(4.2K)$ should also be used for the study of lattice defects in pure iron.

(4) The scattering by the internal magnetic field within each domain is thought to be a main origin of the resistivity increase with increasing the current density without applied fields and of the resistivity decrease under low applied longitudinal magnetic fields, rather than the scattering by domain-walls.

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