Anisotropy of the size effect in the electrical resistivity of high-purity Al single crystals

Anisotropy of the size effect in the electrical resistivity of high-purity Al single crystals

E Hashimoto† and Y Ueda‡

† Hiroshima Synchrotron Radiation Centre, Hiroshima University, Higashi-Hiroshima 739-8526, Japan
‡ Department of Physics, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

Abstract. To clarify the anisotropy of the dc size effect in Al, measurements have been made of the electrical resistivity $\rho_{4.2\,K}$ of high-purity Al single crystals (RRR $\simeq 50\,000$) at 4.2 K. The specimen surfaces were set parallel to each of three crystallographic planes, {100}, {111} and {110}, and the axis orientations were parallel to $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$. The main results were the following. (1) The size effect increased in the following order of the surface orientations: {110}, {111}, {100}. (2) For the size effect due to a {110} surface, the Fuchs–Sondheimer theory with $\rho_b \ell_b = 0.82$ fΩ m^2 gave a good description, while, for the size effect due to {100} and {111} surfaces, substantial disagreement with the theory was suggested for the very thick specimens. (3) For each surface orientation, $\rho_{4.2\,K}$ for sufficiently thin specimens was independent of the axis orientation within the experimental error; i.e. the size effect was independent of the direction of current flow. (4) However, as the specimen thickness increased, strong anisotropy of $\rho_{4.2\,K}$ with respect to the current direction appeared: $\rho_{4.2\,K}$ increased in the following order of directions: $\langle 110 \rangle$, $\langle 111 \rangle$, $\langle 100 \rangle$. Results (3) and (4) suggest an anisotropy effect of the bulk resistivity ρ_b in high-purity Al.

1. Introduction

The anisotropy of the size effect in the dc electrical resistivity of Al has aroused a considerable amount of interest since the first measurement made by Risnes and Sollien [1]. This anisotropy is closely related to the following two effects. One is the effect due to the anisotropy of the Fermi surface, and the other is the effect due to the anisotropy of the relaxation time of the conduction electrons. However, the origin of the anisotropic size effect has still not been clarified because of the lack of systematic studies on well-defined single crystals. In this paper, we present an experimental study on the anisotropic size effect in high-purity Al single crystals.

2. Experimental procedure

Specimens were prepared by spark erosion from a zone-refined Al rod with a residual resistance ratio RRR ($\equiv R_{300\,K}/R_{4.2\,K}$) of about 50 000 in the bulk [2]. Single-crystal plates, 0.2–2 mm thick, were first cut parallel to each of three crystallographic planes {100}, {111} and {110} from nearby parts of the rod. Then they were cut into straight strips approximately 3 mm by 20 mm to serve as the specimens. The specimen axes were set parallel to the

$\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ directions. After cutting, the specimens were chemically etched with aqua regia and rinsed with distilled water to remove contamination and damaged layers on the surface. Then two pairs of electrodes, 0.3 mm thick wires made of zone-refined Al, were spot-welded onto each specimen for the dc four-probe measurement. The potential electrodes were placed sufficiently far inside to avoid end effects. The specimens thus prepared were lightly etched with aqua regia, annealed at 300 °C for 3 h in air and furnace cooled to room temperature.

The crystallographic orientation of the specimens was determined by the transmission Laue method to an accuracy of $\pm 1°$. Hereafter, we use the following abbreviated notation: $\{100\}\langle 110 \rangle$, for instance, indicates that the surface orientation of the specimen is $\{100\}$ and the axis orientation is $\langle 110 \rangle$.

The resistance measurement at 4.2 K was performed using a superconducting chopper amplifier with a voltage sensitivity of ± 2 pV. The specimen was shielded with a super-conducting Pb can to avoid the influence of external fields such as the Earth's field. A dc current through the specimen was set at 0.5–1 A after making sure that the influence of Joule heat, as well as magnetoresistance due to the self-field of the measuring current, was negligible in the measurement. The resistivity of the specimens at 4.2 K, $\rho_{4.2\,K}$, was determined from the relation $\rho_{4.2\,K} = (\rho_{300\,K}/R_{300\,K})R_{4.2\,K}$, where $R_{4.2\,K}$ and $R_{300\,K}$ are the resistances measured at 4.2 and 300 K, respectively, and $\rho_{300\,K}$ the resistivity at 300 K: $\rho_{300\,K} = 27.33$ nΩ m for high-purity Al [3]. The resistance at 300 K was measured using a dc comparator potentiometer with a sensitivity of ± 0.5 nV (Guildline, Model-9930).

The thickness d of the specimens was determined from the following relation: $d = (\ell_p/w)(\rho_{300\,K}/R_{300\,K})$. The width w of the specimen and the distance ℓ_p between the potential electrodes were measured with a travelling microscope with a resolution of 0.01 mm.

As already described, the specimens were prepared from a single-crystal rod, grown by repeating zone-refining procedures. Although they were cut from nearby parts of the rod, the possibility existed that an inhomogeneous distribution of impurities in the rod could give rise to systematic errors in the measurements. This possibility was checked for in the following two ways. The first way was to examine the resistivity distribution over the parts used for the preparation of each specimen set for the same crystallographic orientation. The measurement on single-crystal specimens, cut from each part to equal thickness and crystal orientation, excluded the possibility that impurities caused unfavourable resistivity differences between the specimen sets. The second way was to make it clear whether the thickness dependence of $\rho_{4.2\,K}$ obtained for each specimen set could be attributed to the intrinsic origin only. For this purpose, the thick specimens in each set were reduced in thickness by spark erosion, and resistivity measurements were made again. The results obtained in this manner also showed no significant effect of the impurity distribution.

3. Results and discussion

Figure 1 shows $\rho_{4.2\,K}$ for the $\{100\}\langle 110 \rangle$, $\{111\}\langle 110 \rangle$ and $\{110\}\langle 110 \rangle$ specimens, plotted as functions of the inverse of the reduced thickness, $P/2A$, where P is the perimeter of a cross section and A the cross-sectional area of a specimen. Since the axis orientation (the direction of current flow) is common, the bulk resistivities ρ_b of these specimens essentially agree with each other. Therefore, as is obvious from the figure, the size effect increases in the following order of the surface orientations: $\{110\}$, $\{111\}$, $\{100\}$. The anisotropic dependence of the bulk resistivity ρ_b on the current direction in high-purity Al has been reported elsewhere [4–7].
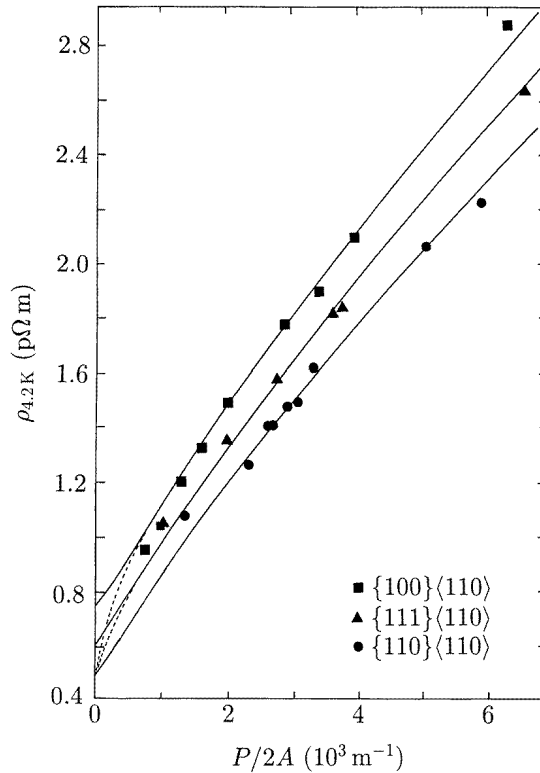
Figure 1. Experimental values of the residual electrical resistivity $\rho_{4.2\,\mathrm{K}}$ for high-purity Al single crystals (RRR $\simeq$ 50 000), plotted as functions of the inverse of the reduced thickness, $P/2A$, for each of three crystallographic orientations $\{100\}\langle110\rangle$, $\{111\}\langle110\rangle$ and $\{110\}\langle110\rangle$. Solid curves show the Fuchs–Sondheimer theory, with $p = 0$, fitted to the experimental data, using $\rho_{\mathrm{b}}\ell_{\mathrm{b}} = 0.82$ fΩ m^2. Broken curves illustrate schematically how $\rho_{4.2\,\mathrm{K}}$ increases with decreasing thickness in the very thick $\{100\}\langle110\rangle$ and $\{111\}\langle110\rangle$ specimens when the contribution of the size effect due to the side surface is negligible.

The solid curves in the figure are drawn according to the Fuchs–Sondheimer theory [8], assuming that the specularity parameter $p = 0$, and that the product of the bulk resistivity and bulk mean free path $\rho_{\mathrm{b}}\ell_{\mathrm{b}} = 0.82$ fΩ m^2 [9, 10]. As the specimens have been etched with aqua regia and annealed in air, the specimen surface is rather rough. Therefore, the surface scattering of conduction electrons is reasonably assumed to be diffuse, i.e. we assume that $p = 0$ [9, 11]. Sambles and co-workers [9, 11] have amply shown that the theory given by Soffer [12] works better than the Fuchs–Sondheimer theory in the field of the size effect in metals. When the surface roughness is large, the two theories agree closely with each other over a wide range of d/ℓ_{b} including the values for the present specimens.

The curves thus obtained fit the experimental data closely, except those on the thick specimens. Deviations from Fuchs–Sondheimer theory for the thick specimens suggest a contribution of the size effect due to the side surface. The orientations of the side surfaces are $\{110\}$, $\{112\}$ and $\{100\}$ for the $\{100\}\langle110\rangle$, $\{111\}\langle110\rangle$ and $\{110\}\langle110\rangle$ specimens, respectively. These side surfaces, as expected from the anisotropic size effect above, give a different size effect from that due to the main surface, thereby resulting in disagreement between theory and experiment. For example, the value of $\rho_{4.2\,\mathrm{K}}$ obtained

for the thickest {110}⟨110⟩ specimen is significantly larger than the prediction based on the Fuchs–Sondheimer theory, while the value for the thick {100}⟨110⟩ specimens is smaller than the theoretical prediction. Also the $\rho_{4.2\,\text{K}}$-value for the thickest {111}⟨110⟩ specimen suggests that the size effect due to the {112} surface is larger than that due to the {111} surface.

As already mentioned, the bulk resistivities ρ_b of the specimens in figure 1 are essentially the same. However, the ρ_b-value adjusted to give a good fit increases with the contribution of the anisotropic size effect. Thus, if the contribution from the side surface above is negligible, a rapid increase in $\rho_{4.2\,\text{K}}$ with decreasing thickness must take place at first in the very thick {100}⟨110⟩ and {111}⟨110⟩ specimens, as illustrated by dotted curves in figure 1. In such conditions, it is very difficult to measure the resistivity of these specimens accurately. Nevertheless, for the size effect due to the {100} and {111} surfaces, there is substantial disagreement with the Fuchs–Sondheimer theory, with $\rho_b\ell_b = 0.82$ fΩ m^2, for the very thick specimens.

In our previous experiments on single-crystal specimens of dilute Al–Ag and Al–Si alloys [13], any orientation dependence of the size effect was less than the experimental error: the size effect in both dilute alloys was well described by the Fuchs–Sondheimer theory with $p = 0$, using $\rho_b\ell_b = 0.82$ fΩ m^2. The solute Ag in Al decreases the relaxation time near the Brillouin zone boundaries, while Si has the reverse effect; therefore, the anisotropy of the relaxation time due to the impurities is not the intrinsic origin of the anisotropic size effect in Al.

A probable explanation for the disappearance of the anisotropy, caused by the addition of the impurities Ag and Si, is that the scattering of conduction electrons from impurities makes the deviation of the electron distribution from the equilibrium isotropic in the steady state [14]. In such a situation, the Fuchs–Sondheimer theory is sure to be a good approximation, since the Fermi surface of Al is nearly a free-electron sphere even though it extends beyond the first Brillouin zone. It is therefore reasonable to expect that the effect of the anisotropy of the distribution function leads to the anisotropic size effect in high-purity Al.

The Fermi surface must meet the Brillouin zone boundaries at right angles, resulting in departures from the free-electron Fermi sphere. As the electron velocity is proportional to the gradient of the energy in k-space, the velocity distribution of the electrons approaching the specimen surface will in general vary depending on the surface orientation. This is probably an important effect, which may cause the anisotropic size effect as shown in figure 1, since the surface scattering affects all the electrons, especially those moving in the direction of the surface normal.

In Al, the structure of the Fermi surface is highly anisotropic near the zone boundaries, as shown in figure 2. On inspection of the geometry of the Fermi surface, especially around the [001] direction, it does appear that the relative number of conduction electrons moving in the [001] direction is larger than that on the free-electron Fermi sphere. Thus, if the specimen surface is parallel to the (001) plane, such electrons are effectively scattered out of their states by the surface scattering. This increases the number of unoccupied states into which an electron travelling in the forward direction will be scattered, leading to an enhancement of the rates of scattering of the electrons. Therefore the apparent resistivity becomes larger than the prediction based on the Fuchs–Sondheimer theory; i.e. $\rho_{4.2\,\text{K}}$ should increase rapidly as the specimen thickness d is decreased to a value comparable with the mean free path of the electrons moving in the [001] direction. With further decrease in thickness, the increase in $\rho_{4.2\,\text{K}}$ will soon become a slow change and accord well with the Fuchs–Sondheimer theory, since the zone boundaries have only a little effect on the surface scattering rate of electrons which move in directions making large angles with the surface
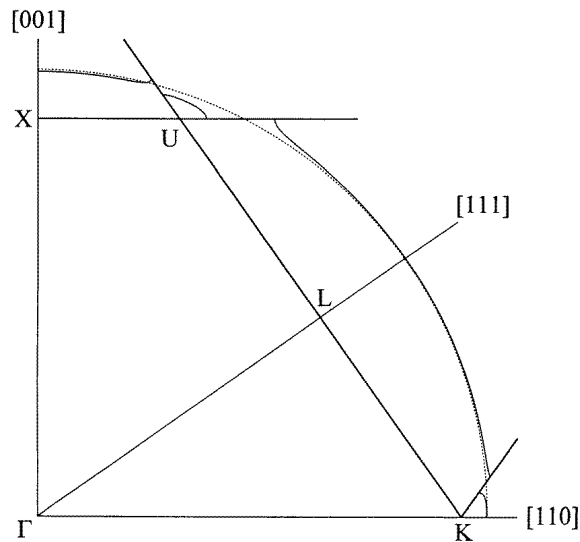
Figure 2. The central $(1\bar{1}0)$ section of the Fermi surface of Al in the extended-zone scheme. The calculations were made in the 4-OPW approximation. The thick lines represent the Brillouin zone boundaries and the dotted curve shows the free-electron Fermi sphere.

normal. In the [110] direction, on the other hand, the Fermi surface intersects with the zone boundaries, but their influence is relatively small as shown in figure 2. The velocity distribution in this direction is nearly free-electron-like. Therefore it is reasonably expected that the Fuchs–Sondheimer theory gives a good description for the size effect due to a {110} surface.

Figure 3 shows $\rho_{4.2\,\mathrm{K}}$ for the {110}⟨100⟩, {110}⟨111⟩ and {110}⟨110⟩ specimens, plotted as functions of $P/2A$. The main feature of the results is that $\rho_{4.2\,\mathrm{K}}$ depends strongly on the axis orientation (the direction of current flow): $\rho_{4.2\,\mathrm{K}}$ increases in the following order of the directions: ⟨110⟩, ⟨111⟩, ⟨100⟩. The degree of this anisotropy, however, decreases in the thin specimens in which the rate of scattering of conduction electrons at the specimen surface is large. As the specimen thickness decreases, the $\rho_{4.2\,\mathrm{K}}$-values of the {110}⟨111⟩ and {110}⟨100⟩ specimens rapidly approach the $\rho_{4.2\,\mathrm{K}}$-value of the {110}⟨110⟩ specimens around $P/2A \sim 3 \times 10^3$ m^{-1} and $\sim 4 \times 10^3$ m^{-1}, respectively. This implies that an explanation of the anisotropy in terms of an anisotropy effect due to the size effect is not very probable.

Another possibility in trying to explain this anisotropy is to consider a breaking in the cubic symmetry due to impurities, assuming that a very small proportion of the impurities remaining in high-purity Al tend to align in a certain direction. But, if this is the case, we cannot predict a decrease in the degree of anisotropy in the thin specimens. Such a model therefore does not work.

Recently, we have found nonlinear I–V characteristics for single-crystal specimens of high-purity Al (RRR $\simeq 100\,000$), cut into strips whose sides are inclined to one another [15]. The result implies that the deviation of the electron distribution induced by the application of an electric field to the equilibrium distribution can no longer be regarded as being a first-order infinitesimal. The deviation of the distribution in the steady state generally depends on the direction of the electric field due to the anisotropic structure of the Fermi surface. This leads to the idea that, in high-purity Al, the electron distribution function does not always
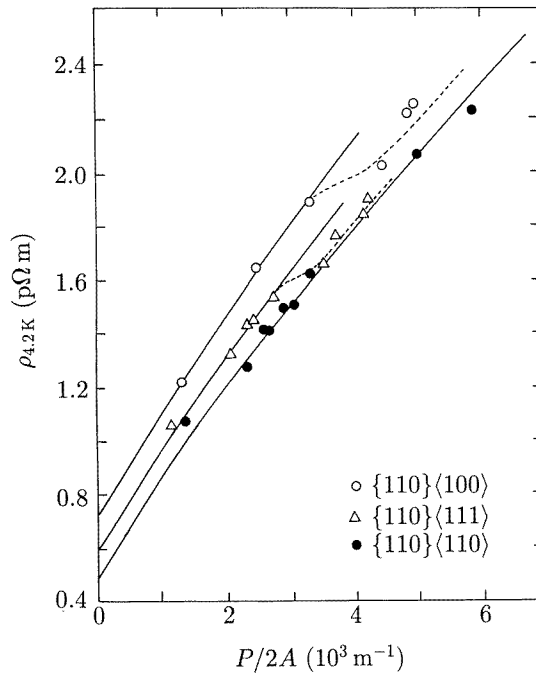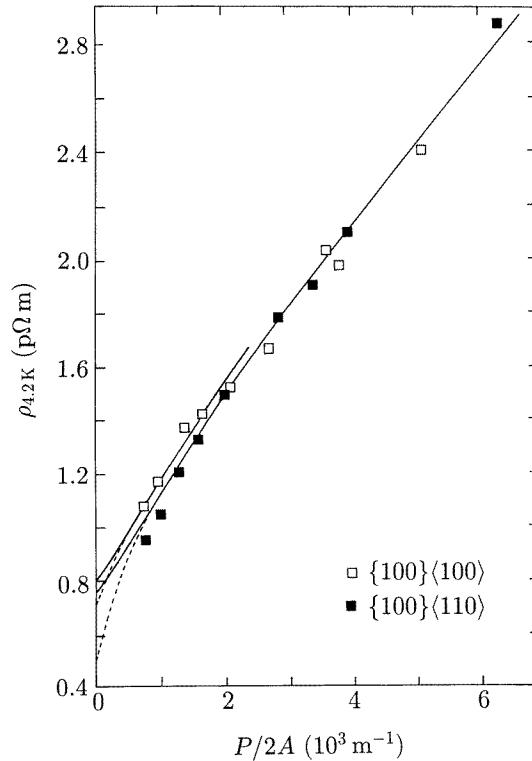
Figure 3. Experimental values of $\rho_{4.2\,\mathrm{K}}$ of high-purity Al single crystals (RRR $\simeq$ 50 000), plotted as a function of $P/2A$ for each of the three crystallographic orientations $\{110\}\langle100\rangle$, $\{110\}\langle111\rangle$ and $\{110\}\langle110\rangle$. The solid curves are theoretical fits based on the Fuchs–Sondheimer theory, with $p = 0$, obtained using $\rho_{\mathrm{b}}\ell_{\mathrm{b}} = 0.82$ fΩ m^2. The broken curves are drawn to guide the eye.

retain its cubic symmetry even though the applied electric field is small. Therefore, we would expect the anisotropic dependence of $\rho_{4.2\,\mathrm{K}}$ on the axis orientation to be a reflection of the anisotropy of the bulk resistivity ρ_{b} in high-purity Al; i.e. ρ_{b} increases in the following order of the directions: $\langle110\rangle$, $\langle111\rangle$, $\langle100\rangle$ [4–7]. The anisotropy of ρ_{b} is noteworthy in relation to electronic transport phenomena, since it has been widely believed that ρ_{b} is isotropic in a normal metal with cubic symmetry such as Al [16].

In that case, the result apparent from figure 3 that the anisotropy decreases in the thin specimens leads to the conclusion that the anisotropy of ρ_{b} does not occur when random scattering effects become sufficient to restore the electrons to their equilibrium distribution. This can also be concluded from our previous findings that the degree of anisotropy of ρ_{b} differs significantly according to the purity level of the specimens: it decreases markedly with decreasing purity level [7].

The solid curves in figure 3 are the predictions based on the Fuchs–Sondheimer theory, with $p = 0$, obtained using $\rho_{\mathrm{b}}\ell_{\mathrm{b}} = 0.82$ fΩ m^2. Each of these curves gives a good fit to the data on the thick specimens, if the contribution from the side surface is negligible. In fact, there is satisfactory agreement between theory and experiment for the thick $\{110\}\langle100\rangle$ specimens whose side surfaces have the same orientation, $\{110\}$, as the main surface. This shows that the Fuchs–Sondheimer theory with a suitable value of $\rho_{\mathrm{b}}\ell_{\mathrm{b}}$ (0.82 fΩ m^2) gives a good description of the size effect due to a $\{110\}$ surface.

Figure 4 shows $\rho_{4.2\,\mathrm{K}}$ for the $\{100\}\langle100\rangle$ and $\{100\}\langle110\rangle$ specimens, plotted as functions of $P/2A$. The anisotropy of $\rho_{4.2\,\mathrm{K}}$ with respect to the axis orientation also occurs for these

Figure 4. Experimental values of $\rho_{4.2\,\mathrm{K}}$ for high-purity Al single crystals (RRR $\simeq 50\,000$), plotted as a function of $P/2A$ for each of the crystallographic orientations $\{100\}\langle100\rangle$ and $\{100\}\langle110\rangle$. The solid curves show theoretical fits based on the Fuchs–Sondheimer theory, with $p = 0$, obtained using $\rho_{\mathrm{b}}\ell_{\mathrm{b}} = 0.82$ fΩ m^2. The broken curves illustrate schematically how $\rho_{4.2\,\mathrm{K}}$ increases with decreasing thickness for the very thick specimens when the contribution from the side surface is negligible: the ρ_{b}-values correspond for each axis orientation to the values in figure 3.

specimens, but its degree is small compared with the results for the {110} specimens shown in figure 3. Besides which, this anisotropy disappears even for a small $P/2A$ value of about 2×10^3 m^{-1}. These results are reasonable, since the rate of scattering of conduction electrons at a {100} surface is larger than that at a {110} surface. The disappearance of the anisotropy in the thin specimens also shows that the size effect is independent of the axis orientation (the direction of current flow) within the experimental error.

4. Summary

In this work, we have measured the electrical resistivity of high-purity Al single crystals (RRR $\simeq 50\,000$) at 4.2 K in order to clarify the anisotropy of the size effect. The general features of the anisotropic size effect in high-purity Al, so far obtained, are summarized as follows.

    (1) The size effect depends strongly on the surface orientation: it increases in the following order of the surface orientations: {110}, {111}, {100}.

    (2) The size effect is independent of the axis orientation (the direction of current flow).

(3) For the size effect due to a {110} surface, the Fuchs–Sondheimer theory, with the parameter $\rho_b \ell_b = 0.82$ fΩ m^2, gives a good description, while, for the size effect due to {100} and {111} surfaces, there is substantial disagreement with the theory for the very thick specimens ($d/\ell_b > 1$).

(4) The anisotropy of the size effect disappears as the purity level of the specimen is decreased [13].

To clarify the anisotropic size effect more quantitatively, it would be necessary to perform high-precision measurements of the resistivity on single crystals of high-purity Al under the condition that $d/\ell_b > 1$.

References

[1] Risnes R and Sollien V 1969 *Phil. Mag.* **20** 895
[2] Hashimoto E and Ueda Y 1994 *Mater. Trans. JIM* **35** 262
[3] Kawata S and Kino T 1975 *J. Phys. Soc. Japan* **39** 684
[4] Hashimoto E, Ueda Y, Tamura H and Kino T 1993 *J. Phys. Soc. Japan* **62** 4178
[5] Ueda Y, Tamura H and Hashimoto E 1994 *J. Phys.: Condens. Matter* **6** L637
[6] Ueda Y, Tamura H and Hashimoto E 1995 *J. Phys.: Condens. Matter* **7** L361
[7] Hashimoto E, Ueda Y and Yamasaki H 1997 *J. Phys. Soc. Japan* **66** 1253
[8] Sondheimer E H 1952 *Adv. Phys.* **1** 1
[9] Sambles J R, Elsom K C and Sharp-Dent G 1981 *J. Phys. F: Met. Phys.* **11** 1075
[10] Ueda Y, Hosoda H and Kino T 1985 *J. Phys. Soc. Japan* **54** 3858
[11] Sambles J R and Elsom K C 1980 *J. Phys. F: Met. Phys.* **10** 1487
[12] Soffer S B 1967 *J. Appl. Phys.* **38** 1710
[13] Yamasaki H, Ueda Y and Hashimoto E 1996 *J. Phys.: Condens. Matter* **8** L399
[14] Kagan Yu and Zhernov A P 1971 *Sov. Phys.–JETP* **33** 990
[15] Ueda Y and Hashimoto E 1997 *Kotai Butsuri (Solid State Physics)* **32** 656 (in Japanese)
[16] Rossiter P L 1986 *The Electrical Resistivity of Metals and Alloys* (Cambridge: Cambridge University Press) ch 1