Deviation from Matthiessen's Rule of Co-Cr and Co-Ni Dilute Alloys

By Y. Fukuda^{*†}, M. Isshiki^{*} and K. Igaki^{*}

The electrical resistivity has been measured on Co-Ni and Co-Cr dilute alloy specimens in the temperature range from 4.2 to 360 K. The deviations from Matthiessen's rule (DMR) derived from the resistivity data have been analysed in terms of the two current model. It is confirmed that a spin mixing term proportional to T^2 is the dominant mechanism of DMR at low temperatures. The large value of the residual resistivity in the spin down subband of the Co-Cr alloy is associated with the virtual bound state of spin down electrons of chromium lying close to the Fermi level of the spin down subband of cobalt.

(Received May 13, 1985)

Keywords: deviation from Matthiessen's rule, electrical resistivity, low temperature, cobalt base alloy, two band conduction

I. Introduction

The mechanism of conduction in ferromagnetic metals and alloys has been investigated by many authors. Campbell *et al.*⁽¹⁾ predicted that Mott's suggestion⁽²⁾ of two parallel currents of spin up and spin down electrons should lead to substantial contributions to the deviation from Matthiessen's rule (DMR) in ferromagnetic alloys. The prediction has been demonstrated by two types of experiments; the first type is measuring the temperature dependence of the DMR in binary alloys⁽³⁾⁻⁽⁸⁾, while the second type is examining the DMR in ternary system of varying composition at fixed temperatures, usually 4.2 K⁽⁹⁾⁽¹⁰⁾.

Many experimental data have been reported on nickel base and iron base alloys which prove the validity of two current conduction in spin up and spin down subbands. However, there is less experimental information on cobalt base alloys. Ross *et al.*⁽⁸⁾ investigated the temperature dependence of the DMR for Co-Sn and Co-Sb alloys. Durand and Gautier⁽⁵⁾ measured the electrical resistivity of cobalt

base dilute alloys of 3 d, 4 d and 5 d transition metals at 4.2, 77 and 297 K. Loegel and Gautier⁽¹¹⁾ reported on the temperature dependence of DMR for Co base binary alloys in the temperature range from 4.2 to 77 K. From the analysis of the DMR, they suggested that the two current model was valid for the cobalt base alloys.

In the present paper, the electrical resistivity of Co-Cr and Co-Ni dilute alloys has been measured precisely in the temperature range from 4.2 to 360 K, and the temperature dependence of DMR derived from the resistivity data is analysed in detail in terms of the two current model.

II. Experimental Details

Pure cobalt was prepared from chloride solution by a purification process⁽¹²⁾ which consisted of anion exchange separation, reduction of the purified anhydrous cobalt chloride by dry hydrogen at 573 K, and electron beam melting in vacuum (1.33×10^{-3} Pa (10^{-5} Torr)). The value of residual resistivity ratio measured on the purified cobalt was 186 after annealing at 1073 K for 86.4 ks (24 h) in Pd-purified hydrogen. Commercial grade pure nickel and chromium with nominal purity of 99.99% purchased from Johnson-Matthey Co. and Materials Research Co., respectively, were purified by the floating zone-refining in dry hydrogen and used for alloying elements. Ex-

^{*} Department of Materials Science, Faculty of Engineering, Tohoku University, Aoba Aramaki, Sendai 980, Japan.

[†] Present address: Research and Development Division, Victor Company of Japan Ltd., Yokohama Plant, 12, 3-chome, Moriya-cho, Kanagawa-ku, Yokohama 221, Japan.

perimental details of the floating zone-refining of Cr were reported by Igaki *et al.*⁽¹³⁾ The residual resistivity ratios of the purified nickel and chromium were 830 and 90, respectively.

The alloys were prepared by arc-melting in pure argon atmosphere. Specimens with the dimension of 1 mm × 1 mm × 40 mm were cut from the sheets prepared by hot rolling at 1023 K. After electrolytic polishing, the specimens were annealed in Pd-purified hydrogen and subjected to the measurement of the electrical resistivity. The electrical resistivity was measured by the standard potential probe method in the temperature range from 4.2 to 360 K.

III. Experimental Results

Relations between temperature and the electrical resistivity measured on the pure cobalt and the alloy specimens were shown in Fig. 1. It can be seen from the figure that the effect of the addition of chromium solute is larger than that of nickel solute. The temperature dependent DMR, $\Delta(c, T)$, is defined by

Fig. 1 Relation between temperature and the electrical resistivity measured on each specimen.

$$\Delta(c, T) = \rho(c, T) - \rho(0, T) - \rho(c, 0), \quad (1)$$

where $\rho(c, T)$ is the measured alloy resistivity, $\rho(0, T)$ the ideal temperature dependent resistivity of the host metal and $\rho(c, 0)$ the residual alloy resistivity. In the present work, the resistivity measured on the pure cobalt was used as $\rho(0, T)$ and $\rho(c, 0)$ was estimated at 4.2 K. The DMR from the other impurity elements contained in both alloy specimens and the pure cobalt can be considered to be cancelled by each other. Such a contribution to $\Delta(c, T)$ should be negligibly small, if any, judging from the low impurity concentrations⁽¹⁴⁾. The values of $\Delta(c, T)$ are plotted against temperature in Fig. 2. It is found that those of $\Delta(c, T)$ show a T^2 dependence at low temperatures and that $\Delta_{Cr}(c, T)$ is larger than $\Delta_{Ni}(c, T)$.

According to the two current model⁽¹⁾, the total residual resistivity $\rho(c, 0)$ is given by

$$\rho(c, 0) = \frac{\rho_t(c, 0) \cdot \rho_i(c, 0)}{\rho_t(c, 0) + \rho_i(c, 0)}, \quad (2)$$

where $\rho_t(c, 0)$ and $\rho_i(c, 0)$ are the residual resistivities in spin up and spin down subbands, respectively, which are assumed to be in-

Fig. 2 Temperature dependence of DMR.

dependent of temperature.

At high temperatures, on the other hand, spin mixing arises and increases with temperature, and finally the electrons have an equal probability of having spin up or spin down. The net solute resistivity $\rho(c, HT)$ at high temperatures is given by

$$\rho(c, HT) = \{\rho_t(c, 0) + \rho_i(c, 0)\} / 4, \quad (3)$$

because the solute resistivity at high temperatures is given by $1/2\{\rho_t(c, 0) + \rho_i(c, 0)\}$ for one spin direction.

Unless $\rho_t(c, 0)$ actually equals $\rho_i(c, 0)$, $\rho(c, HT)$ is greater than $\rho(c, 0)$. In this case, the DMR at high temperatures, $\Delta(c, HT)^{(6)}$ is given by

$$\begin{aligned} \Delta(c, T) &= \rho(c, HT) - \rho(c, 0) \\ &= \frac{\{\rho_t(c, 0) - \rho_i(c, 0)\}^2}{4\{\rho_t(c, 0) + \rho_i(c, 0)\}}. \end{aligned} \quad (4)$$

It is known from the analysis mentioned above

$$\Delta(c, T) = \rho(c, 0) \left[\frac{\{\sigma_t(c, 0) - \sigma_i(c, 0)\}^2}{\sigma_{tl}(T)\{\sigma_t(c, 0) + \sigma_i(c, 0)\} + 4\sigma_t(c, 0)\sigma_i(c, 0)} \right], \quad (5)$$

Fig. 3 Concentration dependence of $\rho(c, 0)$ and $\Delta(c, HT)$.

that the DMR increases gradually and becomes constant as the temperature increases, and that the larger than difference between $\rho_t(c, 0)$ and $\rho_i(c, 0)$, the larger the DMR.

The residual resistivities of each spin band can be calculated from the measured values of $\rho(c, 0)$ and $\Delta(c, HT)$ using eqs. (2) and (4). The concentration dependence of the measured values of $\rho(c, 0)$ and $\Delta(c, HT)$ is shown in Fig. 3, and $\Delta(c, HT)$ is estimated at 360 K. The obtained values of the parameters are summarized in Table 1.

IV. Discussion

The temperature dependence of DMR is discussed first in order to confirm the validity of the two current model for cobalt base alloys. According to Farrell and Greig⁽⁶⁾, the temperature dependence of DMR, $\Delta(c, T)$, is given by

where $\sigma_t(c, 0) = 1/\rho_t(c, 0)$ and $\sigma_i(c, 0) = 1/\rho_i(c, 0)$. σ_{tl} indicates the conductivity regarding spin mixing. As seen from Fig. 2, T^2 dependence of DMR is clearly observed at low temperature range, therefore, σ_{tl} is proposed to be proportional to T^{-2} . The coefficient A in $\sigma_{tl}(T) = AT^{-2}$ is estimated to be $1.6 \times 10^{12} \text{ K}^2/\Omega \cdot \text{m}$. AT^5 term, which is reported on Co-Cr alloy by Loegel and Gautier, is not found in the present experiments. They also suggested the existence of T^5 term in $\rho(0, T)$ at low temperatures. However, Isshiki *et al.*⁽¹⁵⁾ reported recently that $\rho(0, T)$ is expressed by a linear combination of T^2 and T^4 terms below

Table 1 The obtained values of parameters in $10^{-8} \Omega \cdot \text{m}/\text{at. \%}$.

	Co-Ni	Co-Cr
$\rho(c, 0)$	0.11	3.91
$\Delta(c, HT)$	0.36	6.10
$\rho_t(c, 0)$	1.80	4.38
$\rho_i(c, 0)$	0.12	35.6
$\rho_t(c, 0)/\rho_i(c, 0)$	15	0.12

Fig. 4 Calculated values of $\Delta(c, T)$ for each specimen.

40 K.

$\Delta(c, T)$ is calculated for each specimen using eq. (5) with the values of parameters shown in Table 1. The calculated results shown in Fig. 4 are in fairly good agreement with the experimental data in Fig. 2. This fact indicates that the two current model adopted in the present work can be successfully applied for cobalt base alloys and that the two current condition is valid for cobalt and cobalt base alloys.

It should be noted that chromium solute gives larger contributions to $\rho(c, 0)$ and $\Delta(c, HT)$ compared with nickel solute, as shown in Table 1. The large $\Delta(c, HT)$ of Co-Cr alloy is attributed to the large difference between $\rho_t(c, 0)$ and $\rho_i(c, 0)$. In the case of Co-Ni alloy, the value of $\rho_t(c, 0)/\rho_i(c, 0)$ is 15 and $\rho_i(c, 0)$ is small. This fact shows that the conduction is dominated by the spin down electrons, and that these electrons do not make s-d transitions.

It is worth noting that the value of $\rho_i(c, 0)$ for chromium solute is rather large. Taking in-

to consideration the results reported on Ni-Cr alloy by Farrell and Greig⁽⁶⁾, this suggests that the virtual bound state of the spin down electrons in chromium is close to the Fermi level of the spin down band in cobalt.

V. Conclusion

Two current conduction is shown to be valid for cobalt base dilute alloys at low temperatures from the analysis of the temperature dependent DMR. A spin mixing term $\sigma_{\uparrow\downarrow}(T)$ is found to be proportional to T^{-2} and to be the dominant mechanism in determining the DMR at low temperatures. The higher value of $\Delta(c, HT)$ in Co-Cr alloys is explained by the larger difference between $\rho_t(c, 0)$ and $\rho_i(c, 0)$, compared with that of Co-Ni alloys. It is proposed that the virtual bound state of the spin down electrons in chromium is close to the Fermi level of the spin down band in cobalt.

REFERENCES

- (1) I. A. Campbell, A. Fert and A. R. Pomeroy: *Phil. Mag.*, **15** (1967), 977.
- (2) N. F. Mott: *Adv. Phys.*, **13** (1964), 325.
- (3) A. Fert and I. A. Campbell: *Phys. Rev. Lett.*, **21** (1968), 1190.
- (4) A. Fert and I. A. Campbell: *J. Physique*, **32** (1971), 46.
- (5) J. Durand and F. Gautier: *J. Phys. Chem. Solids*, **31** (1970), 2773.
- (6) T. Farrell and D. Greig: *J. Phys. C*, **1** (1968), 1359.
- (7) J. W. F. Dorleijn and A. R. Miedema: *J. Phys. F*, **7** (1977), L23.
- (8) R. N. Ross, D. C. Price and G. Williams: *J. Phys. F*, **8** (1978), 2367.
- (9) J. W. F. Dorleijn and A. R. Miedema: *J. Phys. F*, **5** (1975), 487.
- (10) J. W. F. Dorleijn and A. R. Miedema: *J. Phys. F*, **5** (1975), 1543.
- (11) B. Loegel and F. Gautier: *J. Phys. Chem. Solids*, **32** (1971), 2723.
- (12) M. Isshiki, Y. Fukuda and K. Igaki: *J. Less-Common Metals*, **105** (1985), 211.
- (13) K. Igaki, M. Isshiki and K. Yakushiji: *Trans. JIM*, **20** (1976), 611.
- (14) M. Isshiki, Y. Fukuda and K. Igaki: *J. Radioanal. Nucl. Chem.*, **82** (1984), 135.
- (15) M. Isshiki, Y. Fukuda and K. Igaki: *J. Phys. F*, **14** (1985), 3007.