DEPENDENCE OF THE ORDINARY HALL CONSTANT ON THE TEMPERATURE AND ALLOYING-ELEMENT CONCENTRATION

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An equation is derived for the Hall constant for the case of a binary disordered solid solution on the basis of two-band theory. The equation explains the change in the sign of the Hall emf at certain alloying-element concentrations. An equation is found for the temperature coefficient of the Hall constant for a compensated metal; this equation explains the decrease in this coefficient with increasing temperature and the change in sign at certain alloying-element concentrations.

Several attempts have been made to find theoretical explanations for the behavior of the ordinary Hall constant in pure metals and in dilute binary solid solutions. Unfortunately, no equations agreeing well with experiment have been found. Nevertheless, it can be shown that a systematic extension of the Wilson–Sondheimer theory reveals an explanation of the experimental dependence of the Hall emf on the temperature and alloying-element concentration in metals.

According to the Wilson–Sondheimer two-band theory [1], the ordinary Hall constant can be written in the following form over a relatively broad range of magnetic fields:

$$R = R_1\left(\frac{\sigma_1}{\sigma}\right)^2 - R_2\left(\frac{\sigma_2}{\sigma}\right)^2 = R_1\left(\frac{\rho_2}{\rho_1+\rho_2}\right)^2 - R_2\left(\frac{\rho_1}{\rho_1+\rho_2}\right)^2, \tag{1}$$

where $\sigma_i = e^2 n_i x_i$ is the electrical conductivity; $\rho_i = 1/\sigma_i$ is the resistivity of the i-th energy band; n_i and $x_i = \tau_i/m_i$ are the electron (i = 1) and hole (i = 2) concentrations and mobilities; e is the electronic charge; τ_i and m_i are the relaxation time and the effective mass, and we have $\sigma = \sigma_1 + \sigma_2$. The Hall constant $R_i = 1/en_i$ for each of the energy bands in the metal participating in the conduction is governed only by the electron (or hole) concentration n_i and thus by the position of the Fermi level E_F with respect to the bottom of the conduction band (or with respect to the top of the band in the case of holes). It is known that E_F depends very weakly on the temperature. When alloying metals are added to the pure metal, E_F is also affected very slightly, even at the concentrations at which very anomalous behavior is observed in several physical properties [2]. In poor conductors such as antimony and bismuth, in which the electron and hole concentrations are many orders of magnitude below the concentrations in ordinary metals, these slight changes in E_F may be important [3]. Since the electron concentration varies slightly as a function of the temperature or the alloying-element concentration, we will below relate all the basic changes in the overall Hall constant of the metal to the corresponding changes in the band resistivities, ρ_1 and ρ_2, in Eq. (1).

The resistivity associated with the i-th energy band can be written as [4]

$$\rho_i = \frac{m_i v_F}{e^2 n_i} \sum_{\kappa} \mu_{i\kappa}, \tag{2}$$

where v_F is the velocity at the Fermi level and where we have

$$\sum_{\kappa} \mu_{i\kappa} = \mu_i(T) + \mu_i(c) + \mu_i(N_b) + \mu_i(N_d) + \ldots, \tag{3}$$

where $\mu_i(T)$ is the coefficient for phonon scattering of electron waves; $\mu_i(c)$ is that for scattering by alloying metals; $\mu_i(N_v)$ and $\mu_i(N_d)$ are the corresponding coefficients of scattering by vacancies and dislocations.

Substituting Eq. (3) into Eq. (2) and then into Eq. (1), we can in principle find the Hall constant as a function of the temperature and the alloying element, dislocation, vacancy, etc., concentrations. In general,

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however, all these dependences are complicated. We will deal with certain particular cases in which the Hall emf is a relatively simple function of these factors.

I. We assume a binary disordered solid solution and we assume that the scattering of electron waves which is responsible for the "residual" resistivity is incoherent. The resistivity is known to be governed by squares of the matric elements of the potential. Following Nordheim, we choose as matrix element

$$V_{\kappa\kappa'} = \sum_n \int \psi_\kappa^* v_n \psi_{\kappa'}\, d\tau, \tag{4}$$

where v_n, the atomic potential, vanishes outside the n-th cell; $\psi_{\kappa'}$ and ψ_κ are wave functions corresponding to the states of conduction electron for which the wave vectors are κ' and κ. In particular, for the i-th band of a disordered solid solution containing a concentration c of atoms of species a and a concentration of 1 −c of atoms of species b we have

$$|V_{\kappa_i\kappa_i'}|^2 = Nc(1-c)(f_{a\kappa_i\kappa_i'} - f_{b\kappa_i\kappa_i'})^2 = Nc(1-c)\,\Delta f_i^2, \tag{5}$$

where $f_{a\kappa_i\kappa_i'} = \int \psi_{\kappa_i}^* v_{na} \psi_{\kappa_i'} d\tau$; and N is the total number of atoms. Within the framework of single-band theory we find the Nordheim residual-resistivity term [5]:

$$\rho_i = A_i c(1-c), \tag{6}$$

$$A_i = 16\pi^3 \frac{m_i^2}{e^2 h^3} \left(\frac{3N}{\pi}\right)^{1/3} \Delta f_i^2. \tag{7}$$

The resistivity of the i-th band thus depends on the alloying-element concentration in the following manner:

$$\rho_i = \rho_{0i} + A_i c(1-c), \tag{8}$$

where $\rho_{0i} \simeq \rho_i(T)$ is the phonon resistivity of the i-th band. (At low temperatures and in highly deformed metals, ρ_{0i} should include the resistivity due to the vacancy and dislocation concentrations.)

Substituting Eq. (8) into Eq. (1), and carrying out some calculations, we find

$$R = \frac{\alpha_1 + \beta_1 c(1-c) + \delta_1 c^2 (1-c)^2}{\alpha_2 + \beta_2 c(1-c) + \delta_2 c^2(1-c)^2}, \tag{9}$$

where $\alpha_1 = R_1\rho_{02}^2 - R_2\rho_{01}^2$, $\beta_1 = (R_1A_2\rho_{02} - R_2A_1\rho_{01})$, $\delta_1 = R_1A_2^2 - R_2A_1^2$,

$$\alpha_2 = (\rho_{01} + \rho_{02})^2, \quad \beta_2 = 2(\rho_{01} + \rho_{02})(A_1 + A_2), \quad \delta_2 = (A_1 + A_2)^2. \tag{10}$$

Using c < 1, we expand (9) in a series:

$$R = R(0) + R'(0)\cdot c + \frac{1}{2}R''(0)c^2 + \ldots \simeq R_0 + B_0(1 - \Delta\cdot c)c, \tag{11}$$

where $R_0 = R(0)$ is the Hall constant of the pure metal, given by Eq. (1), except that the σ_i values for pure metals are used; after lengthy calculations we find we can write $B_0 = R'(0)$ and $\Delta = R''(0)/2R'(0)$ as

$$B_0 = 2(A_2\rho_{01} - A_1\rho_{02}) \frac{R_2\rho_{01} + R_1\rho_{02}}{(\rho_{01} + \rho_{02})^2}, \tag{12}$$

$$\Delta = 1 + \frac{2(A_1 + A_2)}{\rho_{01} + \rho_{02}} - \frac{2(R_1A_2\rho_{02} + R_2A_1\rho_{01}) + (R_2 + R_1)(A_2\rho_{01} + A_1\rho_{02})}{2(R_2\rho_{01} + R_1\rho_{02})(\rho_{01} + \rho_{02})}. \tag{13}$$

The expressions for Δ and B_0 simplify considerably for an extremely important and broad class of conductors – compensated metals ($R_1 = R_2 = 1/en$):

$$\Delta = 1 + \frac{A_1 + A_2}{\rho_{01} + \rho_{02}} = 1 + e^2 n(A_1 + A_2)\frac{x_1 x_2}{(x_1 + x_2)}, \tag{14}$$

$$B_0 = 2R_1 \frac{A_2\rho_{01} - A_1\rho_{02}}{(\rho_{01} + \rho_{02})^2} = 2e(A_2x_2 - A_1x_1)\frac{x_1x_2}{(x_1 + x_2)^2}. \tag{15}$$

In contrast with the case of the Nordheim resistivity, the Hall constant may either decrease or increase, dependent on the sign of B_0 in Eq. (11). The sign of B_0 is governed by the sign of the factor $(A_2\rho_{01} - A_1\rho_{02})$ in Eq. (12):

$$A_2\rho_{01} - A_1\rho_{02} = 16\pi^3 \frac{1}{e^2h^3}\left(\frac{3N}{\pi}\right)^{1/3} (\rho_{01}m_{02}^2\Delta f_2^2 - \rho_{02}m_{01}^2\Delta f_1^2). \tag{16}$$

TABLE 1

Alloy	R_0	B_0	Alloy	R_0	B_0	Alloy	R_0	B_0
Pd—Ag	—	— [13]*	Au—Ag	—	— [22]	Pb—Sn	+	— *
Pd—Au	—	— [14]	Cu—Ni	—	— [19]	Pb—Tl	+	— [16]
Pd—H	—	— [15]	Ni—Cu	—	— [19]	Pb—In	+	— [16]
Pd—Ru	—	— [13]	Ni—Ti	—	— [21]	Pb—Hg	+	— [16]
Pd—Mo	—	— [13]	Ni—V	—	— [21]	Mg—Li	—	+ [16]
Pd—Rh	—	— [13]	Ni—Cr	—	— [21]	Mg—Ag	—	+ [23]
Pd—Nb	—	— [13]	Ni—Mn	—	— [21]	Mg—Cd	—	+ [16]
Pd—Zr	—	— [13]	Ni—Co	—	— [20]	Mg—Al	—	+ [16]
Ag—Pd	—	— [11]	Fe—Ni	—	— [18]	Al—Mg	—	+ [16]
Ag—Pt	—	— [11]	Fe—Co	+	— [17]	Al—Si	—	+ [16]
Ag—Au	—	— [22]	Fe—W	+	— *	Al—Ge	—	+ [16]
						Al—Zn	—	+ [16]

From Eq. (16) we easily find

$$B_0 > 0 \ \text{for} \ \frac{m_2 n_2 \tau_2}{m_1 n_1 \tau_1} > \frac{\Delta f_2^2}{\Delta f_1^2} \ \text{and} \ B_0 < 0 \ \text{for} \ \frac{m_2 n_2 \tau_2}{m_1 n_1 \tau_1} < \frac{\Delta f_2^2}{\Delta f_1^2}\,. \tag{17}$$

Experimentally, we can determine the sign and magnitude of B_0 from the dependence of the Hall constant on the alloying-element concentration. Table 1 shows the signs of B_0 and those of R_0 which we found from the literature and from our own experiments (the latter are denoted by asterisks).

Using Eq. (11) we can easily find an explanation for the change in the sign of the ordinary Hall constant at certain alloying-element concentrations: if R_0 and B_0 in Eq. (11) have different signs, an increase in the concentration of the alloying element may result in a situation in which we have $|B_0 c(1-\Delta c)| = R_0$. Then a further increase in concentration c will change the sign of the Hall constant; such a sign change has in fact been observed in iron–cobalt [16], lead–thallium, lead–indium, lead–mercury, magnesium–cadmium [15], and other alloys.

We see from Eq. (11), which holds within a factor on the order of $c^3/3!$, that with

$$c = 0.5\,\Delta^{-1} \tag{18}$$

we will observe an extremum in the Hall constant. In alloy systems such as Co–Ni [18], Cu–Ni [19], Au–Ag [22], Pb–Tl [16], Pd–Ag [13], and Pd–Au [14], for which experiments have been carried out over a wide range of alloy concentrations, this extremum has been observed. Since we generally have $\Delta \neq 1$, the extremum should shift toward a concentration of c = 0.5, in agreement with experiment.

II. No satisfactory explanation has been offered for the behavior of the temperature coefficient of the Hall constant. Gmöhling and Hagmann [24] attempted to explain the change which they observed in this coefficient in their palladium alloys in terms of a temperature dependence of the concentration of conduction electrons in turn due to thermal expansion and a change in the Fermi energy. However, their theoretical estimates of the temperature coefficient turned out to be on the order of hundredths of the experimental values. Taking note of the pronounced paramagnetism, the maximum in the susceptibility $\varkappa$ at 80°K, and the similarity between the temperature dependences of $\varkappa$ and R in palladium, Allison and Pugh [25] suggested that the temperature-dependent part of the coefficient in palladium–silver alloys was due to the extraordinary Hall effect. However, this explanation seems unconvincing, since the ordinary Hall constant depends on the temperature in all metals.

Without using any arbitrary assumptions we can explain the features of the temperature dependence of the Hall constant within the framework of two-band theory. Let us consider the case of compensated metals ($R_1 = R_2 = 1/en$), which includes palladium. According to Eq. (1) we then have

$$R = \frac{1}{en} \cdot \frac{\Delta\sigma}{\sigma}\,, \quad \Delta\sigma = \sigma_1 - \sigma_2 = 1/\rho_1 - 1/\rho_2\,. \tag{19}$$

After simple calculations, using (19), and

$$\frac{d\sigma}{dT} = -\frac{1}{\rho_1^2}\frac{d\rho_1}{dT} - \frac{1}{\rho_2^2}\frac{d\rho_2}{dT}\,, \quad \frac{d(\Delta\sigma)}{dT} = \frac{1}{\rho_2^2}\frac{d\rho_2}{dT} - \frac{1}{\rho_1^2}\frac{d\rho_1}{dT}\,, \tag{20}$$

we find the temperature coefficient of the Hall constant (γ) to be

$$\gamma = -\frac{1}{n}\frac{dn}{dT} + \frac{1}{\Delta\sigma}\frac{d(\Delta\sigma)}{dT} - \frac{1}{\sigma}\frac{d\sigma}{dT} = -\frac{1}{n}\frac{dn}{dT} - 2\alpha_1\frac{1-\varepsilon\delta}{1-\delta^2}, \tag{21}$$

where $\alpha_i = (d\rho_i/dT)/\rho_i$ is the temperature coefficient of the resistivity of the i-th band, and we have $\delta = \rho_1/\rho_2$ and $\varepsilon = (d\rho_2/dT)(d\rho_1/dT) = (\alpha_2/\alpha_1)/\delta$.

Let us consider some limiting cases of Eq. (21).

1. <u>High Temperatures</u>. Here we have $\rho_1 = a_1T + \rho_{10}^*$ and $\rho_2 = a_2T + \rho_{20}^*$; and ρ_{10}^* and ρ_{20}^* are the residual resistivities of the two bands. Under the condition $a_1 \neq a_2$, the denominator in the second term in this equation is finite, even as $T \to \infty$, but the numerator, $1 - \varepsilon\delta = 1 - (a_1a_2T + a_2\rho_{10}^*)/(a_1a_2T + a_1\rho_{20}^*)$, vanishes as $T \to \infty$. Then the temperature coefficient of the Hall constant is governed by the extremely small quantity

$$\gamma' = -\frac{1}{n}\frac{dn}{dT}, \tag{22}$$

which yields a temperature coefficient for the Hall constant for palladium on the order of $4 \cdot 10^{-5}$ deg^{-1} [24], more than an order of magnitude below the experimental values at room temperatures, at which the term

$$\gamma'' = -2\alpha_1\delta(1-\varepsilon\delta)/(1-\delta^2), \tag{23}$$

which is a fraction of the quantity $2\alpha_1 \sim 10^{-2}$-10^{-3}, cannot be neglected. Equation (21) thus correctly reflects the well-known decrease in the temperature coefficient of the Hall constant in metals as the temperature is raised, and it reflects the very small temperature coefficient of the Hall constant at room temperature or higher.

2. Let us consider the change in the alloying-element part of the resistivity on the basis of Nordheim law (7). We expand $\delta = \delta(c)$ in a series and retain the first three terms; after some calculation, we find

$$\delta = \frac{\rho_{01}}{\rho_{02}} + \frac{A_1\rho_{02} - A_2\rho_{01}}{\rho_{02}^2}c(1 - \Delta^* \cdot c), \tag{24}$$

where Δ^* is a new constant, a particular case of which is described below [see Eq. (26)]. At high temperatures we have $\rho_{0i} \simeq a_iT$; i.e., we can neglect the role of vacancies and dislocations in determining ρ_{0i}. In this case the numerator in Eq. (21) becomes

$$1 - \varepsilon\delta = \frac{A_2a_1 - A_1a_2}{a_1a_2T}c(1 - \Delta^*c), \tag{25}$$

where A_1 and A_2 are given as before by Eq. (7).

Since, in the first approximation, a_i and A_i do not depend on the alloying-element concentration, we would expect, at concentrations above $c^* = 1/\Delta^*$, the sign of γ'' to change; this change has in fact been observed experimentally [24]. Using the method of least squares, we find from the data of [24] that the concentration c^* at which this change occurs is $c^* = 5.5$ at.% Ag for Pd–Ag and $c^* = 8.75$ at.% Au for Pd–Au. Using Eq. (21), we can find $c^* = 1/\Delta^*$ theoretically from data on the phonon resistivity of palladium, $\rho(T) = 9.1$ μΩ·cm (0°C) [8] and the constants† $A = 1.0 \cdot 10^2$ (Pd–Au) (the concentrations are given in relative units) and $A = 1.4 \cdot 10^2$ (Pd–Ag) [21]. Let us assume that the phonon resistivity of band 2 differs from the overall phonon resistivity by the same factor by which constant A_2 differs from the overall factor A for all the bands. Then from

$$c^* = 1/\Delta^* = a_2T/(a_2T + A_2) \simeq aT/(aT + A) \tag{26}$$

we find $c^* = 8.3 \cdot 10^{-2}$ (8.3 at.%) for Pd–Au and $c^* = 6.1 \cdot 10^{-2}$ (6.1 at.%) for Pd–Ag. These values differ little from the experimental values given above, offering further support for Eq. (21). We see from (26) that c^* depends strongly on the temperature.

By studying the Hall constant and the electrical resistivity as functions of the temperature and the concentration of the alloying element along with changes in the signs of the Hall constant and the temperature coefficient of the Hall constant; and by determining the maximum of the Hall constant through the use of Eqs. (11), (21), (16), (18), and (26), using arguments based on the model; we can determine important parameters of the energy bands, particularly if we supplement this study with study of the heat capacity, the de Haas–Van Alphen effect, etc.

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†Here A is the coefficient in the residual-resistivity equation (6), averaged over all bands participating in the conduction; this constant is usually determined experimentally.

Significantly, Eq. (4) is based on the assumption that the electron waves are scattered independently, and it neglects several interference effects, e.g., the interaction between alloying-element atoms and dislocations, that between vacancies and dislocations, and that between alloying-element atoms. In several cases these interactions produce a nonmonotonic change in the potential energy of the crystal [12]. These effects can be taken into account in matrix element (5) if we discard the original restrictions. We can retain the mathematical formalism here, but we must recall that $f_{a\kappa_i\kappa_i'}$ and $f_{b\kappa_i\kappa_i'}$ in Eq. (6) change nonmonotonically at low concentrations (on the order of 0.1 at.%) of the alloying element. Since at $c \sim 0.001$ Eq. (11) can be written as $R = R_0 + B_0 c$, this nonmonotonic behavior affects the Hall constant through coefficients A_i [see (8)] in Eq. (12). In this case the pronounced extrema of the Hall constant which have been observed [5-7, 9-11, etc.] become understandable. However, analysis of this anomalous behavior lies outside the scope of this paper and must be taken up separately.

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