TEMPERATURE DEPENDENCE OF THE HALL EFFECT AND THE PARAMAGNETIC

SUSCEPTIBILITY OF ZIRCONIUM AND RHENIUM

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The temperature dependences of the Hall field, paramagnetic susceptibility, and electrical resistivity of polycrystalline Zr and Re were investigated in the 77-350°K temperature range. An anomalous Hall field was found in the investigated nonferromagnetic transition metals; it varied with temperature as T². The relationships of the Hall coefficient with the Pauli susceptibility χ (R* $\propto \chi$) and the electrical resistivity ρ (R* $\propto \rho^2$) were found. It was concluded that a large fraction of the d electrons in Zr and Re was in the collective state.

MANY experimental investigations of the Hall effect in the paramagnetic region have been carried out recently in order to verify a number of theories dealing with the temperature dependence of the spontaneous Hall effect in ferromagnetic metals. It has been established that in all ferromagnetic metals above the Curie temperature^[1-3] and all rare-earth metals above the Neel temperature^[4-6] the experimentally measured Hall field E has the classical (normal) component E_n , which is practically independent of temperature, as well as a considerable anomalous component of the field E_a , which depends strongly on temperature. There have been fewer experimental investigations of the anomalous Hall field, and particularly of its temperature dependence, in nonferromagnetic transition metals.

The present paper deals with the temperature dependences of the Hall field, paramagnetic susceptibility, and electrical resistivity of two nonferromagnetic transition metals: Zr (4d) and Re (5d). The Hall effect of Zr has been investigated before.^[7-10] However, the published results have yielded no definite quantitative relationships for the temperature dependence of the Hall effect. Moreover, the temperature dependences of the paramagnetic susceptibility and electrical resistivity have usually not been investigated in the same samples. As far as the present authors are aware, the temperature dependence of the Hall effects in Re has not yet been investigated at all.

RESULTS OF MEASUREMENTS AND DISCUSSIONS

The Hall effect and the paramagnetic susceptibility were investigated using Zr and Re samples with electrical resistivity ratios $\rho(300^{\circ} \text{K})/\rho(4.2^{\circ} \text{K}) = 27$ for Zr and $\rho(300^{\circ} \text{K})/\rho(4.2^{\circ} \text{K}) = 38$ for Re. The Hall field was proportional to the magnetic field intensity throughout the investigated range of temperatures (77–350°K) and magnetic fields (H_{max} = 15 kOe); the magnetic susceptibility of the samples was independent of the magnetic field intensity.

The temperature dependences of the Hall coefficient $R^* = E/H$, determined from the tangents of the slopes of the E(H) isotherms, are given in Fig. 1 (curves denoted by 1). It is evident from this figure that the Hall

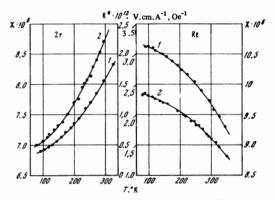


FIG. 1. Temperature dependences of the Hall coefficient R* (curves 1) and of the paramagnetic susceptibility χ (curves 2) of Zr and Re.

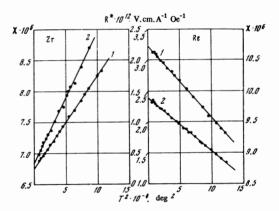


FIG. 2. Dependences of the Hall coefficient R^* (curves 1) and of the paramagnetic susceptibility χ (curves 2) of Zr and Re on the square of temperature.

field in Zr and Re depends strongly on temperature; in Zr, the Hall field increases, while in Re, it decreases when the temperature is increased. However, the temperature dependence of the Hall fields of Zr and Re are both described satisfactorily, as shown in Fig. 2 (curves 1), by a quadratic law, i.e.,

$$R^* = a + bT^2, \tag{1}$$

where a and b are constants which are independent of temperature: $a = 2.6 \times 10^{-13} \text{ V} \cdot \text{cm} \cdot \text{A}^{-1} \cdot \text{Oe}^{-1}$, $B = 1.5 \times 10^{-17} \text{ V} \cdot \text{cm} \cdot \text{A}^{-1} \cdot \text{Oe}^{-1} \cdot \text{deg}^{-2}$ for Zr and $a = 3.2 \times 10^{-12} \text{ V} \cdot \text{cm} \cdot \text{A}^{-1} \cdot \text{Oe}^{-1}$, $b = -1.2 \times 10^{-17} \text{ V} \cdot \text{cm} \cdot \text{A}^{-1} \cdot \text{Oe}^{-1} \cdot \text{deg}^{-2}$ for Re.

Thus, the investigated transition metals (Zr, Re) exhibit the anomalous component of the Hall field Ea and the experimentally determined dependence of the Hall field on T is due to the temperature dependence of E_{a} . In this connection, we should note that the absolute value of the anomalous Hall field Ea of ferromagnetic metals always decreases with increasing temperature in the paramagnetic region, following the Curie-Weiss law, while in the case of Zr and Re the anomalous Hall field is proportional to T^2 . This is the distinguishing characteristic of the behavior of the Hall effect in the investigated nonferromagnetic transition metals. It is also worth mentioning that if the anomalous component of the Hall field is ignored in the determination of the effective number of carriers n^* from the value of E/H. as it is done usually, the value of n* may differ considerably from the true value. The classical Hall field should be determined from measurements at low temperatures because the anomalous Hall field disappears, according to the theory, at $T = 0^{\circ} K$.

In order to determine the relationship of the anomalous Hall field with the susceptibility and electrical resistivity, we used the same Zr and Re samples to measure the temperature dependences of χ and ρ . The results obtained for the volume susceptibility, χ (T) are presented in Figs. 1 and 2 (curves 2). We can see that the paramagnetic susceptibility of Zr and Re is proportional to T², like the Hall field.

It is known that the susceptibility of the spin paramagnetism of metals can be represented approximately in the form^[11]</sup>

$$\chi = 2\mu_B^2 N(\xi_0) + \frac{(\pi k \mu_B)^2}{3} \left[N''(\xi_0) - \frac{(N'(\xi_0))^2}{N(\xi_0)} \right] T^2,$$
(2)

where $N(\xi_0)$ is the density of electron states at the Fermi surface; ξ_0 is the Fermi level at $T = 0^{\circ} K$; $N'(\xi_0) = [dN(\epsilon)/d\epsilon]_{\epsilon=\xi_0}$ and $N''(\xi_0) = [d^2N(\epsilon)/d\epsilon^2]_{\epsilon=\xi_0}$ are derivatives of the function N(ϵ) at the Fermi surface; $\mu_{\rm B}$ is the Bohr magneton; k is the Boltzmann constant. We shall show later that the chief contribution to the susceptibility of Zr and Re is made by the Pauli paramagnetism, while the contribution of the Langevin paramagnetism is negligibly small. Consequently, the temperature dependence of the paramagnetic susceptibility of Zr and Re is governed by the temperature dependence of the Pauli paramagnetism ($\chi_{\mbox{P}} \propto T^2),$ in agreement with our experimental observations. The different nature of the temperature dependence of the susceptibility χ for Zr and Re (χ increases proportionally to T^2 for Zr and decreases in the case of Re) is possibly due to the fact that in the case of Zr the derivative $N''(\xi_0)$ $> [N'(\xi_0)]^2 / N(\xi_0)$, and for Re $N''(\xi_0) < [N'(\xi_0)]^2 / N(\xi_0)$. It is possible that the anomalous temperature dependence of the susceptibility in the case of $Zr (d\chi/dT > 0)$ is due to the fact that the Fermi level (ξ_0) lies close to a minimum of the $N(\epsilon)$ curve, where $N'(\epsilon) = 0$. This is likely to be due to an overlap of the energy bands.

The magnetic susceptibility found by direct measurements represents, in general, a sum of a number of susceptibilities:

$$\chi = \chi_d^{(1)} + \chi_d^{(2)} + \chi_l + \chi_L + \chi_{P0}, \qquad (3)$$

where $\chi_d^{(1)}$ is the diamagnetic susceptibility of atoms; $\chi_d^{(2)}$ is the diamagnetic Landau susceptibility; χ_l is the orbital component of the susceptibility; χ_L and χ_{PO} are, respectively, the Langevin and Pauli (including the exchange interaction) susceptibilities.

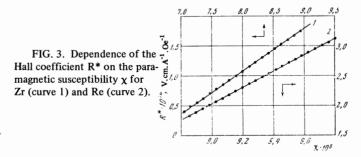
The electronic components of the specific heat, $\gamma = 2.89 \times 10^{-3} \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-2}$ for $\text{Zr}^{[12]}$ and $\gamma = 2.3 \times 10^{-3} \text{ J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-2}$ for Re, ^[13] were used to determine the electron state density $N(\xi)$ near the Fermi surface and Eq. (2) was used to calculate (at low temperatures) the Pauli component of the susceptibility, $\chi_{\mathbf{P}}$. Comparison of the calculated values with the experimental data, corrected for the diamagnetism of ionic cores $\chi_{d}^{(1)} = -27 \times 10^{-6} \text{ cm}^3/\text{mole}$ (Zr) and -36 $\times 10^{-6}$ cm³/mole (Re) and for the Landau diamagnetism of the s electrons, showed that $\chi_{exper} \gg \chi_{calc}$. It is usual to attribute this difference to the fact that the derivation of Eq. (2) from the band theory ignores the exchange interaction between electrons. On the other hand, the orbital paramagnetism (χ_l) , particularly in the case of Zr, can make a definite contribution to the susceptibility. According to an estimate reported in ^[14], χ_l for Zr is approximately 100×10^{-8} cm³/mole. It has been demonstrated in ^[15] that when the exchange interaction between electrons is taken into account, the spin component of the susceptibility (at $T = 0^{\circ} K$) is given by $\chi_{PO} = 2 \mu_B^2 N(\xi) (1-\alpha)^{-1}$, where the correction factor due to the exchange interaction, $(1-\alpha)^{-1}$, is determined from the experimental data and its value is about 2-3.

Thus, analysis of the experimental results shows that the Langevin component of the susceptibility χ_L is negligibly small. We therefore reach the conclusion that the degree of delocalization of the d electrons is high in Zr and Re. The conclusion regarding delocalization is supported also by the value of the electronic component of the specific heat, which is relatively large for Zr and Re.

As already demonstrated, the paramagnetic susceptibility of Zr and Re varies, like the Hall field, proportionally to the square of temperature. Therefore, the Hall field and the susceptibility are related by a simple linear dependence (cf. Fig. 3):

$$R^{\star} = c + d\chi, \tag{4}$$

where c and d are constants independent of temperature: $c = -10.1 \times 10^{-12} \text{ V} \cdot \text{cm} \cdot \text{A}^{-1} \cdot \text{Oe}^{-1}$, $d = 1.35 \times 10^{-6} \text{ V} \cdot \text{cm} \cdot \text{A}^{-1} \cdot \text{G}^{-1}$ for Re and $c = -4.6 \times 10^{-12} \text{ V} \cdot \text{cm} \cdot \text{A}^{-1} \cdot \text{Oe}^{-1}$, $d = 7.1 \times 10^{-7} \text{ V} \cdot \text{cm} \cdot \text{A}^{-1} \cdot \text{G}^{-1}$ for Zr. It follows that the experimentally observed quadratic



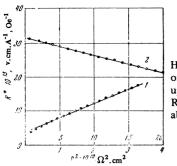


FIG. 4. Dependence of the Hall coefficient R^* of the square of the resistivity ρ for Zr (curve 1, upper scale along the abscissa) and Re (curve 2, lower scale along the abscissa).

temperature of the anomalous Hall effect may be due to the temperature dependence of the Pauli paramagnetism of Zr and Re. However, it must be mentioned that the temperature dependence of the anomalous Hall field E_a may also be due to a relationship of this field with the electrical resistivity. In fact, according to the theory^[16-18] which assumes that carriers are scattered mainly by phonons, the anomalous Hall coefficient is proportional to the square of the electrical resistivity. Measurement of the electrical resistivity ρ in the investigated range of temperatures show that ρ varies proportionally to temperature and therefore the dependence $R^* \propto T^2$ may be the consequence of the dependence $R \propto \rho^2$, which is presented in Fig. 4.

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²I. K. Kikoin, E. M. Buryak, and Yu. A. Muromkin, Dokl. Akad. Nauk SSSR 125, 1011 (1959) [Sov. Phys.-Dokl. 4, 386 (1959)].

³D. I. Volkov and T. M. Kozlova, Fiz. Metallov Met-

alloved. 20, 355 (1965).

⁴N. A. Babushkina, Fiz. Tverd. Tela 7, 3026 (1965) [Sov. Phys.-Solid State 7, 2450 (1966)].

⁵D. I. Volkov, T. M. Kozlova, and G. A. Shafigullina, Fiz. Metallov Metalloved. 27, No. 1 (1969).

⁶N. V. Volkenshtein and G. V. Fedorov, Fiz. Tverd. Tela 7, 3213 (1965) [Sov. Phys.-Solid State 7, 2599 (1966)].

⁷T. G. Berlincourt, Phys. Rev. 114, 969 (1959).

⁸S. Foner, Atomic Energy Commission Report, NYO-7257, Suppl. 2.

⁹V. Frank, Appl. Sci. Res. B7, 41 (1958).

¹⁰N. V. Volkenshtein and É. V. Galoshina, Fiz. Metallov Metalloved. 20, 475 (1965).

¹¹ H. A. Bethe and A. Sommerfeld, Elektronentheorie der Metallen (Russ. Transl., ONTI, 1937).

¹²I. Esterman, S. A. Friedberg, and J. E. Goldmann, Phys. Rev. 87, 582 (1952).

¹³ D. H. Parkinson, Rep. Progr. Phys. 21, 226 (1958).
¹⁴ M. Shimizu and A. Katsuki, J. Phys. Soc. Japan 19, 1856 (1964).

¹⁵ J. Friedel, G. Leman, and S. Olszewski, J. Appl. Phys. **32**, 325S (1961).

¹⁶Yu. P. Irkhin and V. G. Shavrov, Zh. Eksp. Teor. Fiz. 42, 1233 (1962) [Sov. Phys.-JETP 15, 854 (1962)].

¹⁷ L. É. Gurevich and I. N. Yassievich, Fiz. Tverd. Tela 4, 2854 (1962) [Sov. Phys.-Solid State 4, 2091 (1963)].

¹⁸ E. I. Kondorskiĭ, A. V. Cheremushkina, and

N. Kurbaniyazov, Fiz. Tverd. Tela 6, 539 (1964) [Sov. Phys.-Solid State 6, 422 (1964)].

¹⁹ E. I. Kondorskiĭ, Zh. Eksp. Teor. Fiz. **55**, 2367 (1968) [this issue, p. 1256].

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¹I. K. Kikoin, Zh. Eksp. Teor. Fiz. 10, 1242 (1940).