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Properties of the Conduction Electrons in the Metals of Group VIII

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The behaviour of the conduction electrons in the eighth group elements was deduced from the results of experiments on vacuum-deposited films, by combining measurements of the electrical resistivity with thickness determinations and optical investigations. The mean free path of the electrons, their concentration, their effective mass, and the proportion of them specularly reflected at the film surfaces (known as the scattering parameter) were calculated by solving a system consisting of the Sondheimer equation for the size-dependence of the film conductivity, the known formulae giving the mean free path at the Fermi level and the plasma wavelength of the electron gas, and the Dingle relation for the scattering parameter in the spectral region of the anomalous skin effect.

The data thus obtained are in reasonable agreement with the generally accepted band structure of the transition metals.

1. Introduction

This paper describes a method for determining the properties of the conduction electrons in the metals of the eighth group based on the study of the charge transport process and the electron-photon interactions in thin films.

When one of the dimensions of a metal specimen becomes very small, as in the case of vacuum-deposited films whose thickness is so reduced as to be of the order of magnitude of the mean free path of the carriers in the bulk metal, then the boundaries of the sample behave as a sort of structural defect, imposing a geometrical restriction on the movement of the charges. To take into account the influence of this limitation on the conduction mechanism a size-effect theory must be developed, leading to a relation between resistivity and thickness which involves both the bulk metal value of the mean free path of the electrons at the top of the Fermi distribution and a parameter describing the average probability of their elastic scattering by the film surfaces.

Spectrophotometric observations of the behaviour of the films in the ultra-violet and infrared regions allow, respectively, the determination of the critical cut-off wavelength (known as the plasma wavelength of the electron gas) at which the metal changes from a reflecting to a transmitting medium and the carriers oscillate collectively because of the Coulomb interaction, and the calculation of the optical constants in the spectral interval of the anomalous skin effect, where only the electrons specularly reflected at the film surfaces can contribute effectively to the charge transfer. From these considerations on the electrical and optical properties of the films one may deduce the number, the mobility, and the freedom of the conduction electrons in the metal.

2. Experimental Procedure

Thin films of Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt were vacuum-deposited by means of an electron beam gun on very smooth, optically polished fused silica substrates at 10^{-8} to 10^{-9} torr and 250° C and subsequently annealed in vacuum at 400° C for 3 h. Both the film thickness and the condensation rate were carefully controlled with a piezoelectric quartz crystal monitor.

Before film deposition, the substrates were degassed by baking *in vacuo* at 300° C and cleaned afterwards by ionic bombardment using a glow discharge at 5 kV. To study the charge transport mechanism, measurements were made of the sheet resistivity of the films,The results of investigations in the thickness range from 100 to 500 Å are illustrated in fig. 1: each of the data points (not shown) were derived by averaging the values obtained for several square-shaped specimens of equal thickness. When the resistances of samples evaporated separately were compared it was noticed that films thicker than 200 Å exhibit a complete reproducibility of the electrical properties, while thinner layers show discrepancies which increase with reduced thickness: however, even in ultrathin specimens 100 Å thick the deviations from the mean values given in fig. 1 are less than 2%.

To investigate the optical characteristics of the samples many observations were carried out, with a double-beam spectrophotometer, of the transmittance and reflectance of ultra-violet and infra-red waves falling at normal incidence on the vacuum side of the film. The analysis was restricted to the thickness range 100 to 500 Å, since films thicker than 500 Å and thinner than 100 Å are, respectively, too absorbing and too transparent for a precise determination of the transmittance.

Both the electrical and the optical tests were performed at room temperature on freshly evaporated films, preserved from air exposure to avoid a chemical contamination of the free surface of the samples due to oxidation or adsorption of some other residual gases, which could produce a decrease in the conductivity and reflecting power.

A reliable interpretation of the experimental results is possible only if the films may be thought of as homogeneous, isotropic, parallel-sided slabs of bulk material. Therefore all the specimens were examined very carefully in the electron microscope and those showing a porous or discontinuous structure were discarded.

3. Theoretical Treatment

The values shown in fig. 1 for the resistivity, ρ_f, and thickness, t, of the film were introduced into the relation [1, 2]

$$\rho_f = \frac{\rho_b}{1 - \frac{3L}{2t}(1-p)\int_1^\infty \left(\frac{1}{x^3} - \frac{1}{x^5}\right)\frac{1-\exp(-tx/L)}{1-p\exp(-tx/L)}\,dx} \quad \ldots . (1)$$

derived by Sondheimer [3] for a free electron gas model and a spherical Fermi surface by inserting the boundary conditions at the film surfaces into the Boltzmann equation for the distribution function of the conduction electrons.

Here ρ_b indicates the resistivity of the bulk metal and p the fraction of electrons incident on the film surfaces which are specularly reflected, called the scattering parameter. L is the mean free path of the electrons at the Fermi level in the bulk metal and may be expressed as a function of the carrier concentration, N, by the relationship

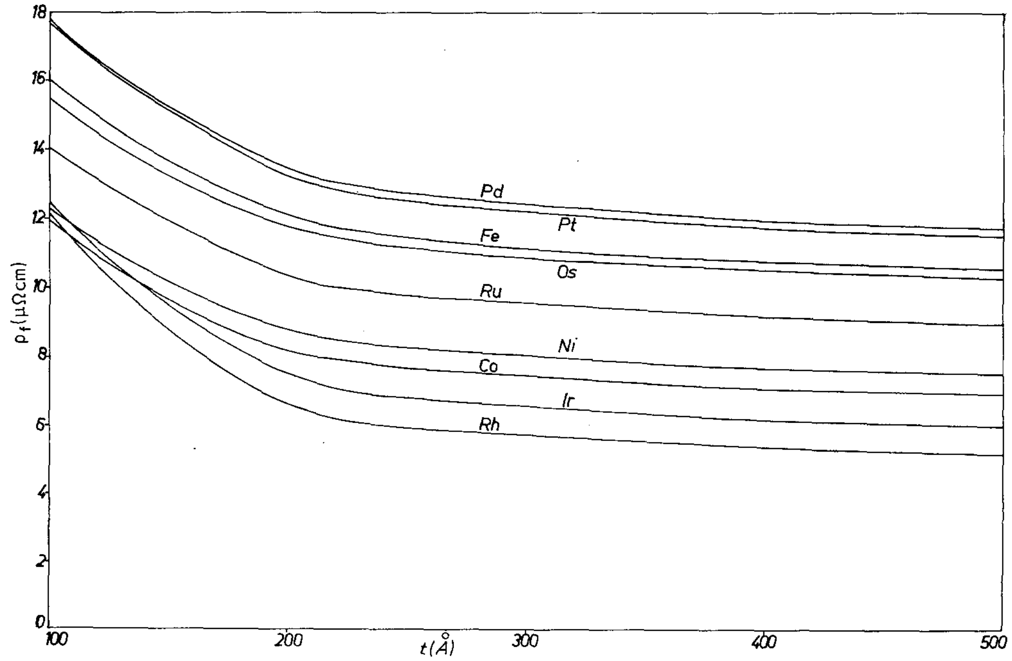

Figure 1 Thickness dependence of the electrical resistivity of vacuum deposited films at room temperature.

$$L = \frac{h}{e^2\rho_b}\left(\frac{3}{8\pi N^2}\right)^{1/3} \qquad (2)$$

where h denotes Planck's constant and e the electronic charge.

On the simplifying assumption that the scattering of the electrons by the surfaces of the film is entirely diffuse, so that $p = 0$, solving equation 1 by repeated integration by parts and making suitable approximations for small and large values of the ratio t/L, one can calculate L; on substituting then in equation 2, N may also be determined. This simplification is, however, unacceptable, as results from previous investigations on the electrical behaviour of vacuum-deposited copper [4] and gold [5] films show. Therefore the evaluation of L and N will require the knowledge of the average probability of elastic scattering of the electrons at the film boundaries, which should depend on the characteristics of the media surrounding the film, and could then be different at the bottom and top surfaces [6]. However, if p_1 and p_2 are the effective electron reflection coefficients for the film-substrate and vacuum-film interfaces, respectively, the film behaves practically as though its scattering parameter is $p = (p_1p_2)^{1/2}$ at both surfaces [7].

To calculate p, a method based on the anomalous skin effect was applied [8, 9]. This effect consists in an abnormally large surface resistance produced by the absorption of high-frequency electromagnetic waves whose penetration into the conductor, expressed by the damping distance or skin depth, is less than the mean free path of the electrons. Under these conditions, only those carriers which travel nearly parallel to the film surfaces, so as to strike them at grazing incidence and remain then inside the skin depth for most of a mean free path, are capable of contributing to the charge transport. Hence the decrease in conductivity associated with the radiation absorption allows one to evaluate the fraction of electrons making glancing collisions with the film surfaces. This corresponds practically to the fraction scattered elastically [10], and may be written [11] as

$$p = 1 + \frac{4\lambda_0}{3}\left(\frac{1}{\pi L} - \frac{2c}{\lambda_\tau v}\right) \qquad (3)$$

Here λ_0 is the plasma wavelength of the electron gas, which can be determined easily by reflectance or transmittance measurements in the ultraviolet, c is the speed of light in vacuum, v is the velocity of the carriers at the Fermi surface, and λ_τ is their relaxation wavelength when their motion is perturbed by the electric field of the radiation producing the anomalous skin effect [12].

These quantities are given by

$$\lambda_0 = \frac{c}{e}\left(\frac{\pi m^*}{N}\right)^{1/2} \qquad (4)$$

$$v = \frac{h}{m^*}\left(\frac{3N}{8\pi}\right)^{1/3} \qquad (5)$$

$$\lambda_\tau = \frac{\lambda^3}{4nk\lambda_0^2}\left[1 + \left(1 - \frac{16n^2k^2\lambda_0^4}{\lambda^4}\right)^{1/2}\right] \qquad (6)$$

where m^* represents the effective mass of the electrons, n and k indicate the optical constants of the film, namely the real and imaginary parts of its complex refractive index, respectively, and λ denotes the wavelength of the perturbing radiation, assumed as monochromatic.

The optical constants of uncoated absorbing films condensed on transparent substrates can be deduced from measurements of the transmittance, T, and reflectance, R, of a wave falling at normal incidence on the vacuum side of the film, by applying the equations [13, 14]:

$$T = \frac{8n_0n_s(n^2 + k^2)}{A\cosh\alpha + B\sinh\alpha - C\cos\beta + D\sin\beta} \qquad (7)$$

$$R = \frac{E\cosh\alpha - F\sinh\alpha - G\cos\beta - H\sin\beta}{A\cosh\alpha + B\sinh\alpha - C\cos\beta + D\sin\beta} \qquad (8)$$

Here n_0 and n_s denote the indices of refraction of vacuum and substrate, respectively, while the Greek and capital letters indicate optical coefficient which may be represented in the form:

$$\begin{aligned}
\alpha &= 4\pi kt/\lambda\,, \quad \beta = 4\pi nt/\lambda\,,\\
A &= (n^2 + k^2 + n_0^2)(n^2 + k^2 + n_s^2) + 4n_0n^2n_s\,,\\
B &= 2n[n_0(n^2 + k^2 + n_s^2) + n_s(n^2 + k^2 + n_0^2)]\,,\\
C &= (n^2 + k^2 - n_0^2)(n^2 + k^2 - n_s^2) - 4n_0k^2n_s\,,\\
D &= 2k[n_0(n^2 + k^2 - n_s^2) + n_s(n^2 + k^2 - n_0^2)]\,,\\
E &= (n^2 + k^2 + n_0^2)(n^2 + k^2 + n_s^2) - 4n_0n^2n_s\,,\\
F &= 2n[n_0(n^2 + k^2 + n_s^2) - n_s(n^2 + k^2 + n_0^2)]\,,\\
G &= (n^2 + k^2 - n_0^2)(n^2 + k^2 - n_s^2) + 4n_0k^2n_s\,,\\
H &= 2k[n_0(n^2 + k^2 - n_s^2) - n_s(n^2 + k^2 - n_0^2)]\,.
\end{aligned} \qquad \ldots. (9)$$

The non-algebraic equations 7 and 8 form a system relating T and R to n and k, that for $t = 100$ to 500 Å may be solved using limited series expansions of the trigonometric functions. Introducing into this system the values of T and R measured with a double-beam spectrophotometer at a suitable wavelength λ in the near infra-red region of the anomalous skin effect, both n and k were calculated.

On substituting these data and those obtained for λ_0 by spectrophotometric investigations in the ultra-violet into equations 6 and 4, respectively, and then inserting values from equations 4, 5, and 6 into equation 3, we can use equations 1, 2, 3, and 4 as a system whose unknowns are L, p, N, and m^*. The calculations may be simplified by reducing equation 1 to

$$\rho_f = \frac{\rho_b}{1 - \frac{3L}{8t}(1 - p)} \qquad (10)$$

which is a sufficiently accurate relation for values of t/L down to 0.1 [15]. The results deduced in this way are given in table I, where m^*/m represents the ratio of the effective to the free electron mass.

TABLE I Summary of the values calculated by the method described in section 3.

Metal	N (electrons/atom)	m^*/m	L (Å)	p
Fe	0.45	1.42	116	0.09
Co	0.60	1.25	142	0.10
Ni	0.58	1.10	131	0.10
Ru	0.55	1.21	132	0.16
Rh	0.75	1.12	195	0.14
Pd	0.48	1.03	115	0.09
Os	0.50	1.19	124	0.17
Ir	0.67	1.11	183	0.16
Pt	0.46	1.03	122	0.12

4. Discussion of Results and Conclusions

The data listed in table I for N, m^*/m, L, and p will now be discussed. The values of N and m^*/m agree satisfactorily with the usually accepted electronic structure of the transition metals, according to which only the electrons in the s band participate in the charge transport, as the contribution of those in the d band may be neglected owing to their large effective mass, and the s band contains about 0.6 electrons per atom with an effective mass of the order of the free mass [16]. The results derived for N can then be used for determining the distribution of the electrons in the energy bands.

In iron, cobalt, and nickel, which are ferromagnetic, the charges must be distributed between the 4s band and the two 3d sub-bands of opposite electron spin orientation according to the simple formulae

$$N_s = N_t + N_m - 10 + 2q \qquad (11)$$

$$N_{d\uparrow} = 5 - q\,, \; N_{d\downarrow} = 5 - N_m - q \qquad (12)$$

where N_s, $N_{d\uparrow}$, $N_{d\downarrow}$, and N_t are the numbers of electrons per atom present in the 4s band, in the two halves of the 3d band, and outside the filled 3p shell, respectively, N_m is the saturation magnetic moment at room temperature, expressed in Bohr magnetons per atom, and q is a parameter taking into account the overlap of the 3d and 4s bands. Determining the value of the saturation magnetisation at $T = 293°$ K by the usual intercept method [17], and making an appropriate correction for the small contribution due to orbital electronic motion by the introduction of the spectroscopic splitting factor, one deduces that in iron, cobalt, and nickel the effective number of Bohr magnetons per atom is, respectively, 2.02, 1.50, and 0.52.

The above considerations may be extended to the paramagnetic elements of group VIII, where the d band shall be taken to hold equal numbers of electrons in both spin directions, as in the ferromagnetic metals above the Curie point, so that equations 11 and 12 will reduce, respectively, to:

$$N_s = N_t - 10 + 2q \qquad (13)$$

$$N_{d\uparrow} = N_{d\downarrow} = 5 - q \qquad (14)$$

where the symbols keep the same meaning as in relations 11 and 12, but refer to 5s and 4d or 6s and 5d bands and to a 4p or 5p shell.

Putting $N = N_s$, deriving the value of q from equations 11 or 13, and inserting it into equations 12 or 14, the results given in table II were found.

TABLE II Distribution of the electrons in the energy bands.

Metal	N_s (electrons/atom)	$N_{d\uparrow}$ (electrons/atom)	$N_{d\downarrow}$ (electrons/atom)
Fe	0.45	4.785	2.765
Co	0.60	4.950	3.450
Ni	0.58	4.970	4.450
Ru	0.55	3.725	3.725
Rh	0.75	4.125	4.125
Pd	0.48	4.760	4.760
Os	0.50	3.750	3.750
Ir	0.67	4.165	4.165
Pt	0.46	4.770	4.770

It must be noted that the distribution of the charges in the energy bands is slightly affected by the thermal agitation, owing to which a certain number of electrons may be excited from the d

band to the s band, leaving behind vacant states at the top of both d sub-bands. Therefore, even in cobalt and nickel we cannot take one $3d$ sub-band as filled, in contrast with the generally accepted electronic structure of these metals at absolute zero [18], based on the assumption that the exchange forces are large enough to ensure a complete alignment of the spins in the absence of thermal effects.

A comparison of the values of N listed in table I shows that the number of electrons in the s conduction band is larger in the family of cobalt ($N_t = 9$) than in that of iron ($N_t = 8$) or nickel ($N_t = 10$). The first result is obvious; the last could indicate that the overlapping of the d and s bands becomes smaller as the d band tends to be filled.

As to the effective mass, it must be emphasised that m^*/m is always higher than unity, and reduces if the atomic number, both in any period and in any family of the eighth group, is increased. This may be explained by supposing that the freedom of the conduction electrons is never complete, but becomes greater as either the number of empty d levels capable of trapping the electrons decreases, or the nearest neighbour distance increases, so as to reduce the Coulomb interaction of the electron gas with the ion cores.

We consider now the mean free paths, which can be compared with those found by the author in recent investigations on the electrical and optical properties of vacuum deposited films of copper [4], gold [5], zinc [19], and transition metals of the vanadium and chromium families [20]. The values of L given in table I for the eighth group elements are lower than in the noble metals, higher than in vanadium, niobium, tantalum, and chromium, and of the same order of magnitude as in molybdenum, tungsten, and zinc. A comparison with the results of previous studies on nickel [21] and on palladium and platinum [22] shows slight discrepancies in the data obtained for L, which must be attributed to differences in the assumptions, since then it was supposed that $m^* = m$, $N = 0.54$ electron/atom, and $p = 0$, whereas now these quantities have been determined by calculations.

L is greater in the metals with the electronic configuration of cobalt than in those of the iron and nickel families. This also occurs for N, and thus by applying the known relation $\rho_b = m^* v / N e^2 L$ one may understand why in any period of the eighth group the middle element is the best conductor. However, ρ_b also depends on v: hence, to improve the knowledge of the charge transport process one must calculate the average electron velocity at the Fermi surface by solving equation 5. The results derived for v, and some other parameters describing the movement of the carriers, such as the relaxation time $\tau = L/v$, the mobility $\mu = e\tau/m^*$, and the Fermi energy $E_F = m^* v^2/2$, are shown in table III.

TABLE III Parameters describing the motion of the conduction electrons.

Metal	v (10^7 cm/sec)	τ (10^{-14} sec)	μ (cm^2/V sec)	E_F (eV)
Fe	8.48	1.37	16.93	2.91
Co	10.81	1.31	18.40	4.16
Ni	12.22	1.07	17.10	4.67
Ru	10.11	1.30	18.87	3.52
Rh	12.10	1.61	25.27	4.66
Pd	11.08	1.04	17.73	3.60
Os	9.89	1.25	18.47	3.31
Ir	11.63	1.57	24.83	4.27
Pt	10.83	1.13	19.27	3.44

As for p, we point out that its values are nearly proportional to those of the cohesive energy of the metals, as was already noticed in the case of the elements of the vanadium and chromium groups [20]. Since the proportion of electrons specularly reflected at the film surfaces should increase as their roughness is reduced, the behaviour of p could indicate that the surfaces become smoother as the interatomic binding forces become stronger.

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