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ON FREE AND BOUND ELECTRONS IN METALS

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ABSTRACT

When the theory of dispersion in an absorbing medium is applied to the values published in recent years for the optical properties of different metals, it follows that bound electrons exist inside the metal comparable in number with that of the free electrons.

IN THEIR new theory of the electric conductivity of metals, Sommerfeld, Houston and Eckart did not have to examine "the essential problem of the degree of dissociation of the metal i.e. the number of free electrons per atom."[1] It is known that if the conductivity of the metallic elements be plotted as a function of the atomic number, the curve obtained shows marked peaks at the beginning of each period or half period (Cu, Ag, Au) and an irregular drop toward the end of the period. With an increasing number of valency electrons the conductivity seems to decrease, and those elements having in their atomic configuration one single outermost electron possess the highest conductivity. Only three elements were an exception when this rule was first observed: Cr, Mo, W, which attain new high values inside their period.[2] But the analysis of their spectra has since shown that these atoms too possess one outermost electron in an uncompleted shell, or that one single electron plays an important part in the emission and absorption of light. Even if instead of this rough comparison the elements are examined at corresponding temperatures and with the same field applied per atom, so as to eliminate as far as possible the influence of crystalline structure, the dependence of the conductivity upon the number of outer electrons is still well marked.[3] It may therefore be assumed that the number of free electrons is about equal to the number of valency electrons.

On the other hand the electric conductivity of the metal is closely connected with its optical properties. The reflective power in the far infra-red region, for example, may be calculated from the specific conductivity of the metal.[4] The better the conductivity, the stronger is the absorption. Down to wave-lengths larger than about 4μ, the metals behave optically as if they contained only free electrons. In the visible spectrum, however, there appear signs of bound electrons which are set into vibration by the incident light waves. We may try to find the relative number of free and bound electrons from a study of the optical properties of the metal in the visible and ultraviolet spectrum. In recent years some new measurements have been published

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[1] A. Sommerfeld, Zeits. f. Physik. **47**, 1 (1928); W. V. Houston, Zeits. f. Physik. **47**, 33 (1928); C. Eckart, Zeits. f. Physik. **48**, 449 (1928); A. Sommerfeld, Naturwiss. **16**, 374 (1928).

[2] O. Feussner, Zeits. f. Physik. **25**, 215 (1924).

[3] H. Cassel, Zeits. f. Physik. **33**, 477 (1925).

[4] R. W. Wood, Physical Optics.

on this interesting but difficult problem, and it seems worth while to examine the results from the point of view of the theory of dispersion and absorption.[5]

The general equation for dispersion and absorption is

$$n^2(1-i\kappa)^2=1+\sum\frac{\zeta/4\pi^2}{\nu_0{}^2+i\nu\nu'-\nu^2}\tag{1}$$

where $(2\pi\nu_0)^2=4\pi e^2f/m=4\pi f/m'$; N is the number of electrons of frequency ν_0 per unit volume; ν_0 the natural frequency of the electrons; f the elastic force (at 1 cm distance) calling the electron to its equilibrium position; $\nu'=r/2\pi m'$ where r is the friction met with by the electrons in crossing the metal; and $\zeta=4\pi Ne(e/m)=4\pi N/m'$.

Separating the imaginary and real quantities and introducing $\lambda=c/\nu$, this equation becomes

$$2n^2\kappa=\sum\frac{\zeta/4\pi^2c^2\lambda\lambda'}{(1/\lambda_0{}^2-1/\lambda^2)^2+1/\lambda^2\lambda'^2}=\sum\frac{C/\lambda\lambda'}{(1/\lambda_0{}^2-1/\lambda^2)^2+1/\lambda^2\lambda'^2}$$

$$n^2(1-\kappa^2)-1=\sum\frac{\zeta/4\pi^2c^2\times(1/\lambda_0{}^2-1/\lambda^2)}{(1/\lambda_0{}^2-1/\lambda^2)^2+1/\lambda^2\lambda'^2}=\sum\frac{C(1/\lambda_0{}^2-1/\lambda^2)}{(1/\lambda_0{}^2-1/\lambda^2)^2+1/\lambda^2\lambda'^2}$$

If the substance considered possesses one class of free electrons ($\nu_0=0$) besides "i" groups of bound electrons, its optical properties will be determined by

$$\begin{array}{rcc} & \text{(free electrons)} & \text{(bound electrons)} \\ 2n^2\kappa= & \dfrac{C\lambda'\lambda^3}{\lambda^2+\lambda'^2}+ & \displaystyle\sum_0^i\frac{C_i/\lambda\lambda_i'}{(1/\lambda_i{}^2-1/\lambda^2)^2+1/\lambda^2\lambda_i'^2} \end{array}\tag{2}$$

$$n^2(1-\kappa^2)-1=-\frac{C\lambda'^2\lambda^2}{\lambda^2+\lambda'^2}+\sum_0^i\frac{C_i(1/\lambda_i{}^2-1/\lambda^2)}{(1/\lambda_i{}^2-1/\lambda^2)^2+1/\lambda^2\lambda_i'^2}\tag{3}$$

The values of C and C_i are subject to the condition that they yield a sum corresponding with the total number of valency electrons inside unit volume of the metal:

	Cu	Ag	Au (one electron per atom)	Na	Ni (two electrons per atom)	Hg
$N\times10^{-22}$	8.5	5.6	6	2.5	18	6.2
C	0.8	0.5	0.5	0.2	1.6	0.6

λ being expressed in 10^3AU.

If the value of the incident wave-length λ exceeds λ' as well as λ_i and λ_i'

$$2n^2\kappa=C'\lambda'=2\pi cm'C'/r\quad\text{or}\quad n^2\kappa=N'/r\nu$$

N'/r may be interpreted as the electric conductivity σ of the metal, and for many metals Hagen and Rubens[6] have established (large λ)

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[5] G. Pfestorf, Ann. d. Physik **81,** 906 (1926); K. Lauch, Ann. d. Physik **74,** 55 (1924); J. Richter, Ann. d. Physik **77,** 81 (1925). See also W. Meier, Ann. d. Physik **31,** 1017 (1910).

[6] E. Hagen and H. Rubens, Ann. d. Physik **11,** 873 (1903).

$$n^2\kappa = \sigma/\nu$$

We may then deduce a minimum value for $\lambda' = 2\pi m'c/r$ by supposing all the electrons inside the metal as free; this gives (in A.U.$\times 10^{-3}$).

Cu,	538;	Ag,	705;	Au,	535;	with one electron per atom
Ni,	29.5;	Hg,	8.5;	Pt,	54;	with two electrons per atom

For the large values of λ', the well known relation $n^2\kappa = \sigma/\nu$ ceases to be quite accurate; and besides, the new theory of conductivity does not confirm fully the expression $\sigma = N'/r$. The exact value of λ', however, is rather indifferent as long as it is large. Another feature for large λ' is that in the visible spectrum the contribution to the value of $2n^2\kappa$ by the free electrons will be small or negligible, so that the presence of bound electrons becomes at once apparent. The part of the free electrons in determining $n^2(1-\kappa^2)$, on the other hand, is well marked, independent of λ' and therefore similar for all good conductors. The presence of free electrons alone causes a steady decrease for $n^2(1-\kappa^2)$ and a steady increase in the value of $2n^2\kappa$, as the wave-length increases. Therefore a graph (Figs. 1 and 2) representing $2n^2\kappa$ and $n^2(1-\kappa^2)$ as a function of the wave-length of the incident light, indicates clearly the regions where bound electrons and the regions where free electrons have a prominent part in determining the optical constants of the metal, and suggests approxi-

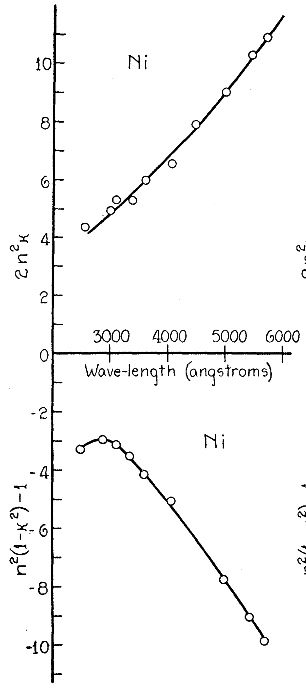

Fig. 1.

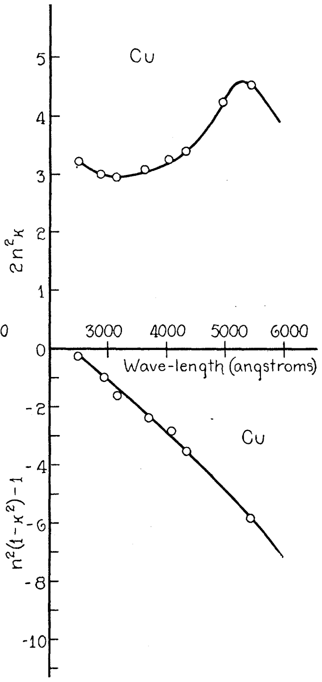

Fig. 2.

mate values for C, λ' and λ as used above. By comparing the new experimental results for Cu, Au and Ni with a sufficient number of theoretical curves calculated from Eqs. (2) and (3), values for C, λ and λ' may be picked out (Table I), which by means of Eqs. (2) and (3) determine the optical properties of these metals within the limit of experimental errors (Table II). In the tables, p_0 is the average number of free electrons per atom, p_1 and p_2 are the average number of bound electrons having natural frequencies corresponding with λ_1 and λ_2 and the values λ_1' and λ_2' as defined above, λ being given in 10^3 A.U.

TABLE I. *Calculated values of C, λ and λ'.*

Metal	Free electrons p_0	λ'	C	Bound electrons 1st kind p_1	λ_1	λ'_1	C_1	2nd kind p_1	λ_2	λ_2'	C_2	λ_3
Cu	0.3	large	0.25	0.1	5.2	10	0.08	0.75	2.0	2	0.6	
Ag (old values)	.6	large	.3					.8	2.2	4	.4	
Au	.6	large	.3	.05	5.2	10	.05	.6	3.0	6	(.3)	(1.5)
Ni	.45	7.5	.7					.45	2.0	2	.7	

TABLE II. *Optical constants of Ni, Cu, Au.*

		$\lambda=$	3	4	5	6
Ni	$2n^2\kappa$	obs	5.0	6.5	9.0	12.3
		calc.	4.3	6.2	9.3	12.6
	$n^2(1-\kappa^2)-1$	obs.	-3.1	-5.0	-8.0	-11.0
		calc.	-3.9	-6.2	-9.1	-11.5
Cu	$2n^2\kappa$	obs.	2.9	3.2	4.2	3.8
		calc.	2.5	2.8	4.8	4.6
	$n^2(1-\kappa^2)-1$	obs.	-1.2	-2.8	-4.9	-7.2
		calc.	$-.6$	-3.4	-4.5	-6.8
Au	$2n^2\kappa$	obs.	5.5	3.4	4.0	2.4
		calc.	5.6	3.7	4.1	3.4
	$n^2(1-\kappa^2)-1$	obs.	$-.1$	-1.6	-7.8	-8.8

The values n and κ are usually certain to ± 0.04 or ± 0.05 units; this causes an uncertainty of 0.8 to 1.2 in the values of $2n^2\kappa$ and $n^2(1-\kappa^2)$. More accurate figures could only be obtained by taking a very large number of readings so as to eliminate the small accidents upon the metallic surface due to the polishing and treatment of the metal. The values for the natural frequencies below $200\mu\mu$ are not reliable, as no readings in this region exist, where the influence of the ν's would appear most plainly. A large number of metals must possess a band at or below $200\mu\mu$ which is decisive for the optical properties. Cu and Au alone appear to have a band of natural frequencies in the visible spectrum; but it comes from a comparatively small number of electrons and may correspond with a forbidden transition. In contrast with Ag, the spectrum of which is almost exclusively due to the single valency electron, Au and Cu atoms show a system of lines built up upon a metastable level.

Sommerfeld has pointed out as a consequence of the Pauli-Fermi distribution of energy, that the electrons in the interior of a metal possess a much higher kinetic energy than would be expected from the older equipartition theory. The kinetic energy per electron, if all the electrons in the volume V or only half the electrons are free, follows from

$$W_0=\frac{3h^2}{40m}\left(\frac{6N}{\pi V}\right)^{2/3}$$

as follows:

for	Cu	Ag	Au	Na	Hg	Ni	
	5.5	3.4	3.6	2	3.6	7.5	Volts
or	3.3	2.1	2.3	1.3	2.2	4.7	Volts

Ag perhaps excepted, these values for the kinetic energy allow bound electrons to be present in the metal, having natural frequencies corresponding with the visible or ultra-violet spectrum. For an accurate comparison it would be necessary to know the influence of the high density of the metal upon its dispersion and absorption.[7]

If the conductivities of the metals are now calculated from Houston's formula, assuming one half of the number of the valency electrons to be free, the agreement with the experimental values becomes better than before. This is the more remarkable as the classical theory of the diffraction of x-rays used in establishing the formula is not well supported by experiment: the influence of temperature having always been found larger than predicted.

The more recent values obtained for the absorption and dispersion of light by metals confirm the older ones in that they require for their explanation the existence of bound electrons inside the metal comparable in number with that of the free electrons.[8]

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[7] K. F. Herzfeld, Phys. Rev. **29,** 701 (1927).

[8] The magnetic properties of single crystals of Zn and Cd, which have recently been studied at my suggestion, and the magnetic susceptibilities of the alkali metals point also to the existence of a certain proportion of bound and shared electrons (Nature **121,** 351 (1928).