THE TEMPERATURE SHIFT OF THE TRANSMISSION BAND OF SILVER

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Abstract

It is shown that by Kronig's quantum theory of dispersion in metals one can account for the shift of the frequency at which maximum transmission is found for silver when the temperature is varied. The calculated rate of shift is in fair agreement with experiment.

It HAS been known for some time that, although for wave-lengths up to 5μ the optical constants of metals show little or no temperature dependence, there is a marked temperature effect in the case of silver in the region of the minimum of reflecting power, around 3160A. Ebeling[1] first noted that raising the temperature from 15°C to 200°C produces a displacement of the reflection minimum toward the red of about 100A and an increase of reflecting power at the minimum from 4.2 to 20 or 30 percent. The reflection measurements of de Selincourt[2] at temperatures from −183 to 156°C showed that a similar effect extended throughout this range. It is to be expected that with the minimum of reflection would be associated one of absorption. Minor's experiments on silver at ordinary temperatures[3] showed minima of absorption index, reflecting power, extinction coefficient, and absorption coefficient at 3140, 3160, 3160, and 3220A respectively. Lord Rayleigh[4] first investigated the effect of temperature on the absorption minimum (transmission maximum) by passing light through silver foil at temperatures from −180 to 254°C. The transmission maximum behaved much in the same manner as the minimum in the earlier reflection experiments.

Quite recently, McLennan, Smith, and Wilhelm[5] with greatly improved methods made measurements on the transmission band of silver at temperatures from 20°C down to −269°C using liquid air, hydrogen, and helium and found the transmission maximum to vary nearly linearly with the temperature over this large range. Before the appearance of the last named paper, the author repeated Lord Rayleigh's experiments with modifications in order to determine the nature of the reported broadening of the transmission band and change in transmission intensity and found that these agreed qualitatively with the reflection experiments of de Selincourt. No quantitative explanation of the shift has been given but one should now be possible in view of

[1] Ebeling, Zeits. f. Physik **32,** 489 (1925).
[2] de Selincourt, Proc. Roy. Soc. **107,** 247 (1925).
[3] Minor, Ann. d. Physik **10,** 581 (1903).
[4] Lord Rayleigh, Proc. Roy. Soc. **128,** 131 (1930).
[5] McLennan, Smith, and Wilhelm, Phil. Mag. **12,** 833 (1931).

the work on the quantum theory of dispersion in metals by Kronig.[6] Extending Kronig's theory, Schubin[7] has shown that the quantum theory indicates the existence of an absorption minimum very near the second line of the resonance doublet of the corresponding metal vapor (for silver this line is found at 3280A). Attention had been called to this coincidence by Ebeling in the paper cited above. Schubin also shows that general qualitative considerations lead one to expect a shift of absorption minimum toward the red with increasing temperature.

In Fig. 1 are shown the experimental values of the frequency at which the absorption minimum occurs for different temperatures as found by various investigators. It is seen that the values found by McLennan and by de Selincourt fall on straight lines. In both of these cases careful photometric measurements were made. Of course, the two lines are quite distinct since one represents transmission maxima and the other minima of reflecting

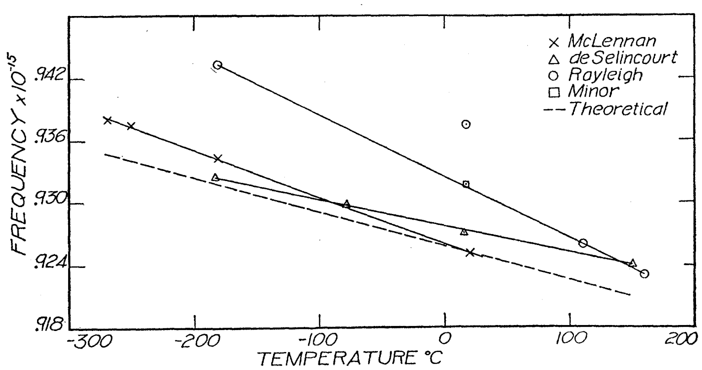

Fig. 1. Frequency of transmission maximum.

power. There is also a difference in the physical condition of the silver used. Three of Lord Rayleigh's values are on a straight line on which Minor's value at room temperature also lies.

The quantum theory of dispersion in metals as given by Kronig is based on Bloch's theory of metallic conduction.[8] The conduction electrons play the part both of free and of bound electrons. These electrons are distributed among their various quantum states according to the Fermi-Dirac statistics. Under the influence of an applied electric field and as a result of collisions with the ions of the crystal lattice, which are in temperature vibration, the conduction electrons make transitions to other states. When the applied electric field is that due to incident light of short wave-length λ, (i.e., less than about 5000A) it is shown that it is possible to neglect the collisions with the lattice.

In Kronig's ideal cubical crystal lattice the quantum states of the conduction electrons are given by three quantities ξ_1, ξ_2, ξ_3.[8] Possible transitions are those to states ξ_1', ξ_2', ξ_3' where

[6] Kronig, Proc. Roy. Soc. **124,** 409 (1929); **133,** 255 (1931).
[7] Schubin, Zeits. f. Physik **73,** 273 (1931).
[8] Bloch, Zeits. f. Physik **52,** 555 (1929).

$$\xi_i' = \xi_i + 2\pi n_i \quad i = 1, 2, 3$$

and n_i is any positive or negative integer. Light of frequency ν will be absorbed by such electrons as can make such transitions under the condition

$$E(\xi_i + 2\pi n_i) = E(\xi_i) + h\nu.$$

According to Kronig, absorption is found under these conditions for $\nu = 0$ (which corresponds to absorption by free electrons under the classical theory) and also for a band $\nu_1 < \nu < \nu_2$ (corresponding to bound electrons) where ν_1 and ν_2 are of the order 10^{15}.

Now, experimentally just such an absorption band is found for silver from $\nu_1 = 0.925 \times 10^{15}$ to $\nu_2 = 1.56 \times 10^{15}$. This is best seen by comparing the conductivity calculated from Minor's experimental values of refractive index (n) and extinction coefficient (K) by Drude's expression

$$2\sigma/\nu = 2n\,\mathrm{K}$$

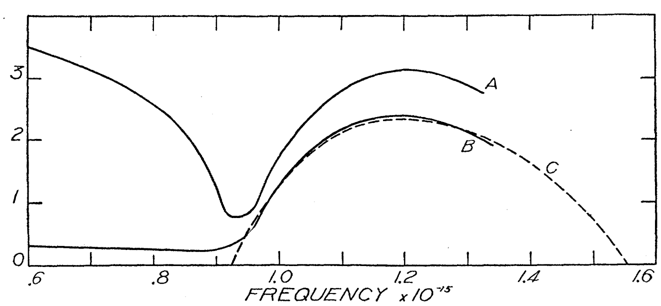

Fig. 2. A, Relative absorption coefficient ($nK\lambda_0/\lambda$) Minor; B, Conductivity$\times 10^{-15}$ calculated from Minor; C, Conductivity$\times 10^{-15}$ by quantum theory.

where σ is the conductivity, with the conductivity calculated from Kronig's formula

$$\sigma = \frac{\pi}{2}\,\frac{\Omega}{\nu}(\nu_2 - \nu)(\nu - \nu_1) \quad \nu_1 < \nu < \nu_2$$

where Ω is a constant for silver. This comparison is made in Fig. 2 where Ω is taken equal to 18. It is seen that ν_1 must have very nearly the value assigned above.

But the lower frequency limit of the absorption band will also be very nearly the upper frequency limit of the transmission band. What we propose to show is that this limit, ν_1, depends on temperature and shifts linearly toward the red with increasing temperature. If the transmission band does not widen appreciably (and the photometric measurements of de Selincourt and of McLennan do not bear out the widening reported by others for which Schubin attempts an account), the rate of shift of transmission maximum with temperature will be very nearly that of ν_1.

Kronig finds, as a theoretical value for ν_1,

$$\nu_1 = \frac{4\pi\omega}{h}(\pi - \rho_0)$$

where

$\omega = \beta(h^2/8\pi^2 ma^2)$
β = binding constant < 1
$\rho_0 = (6\pi^2 K)^{1/3}$
$2K$ = number of conduction electrons per cell
a = the lattice constant.

Thus

$$\nu_1 = \frac{\beta h(\pi - \rho_0)}{2\pi m a^2}$$

where a alone is supposed to vary with temperature according to this theory. Putting $a = a_0(1 + \alpha t)$ where α is the coefficient of linear expansion for silver and t is the temperature on the Centigrade scale and putting

$$\nu_0 = \frac{\beta h(\pi - \rho_0)}{2\pi m a_0^2}$$

we get

$$\nu_1 = \frac{\nu_0}{(1 + \alpha t)^2} = \nu_0(1 - 2\alpha t + \cdots)$$

$$\frac{d\nu_1}{dt} = -2\alpha\nu_0 = -2 \times 19 \times 10^{-6} \times 0.925 \times 10^{15}$$

$$= -3.5 \times 10^{10} \text{ very nearly.}$$

Based on this calculation, a theoretical curve is shown in Fig. 1 for comparison with experiment. Its slope is seen to lie between that of McLennan's curve for transmission maxima and that of de Selincourt's curve for minima of reflecting power.

In conclusion the author wishes to thank Professor H. A. Wilson for suggestions and criticisms in connection with the above work.