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DEPENDENCE OF ULTRA-VIOLET REFLECTION OF SILVER ON PLASTIC DEFORMATION

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Abstract

The change in electrical conductivity of metals with mechanical strain suggests the possibility of a dependence of optical reflecting power on plastic deformation. To study this matter, and to obtain additional evidence with regard to the nature of cold working, the behavior of the minimum of reflecting power of silver in the near ultra-violet (at 3160A according to Hagen and Rubens) was examined for silver surfaces of varying degrees of strain, produced by vigorous and moderate polishing, etching, and electroplating. Reflection curves were obtained by measuring directly, by means of two quartz photoelectric cells, incident and reflected intensities. It is shown that the minimum is very low and lies at 3160A, in accordance with Hagen's and Rubens' measurements, only for highly polished plates. For unstrained surfaces it is shifted to lower wave-lengths by about 20A and the reflecting power rises appreciably. The results presented in the paper, as well as other allied phenomena, are accounted for by assuming a change in the number of free electrons and a consequent change in the index of refraction of the metal.

Introduction

THE effects of cold working upon metals are usually explained by assuming two distinct types of changes in the arrangement of the crystal lattice: translational slipping of portions of the crystal along important crystallographic planes and the process commonly known as twinning. Although metallurgists have been fairly successful in assigning the observed features of plastically deformed metals to these two causes, there has recently been an accumulation of evidence pointing to their inadequacy for an exhaustive explanation of electrical properties of cold worked metals. Geiss and van Liempt[1] present a summary of observations which cannot be accounted for by reference to changes in the geometrical configuration of the crystal. The authors are led to suggest a deformation of electronic orbits accompanying the rearrangement of atoms. However, they advance this hypothesis on purely speculative grounds.

The original object of the experiment described in this paper was to decide, by studying with some precision those properties of plastically deformed metals which do not depend on atomic arrangement, whether or not such assumptions are necessary. The reflecting power R of Ag in the ultra-violet was selected for the following reasons: *a*.—If the fundamental assumptions of Drude's theory are correct, R is determined in the ultra-violet region by electrons only, free or bound. (The reasoning in this paper will be consistently classical, since the quantum theory is not readily applicable to the phenomena of reflection and dispersion.) The residual ray frequencies

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[1] W. Geiss and J. A. M. van Liempt, Zeits. f. Metallk. **18**, 216–218 (1926).

for silver as computed roughly from Madelung's theory lie at about 75μ, while the electronic resonance frequencies fall in the near ultra-violet. *b.*—Ag has a sharp minimum of reflection at 3160A, which, it was hoped, would be particularly sensitive to changes. *c.*—Ag is capable of sustaining high degrees of plastic deformation, which can be easily produced. Polishing is known to cause very severe surface strains. *d.*—A silver surface is not likely to undergo rapid chemical changes; disturbing effects resulting from impurities are less likely to arise than with other metals. *e.*— Optical constants of silver are accurately known; they have always been obtained for highly polished surfaces.

EXPERIMENTAL METHOD

To carry out the investigation it was necessary to use a method not dependent on specular reflection; furthermore it had to permit a comparison of reflecting powers of specularly and diffusely reflecting specimens. Photographic methods were not employed (except as a check) because of the uncertainty that attends densitometer readings taken on plates which are given very unequal times of exposure. Hence it seemed preferable to make direct photometric measurements. Figure 1 illustrates the experimental arrangement.

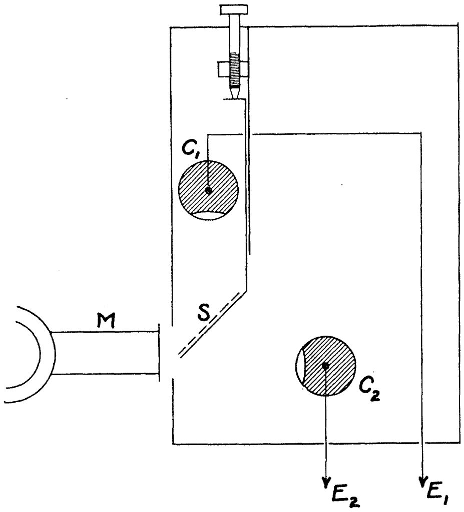

Fig. 1. Diagram of apparatus.

The light source used (not shown in the figure) was a mercury quartz lamp. An iron arc, preferable because of its greater abundance of lines, was not sufficiently steady in its performance to give good results. It will be noticed that the precision of the results is unaffected by intensity variations, but depends essentially on the constancy of the position of the light source. The mercury arc was found to emit a moderately strong continuous spectrum if it was operated with high current densities. This latter condition was suitable for taking readings. After passing through a Gaertner monochromator the light was admitted to a tin box containing the silver plate and the measuring devices. The dispersion of the optical system was such that a spectral line in the region under investigation had a width of about 12A as measured on the drum of the monochromator.

The interior of the box and all parts exposed to the light were coated with lamp black. A silver plate *S* rested on an inclined holder, which could be made to move vertically by means of a spring and a screw extending through the top of the box. By turning the screw the relative amounts of light falling on S and passing below the holder were adjusted. C_1 and C_2 are photoelectric cells measuring reflected and directly transmitted light respectively. They are made completely of quartz, Pyrex cells with quartz windows having proved unsatisfactory. It was attempted for some time to construct two photo-cells (potassium cells) with similar characteristics for the complete region of measurements, but without success. There was a change in the ratio of the sensitivities of the two cells in different portions of the spectrum. This variation had to be determined by calibrations. The cells used in the experiment were carefully tested and shown to have a linear intensity-current relation for intensities of the order of magnitude here used. Readings were taken both with white light and various definite ultra-violet wavelengths selected at random. Each cell was connected with a separate electrometer kept in a different compartment of the same case. Deflections could be observed on the same scale through a longitudinal slit in the wall of the box. Measurements were made by the rate method. The electrometers could be used at very low sensitivities (400 mm per volt) during the greater part of the experiment, the photo-currents being of the order of 10^{-13} amperes.

At the beginning of a series of observations the top screw was adjusted until a suitable ratio of deflection rates was obtained. This adjustment was maintained until all readings on a single plate were taken. The apparatus was repeatedly calibrated, usually after three sets of readings had been made on different specimens which were to be compared. This was done by inserting in place of S a totally reflecting quartz prism, designed to deviate the incident beam upward through an angle of 90°. The absorption of the quartz was assumed to be non-selective over the range of measurements.

The preparation of the silver surfaces needs a few words of comment. Two different conditions of plastic deformation were imposed by moderate and vigorous polishing. Moderate polish was produced by rubbing the specimen on emery and fine sand paper, while high polish was the result of grinding and subsequent careful buffing. The former surface was fairly regularly reflecting, but showed a multitude of minute scratches, while the latter appeared highly specular and exhibited no irregularities visible to the naked eye. "Unstrained" surfaces were prepared by slow etching in dilute nitric acid. They showed a distinctly crystalline structure of fine grain. The "electrolytic" plate carried a deposit produced with current densities of 1.5 milliamperes per cm^2 in a bath of $KAg(CN)_2$. All plates were of dimensions $2\times 4\times 0.1$ cm. To avoid the formation of disturbing impurities on the plates or at least to insure the existence of similar surface films the specimens were washed in alcohol and rinsed in distilled water after their preparation. It was found, however, that great precautions of this character were unnecessary to obtain reproducible results in the spectral region of primary interest.

Experimental Results

The range of investigation extended from 2500A to 3500A. Only the significant portion of the curves, that covering the minimum, is reproduced.

Readings about and below $\lambda = 2500$A were found to be irregular and incapable of reproduction within the limit of experimental error. The cause of such variations appears to be the disturbing action of occluded impurities which overshadow the spectral peculiarities of the silver surface. For accurate determinations in this region it will be necessary to place the plates in a vacuum.

The values of R plotted against λ represent in all cases reflecting powers at an angle of incidence of 45°, not at normal incidence. For comparison, R has been assumed arbitrarily to be 1 for some wave-length in the visible portion of the spectrum, and all other points have been adjusted accordingly. This procedure, which was applied equally to all curves compared on a single diagram, may possibly introduce an unavoidable constant error throughout. However, it can not vitiate the conclusions of the paper.

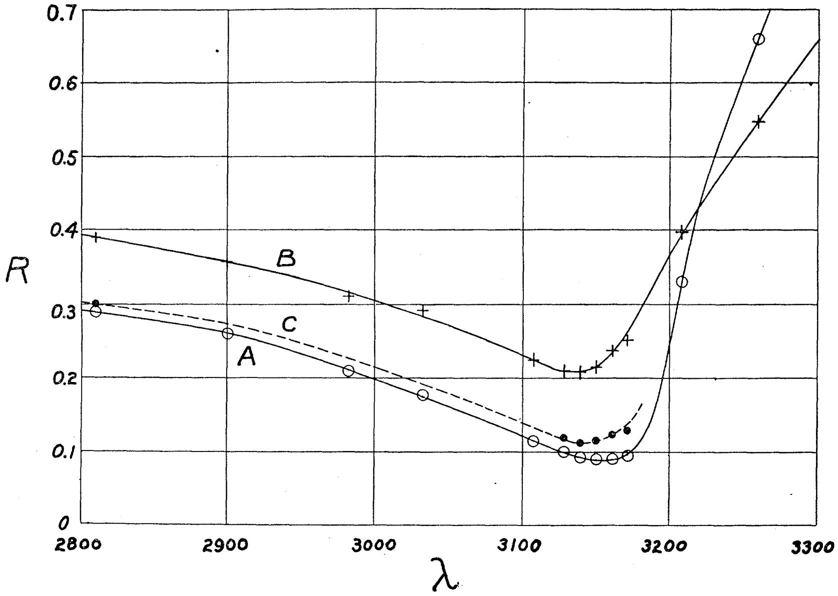

Fig. 2. Reflecting power curves. *A*, highly polished plate. *B*, etched plate. *C*, highly polished plate after heating.

Curve *A* in Figure 2 refers to the reflecting power of a highly polished plate. For this curve, particular care has been taken in determining R for visible light ($\lambda = 5400$A was the wave-length for which these three curves were normalized), so that the actual height of the ordinates at the minimum should be correct and in agreement with results obtained by absolute methods of measurement. Computing the minimum ordinate on the basis of Minor's data[2] the value 0.0883 is found[3] while the experimental height is 0.088. An accurate location of the minimum on the wave-length scale afforded some

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[2] R. S. Minor, Ann. d. Physik **10**, 617 (1903).

[3] Cf. table on p. 11.

difficulties. Calibration curves without the silver plates could not be taken with a precision equal to that of the actual measurements, the electrometer deflection being more rapid. (Reducing the intensity of the light source introduced erratic readings as it entailed a shift of the center of illumination and a consequent change in the relative amounts of transmitted and reflected light.) The error due to the uncertainty in the calibration affects only the absolute position of the minima, not their distance apart. For curve *A* the minimum lies at 3157A, and the range of uncertainty is estimated to be about ±5A. Curve *B* represents the reflecting power of an etched surface. There is a slight irregularity to the right of the minimum which occurs on almost all curves taken for etched samples. Though this feature can not be said definitely to be real, it is probable that there is a fine structure.

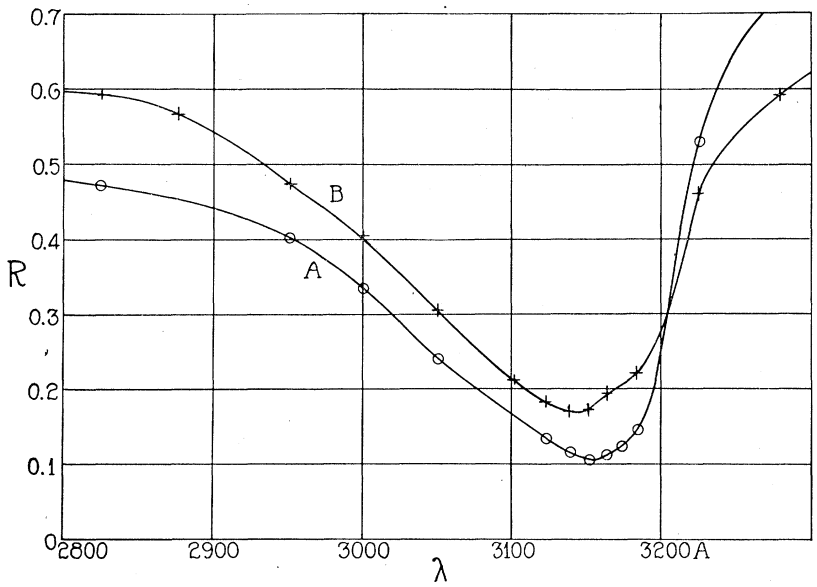

Fig. 3. Reflecting power curves. *A*, highly polished plate. *B*, moderately polished plate.

Curve *C* illustrates the behavior of a silver plate which was first highly polished and subsequently heated for a few minutes above the annealing temperature. It shows that the changes which are due to polishing are partly reversible if the metal is allowed to free itself from strain.

In Figure 3 the optical behavior of a moderately polished surface *B* is compared with that of a highly polished one *A*, while in Figure 4 *B* is an electrolytic plate and *A* a highly polished one.

The experimental method here outlined, if applied carelessly, is susceptible to errors for several reasons. First, proper account has to be taken of the variations in the spectral sensitivities of the two photo-cells. They necessitate frequent calibrations such as were referred to previously. Another very annoying source of error is the lack of parallelism of the two monochromator slits. If a spectral line, the inclination of which is determined by the position of the collimator slit, makes a small angle with the second slit, the various portions of this slit will be illuminated successively as the line passes across it, and the constant ratio of the amounts of reflected and transmitted light as fixed by the position of the top screw will be disturbed. It is therefore necessary to make an extremely fine adjustment of the monochromator. Small residual disturbances of this character which could not be eliminated were rendered ineffective by calibrating the arrangement exactly for the wave-lengths at which measurements of R were made. For the diffusely reflecting surfaces selective action of photo-cell C_1 was to be expected on account of partial polarization of the reflected light. This matter was investigated by introducing a ground quartz plate in place of S and taking readings. Thus it was found that the sensitivity of C_1 did not increase markedly up to about 3500A, where a change, attributed to selective photoelectric emission, became noticeable. Potassium is well known to behave in this way, its maximum selective effect occurring at 4350A.

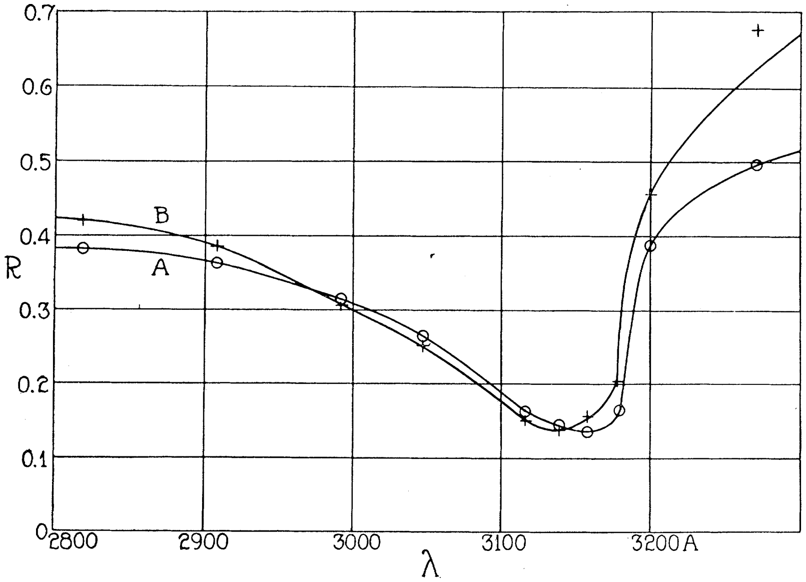

Fig. 4. Reflecting power curves. A, highly polished plate. B, electrolytic plate.

The experimental results, as apparent from the curves, can be summarized as follows: Cold working displaces the minimum of reflecting power of silver to longer wave-lengths by about 20A (in the extreme case of Fig. 2) and causes it to be more pronounced. High polish, regarded as an extreme form of plastic deformation, reduces the ordinate at the minimum by about one half.

It may be objected that the results here stated are not consequences of cold working, but arise from the difference in smoothness of the surfaces.

There is indeed an effect of this character, and its magnitude requires investigation. If the wave-length of light becomes smaller than the size of pits in the surface, it may, under suitable conditions, undergo several reflections. Its intensity will thereby be reduced. Hence an uneven surface should show diminished reflection for small wave-lengths. At the minimum the opposite is observed. Another influence will result from the difference in inclination of the small reflecting portions of a rough surface. Consider a rough surface as being made up of small facets of equal area, whose normals have a certain angular distribution about the normal of the "plane" surface. The latter was inclined, in this experiment, at an angle of 45° to the incident parallel light. Let $p(\theta)$ be a distribution function measuring the proportional number of facets the normal of which is inclined at θ to the parallel incident light, such that $\int_{-45°}^{135°} p(\theta)d\theta=1$. For any angle of incidence θ the reflecting power of a metal surface is given by

$$R(\theta)=\frac{1}{2}\left\{\frac{n^2(1+k^2)-2n\cos\theta+\cos^2\theta}{n^2(1+k^2)+2n\cos\theta+\cos^2\theta}+\frac{n^2(1+k^2)\cos^2\theta-2n\cos\theta+1}{n^2(1+k^2)\cos^2\theta+2n\cos\theta+1}\right\} \tag{1}$$

Here n=index of refraction; nk=index of absorption. Neglecting a constant multiplier, which in the experiment is disposed of by the indicated process of adjusting the values of R, the reflecting power of a diffusely reflecting surface at a general angle of incidence 45° becomes

$$R=\int_{45°-\delta}^{45°+\delta} p(\theta)R(\theta)d\theta \tag{2}$$

where δ is one quarter of the angle subtended by the diameter of the transparent area of C_1 at S. This integral, evaluated for all wave-lengths, gives the values of R over the spectral range. They will not, in general, agree with those obtained from (1). (2) was evaluated for $\lambda=3130$A, $\lambda=3150$A. $\lambda=5400$A, using Minor's[2] data for n and nk. The difference between (1) and (2) will evidently be greatest for the case $p(\theta)=0$ if $\theta<(45°-\delta)$ and $\theta>(45°+\delta)$; $p(\theta)=$const. if $(45°-\delta)\leq\theta\leq(45°+\delta)$, the constant being chosen in accordance with $\int p(\theta)d\theta=1$. This amounts to assuming all facet orientations as equally probable, while actually there will be a preponderance of facets having their normals nearly coincident with the general normal of the surface. For this extreme case

$$R=\overline{R(\theta)} \tag{3}$$

where the average is taken between $(45°-\delta)$ and $(45°+\delta)$. Taking $\delta=5°$, the following figures are obtained:

	$R(\theta)$ (Specular reflection)	R(diffuse reflection)
5400A	0.938	0.939
3150A	0.073	0.073
3130A	0.083	0.084

It is apparent that the experimental results are not due to surface roughness.

After the displacement of the minimum had been measured in this manner the reflection spectrum from silver plates illuminated by a carbon arc was photographed, first by means of a small grating, then, to get greater dispersive power, with a prism spectrograph. The first photographs showed a definite indication of the shift, while the latter (dispersion about 15A/mm) permit a comparison as to its order of magnitude, which checks well with conclusions from the curves. Densitometer readings were not made.

Hagen and Rubens[4] found that the reflecting power of Ag depends to some extent on the age of the surface. R at the minimum is greater for "old" silver than for a freshly polished surface. In the present work this was also found to be the case. R at the minimum rose through a succession of intermediate values by an amount of 37 percent after 15 days, the plate being kept near the radiator of the research room (temperature about 85°F). Another plate polished in the same manner at the same time was placed in a glass tube, which was evacuated and deposited at the same place. Its minimum reflecting power showed no change on examination after 15 days. Moreover, a highly polished plate exposed to evaporating SC_2 acquired an increase in R of 12 percent within one hour. Hence this effect is attributed to the formation of impurities, probably sulfide, on the reflecting surface. Any foreign substance could reasonably be assumed to obliterate the spectral peculiarities of metallic silver in the region of the minimum. Accompanying changes in R in the farther ultra-violet were measured, but appear erratic. The position of the minimum is not noticeably altered by ageing of this type.

Discussion of Results

A change in R can be accounted for by a variation of two parameters: n and k. The trend of both is sketched in Fig. 5, which is taken from Minor's[2] paper. The rapid downward slope of n is characteristic of a narrow transmission band. It is difficult to produce agreement with the experimental findings by assuming changes in k. A simple shift of the k-minimum to the left will not displace the minimum of R. At any rate such procedure would seem very arbitrary. The curve shows, on the other hand, that the minimum of k lies at 3140A, not at 3160A, where that for R is found. It is the rapid slope of n which causes the latter to appear 20A beyond the former. Tilting the straight line portion of the curve about a fixed point for which n is about 1.1 so that $dn/d\lambda$, whose value for the polished surface is $-0.006/\text{A}$, becomes $-0.0032/\text{A}$, moves the minimum of R to 3140A. This reduction in the rate of variation of n with λ is chosen, *a*) on account of its simplicity, all other possible methods of accounting for the displacement being more complicated, *b*) because of its influence on other properties. It is well known that, on the basis of the classical dispersion theory, $dn/d\lambda$ depensd in a definite manner upon the number of bound electrons vibrating with a resonance frequency which lies on the short wave-length side of the trans-

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[4] R. Hagen and H. Rubens, Ann. d. Physik **8**, 1–21 (1902).

mission band. If this number decreases the slope of n at the point in question becomes less steep.[5] We shall assume, therefore, that for an unstrained surface the number of electrons vibrating with a certain ultra-violet frequency is smaller than that for a polished one. Therefore, relieving the surface from strain affects the values of k for two reasons. (1) The maximum of k will be reduced in proportion to the decrease in the number of bound electrons of the resonance frequency, which follows directly from

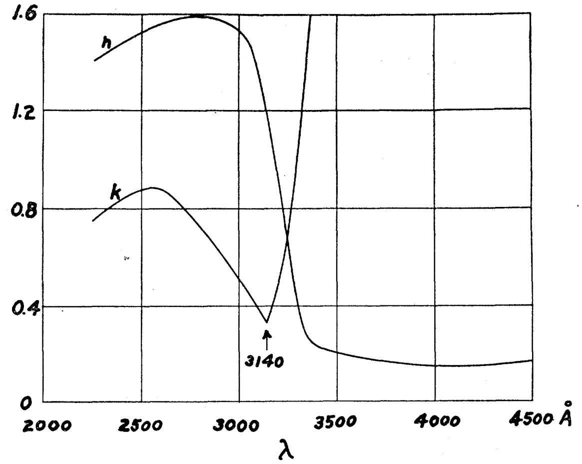

Fig. 5. Variations of n and k with λ.

$$n^2k=A\sum_i\frac{n_i\omega l_i}{(k_i^2-\omega^2)+4\omega^2l_i^2},$$

where A is a constant, n_i the number of resonating electrons of frequency k_i, and l_i a damping factor. The effect of neighboring frequencies is here neglected. The effect upon the minimum of k can not be calculated since it depends essentially on other resonance frequencies, but if conditions in the latter frequencies remain fixed it is probably small. (2) The electrons which, in the undeformed state, are no longer constrained to vibrate with a definite frequency must be supposed to be free. Their presence adds to k the amount $C/2\omega n^2$, C being the conductivity due to these electrons. If the curves in Fig. 5 are redrawn in qualitative agreement with these considerations, the values for R obtained from them are in accord with experimental observation. The hypothesis here outlined also agrees with the reduction of electrical conductivity which occurs with plastic deformation.

M. de Sélincourt[6] has shown that heating a silver surface causes the minimum of R to be displaced to longer wave-lengths. His explanation seems unsatisfactory to the writer, since it is out of harmony with accepted theories

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[5] Numerical calculations can easily be made; but they have little meaning since the value of the resonance frequency is not known. See note added in correction of proof.

[6] M. de Sélincourt, Proc. Roy. Soc. A107, 247–254 (1925).

of metallic reflection (the effect of bound electrons is neglected, the occurrence of the minimum being attributed to lack of resonance of free electrons) and it shows no connection with the decrease in electrical conductivity. The assumptions made in the present paper account well for the changes found by M. de Sélincourt, if heating, as well as cold working, is supposed to reduce the number of free electrons, i.e. bind some electrons into vibrational frequencies. Cooling would then shift the minimum to shorter wave-lengths and raise it, which is actually shown in his curves, while heating would displace it still further to greater wave-lengths. ($dn/d\lambda = -0.012/\mathrm{A}$ causes it to appear at 3180A.) The shallowness of the minimum at 150° does not follow from a change in the slope of the n-curve; it would call for a more radical modification which would result, for instance, if other resonance frequencies were affected.

It is interesting to apply the hypothesis, here found valid to explain the effects of plastic deformation on the reflecting power of silver, to other known influences of cold working on optical properties. Lord Rayleigh[7] and Lummer and Sorge[8] have shown that polishing changes the sign of Δ, the phase-difference between the components of the reflected amplitude vibrating in and perpendicular to, the plane of incidence. The latter authors have also discussed the incompetence of Drude's theory of surface layers for explaining this effect. They used a glass prism with $n = 1.5196$ for $\lambda = 5460\mathrm{A}$. It would follow from our assumption that polishing increases the number of electrons vibrating with a resonance frequency in the ultra-violet. The consequent effect on n in the visible region of the spectrum is an increase as is apparent from the dispersion curve for glass. Denoting the new index of refraction by n', we have $n' > n$. Passing from the polished surface into the prism we should encounter surface layers whose indices of refraction vary from a maximum value n_m to n. But according to Drude's theory,

$$\tan \Delta = \frac{4\pi}{\lambda} \frac{n^2}{1-n^2} \frac{\sin \alpha \tan \alpha}{\tan^2 \alpha - n^2} \int_0^d \frac{(n'^2-1)(n'^2-n^2)}{n'^2} dl,$$

where α = the angle of incidence. (See Fig. 11 on page 339 of Lummer and Sorge's paper.) l is the distance of an infinitesimal surface layer with index of refraction n' from the regular prism surface. The change in sign of Δ can only be caused by a change in the sign of the integral, which is negative as long as $n' < n$. Drude assumed the surface layers to be occluded air, hence there should be no change in sign. Strain will produce a surface film of glass with $n' > n$, which renders it possible for the preponderance of surface layers dl to have an index of refraction greater than n, and for the integral to change sign.

In concluding the writer wishes to express his gratitude for the encouragement he received from the members of the department throughout

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[7] Lord Rayleigh, Phil. Mag. **16**, 444–449 (1908).

[8] O. Lummer and K. Sorge, Ann. d. Physik **31**, 325–342 (1910).

his work, particularly to Professor McKeehan, who suggested the problem, and under whose sympathetic guidance it was a pleasure to carry on the investigation.

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March 11, 1929.

Note added in proof:—More detailed calculations have been carried out on the basis of the following assumptions:

1. The frequencies corresponding to the two persistent spectral lines $\lambda_2 = 2413$A (spark) and $\lambda_1 = 3280$A may be considered as principally responsible for the value of the index of refraction at the minimum. λ_1 involves the neutral state of the atom.

2. Cold working changes only the number of electrons per atom (n_1) vibrating with frequencies corresponding to λ_1.

For Δn_1, the change in n_1 due to plastic deformation, one easily derives

$$\Delta n_1 = -\Delta\left(n\frac{dn}{d\lambda}\right)(\lambda_1^2-\lambda^2)^2/A\lambda\lambda_1^4, \quad \text{where } A = \frac{Ne^2}{4\pi^2c^2m}\cdot$$

We find for n_1 the value 0.023, indicating that only about 2 percent of the silver atoms are in their neutral state; and for Δn_1 due to plastic deformation, by inserting the experimental value for $\Delta(ndn/d\lambda)$ at the minimum,

$$\Delta n_1 = -0.008,$$

which is equivalent to a reduction of the number of neutral atoms by about one-third. This would call for a change in electrical conductivity of about 0.8 percent.