CONCERNING THE REFLECTION POWER OF METALS IN THIN LAYERS FOR THE INFRARED

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Abstract

The reflection power of metals for the infrared and the visible spectra has been studied with special regard to the dependence of R upon the thickness of the reflecting layer. A new equation governing this relation has been developed.

The annoying fact that silvered surfaces, such as those used in infrared spectroscopy, tarnish rather rapidly when exposed to the gases usually present in laboratory air, has started many infrared experimenters on the search for a remedy or a substitute for silver. The results of these investigations are much varied. Some have found relief by simply covering the freshly silvered surface with an extremely thin protective film of collodion. Others[1] have suggested distilling a thin layer of quartz upon the surface in order to prevent the harmful gases from coming into contact with the metal. The majority of investigations however have been concerned with the use of some metal other than silver, such as gold, platinum, steel, antimony and many alloys.

We found here in this institute an antimony mirror which had been exposed to laboratory gases for two years. As this still appeared perfectly fresh and showed absolutely no traces of tarnish, we at once decided to antimony our spectrometer mirrors. The process which we used, distillation in high vacuum, though apparently simple, presented a number of very interesting complications which we wish to describe at this time.

The apparatus used embodied the essential features described in the papers of Pohl and Pringsheim,[2] Pfund,[3] Burger and van Cittert,[4] and Murmann.[5] It consisted chiefly of a bell jar, evacuated to approximately 10^{-4} mm, in which the distillation was effected. Bits of metallic antimony were contained in a small quartz tube or oven of 2 mm inside diameter, which was heated to a bright red by a spiral of tungsten wire. Above this oven, which was mounted vertically, the glass surface which was to be coated with antimony was supended. To obtain a deposit of uniform thickness the distance from the oven to the glass surface had to be about 10 cm. Precaution had to be taken in heating the oven, for if it was too rapidly or too unevenly heated the bits of antimony were shot out as if from a cannon.

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1 H. C. Burger and P. H. van Cittert, Zeits. f. Physik **66**, 218 (1930).

2 R. Pohl and P. Pringsheim, Verh. d. D. Phys. Ges. **14**, 46 (1912).

3 A. H. Pfund, R.S.I. **1**, 397 (1930).

4 H. C. Burger and P. H. van Cittert, reference 1.

5 Hans Murmann, Zeits. f. Physik **54**, 741 (1929).

As the process begins the antimony condenses as a thin highly transparent metallic film, of a light brownish color. This gradually increases in opacity and reflection power remaining always quite uniform in its appearance. At a certain stage in the process, depending upon the speed with which the distillation is carried on, the surface remains no longer uniform but becomes covered with spots. These are always round, more opaque than the surrounding layer, and have a relatively high reflection power. With the appearance of these spots the process should at once be interrupted and the mirror removed from the apparatus. If this is done at the right time, these spots, which we shall refer to as the second modification of antimony, increase in number, and expand always however remaining circular in form. They merge one with another to form larger areas, and after a period of time varying from 5 minutes to half an hour, this process completes itself and the mirror is composed entirely of the second modification. This is obviously the desired modification for it is more opaque and possesses for visible light a much higher reflection power than the first layer which forms. By gently warming the glass the speed of this transformation from the first modification into the second can be greatly increased.

If, however the distillation process is allowed to continue after the formation of these spots, another series of changes takes place. While the process is going on the spots increase in size and number and merge to form larger spots just as before. In addition, however, some kind of a "third modification" begins to form as a dark speck at the centers of the original spots. These specks, usually about 0.5 mm in diameter, do not increase in size, but remain fixed. When the mirror is finally taken out of the vacuum the second modification grows a bit, but usually not sufficiently to cover the entire mirror, with the result that in the end one has a mirror consisting of what is apparently three distinct forms of antimony.

This process of spot formation is exactly the same that found by Murmann[6] and described by him in detail. He investigated carefully some of the optical and electrical properties of the first and second forms of the antimony and as a result of his studies believed that the first form was an unstable amorphous modification which changed over into the stable crystalline second form. Evidence was also found by him for the existence of two analogous modifications in the case of silver. In all cases he found that the physical properties of the various modifications were radically different.

The spectrometer was equipped with three concave and two plane mirrors prepared in the manner described above, all five being of the so-called second form of antimony. These mirrors appeared to be optically perfect, however, when the instrument was tested for radiation of 52μ wave-length, the microradiometer deflections were entirely unsatisfactory, being extremely small. This suggested that one or more of the mirrors had for these wave-lengths an exceptionally low reflection power, for the same instrument equipped with silver mirrors had previously given nice deflections.

[6] Hans Murmann, reference 5.

In order to investigate this point a rocksalt reststrahlen apparatus, shown in Fig. 1, was assembled and for each of the mirrors the percentage reflection was roughly determined. Each mirror was in turn substituted for the freshly silvered plane mirror M_2, whose reflection power was assumed to be 100 percent. Since the effect for which we were looking was so large, the errors introduced by the approximations made in these measurements played a very small role. The results were rather surprising. The four antimony mirrors had reflection powers ranging from 42 percent to 80 percent, while a platinum mirror had $R=92$ percent and an old badly tarnished silver mirror, 96 percent.

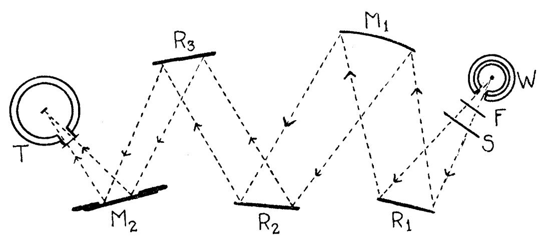

Fig. 1. Reststrahlen apparatus. W=Welsbach mantel, F=soot filter, R=rock-salt plates, T=microradiometer, S=glass shutter, M=silver mirrors.

The well-known formula for the reflection power of metals taken from Drude, reads

$$R = 100 - \frac{200}{(\sigma T)^{1/2}}$$

where σ is the conductivity expressed in e.s.u., and T is the period of the incident electromagnetic wave. This can also be expressed in the form,

$$R = 100 - \frac{36.5}{(x\lambda)^{1/2}}$$

where x is the reciprocal of the resistance in ohms for a conductor 1 m long and 1 mm cross-section, and λ is the wave-length expressed in μ. Taking for x the value $1/0.4$ or 2.5, we should expect antimony to have a reflection power for $\lambda=50\mu$ of 96.7 percent. Rubens and Hagen[7] in their work on the reflection power of metals did not measure antimony. However, from their work on other metals we know that the above formulas are accurate, and therefore theoretically we should expect an antimony mirror to have a reflection power throughout the far infrared of over 90 percent. Why then these particularly low values at 52μ?

The value taken for x, the conductivity, in the above equation was of course measured on massive antimony. If in such thin sheets prepared as described above the conductivity should be exceptionally low, then such low values of R could result. Indeed Murmann found that the resistances of mirrors of the first modification of antimony were in the order of 10^5 ohms. These

[7] H. Rubens and E. Hagen, Ann. d. Physik **8**, 1 (1902).

same mirrors, after the transformation to the second modification was complete, showed resistances of only 10^2 ohms. This, assuming that the thicknesses were in the two modifications the same, indicated that the value of the conductivity of the first form was extremely small in comparison with that of the second modification. Our mirrors, though all of the second form may still have possessed smaller values of x than 2.5.

Further discussion of this problem, however, led us to a new and entirely different question regarding the reflection power of metals. To just what extent and in what manner does the reflection power depend upon the thickness of the reflecting layer? From Drude we took as a starting point the equation expressing the ratio of the reflected amplitude to the incident amplitude in the case of non-absorbing substances.* This formula, as stated by Drude in his "Lehrbuch der Optik," reads

$$\frac{E_n}{E_i}=\frac{(e^{ip}-e^{-ip})(\epsilon_1-\epsilon_2)}{e^{ip}(\epsilon_1{}^{1/2}-\epsilon_2{}^{1/2})^2-e^{-ip}(\epsilon_1{}^{1/2}-\epsilon_2{}^{1/2})^2}. \tag{1}$$

where E_r is the reflected amplitude; E_i the incident amplitude; ϵ_1 the dielectric constant of medium 1; ϵ_2 the dielectric constant of medium 2; $p=2\pi d/\lambda(n-ik)=\alpha-i\beta$; $\alpha=2\pi nd/\lambda$; $\beta=2\pi kd/\lambda$. In our particular example, i.e., a metal surface in air, we can set

$$\epsilon_1=1 \text{ and } \epsilon_2{}^{1/2}=n-ik$$

where n and k are the optical constants of the metal in question. Rewriting Eq. (1), we get

$$\frac{E_r}{E_i}=\frac{(e^{i\alpha}e^{\beta}-e^{-i\alpha}e^{-\beta})(1-n^2+k^2+2ink)}{e^{i\alpha}e^{\beta}(1+n-ik)^2-e^{-i\alpha}e^{-\beta}(1-n+ik)^2}. \tag{2}$$

If this equation is now multiplied by its complex conjugate, we then have

$$\frac{E_r{}^2}{E_i{}^2}=\frac{[e^{2\beta}+e^{-2\beta}-2\cos(2\alpha)][(1-n^2+k^2)^2+4n^2k^2]}{e^{2\beta}[(1+n)^2+k^2]^2+e^{-2\beta}[(1-n)^2+k^2]^2-2\cos(2\alpha)[(1-n^2-k^2)^2-4k^2]-2\sin(2\alpha)[4k(1-n^2-k^2)]}. \tag{3}$$

Setting

$$[(1+n)^2+k^2]=U$$
$$[(1-n)^2+k^2]=V$$

and introducing an angle ψ, defined by

$$\tan\psi=\frac{2k}{n^2+k^2-1}$$

Eq. (3), by the application of a trigonometric transformation, becomes,

$$R=\frac{E_r{}^2}{E_i{}^2}=\frac{[e^{2\beta}+e^{-2\beta}-2\cos(2\alpha)]UV}{e^{2\beta}U^2+e^{-2\beta}V^2-2UV\cos(2\psi)\cos(2\alpha)+2UV\sin(2\psi)\sin(2\alpha)} \tag{4}$$

* This equation takes into account possible interference effects arising from multiple reflection of the radiation between the two surfaces of the non-absorbing body.

or

$$R = \frac{[e^{2\beta} + e^{-2\beta} - 2\cos(2\alpha)]UV}{e^{2\beta}U^2 + e^{-2\beta}V^2 - 2UV\cos 2(\alpha + \psi)} \tag{5}$$

Applying now the formula

$$\cos 2x = 1 - 2\sin^2 x$$

we get the final expression

$$R = R_\infty \frac{(e^\beta - e^{-\beta})^2 + 4\sin^2\alpha}{(e^\beta - R_\infty e^{-\beta})^2 + 4R_\infty \sin^2(\alpha + \psi)} \tag{6}$$

where

$$R_\infty = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} = \frac{V}{U}$$

$$\alpha = \frac{2\pi n}{\lambda} d \qquad \beta = \frac{2\pi k}{\lambda} d$$

$$\tan\psi = \frac{2k}{n^2 + k^2 - 1}$$

This Eq. (6), is the general expression giving the reflection power of a plane parallel plate of an absorbing substance as a function of the plate thickness, d. That it expresses correctly the extreme cases can easily be seen. Since d enters only in α and in β it is clear that

(1) when $d \ll \lambda$, i.e. an extremely thin plate, α and β will each be equal to zero, and therefore R will be also zero.

(2) when $d \ll \lambda$, or in case of a very thick plate, the terms $4\sin^2\alpha$ and $(4R_\infty \sin^2(\alpha+\psi))$ may be neglected in comparison with the exponential terms. Also the negative exponentials vanish, leaving the result $R = R_\infty$.

Using this equation we have made calculations of several interesting numerical examples. With values of n and k so chosen as to typify both good and

TABLE I. *Calculated reflection powers and percentage transmissions as functions of the thickness of the metal layer. d=thickness in μ, R=percentage reflection, D=percentage transmission.*

$\lambda=0.59\mu$						$\lambda=25\mu$								
$n=0.18$, $k=3.67$			$n=3.04$, $k=4.94$			$n=k=40$			$n=k=70$			$n=k=200$		
d	R	D	d	R	D	d	R	D	d	R	D	d	R	D
.0051	12.98	82.3	.0019	6.8	58.3	.001	12.7	79.0	.00056	16.8	33.8	.00019	40.7	11.4
.0128	48.0	45.4	.0095	42.2	13.7	.005	44.6	11.0	.00284	61.0	4.7	.00099	81.4	9.0
.0256	79.2	14.7	.019	64.7	4.4	.01	65.4	4.0	.00568	77.5	1.5	.00199	90.1	2.5
.0503	93.1	1.8	.0285	68.4	1.48	.02	79.0	1.2	.0114	88.3	.4	.0039	94.7	.7
.128	95.1	—	.038	70.0	.6	.05	90.9	.2	.0284	97.0	—	.0099	97.6	—
						.10	94.3	—	.0568	97.1	—	.0199	98.7	—

$\lambda=50\mu$														
$n=k=10$			$n=k=30$			$n=k=60$			$n=k=100$			$n=k=300$		
d	R	D	d	R	D	d	R	D	d	R	D	d	R	D
.0398	4.47	31.0	.01	28.3	22.0	.0066	61.5	6.9	.0008	20.3	38.5	.00026	62.7	8.1
.0797	13.25	13.2	.0265	54.9	6.1	.0132	72.5	2.6	.0039	69.5	2.6	.0013	89.4	.4
.1594	31.3	7.8	.053	73.0	2.0	.0264	85.2	.6	.008	83.5	.8	.0026	94.0	—
.318	63.9	4.0	.10	84.6	.6	.066	93.4	—	.02	92.7	.1	.0066	97.4	—
.637	78.0	1.2	.417	92.9	—	.132	96.4	—	.04	96.2	—	.0132	98.8	—
.797	81.2	.7							.08	97.5	—	.026	99.1	—

bad conductors, we have calculated R as a function of the thickness d for $\lambda = 0.59\mu$, 25μ and 50μ. To supplement these values of R, we have also in every

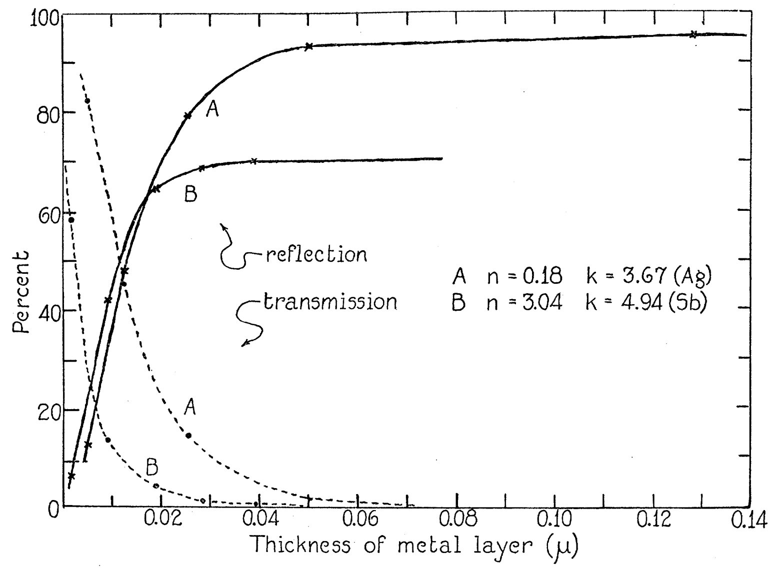

Fig. 2. Calculated reflection powers and percentage transmission for $\lambda = 0.59\mu$ as functions of the thickness of the metal layer.

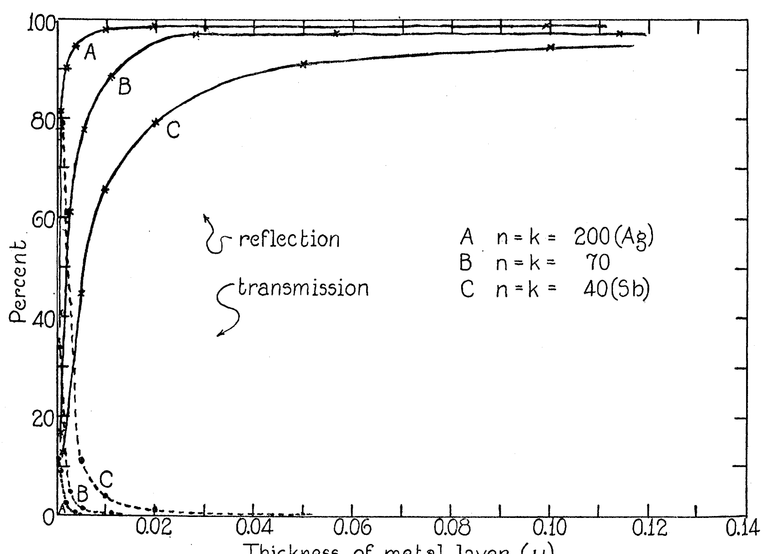

Fig. 3. Calculated reflection powers and percentage transmission for $\lambda = 25\mu$ as functions of the thickness of the metal layer.

case given the percentage transmission D, for the calculation of which an equation exactly analogous to the reflection power equation was used. This is essentially the same as that used by Czerny[8] and by Murmann and, with the same abbreviations as are noted above, it reads

$$D = \frac{(1 - R_\infty)^2 + 4R_\infty \sin^2\psi}{(e^\beta - R_\infty e^{-\beta})^2 + 4R_\infty \sin^2(\alpha + \psi)} \tag{7}$$

In making these calculations we made use of the fact that in the region of long wave-lengths $\kappa = 1$. From this it follows that $n = k$. Further, if we neglect the effect of terms of higher orders, we can also set $n^2 = \sigma\tau$ (where σ is again the conductivity expressed in e.s.u. and τ is the period of the incident radiation).

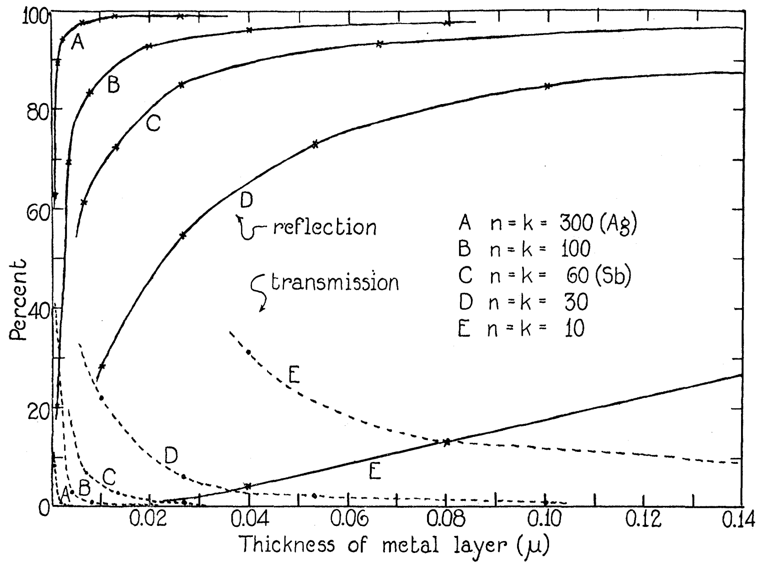

Fig. 4. Calculated reflection powers and percentage transmission for $\lambda = 50\mu$ as functions of the thickness of the metal layer.

From this latter condition we find that for $\lambda = 50\mu$ the refractive index of silver is equal to 307, while for antimony $n = 61$. For $\lambda = 25\mu$, these values are $n = 217$ and $n = 43$ respectively. Certain examples were therefore calculated and the results are given in Table I and Figs. 2, 3 and 4. The extent and manner in which the reflection power depends upon the thickness of the metal layer as is indicated by these calculations is rather surprising. For a given mirror to be "suitable" for use in any particular spectral region, we shall require that it be thick enough to have let us say, 99 percent of its R_∞ for those wave-lengths. Hence in discussing the calculations mentioned we shall center our attention only upon those thicknesses for which $R = 0.99\, R_\infty$.

From the tables and curves we find the following results for silver;

(1) For $\lambda = 0.59\mu$ $d = 0.080\mu$

(2) " $\lambda = 25\mu$ $d = 0.010\mu$

(3) " $\lambda = 50\mu$ $d = 0.012\mu$

[8] M. Czerny, Zeits. f. Physik **65**, 600 (1930).

This means that a silvered mirror 0.012μ thick, while it is for visible light still 40 percent transparent and has a reflection power of only $0.45\ R_\infty$, is according to our above requirement perfectly suitable for use in the far infrared. For use in the visible spectrum the layer of silver must be at least 6 times as thick as that required of a silver mirror intended for infrared use.

However, when we examine the case of antimony, a poorer conductor, we find that the thickness plays a very different role and the above relations are almost exactly reversed. We see that for antimony

(1) For $\lambda = 0.59\mu \quad d = 0.032\mu$

(2) " $\lambda = 25\mu \quad d = 0.10\mu$

(3) " $\lambda = 50\mu \quad d = 0.11\mu$

Thus an antimony mirror 0.03μ thick is just opaque for visible light, and has in this region $R = 0.99\ R_\infty$. The same mirror however has for the infrared $R = 0.90\ R_\infty$ and is therefore unsuitable. The antimony layer if it is to be used in the infrared must be at least 3 times as thick as that which is suitable for use in visible light.

Comparing these two cases we see that for use in the visible spectrum the thickness required for a suitable silver mirror is about 2 times that required for an antimony mirror. On the other hand however, for use in the infrared an antimony mirror must be about 10 times as thick as a suitable silver mirror.

By weighing two of our mirrors before and after the removal of the antimony layer, we found that the thicknesses of the latter were 0.19μ and 0.18μ respectively. From our curves we should expect mirrors of these thicknesses to have their full reflection power, or in this case 96.7 percent. These two however, according to our rough measurements had reflection powers of only 77 percent and 74 percent respectively.

The reflection power for such thin metal layers is a complicated function of σ, n and k, and through them of d, the layer thickness. Low values of R, assuming that the polish of the surface is perfect, must be attributed to the influence of some one or some combination of these quantities. In all of the above discussions and calculations we have assumed that metals in these thin layers possessed normal values of σ, n and k. It is entirely possible, however, and even probable, that σ for the second modification of antimony is still lower than the normal value. The optical constants too, due to the manner in which the mirrors were prepared and to the extreme thinness of the layers may vary somewhat from the accepted values.

As the questions raised by these observations in regard to the reflection power of metals in thin layers are still unsettled it is planned that further work along this same theme shall be carried out in this institute, and it is hoped that by obtaining more exact values of R, σ, n, k, and d answers to all of these questions may be found.