THE SCATTERING OF LIGHT BY THIN METALLIC FILMS.

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1. *Introduction.*

MUCH work has been done during the past few years by various authors on the optical properties of thin metallic films obtained by cathodic sputtering and evaporation in vacuo. But their attention has been so far confined mostly to reflection and transmission of light by thin metallic films. The phenomenon of scattering of light by these films, which is perhaps more striking and characteristic of them, has been more or less neglected.

Ramdas[1] studied the scattering of light by polished metallic surfaces. He found that much of the light scattered was due to microscopic irregularities in the surface. He also found that observed parallel to the surface with normally incident unpolarised light with a double image prism, the component of the scattered light with its vibrations in the plane of observation was very intense while that with its vibrations perpendicular was weak. In order to examine metallic surfaces free from irregularities he later obtained deposits of gold on freshly split mica surfaces by cathodic sputtering.[2] The mica-metal contact surface of these films exhibited metallic reflection and scattered very little light, much less in fact, than a clean mercury surface. This paper deals with an entirely different and far more striking phenomenon exhibited by extremely thin films of metal obtained by evaporation in vacuo and also cathodic sputtering.

2. *Some Preliminary Observations.*

During silvering the plates of a Fabry and Perot interferometer by evaporation of silver in vacuo, in the apparatus shown in Fig. 2, a deposit of silver of varying thickness like a wedge, was obtained on the walls of the glass jar in which it was done. The colour of the film by transmitted light varied from the characteristic blue of silver in the thickest part which showed metallic reflection, to a purple and finally an orange yellow. The thinnest portions which were orange yellow by transmitted light appeared greenish by reflected light and the portions which were purple by

[1] L. A. Ramdas, *Proc. Ind. Assoc. Sci.*, 1925-26, **9**, 129-143.

[2] *Ibid.*, 1925-26, **9**, 323-327.

transmission appeared a pale yellow by reflection. But by scattered light these thinner portions presented a remarkable appearance. The scattering of light by these portions of the film was so intense as to be capable of being demonstrated to a large audience. The scattering was observed to begin just where the metallic reflection fell off and the scattered light was an intense orange yellow in colour. The thinnest portions which were orange yellow by transmitted light appeared a green by scattered light. Photographs of a strip of the deposit on the jar taken by transmitted, reflected and scattered light are given in Fig. 1. The photograph by scattered light was taken through a red filter using a carbon arc for illuminating the jar obliquely. The source of light in the other two cases was a piece of Bristol board illuminated by a carbon arc. It is clear from the photographs that the scattering begins very suddenly just where the reflection weakens, at about 5·5 on the scale in B and continues till the thickness of the film becomes zero (about 8·0 on the scale).

Examination of the scattered light with a nicol showed that just as in the case of the metallic surfaces examined by Ramdas,[3] with normally incident unpolarised light, the direction of observation being almost parallel to the film, the component with its electric vector in the plane of observation was much more intense than the one with its electric vector perpendicular. If this scattering were the ordinary Rayleigh type of colloidal scattering, then the component with its electric vector perpendicular to the plane of observation should have been stronger than the one with its vector in the plane of observation. This follows from Mie's[4] theory and is found to be the case for the light scattered by colloidal gold and silver. Hence the scattering by thin films of metals must essentially be a surface effect different from the ordinary type of colloidal scattering. This remarkable property and the fact that the thicker portions did not scatter any light whatever made it desirable to study this phenomenon more fully using films of various metals.

3. *Preparation of the Films.*

Films of silver, aluminium and tin were obtained on clean glass or freshly split mica surfaces, by evaporation in vacuo in a modification of the well known apparatus of Ritschl,[5] shown in Fig. A. A conically wound spiral

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[3] *Loc. cit.*

[4] G. Mie, *Ann. der Physik*, 1908, 25, 427.

[5] R. Ritschl, *Zs. Physik*, 1931, **69**, 578.

See also

C. H. Cartwright, *Rev. Sci. Instr.*, 1932, **3**, 298.

C. H. Cartwright and J. Strong, *Phys. Rev.*, 1931, **2**, 189.

R. C. Williams and G. B. Sabine, *Astrophys. Journ.*, 1933, **77**, 316.

B of 30 gauge tungsten wire was firmly attached to two supports AA of thick copper wire. These supports which also served as electrical leads for the spiral, passed through C, the brass bed plate of the apparatus. They were insulated by means of glass bushes and the joint made vacuum-tight with sealing wax. The glass plate D on which the metallic deposit was to be obtained was kept inclined inside the jar E as shown. A small piece of the metal to be evaporated was kept in B, the joint between the jar and the bed plate was rendered vacuum-tight with a putty supplied by Metropolitan Vickers and the apparatus was evacuated by means of F with an oil

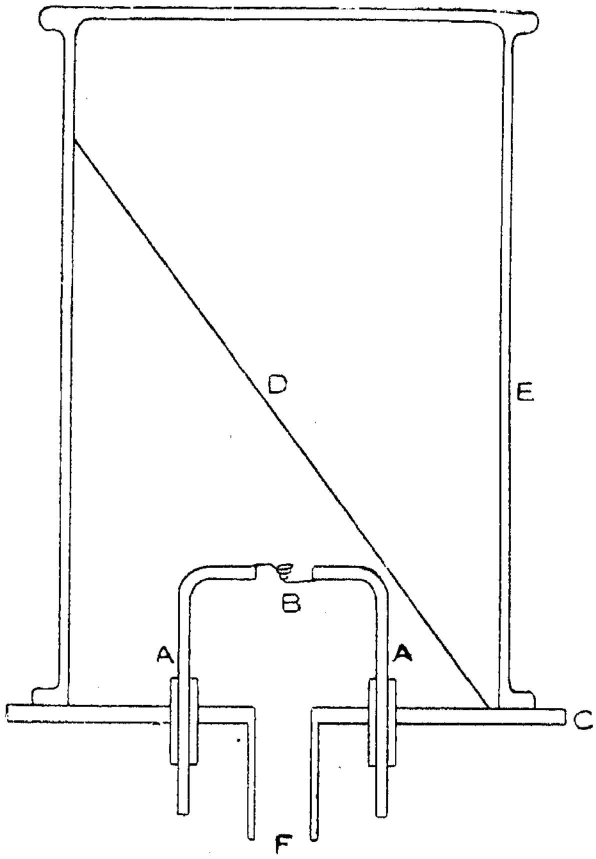

Fig. A.

diffusion pump capable of maintaining a vacuum of 10^{-6} mm. of mercury. After complete evacuation the metal in B was evaporated by passing a current of about 6 to 7 amperes through the tungsten spiral. The current and the time of evaporation depend upon the particular metal used. For instance silver films could easily be prepared with a current of 7 amperes in about 5 minutes.

4. *Detailed Study of Silver Films.*

A number of silver films were obtained by the above method on glass plates previously cleaned with chromic acid, washed with distilled water and dried in a closed cupboard to minimise the settling of dust. The silver films thus obtained were very thick in the centre and thinned off towards the edges. By transmitted light the central portion was deep blue in colour. The colour progressively varied towards the edges from deep blue in the centre, in the sequence—light blue, bluish purple, purple, reddish purple and orange yellow—just as in the case of the deposit on the jar mentioned earlier. The deep blue portions were highly reflecting, and the light blue portions also showed metallic reflection but with diminished intensity. The purple portions appeared pale yellow by reflected light and the orange yellow portions appeared a light green. The light reflected by these thin portions was extremely feeble. But by scattered light the film had a remarkable appearance, the portions with metallic reflection appearing quite black and invisible, while the outer portions were successively brilliant orange and green in colour. The intense orange scattering was manifest just where the metallic reflection fell off, while the thinnest portions appeared green. Examination with a nicol showed that with normally incident unpolarised light, the direction of observation being almost parallel to the surface of the film, the component with its electric vector in the plane of observation was much more intense than the one with its electric vector perpendicular.

In order to test whether the above phenomenon was in any way influenced by the nature of the surface of deposition of the film, a number of silver films were obtained on freshly split surfaces of mica. Photographs of an evaporated silver film on mica, obtained by reflected, scattered and transmitted light are given in Figs. 2, 3 and 4 respectively. Fig. 2 was obtained by photographing the silver film by reflected light using a piece of Bristol board illuminated by a carbon arc as the source of light. Fig. 3 was obtained by photographing the film illuminated by the light from a carbon arc at grazing incidence. Fig. 4 was obtained by photographing the film by transmitted light using a piece of Bristol board illuminated by a carbon arc as the background. From the photographs it can be seen that the metallic reflection ends abruptly and the scattering begins in an equally abrupt manner where the metallic reflection ends. The white spots and streaks in the photographs are due to imperfections in the mica.

5. *Films of other Metals.*

Films of aluminium and tin obtained by evaporation in vacuo also show the scattering of light phenomenon described in this paper, but not so strikingly as silver. Neither do they show such remarkable colours by transmitted and reflected light as silver films. The light scattered by films of aluminium and tin also exhibits anomalous depolarisation which is characteristic of metallic surfaces, in very much the same way as silver films. With a heating current of 6 to 7 amperes films of the above metals could be obtained in 4 to 5 minutes. With this current it takes about an hour to prepare a gold film. But it will probably be contaminated with tungsten since a tungsten filament by itself gives an easily discernible film with 7 amperes in about half an hour. For this reason gold and copper films were prepared by cathodic sputtering, as explained later.

6. *Sputtered Films.*

Some films of silver, copper and gold were obtained by sputtering on freshly split mica from a circular cathode of silver about 5 mm. in diameter. Films similar to the evaporated ones were obtained, the thinner portions of which showed exactly similar phenomena. But the central thick portions also scattered light quite intensely as observed by Ramdas[6] in some sputtered deposits, probably due to very coarse granular structure.

Another property of the sputtered films is perhaps worth mentioning. They exhibit coloured rings of the type observed by Wood, Edwards and others,[7] both by reflection and by transmission. With obliquely incident light these colours are different when viewed through a nicol with the direction of vibration parallel to the film, to what they are when it is perpendicular. The reflection colours with the nicol parallel to the film are the same as the transmission colours with the nicol perpendicular; and also, they are complementary with the reflection colours obtained with the nicol perpendicular.

7. *Examination of the Films under a Microscope.*

Examined by transmitted light under a microscope the silver films as also films of other metals do not reveal any kind of a structure even with the highest powers which can be used without oil-immersion. Only the colour of the film is visible, which is itself quite continuous and structureless. A more thorough examination of the scattered light is possible with the "Ultra-opak" microscope recently introduced by Leitz and used by Sir C. V. Raman[8] for the examination of the plumage of birds. The brilliant colour of the scattered light is very clearly visible in this microscope. Only the faintest semblance of a structure is seen, which is but imperfectly resolved. The colour itself is quite uniform and does not show any discontinuity. It is hard to say definitely whether the films have a structure or not without further examination with higher powers and more intense illumination than what was used.

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[6] *Loc. cit.*

[7] R. W. Wood, *Phil. Mag.*, 1902, **4**, 428.
H. W. Edwards, *Phys. Rev.*, 1931, **38**, 166.
L. I. Bockstahler and C. J. Overbeck, *Phys. Rev.*, 1931, **37**, 465.

[8] Sir C. V. Raman, *Proc. Ind. Acad. Sci.*, 1934, **1**, 3.

8. *Electrical Conductivity of the Films.*

In order to find out whether there is any sudden fall in electrical conductivity where the scattering of light begins, the silver film on mica was divided into parallel strips 7 or 8 mms. long and about 2 mms. wide by ruling lines with a pointed piece of wood. A suitable contact piece was made out of two strips of silver foil about a millimetre wide, firmly secured 2 mms. apart on a piece of mica. The strip of the silver film whose resistance was to be measured was kept on the contact piece and weighted down by a 100 gram weight in order to ensure good contact between the strips of foil and the film. The results obtained are given in Table I. Resistances below 100,000 ohms were measured with a post office box and the rest with an Evershed "Megger".

TABLE I.

No. of strip	Colour by transmission	Colour by reflection	Colour by scattering	Electrical resistance ohms
1	Deep blue, almost opaque	White, metallic	Invisible by scattered light	1·1
2	do.	do.	do.	2·0
3	do.	do.	do.	2·5
4	do.	do.	do.	2·8
5	do.	do.	do.	2·9
6	Blue	do.	do.	3·9
7	do.	do.	do.	4·8
8	Light blue.	Slightly feebler metallic reflection	do.	5·8
9	do.	do.	do.	7·7
10	do.	do.	do.	8·4
11	do.	do.	do.	13·6
12	Bluish purple	Pale yellow, metallic reflection absent	Intense orange start of scattering	55·7
13	Purple	do.	do.	..
14	do.	do.	do.	207
15	do.	do.	do.	100,000
16	do.	do.	do.	100×10^6
17	do.	do.	do.	Infinite
18	Orange yellow	Green, feeble	Green	do.
19	do.	do.	do.	do.
20	do.	do.	do.	do.

From the Table it is clear that the film can be divided roughly into three portions: a metallic part where it is highly conducting, a part where the resistance is high but finite and a part where the resistance is infinite.

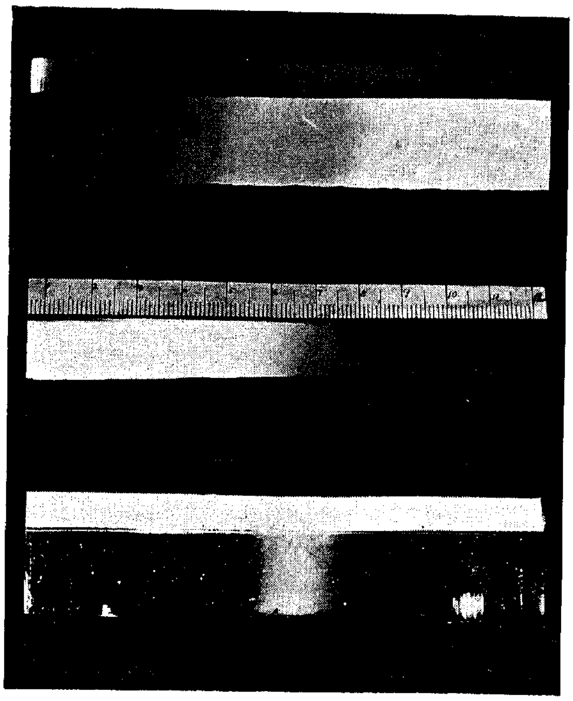
The first of these parts does not scatter any light, the second appears orange and the third green by scattered light. The metallic portion of the film is definitely crystalline as shown by X-ray observations. One can think of the film as existing in three different states: a crystalline state where there is complete regularity of arrangement of atoms in a lattice and consequently very little scattering, a two-dimensional gaseous state with random distribution, and an intermediate state between the two. The intermediate state is the one in which the film is orange by scattered light and has a high but finite resistance. The two-dimensional gaseous state is the one in which the film is green by scattered light and has infinite resistance.

In view of the facts described in the present paper, any explanation of the colours of thin metallic films based merely on the optical constants of metals, *viz.* refractive index and absorption cofficient, measured in the crystalline condition would necessarily be incorrect. More detailed quantitative investigations of the scattering of light by thin films of metal and its correlation with colours by reflection and transmission and with electrical resistance are now in progress.

It is with much pleasure that I take this opportunity to express my sincere thanks for the kind and helpful interest which Sir C. V. Raman has taken in this work.

Summary.

Observations on a new kind of light scattering shown by thin films of metals obtained by evaporation in vacuo and cathodic sputtering are described. The light scattered by such films exhibits anomalous depolarisation characteristic of metallic surfaces. It is thus essentially a surface effect and not the ordinary Rayleigh type of colloidal scattering. The portions of the film which are thin enough to show this effect are found to have no metallic reflection and either a large or else a practically infinite electrical resistance. It is suggested that the metallic film has three possible different states: a crystalline state with metallic properties, a two-dimensional gaseous state which is not metallic and is non-conducting, and thirdly an intermediate state with high electrical resistance. An evaporated silver film in the first state scatters little light and is black by scattered light. In the intermediate state, it scatters bright orange yellow light, and in the gaseous state, a bright green. Observations on the colours of the film by transmission and reflection examined with a nicol are also recorded. It is hoped that a more detailed quantitative investigation of the scattering of light by thin films of metals will throw light on their nature.



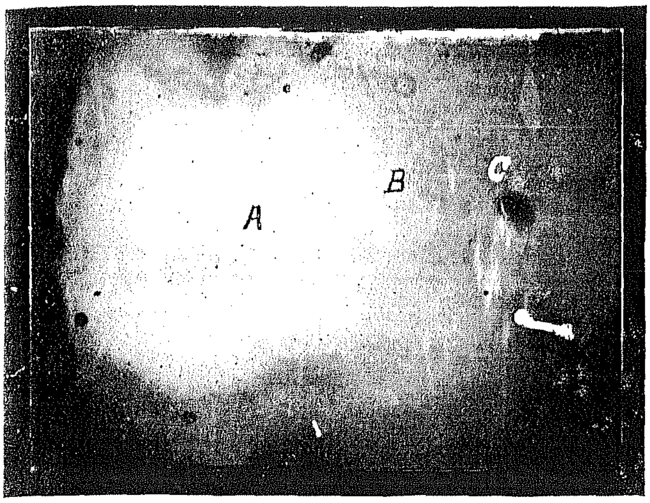
A—Transmitted.

B—Reflected.

C—Scattered.

Fig. 1.

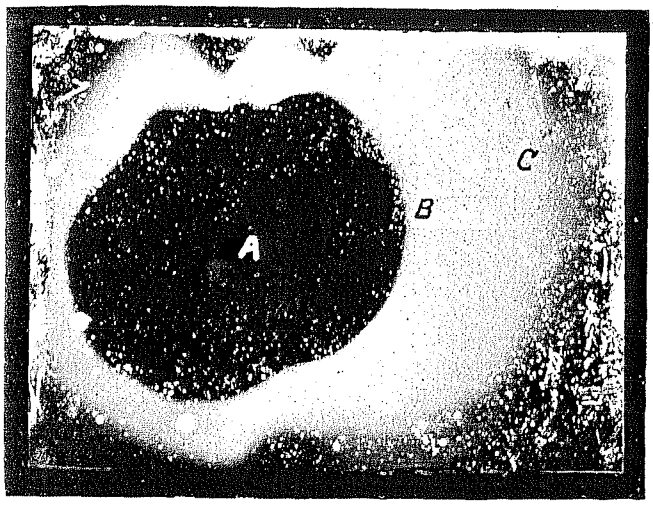
FIG. 2.



Reflected.

A—Metallic reflection.
B—Pale yellow reflection.
C—Pale green reflection.

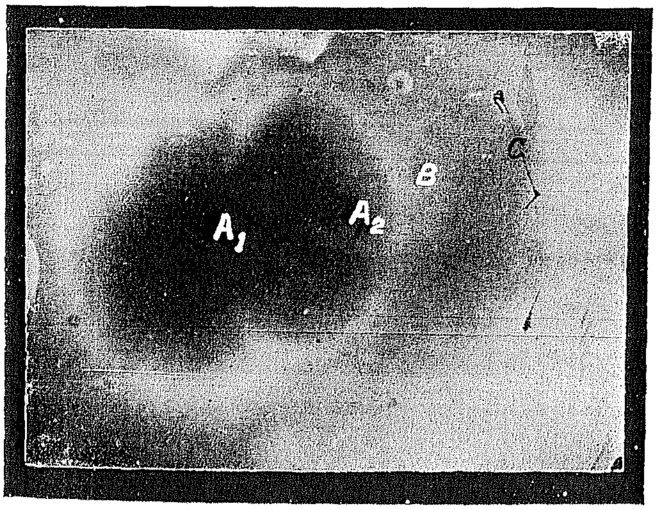
FIG. 3.



Scattered.

A—Black. No scattering.
B—Orange yellow scattering.
C—Green scattering.

FIG. 4.



Transmitted.

A_1—Deep blue.
A_2—Light blue.
B—Purple.
C—Yellow.