

than the theoretical values and are of the opposite sign. However, we have considered neither perturbations from higher terms of the  $3d^7$  configuration or from other excited states, nor mixing between the  $\Gamma_4$  states of  $^4F$  and those of  $^4P$ .<sup>7</sup> Both effects can change the calculated coefficients significantly. Study of these questions is in progress.

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<sup>1</sup>A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

<sup>2</sup>G. F. Koster and H. Statz, Phys. Rev. **113**, 445 (1959).

<sup>3</sup>B. Bleaney, Proc. Phys. Soc. (London) **A73**, 939 (1959).

<sup>4</sup>M. Dvir and W. Low [Proc. Phys. Soc. (London) **75**, 136 (1960)] have observed a spectrum for  $Ce^{3+}$  in  $CaF_2$  which is similar to that predicted by Bleaney (reference 3). However, the angular variation was found to deviate somewhat from Bleaney's result.

<sup>5</sup>K. D. Bowers and J. Owen, Reports on Progress in Physics (The Physical Society, London, 1955), Vol. 18, see p. 349; J. M. Baker, W. Hayes, and D. A. Jones, Proc. Phys. Soc. (London) **A73**, 942 (1959); T. P. P. Hall and W. Hayes, J. Chem. Phys. **32**, 1871 (1960); W. Low and M. Weger, Phys. Rev. **118**, 1130 (1960). The resonance in ZnS reported in the last article was not positively identified. However, the resolution of the eight-line hyperfine structure by the present authors (in presumably less-strained crystals) makes its identification as due to cobalt conclusive.

<sup>6</sup>For a summary of terms in the actual Hamiltonian, see reference 1 or W. Low, Paramagnetic Resonance in Solids (Academic Press, New York, 1960), p. 43.

<sup>7</sup>A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 173 (1951).

## EXPERIMENTAL VERIFICATION OF RADIATION OF PLASMA OSCILLATIONS IN THIN SILVER FILMS\*

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About two years ago Ferrell<sup>1</sup> predicted that plasma oscillations in a thin metal film of suitable thickness should give off a photon radiation of plasma frequency  $\omega_p$ . The detection and investigation of this radiation would give experimental evidence of plasma oscillations and furthermore would be a useful tool for measuring the energy of the plasmon more precisely than is possible by the electron energy-loss experiments.<sup>2</sup>

Ferrell<sup>3</sup> suggested using silver films for detecting plasma radiation. Plasmons in silver are expected to have an energy of 3.75 eV corresponding to a wavelength of 330 m $\mu$ .<sup>4</sup> Therefore, for radiation experiments with silver, quartz optics can be used.

In the work reported here, self-supported silver films were bombarded with 25-keV electrons. Care was taken for the electron beam to interact only with the specimen so that all radiation found necessarily had come from the silver film. To record the radiation a small quartz spectrograph was placed on the same side of the specimen as the incident electron beam. Its resolution was found to be about 10 m $\mu$ . As the spectrograph

could not be calibrated absolutely, optical filters were used to fix a point in the spectrum. The dispersion was known from calibration measurements with a helium spectrum. The total number of electrons having passed the specimen could be determined, and yielded a relative measure for the exposure of the photographic film.

The spectrum of the radiation from a silver film was found to consist of a rather sharp line at  $330 \pm 10$  m $\mu$  and a broad continuum at the long-wavelength side of the line; for shorter wavelengths the intensity rapidly falls to zero [see Fig. 1(a)]. Similar experiments with gold films with the same exposure yield only a weak continuum decreasing with wavelength.

As an experimental test whether the radiation was really caused by plasmons, we studied the dependence of the intensity on film thickness, which, as Ferrell<sup>1</sup> pointed out, ought to be as shown in Fig. 1(d). The experimental results [Fig. 1(a)-(c)] clearly demonstrate that the dependence of the line intensity on thickness agrees with the theoretical prediction, showing two maxima [Fig. 1(a) and (c)], the second one much

lower than the first, and the minimum equal to zero between them [Fig. 1(b)], while the intensity of the continuum apparently shows another dependence on thickness. From this fact it follows clearly that the radiation of the line is caused by

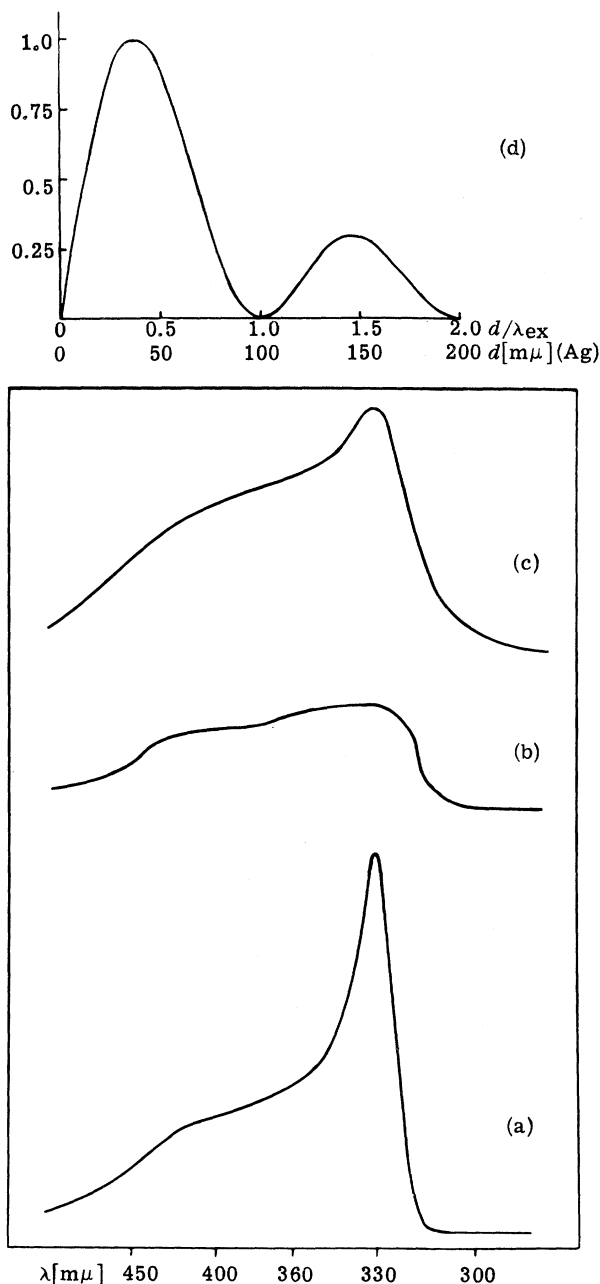


FIG. 1. Photometer curves of 3 spectra of the radiation from silver films of various thickness  $d$ : (a)  $d = 45 \text{ m}\mu$ ; (b)  $d = 85 \text{ m}\mu$ ; (c)  $d = 150 \text{ m}\mu$ . (d) Photon yield (in arbitrary units) per incident electron,  $Y$ , vs  $d/\lambda_{\text{ex}}$ .  $\lambda_{\text{ex}} = \lambda_p v/c$ ;  $\lambda_p$  = plasmon wavelength;  $v$  = velocity of the incident electrons. Lower scale of (d) is specified for Ag films bombarded by 25-kev electrons.

plasma oscillations, since no other known process gives this dependence on thickness. As a result it is demonstrated that plasmons really can radiate, and furthermore that in silver plasmons exist with  $\hbar\omega_p = 3.75 \pm 0.1 \text{ ev}$ .

There should exist a corresponding peak in the electron energy-loss spectrum. In all transmission experiments on silver a low-lying loss was found at 3.4 ev.<sup>2,5</sup> This value lies beyond the limit of error of the radiation experiment. Therefore the energy-loss spectrum was measured with the same silver films as used for detecting the radiation.<sup>6</sup> As Fig. 2 shows, the shape and width of the low-lying loss line agrees with that of the radiation line. The value of this loss altered a little from one measurement to the next, always lying between 3.4 and 3.6 ev. The difference between the results of the energy-loss and radiation experiments can be explained by the fact that the loss is superimposed on the slope of the no-loss peak. Therefore the maximum of the loss appears shifted towards the top of the zero peak and the measured value is too low. An estimation of the shift showed the right order of magnitude (some 0.1 ev). Probably this fact also caused the measured loss value to fluctuate. As a conclusion the radiation experiment already now yields a better, more reliable value of the plasmon energy than the energy-loss experiments, in spite of the hitherto rather rough method of wavelength determination.

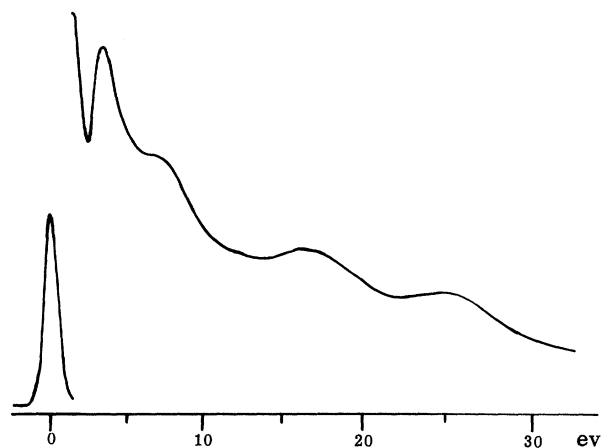


FIG. 2. Electron energy loss spectrum of a silver film ( $d = 45 \text{ m}\mu$ ) (photometer curve). The no-loss peak was shielded during most of the exposure of the spectrum. Thereby its shape was preserved and the zero point of the loss axis could be fixed precisely. The losses of this spectrum are  $3.59 \pm 0.03$ ,  $7.4 \pm 0.2$ ,  $17.0 \pm 0.5$ , and  $25.5 \pm 0.5 \text{ ev}$ .

The author wishes to express his thanks to Professor Ferrell for helpful advice and important suggestions, and to Professor Rollwagen, director of this institute, for his constant interest in this work. He is also indebted to Mr. Fischer and Mr. Otto for their performance of the energy-loss experiments.

\*A more detailed report of this work will be submitted to the *Zeitschrift für Physik*.

<sup>1</sup>R. A. Ferrell, *Phys. Rev.* **111**, 1214 (1958).

<sup>2</sup>L. Marton, L. B. Leder, and H. Mendlowitz, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 183.

<sup>3</sup>R. A. Ferrell (private communication).

<sup>4</sup>H. Fröhlich and H. Peltzer, *Proc. Phys. Soc. (London)* **A68**, 525 (1955).

<sup>5</sup>H. Watanabe, report submitted to the Gatlinburg Conference on Penetration of Charged Particles in Matter, 1958 (unpublished).

<sup>6</sup>The measurements of the loss spectra were performed by J. Fischer and A. Otto of this institute with a Möllenstedt-type analyzer.

### PLASMON RERADIATION FROM SILVER FILMS

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A straightforward application of the free electron theory of metals would indicate the possibility of a plasma oscillation of the valence electrons at a frequency dependent on their density. It has been conjectured<sup>1</sup> that the characteristic losses of energy suffered by high-energy electrons traversing thin metallic films can be attributed to the excitation of these plasmons with a characteristic frequency determined through  $\Delta E = \hbar \omega_p$ .

However, this explanation of the losses is not universally accepted.<sup>2</sup> For this and other reasons stated in his paper, Ferrell<sup>3</sup> has suggested a crucial test of the plasmon theory. He states that, at certain ratios of film thickness to incident electron velocity, plasmons would be excited which could be expected to decay through photon emission at a frequency  $\omega_p$ . Although the level of this radiation is expected to be small, it differs from anticipated background in its dependence of intensity on electron velocity and its angular distribution about the normal to the film. The width of the line should also depend strongly on angle of observation, through the relation

$$\tau_r^{-1} \propto \sin \theta \tan \theta, \quad (1)$$

where  $\theta$  is the angle from the normal and  $\tau_r$  the radiative mean life.

Although we originally planned to work with sodium films, we found it impossible to keep them continuous and clean in our apparatus. We now are working with thin silver films, in which the predictions of the free electron theory are less clear-cut but the experiment itself more

simple. We deposit films of the order of 500 Å thick and transfer them to cover a slit 1 mm wide at the target end of an electron gun structure providing 22-keV electrons normally incident on the film. The entire gun structure is capable of rotation about a slit serving as the input to a diffraction spectrometer which, with the exception of input lenses and a quartz window, is located entirely outside the vacuum system. The signal is taken from a photomultiplier and read beyond an amplifier and phase detector, which eliminates noise having no relation to the modulated beam.

As shown in Fig. 1(a), we find a peak in the spectrum taken at 30° from the film normal; it has

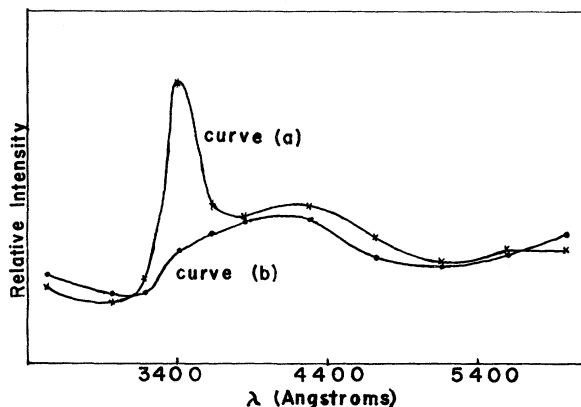


FIG. 1. Intensity of radiation vs wavelength at two different angles from normal of silver film. Thickness of film 500 Å; beam voltage 22 kv. (a)  $\theta = 20^\circ$ . (b)  $\theta = 75^\circ$ .