Observation of Radiative Decay of Surface Plasmons in Small Silver Particles

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The radiation resulting from decaying surface plasmons in small metallic particles has been observed for the first time. The surface plasmons were excited in colloidal silver by x rays. The spectrum of the observed radiation is presented and compared with theoretical predictions.

Surface plasmons (SP) in metallic films have been studied intensely over the last fifteen years, both experimentally and theoretically.[1] In particular, the possibility of radiative decay of SP in films has been examined systematically. However, because of momentum conservation, the direct decay of a SP to a photon is prohibited for a plane geometry. Surface irregularities, surface grating, or coupling to other elementary excitations have been used to provide the missing momentum and thereby make the radiative decay of SP in films possible.[1] On the other hand, for a spherical geometry the direct decay of SP to photons is not prohibited by any selection rules and should be observable provided that the cross section for the process is appreciable. Theoretical estimates by Crowell and Ritchie[2] indicate that the latter condition is fulfilled.

The existence of SP in metallic spherical particles has been demonstrated experimentally by optical absorption,[3,4] high-energy electron loss measurements,[4-6] and inelastic x-ray scattering.[7] To the best of our knowledge, the experiments reported in the present communication constitute the first direct observation of the radiation resulting from the decay of SP in spherical particles.

The samples used in the present experiments consisted of colloidal silver deposited on a substrate. In some of the samples, stabilizing agents such as gelatine and sodium citrate were used; in these cases the silver particles were surrounded by the stabilizing agent. Electron microscope photographs of the samples were taken. In the case where no stabilizing agent was used, the silver particles tended to form closely packed clusters of irregular shape. The mean diameter of the particle was about 130 Å in this case. For the samples treated with a stabilizing agent the silver particles were rather well separated. The mean diameter was about 120 Å for the case of gelatine and 50 Å for the case of sodium citrate. The samples were painted onto a rotatable target to a thickness that made them opaque and were inserted in a vacuum chamber. By turning each facet of the target they could be brought into an x-ray beam coming from a closed x-ray tube at a distance of 10 cm. The tube had an iron anticathode and carried 8 mA at 30 keV. The radiation emitted from the target entered an uv spectrometer, and the spectrum was measured point by point with a photomultiplier. Details of the experimental apparatus will be given elsewhere.

Figure 1 shows the spectrum of the emitted radiation for the case where gelatine was used as a stabilizing agent. Quite similar results were obtained with the other stabilizer. The radiation consists of a band peaked at 400 nm with a half-width of 75 nm. The corresponding energy is 3.10 ± 0.30 eV.

Figure 2 shows the spectrum for the case where no stabilizing agent was used. Again a clear peak appears which is shifted to higher energies relative to the case of Fig. 1. The maximum occurs now at 310 nm with a half-width of 25 nm. The corresponding energy is 4.0 ± 0.17 eV. Note that the accuracy in the present case is higher than when a stabilizing agent has been used.

To exclude the possibility that the observed radiation may arise from a source other than the

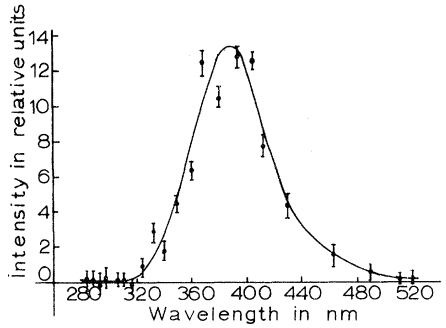

FIG. 1. Spectrum of the plasma radiation from colloidal silver embedded in gelatine.

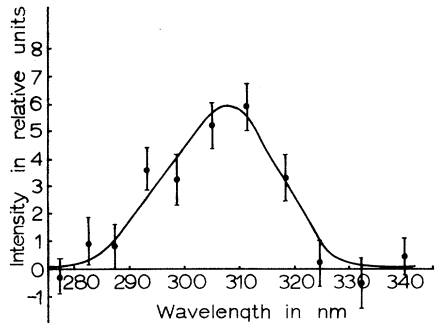

FIG. 2. Spectrum of the plasma radiation from dry colloidal silver without stabilizing agent.

colloidal silver samples, we performed measurements when no sample was deposited on the target as well as when pure gelatine was deposited. In both cases the results were negative. We have also deposited a metallic silver film on the target and the result was again negative.[8] This is a clear demonstration that the observed radiation arises from silver in its colloidal form.

We attribute the observed radiation to the decay of SP in the metallic silver particles. The incoming x rays excite the SP,[7] which in turn, because of their coupling with the radiation field, decay to photons.[2] According to theoretical calculations[2,9,10] the eigenfrequencies of the SP in spherical particles (which by energy conservation is the same as the frequency of the emitted radiation) is given by

$$\epsilon_m(\omega) = -(l+1)l^{-1}\epsilon_d, \qquad (1)$$

where $\epsilon_m(\omega)$ is the dielectric function of the spherical metallic particle, ϵ_d is the dielectric constant of the surrounding material, and l is a positive integer, characterizing the different modes. As a result of the smallness of the spherical particles, only the lowest mode ($l=1$) is expected to be appreciably excited.[5] Equation (1) has been derived[9] on the basis of electrostatic theory. Retardation effects[1] are important when the quantity $\omega R\epsilon_d^{1/2}/c$ becomes comparable to or larger than unity[11] (ω is the eigenfrequency, R is the radius of the spherical particles, and c is the speed of light); for the present case, however, the correction due to retardation effects is of the order of 1% and thus negligible.[11]

For the case of Fig. 1, $\epsilon_d = 2.37$. The dielectric function $\epsilon_m(\omega)$ of silver has been calculated by Ehrenreich and Phillipp.[12] Kreibig[4] has demonstrated that the real part[13] of ϵ_m does not depend on the size of the spherical particle for $R \geq 50$ Å. Using for $\epsilon_m(\omega)$ the values of Ref. 12 and $\epsilon_d = 2.37$, we find that the theoretical prediction for the eigenfrequency of SP in the present case is $\omega_{SP} = 3.0$ eV. This theoretical value is in rather good agreement with our experimental value of 3.10 eV. Good agreement is also obtained if the results of the present measurement are compared with the experimental data of Refs. 3 and 4. Thus Kreibig and Zacharias[4] obtained $\omega_{SP} = 2.99$ eV for silver particles embedded in gelatine and $\omega_{SP} = 3.1$ eV for silver particles in glass ($\epsilon_d = 2.25$); Doremus[3] found that $\omega_{SP} = 3.05$ eV for silver particles in glass. The small discrepancies may be understandable in terms of uncertainties in $\epsilon_m(\omega)$ in a region where $\epsilon_m(\omega)$ is changing rapidly.

For the case where no stabilizing material was used (Fig. 2), and if we assume that the spherical particles are surrounded by air ($\epsilon_d = 1$), we obtain from Eq. (1) $\omega_{SP} = 3.3$ eV. This value is to be compared with the experimentally observed $\omega_{SP} = 4.0$ eV. This rather large discrepancy is due partly to the considerable compacting together of the spheres when there is no ponderable medium separating them. This clustering effect effectively changes the geometry from the assumed spherical shape to a quite irregular one, for which Eq. (1) is no longer valid. Since this irregular geometry is in a sense intermediate between the two extremes of a film and a sphere, we expect in general an increase in the eigenfrequency predicted by Eq. (1). Similarly, the presence of oxides or impurities may be partly responsible for the observed discrepancy.

In conclusion, we have observed radiation following bombardment by x rays of colloidal silver. We have demonstrated that the spherical silver particles are the source of this radiation. In the experimentally controllable case where gelatine was surrounding the spherical particles, the frequency of the observed radiation agrees well with the frequency of SP in spheres, as predicted theoretically and as determined experimentally. Thus we identify the observed radiation as due to the radiative decay of SP following their excitation by the x-ray beam.

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[8]One expects that there would be some transition radiation from the silver film due to the electrons released by the x rays. According to the estimations in Ref. 2, the intensity of such transition radiation is a little less than the intensity of radiation produced from the decay of SP in spherical particles excited by the same electrons. Since SP in spherical particles can, in addition, be excited directly by x rays although x rays do not produce transition radiation in films, we expect that the observed radiation from SP in silver spheres should be considerably more intense than the indirectly produced transition radiation in silver film. The present experiment suggests that the observed radiation from colloidal silver is at least 10 times more intense than the transition radiation from the silver film generated indirectly by the x-ray beam.
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[13]The $\mathrm{Im}\epsilon_m(\omega)$ increases with decreasing size because of surface scattering.

Magnetic Field Dependence of Cyclotron-Resonance Linewidth in the Quantum Limit*

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We show that an electron-impurity interaction with a screening radius longer than the cyclotron radius gives rise to a cyclotron-resonance linewidth for a nondegenerate semiconductor in the quantum limit, which increases and approaches a constant value with increasing magnetic field. This is in contradiction to earlier theoretical work of Kawamura *et al.* and to the interpretation of the recent experimental work of Apel *et al.*, both of which are discussed in the light of this calculation.

With the advent of lasers, a number of experimental studies of the cyclotron resonance in semiconductors at infrared frequencies have been reported.[1,2] Of particular interest are the recent experiments of Apel, Poehler, and Westgate,[2] which investigate the shape of the resonance absorption line in the quantum limit and seem to suggest a narrowing of the line with increasing magnetic field B. Apel, Poehler, and Westgate[2] point out that such behavior is in conformity with the theoretical results of Kawamura *et al.*[3] and Kawabata,[4] who have calculated the field dependence of the resonance linewidth in the quantum limit due to unscreened ionized impurity scattering and found, respectively, a *narrowing* $\propto B^{-1/4}$ for "adiabatic" scattering and a *narrowing* $\propto B^{-1}$ for "nonadiabatic" scattering.

We point out below that the suggested narrowing of the cyclotron resonance line with increasing field should *not* be considered a settled matter because of inadequate theoretical understanding. In fact, we have found that long-range screened ionized impurity scattering causes the resonance line of a nondegenerate semiconductor in the quantum limit to *broaden* and level off to a constant value with increasing magnetic field. In general, the field dependence of the linewidth is very sensitively dependent on the detailed form of the scattering interaction, as is to be expected from the field dependence of magnetoresistance in the quantum limit.

Our calculation is carried out with the help of