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Surface-Plasmon Excitation in Small Spherical Graphite Particles by X Rays*

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X-ray scattering experiments have been carried out on dried colloidal graphite, for scattering angles $\varphi = 0°$ and $\varphi = 10°$, using Cr$K\beta_1$ line as a primary radiation. The spectrum for $\varphi = 0°$ shows a faint new component shifted by 13 ± 1 eV from the primary line; the same line was also found for a scattering angle $\varphi = 10°$. If the dried colloidal graphite was replaced by dried colloidal graphite embedded in gelatine, the new component moved to a position shifted by 10 $\pm$ 1 eV from the primary line. The corresponding experiments with polycrystalline graphite did not show such components. These new components can be attributed to a plasmon excitation on the spherical surface of each particle of colloidal graphite. This experiment shows that surface plasmons can be excited in small spherical particles independently of the scattering angle.

I. INTRODUCTION

In recent years, surface plasmons in small spherical particles have been investigated using fast electrons by Kreibig and Zacharias[1] for Ag and Au, by Doremus[2] for Ag and Au, and by Fujimoto and Komaki[3] for Al. Recently, Kokkinakis and Alexopoulos[4] observed surface plasmons in small spherical particles of Ag using x rays.

The study of graphite has received much attention in plasmon investigation because of the two kinds of bulk plasmons, one of low energy (7 eV) due to the π electrons and one of high energy (25 eV) due to π and σ electrons.[5] The existence of both these types of plasmons was established with electron-energy-loss experiments,[6-9] optical measurements,[10] and x-ray-scattering experiments.[11-14]

Recently, the excitation of surface plasmons of colloidal graphite was reported using x-ray techniques.[15] In the present paper a complete report of the experiment is presented. Zero- as well as nonzero-scattering-angle configurations were employed and two different dielectric environments were used for the colloidal-graphite particles.

II. EXPERIMENTAL PROCEDURE

The experimental investigation involves the observation and examination of the transmission spectrum of the radiation produced by a Cr x-ray tube. The radiation was analyzed by a curved-crystal spectrometer and detected by a Geiger counter. The region investigated was the $K\beta_1$ line and the near region towards lower energies. Due to the natural width (3.14 eV) of the line[16] and other experimental limitations, the resolution of the instrument was about 1880. The apparatus has been described in detail elsewhere.[11,17] For the scattering angle $\varphi = 0°$, the following modification was made (Fig. 1): The sample S was positioned just in front of the window of the x-ray tube with its center approximately on the Rowland circle. The scattering angle φ indicated in Refs. 11 and 17 is not shown in Fig. 1 being equal to 0°. It was found that the background was considerably reduced by using a lead shield B. The samples were prepared from colloidal Acheson graphite and were left

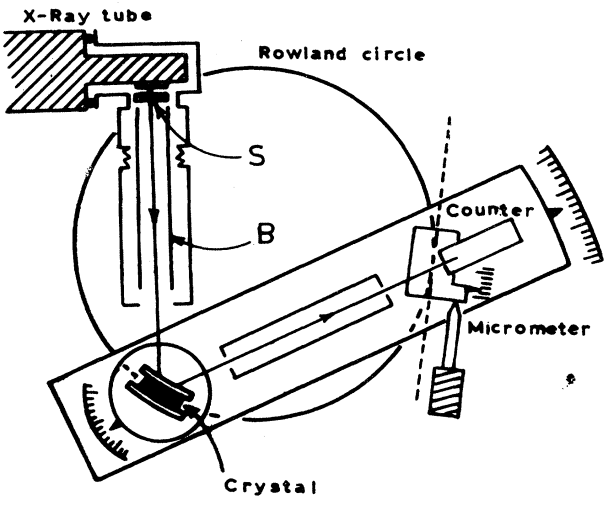

FIG. 1. Experimental set up for $\varphi = 0°$.

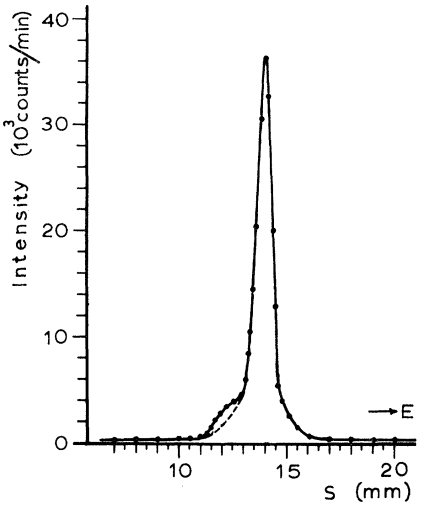

FIG. 2. Spectrum of colloidal graphite at $\varphi = 0°$. On the abscissa, S represents vernier readings of the micrometer along the Rowland circle. The energy E increases towards the right. The statistical error is too small to be indicated.

to dry after been pressed into the form of a slab. The thickness d was chosen according to the relation

$$d = \cos(\tfrac{1}{2}\varphi)/\mu \quad ,$$

where φ is the scattering angle and μ is the linear absorption coefficient. Other samples consisted of dried colloidal graphite after it had been dissolved in a gelatine solution. The mean particle size of the colloidal sample was found by electron microscopy equal to about 130 Å. X-ray diffraction showed that this material was essentially crystalline. Nuclear-reactor-grade polycrystalline graphite was also used as a comparison.

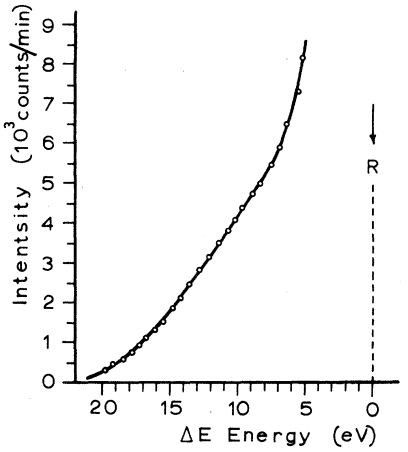

FIG. 4. Spectrum of polycrystalline graphite at $\varphi = 0°$ in the vicinity of 13 eV. R indicates the position of the Rayleigh line.

A. Scattering Angle $\varphi = 0°$

Because of the high counting rate, the lowest possible power was used ($U = 20$ kV, $i = 6$ mA). Figure 2 shows the spectrum of the colloidal-graphite sample obtained by moving the slit of the Geiger counter along the Rowland circle. Figure 3 shows a region of the spectrum on the low-energy side. The abscissa gives the energy shift from the peak of the primary line. We note that a new component appears in this region shifted by 13 ±1 eV. The width of this new component is the

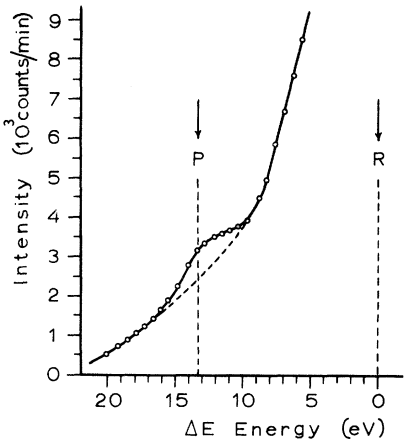

FIG. 3. Spectrum of colloidal graphite at $\varphi = 0°$ in the vicinity of 13 eV. R and P indicate the positions of the Rayleigh line and plasmon line, respectively. The statistical error is too small to be shown.

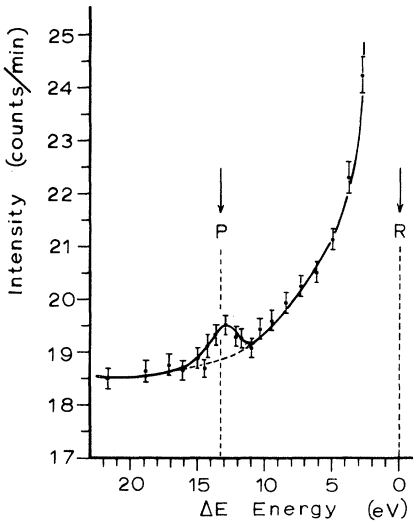

FIG. 5. Spectrum of colloidal graphite at $\varphi = 10°$ in the vicinity of 13 eV.

same as that of the primary line, i.e., 3.14 eV. Figure 4 shows the corresponding spectrum from the sample of polycrystalline graphite taken under the same conditions. Since in this spectrum no additional component exists, the new component in Fig. 3 is ascribed to the colloidal state of graphite.

B. Scattering Angle $\varphi = 10°$

In this experiment the maximum power available ($U = 26$ kV, $i = 34$ mA) was used. The sample of the dried colloidal graphite was positioned at a distance about 8 cm from the window of the x-ray tube and approximately on the Rowland circle. A portion of its spectrum is shown in Fig. 5. The statistical errors are indicated with vertical lines. The new component was found again at 13 ± 1 eV, i.e., at the same position as in the experiment of $\varphi = 0°$, which means that no important dispersion exists, at least up to $\varphi = 10°$. This new component had the same width as in the first experiment, with a peak intensity about $\frac{1}{15}$ of the Rayleigh line.

In the next experiment, the colloidal sample was replaced by the sample of dried colloidal graphite embedded in gelatine; the corresponding spectrum (Fig. 6) exhibits a component shifted by 10 ± 1 eV from the primary line. The intensity of this component was also $\frac{1}{15}$ of the Rayleigh line and its width was the same as that of the primary line. The shift from 13 to 10 eV as is explained below, is due to the dielectric properties of the medium surrounding the spherical graphite particles. The spectrum of polycrystalline graphite taken under the same conditions shows no additional component of comparable intensity in the regions about 13 and 10 eV.

III. DISCUSSION

According to the theory of Crowell and Ritchie[18] and Fujimoto and Komaki[3] about the plasmon creation on the surface of small spherical particles, the energy of such a plasmon is given by the relation

$$\hbar\omega_L = \frac{\hbar\omega_p}{\{1 + [(L+1)/L]\epsilon_\alpha\}^{1/2}} \quad , \tag{1}$$

where $\hbar\omega_p$ is the energy of the bulk plasmon, L is an integer whose value depends on the particle size (in the present experiment $L = 1$), and ϵ_α is the dielectric constant of the medium surrounding the spherical particles; in the following we take

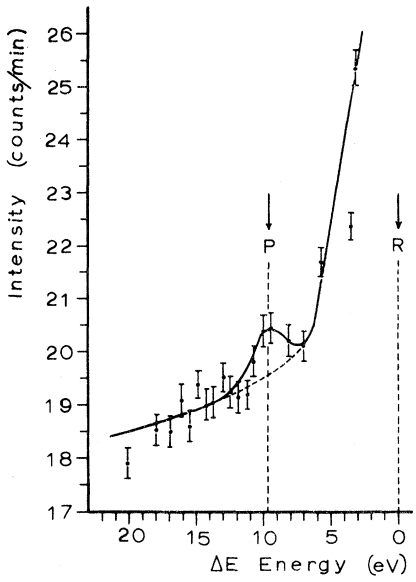

FIG. 6. Spectrum of colloidal graphite embedded in gelatine at $\varphi = 10°$ in the vicinity of 10 eV.

$\epsilon_\alpha = 1$ for the sample of dried colloidal graphite assuming air as the surrounding medium. For the sample of colloidal graphite embedded in gelatine, we take $\epsilon_\alpha = 2.37$.[4]

If we assume that the new component is due to energy loss by exciting surface plasmons, then by setting $\hbar\omega_L = 13.2$ eV and $\epsilon_\alpha = 1$, we obtain for the bulk plasmon the value $\hbar\omega_p = 23$ eV. The same value results from the experiment of colloidal graphite in gelatine if one sets $\hbar\omega_L = 9.8$ eV and $\epsilon_\alpha = 2.37$.

We will compare this value 23 eV with the high-energy bulk plasmon found in other experiments. No exact value can be given probably because it depends on the density of the sample used and the type of preparation.[7,10] The values vary from 19 to 29.8 eV.[9,13]

The present experiment shows that surface plasmons can be produced in small spheres by x rays even at $\varphi = 0°$ scattering angle. As the energy of the surface plasmon was found independent of the scattering angle, we conclude that no important dispersion exists, at least up to $\varphi = 10°$. This finding coincides with the existing theory.[3,18] This present experiment also verifies the validity of formula (1).

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Electron-Paramagnetic-Resonance Study of $3d^5$ Ions in Mixed-Polytype Zinc Sulfide

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Mixed-polytype ZnS single crystals doped with various $3d^5$ ions (Cr^+, Mn^{++}, and Fe^{3+}) have been examined by electron-paramagnetic-resonance techniques. It was found that three kinds of sites exist in these crystals, one of cubic and two of axial symmetry around the *c* axis of these "hexagonal" crystals. None of the axial centers correspond to the one characteristic of a true wurtzite crystal. A model of the crystallographic nature of these centers based on a point-charge calculation is proposed which allows a qualitative understanding of the experimental facts.

I. INTRODUCTION

Optical measurements on "hexagonal" ZnS crystals doped with various $3d^n$ ions (Cu^{2+},[1,2] Cr^{2+},[3] and Fe^{2+} [4]) have demonstrated the existence of centers of axial symmetry in these crystals in addition to the known "cubic" centers. In reality, these so-called "hexagonal" crystals are of mixed-polytype structure, and one can have several different axial sites, at least in principle. Furthermore, the splittings of levels due to the low-symmetry fields add to the complexity of the optical spectra.

The observation of electron-paramagnetic-resonance (EPR) signals of $3d^5$ ions whose ground state is an orbital singlet (Cr^+, Mn^{2+}, and Fe^{3+}) eliminates the complexity due to orbital splitting and gives clear evidence of the axial-symmetry centers. We have thus detected *two* kinds of axial sites in these crystals (in addition to cubic) for each of the isoelectronic doping ions. These two sites, whose spin-Hamiltonian parameters we measured, are occupied with about equal numbers of doping ions.

The axial field parameters vary greatly from one ion to another, and for some ions, from one site to the other. For Fe^{3+}, moreover, second-order terms in the spin-Hamiltonian formalism are important; this necessitates special care in the evaluation of the spectra, and a formalism to this end has been developed.

A point-charge crystal-field calculation on various polytype structures permits one to explain the presence of these centers, as well as the fact that not more than two different axial sites appear in these crystals; none of which corresponds to the site characteristic of a true hexagonal (wurtzite) structure.

The three $3d^5$ centers play important roles in the luminescence mechanisms in ZnS. Mn^{2+} is well known for its yellow-orange emission; Cr^+ is a filled electron trap. Fe^{3+} is a recombination center in the middle of the forbidden gap.

The specific influence of the axial sites on the luminescence of these crystals is at present being studied in this laboratory.

II. EXPERIMENTAL

All samples used were synthetic and growth doped. They are all of those commercially called "hexagonal", although their contents in "hexagonalicity" is widely variable. We have examined bulk single crystals of three different origins: (i) vapor-phase-grown crystals of the Research Insti-