

## Excitation of Plasmons with X-rays

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*Dedicated to Professor Dr. G. Borrmann on the occasion of his 65th birthday*

A short review is given of plasma phenomena produced in solids by impinging X-rays. The first category refers to bulk plasmons due to X-ray photons scattered on solids. They are observed through the appearance of a new component in the spectrum of the scattered radiation. The energy shift increases slightly with scattering angle but eventually the dispersion stops. A second category of phenomena consists in the light emitted by decaying surface plasmons. They are excited by photoelectrons produced in colloidal materials by X-rays. The spectrum shifts with the dielectric constant of the stabilizing medium.

The excitation of plasma oscillations in solids has been extensively studied from the characteristic energy losses of electrons passing through thin films of material. Several other methods have also been successful, as for example optical ones (reflectivity, absorption etc.). In the present article a short review is given of plasma excitations due to X-ray photons impinging on solids of low atomic number. Such effects were first observed during spectrometric analysis of X-ray radiation scattered on Li, Be and graphite under conditions of small momentum transfer<sup>1</sup>. Beyond the usual Rayleigh line and Compton band a third spectral component was observed. It has approximately the same width as the primary line and is shifted towards lower energies by an amount that corresponds to the plasmon energy as determined by other methods. This effect could be attributed to photons that had lost part of their energy during the scattering process and produced plasma excitations.

The possibility of such excitations had been predicted theoretically by Nozieres and Pines<sup>2</sup> under the condition that the momentum transfer be smaller than a theoretically determined critical value. They also predicted a dispersion consisting in a quadratic dependence of the plasmon energy on the wave number. By more accurate measurements Priftis<sup>3</sup> has indeed detected such a dispersion in the region of small wave numbers, roughly with the theoretically computed dependence. The experiments were extended up to a region of higher wave numbers by Miliotis<sup>4</sup> on Be with a different spectro-

meter and with a different primary wave length. He found that the plasmon line could be detected much beyond the theoretically evaluated critical value. Another interesting feature was a break in the dispersion curve near the position of the critical wave number. In the meantime other research groups using varying techniques have confirmed the above results. Their findings are given below.

All measurements up to now are restricted to the materials Li, Be and graphite, materials of low atomic number, because the momentum condition demands a soft X-ray radiation which however is strongly absorbed in materials of higher atomic number without a considerable increase of the Compton and the plasmon component.

### Lithium

The initial measurements<sup>3</sup> were carried out with  $\text{CrK}\beta$  radiation with scattering angles that corresponded to wave vectors  $\mathbf{k}$  between 0.26 and 0.79  $\text{\AA}^{-1}$ . The energy shift of the plasmon line from the primary line was found to change slightly with increasing wave vector. If plotted against  $k^2$  a straight line resulted with a slope agreeing with theoretical predictions. Extrapolation to the scattering angle of  $0^\circ$  gives a plasmon energy of 8.1 eV which agrees with values found by other methods.

The above results were confirmed by Alexandropoulos<sup>5</sup> with  $\text{CuK}\alpha$  radiation and for wave vectors extending up to 1  $\text{\AA}^{-1}$ . This value is slightly beyond the critical wave vector  $k_c = 0.9 \text{\AA}^{-1}$ , however not sufficiently in order to decide if the plasmon energy continues to shift proportional to  $k^2$  beyond  $k_c$  or if there is a break in the dispersion curve.

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### Beryllium

Measurements<sup>3</sup> carried out with CrK $\beta$  radiation in the region of  $k = 0.26$  to  $0.79$  showed a well visible dispersion. Extrapolation to  $k = 0$  gave a plasmon value of  $20.7$  eV.

The experiment was repeated by Miliotis<sup>4, 6</sup> with CuK $\beta$  radiation and extended to  $k = 1.95$  which definitely reached beyond the theoretically computed  $k_c = 1.3$ . The energy shift, as mentioned, showed a straight line when plotted versus  $k^2$  up to about the value  $k = 1 \text{ \AA}^{-1}$ . The slope agrees with the theoretically expected one. From there onwards up to  $k = 1.95$  the plasmon energy increased very little. Extrapolation of the initial part to  $k = 0$  gave  $19.4$  eV for the plasmon value.

Tanokura Hirota and Suzuki<sup>7</sup> in a similar experiment with CuK $\alpha$  and later<sup>8</sup> with CrK $\alpha$  confirmed the existence of a dispersion.

Suzuki and Tanokura<sup>9</sup> repeated their experiment in a wide region of  $k$  values using  $\beta$  lines in the primary radiation, which are single lines and thus allow a more accurate separation of the plasmon line. Reliable determination of the energy shift could be obtained up to about  $2 \text{ \AA}^{-1}$ . The dispersion curve was found to be linear in  $k^2$  without a break and with a slope smaller than in the experiment of Miliotis.

In view of the discrepancy in the form of the dispersion curve, Marinou<sup>10</sup> repeated the experiment with a stronger X-ray source and obtained the same result as Miliotis, i. e. a dispersion curve initially linear in  $k^2$  with break at about  $k = 1 \text{ \AA}^{-1}$ . From there onwards the plasmon line shifted very little.

### Bulk Graphite

The excitation of a plasma line of  $6.5$  eV was first observed with CrK $\beta$  for small momentum transfers<sup>1, 3</sup>.

Suzuki, Kishimoto, Kaji and Suzuki<sup>11</sup> using the somewhat harder radiation of CrK $\alpha$  discovered a second plasmon line at  $27$  eV.

More extensive measurements with CrK $\beta$  in a wide range of  $k$ -values by Suzuki and Tanokura<sup>12</sup> showed that both lines shifted considerably with increasing  $k$  values. For example, the first line attributed to  $\pi$ -electrons, shifted from  $7$  eV to  $35$  eV. Similarly the high energy plasmon, attributed to  $\sigma$ - and  $\pi$ -electrons, shifted from  $25$  to  $60$  eV. No break in the dispersion curve was found.

### Colloidal Graphite

Koumelis, Leventouri, and Alexopoulos<sup>13</sup> investigated the plasmon line for  $k = 0$ , i. e. analysed spectrometrically the direct beam after letting it pass directly through the sample. No convincing indication of a shifted line was observed when the sample was a slab of polycrystalline graphite of "nuclear" quality. This agrees with the theoretical prediction that electromagnetic radiation cannot couple with longitudinal oscillations so that bulk plasmons cannot be excited. When, however, the sample was replaced by a slab of dried colloidal graphite of Aquadag quality, a line appeared shifted by  $13$  eV. This was attributed to surface plasmons.

According to Mie's theory surface plasmons can occur in spheres if

$$\epsilon_i = -[(l+1)/l] \epsilon_a, \quad (1)$$

where  $\epsilon_i$  and  $\epsilon_a$  are the dielectric constants of the spherical particles and the surrounding material.  $l$  is a positive integer characterizing the different modes.

Setting  $\epsilon_a = 1$  (air) and  $l = 1$  we obtain for  $\epsilon_i$  the condition  $\epsilon_i = -2$ . The optical constants of graphite have been determined by Taft and Philipp<sup>14</sup>. From their curve we obtain for the surface plasmon the value  $14$  which agrees well with the value  $13$  eV.

The same line was observed by Koumelis and Leventouri<sup>15</sup> when CrK $\beta$  radiation was scattered under an angle of  $10^\circ$ . Thus no dispersion of surface plasmons could be detected between  $0^\circ$  and  $10^\circ$  scattering angle, a fact that has theoretically been predicted<sup>16, 17</sup>.

In order to investigate Mie's theory with a different surrounding material the colloidal graphite was mixed with gelatine before drying. The line shifted from  $13.2$  eV to  $9.8$  eV. Inserting  $\epsilon_a = 2.37$  in Eq. (1) we obtain  $\epsilon_i = -4.74$  a value that does not occur in<sup>14</sup>.

### Secondary Effects of X-rays on Colloidal Silver

X-rays can also excite plasma oscillations indirectly through the intermediary of photoelectric or Compton-electrons, which are generated in the material. If the oscillations are excited in small spheres their decay would be coupled to the emission of photons. Crowell and Ritchie<sup>16</sup> showed theoretically that such surface plasmons should emit a relatively intensive radiation upon decay. This was

verified by Kokkinakis and Alexopoulos<sup>18</sup> by studying the radiation emitted when colloidal silver was irradiated with X-rays. The experiment consisted in irradiating a target and analyzing the emitted photons in a UV spectrometer.

When the target was covered with colloidal silver without a stabilizing agent, a band of photons appeared in the region of  $4.0 \pm 0.2$  eV. When the silver colloid was prepared with a gelatine stabilizer, the emission band shifted to  $(3.1 \pm 0.3)$  eV. A target of pure gelatine or of metallic silver emitted no radiation in the region covered by the UV spectrometer.

For the above two cases relation (1) gives the following values of  $\epsilon_i$ :  $-2$  (without stabilizer,  $\epsilon_a = 1$ ) and  $-4.74$  (with gelatine stabilizer,  $\epsilon_a = 2.37$ ), which according to the optical constants determined by Ehrenreich and Philipp<sup>19</sup> correspond to 3.6 eV and 3.12 eV as values of the surface plasmon energy.

The observed deviation of 0.4 eV in the former case, can be ascribed to both the steepness of the curve of the real part of the optical constants in the region in question, or perhaps to the assumption  $\epsilon_a = 1$ , since spherical particles may build clusters or may be covered with oxides. In the case of a stabilizer there is a complete agreement.

More recent experiments by Kokkinakis<sup>20</sup> with gold colloid without and with a gelatine stabilizer gave for the surface plasmons the energy values 3.2 eV and 2.5 eV respectively. From relation (1) and the optical constants of gold determined by

Doremus<sup>21</sup> we obtained 2.87 eV and 2.45 eV as corresponding values of energy.

Concerning the energy  $\hbar \omega_s$  of surface plasmons in spheres, the current theory<sup>16, 17</sup> leads to a formula valid only for free electrons:

$$\hbar \omega_s = \hbar \omega_p [1 + (\{l+1\}/l) \epsilon_a]^{-1/2}. \quad (2)$$

Table 1 shows resulting computed values of the bulk plasmons as compared with currently accepted values.

Although there is no reason to accept the validity of Eq. (2) for colloidal graphite and there are many reasons against assuming the plasma in colloidal silver as consisting of free electrons, the application of this formula to the materials studied does not give unacceptable results.

### Conclusion

At the present moment experimental findings of bulk plasmons excited by X-rays agree with existing theoretical models as regards their energy and initial dispersion. However, two facts are unaccountable for: a) the bulk plasma continues to show well defined oscillations for wave vectors beyond the value  $k_c = \omega_p/v_F$  at least for plausible values of  $v_F$  and b) the dispersion does not continue to increase linearly with  $k^2$  but saturates beyond  $k = k_c$ . The second fact has only been observed in beryllium and by the Athens group. A theoretical treatment of these phenomena would be gratifying.

| Material | surrounding material | $\hbar \omega_s$ exp. | $\hbar \omega_p$ calc. from formula (2) | $\hbar \omega_p$ from other experiments                          |
|----------|----------------------|-----------------------|---|--|
| graphite | air                  | 13,2 eV               | 23 eV                                   | } 25 eV <sup>14</sup><br>19 to 30 (other experimenters)          |
| graphite | gelatine             | 9,8                   | 23                                      |  |
| silver   | air                  | 4,0                   | 6,92                                    | } 9,2 eV <sup>22</sup><br>7,3 <sup>23</sup><br>7,5 <sup>19</sup> |
| silver   | gelatine             | 3,1                   | 7,4                                     |  |

Table 1.

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## An Absolute Atomic Scattering Factor for Germanium Obtained by Anomalous Transmission in a Bicrystal

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Using the newly developed method of dynamical interference between anomalously transmitted waves in a crystal containing a non-diffracting zone<sup>1</sup>, we have measured the real part of the atomic scattering factor for germanium at the value of  $\sin \theta/\lambda$  corresponding to the 220 Bragg reflection. The result,  $f_0 = 23.79 \pm 0.08$  electron units is in excellent agreement with values obtained in perfect crystal intensity measurements<sup>2,3</sup> and from triple crystal rocking curve studies<sup>4,5</sup> but significantly differs from the value obtained using Pendellösung fringes<sup>3</sup>. Finally, we seek to assess the reliability of each method by comparison with the corresponding results for silicon, concluding that the error probably lies in the Pendellösung result.

### Introduction

Provided that adequately homogeneous crystals, free from dislocations and planar defects, can be obtained there are several dynamical diffraction effects which may be used to obtain accurate values of structure factors without the need for accurate *absolute* intensity measurements.

Structure factors for germanium had already been obtained from absolute integrated intensity measurements by DeMarco and Weiss<sup>2</sup> when, in 1968, Batterman and Patel<sup>3</sup> made structure factor measurements on germanium using both the Bragg case integrated intensity and the Pendellösung methods. They found significant differences between the results obtained by the two methods. Similar differences seemed to be evident in the silicon data then available though, as we will see later, the Pendellösung results for silicon have since been revised. From measurements of the intrinsic diffraction profiles of germanium using a triple-crystal diffractometer Nakayama, Kikuta and Kohra<sup>4</sup> (1971) and Persson, Zielinska and Gerward<sup>5</sup> made quite independent structure factor measurements which seem to favour the previous integrated intensity results rather than Batterman and Patel's Pendellösung

values. In an attempt to provide more independent evidence, we have used the method devised by Hart and Milne<sup>1</sup> to measure the absolute structure factor for the 220 Bragg reflection from germanium.

This interference effect, produced by a non-diffracting zone in a crystal, is in principle quite different from the Pendellösung effect because only one branch of the dispersion surface is involved. The method is described in detail in the original paper<sup>1</sup> where it was applied to silicon, yielding scattering factors within 0.1% of those obtained using Pendellösung fringes. Let us briefly recall the relevant theory and the approximations involved.

### Theoretical Background

We record the interference pattern obtained when a narrow divergent incident ribbon beam is Bragg reflected by a thick, perfect crystal which contains a narrow gap (Figure 1). Within the Borrmann fan various pairs of ray-paths, such as those illustrated, are possible between the point of incidence and the exit points. For a gap of zero thickness the pair of rays coalesce into one and these interference fringes disappear. In reciprocal space the two ray bundles are described by tie points A and B giving rise to energy flows inside the crystal inclined at angles  $\alpha$  and  $\beta$  respectively to the Bragg planes.

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