

X-ray Raman scattering in colloidal and polycrystalline graphite



C. N. KOUMELIS AND C. A. LONDOS

Physics Laboratory, University of Athens, 104 Solonos Street, Athens 144, Greece

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Raman scattering was measured in colloidal and polycrystalline graphite for a scattering angle 45°, using X-ray CrKβ radiation and a mosaic graphite analysing crystal spectrometer without collimators. The use of such a spectrometer was necessary because of the weakness of the Raman effect.

For the colloidal graphite, an energy shift of ΔE = 288.3 ± 0.6 eV from the primary line was observed. For the polycrystalline graphite, the above shift was ΔE = 284.9 ± 0.5 eV. These shifts can be ascribed to the transition of the 1s electrons onto and above the Fermi level, constituting the so-called Raman band.

In the polycrystalline graphite, an additional anomaly was observed in the spectrum, beyond the Raman band towards the low energies, i.e., in 311 eV. This fine structure is a verification of the Weaire-Thorp concept about the difference in the spectra, due to the short-range and long-range order.

On a mesuré la diffusion Raman dans le graphite colloidal et le graphite cristallin, pour un angle de diffusion de 45°, en utilisant le rayonnement X Kβ de Cr et un spectromètre à cristal analyseur mosaïque de graphite sans collimateur. L'utilisation d'un tel spectromètre était nécessaire par suite de la faiblesse de l'effet Raman.

Dans le cas du graphite colloidal, on a observé un décalage d'énergie ΔE = 288,3 ± 0,6 eV par rapport à la raie primaire. Dans le cas du graphite polycristallin, le décalage était ΔE = 284,9 ± 0,5 eV. Ces décalages peuvent être attribués à la transition des électrons 1s sur le niveau de Fermi et au-dessus pour constituer la bande appelée bande Raman.

Dans le graphite polycristallin, on a observé une anomalie additionnelle du spectre, au-delà de la bande Raman vers les basses énergies, à 311 eV. Cette structure fine constitue une vérification du concept Weaire-Thorp de la différence dans les spectres due à l'ordre à courte et à longue portée.

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Introduction

The Raman effect in solids has been examined by many investigators since the discovery of the Compton effect. In recent years, the Raman effect in carbon, has been studied in pyrolytic graphite (1) and in polycrystalline and amorphous graphite (2-4).

Raman effect in carbon is expected within a distance of about ΔE = 284 eV from the primary line (5, 6).

From a theoretical standpoint, the problem has been examined by Mizuno and Ohmura (7), Eisenberger and Platzman (8), Kuriyama (9), and Babuskin (10).

According to the theory of Misuno-Ohmura (7,11) the differential cross section calculated in the dipole approximation is proportional to:

$$\int_E \frac{d^2k}{|\nabla_k E|} \left[\int_r \Psi_f^*(r) \cdot r \cdot \Psi_i(r) \cdot d^3r \right]^2$$

where $\Psi_i(r)$ represents the orbital of K-electrons, and $\Psi_f(r)$ is the final wave function.

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In the amorphous graphite, due to the lack of periodicity, the final wave function is more localized than that in the polycrystalline one. Moreover, the density of states:

$$\int_E \frac{d^2k}{|\nabla_k E|}$$

is redistributed, so that a difference in the two spectra is expected.

In the present work, using a spectrometer giving strong intensities, we studied the spectrum of colloidal and polycrystalline graphite from the primary line up to and beyond the Raman band. The aim was to examine the Raman spectrum of graphite in both forms, in order to verify the existence of differences in the two spectra, especially to the lower energies, where Suzuki *et al.* (3) observed small humps.

Experimental Details

The spectra were studied for a scattering angle 45°. The spectrometer had no collimators and CrKβ was used (24 mA, 34 kV). The analysing crystal was a Union Carbide mosaic graphite crys-

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* PRESENT ADDRESS: Institut of Mineralogy

Univ. of Athens, Aeo Ilissia, Athens 621

tal and the reflecting planes were the (0006). For a distance of 200 cm between the scatterer and the analysing crystal, the resolution of the instrument was low, i.e., 274, but the intensities were strong enough.

The scatterers were (i) polycrystalline graphite and (ii) a slab prepared from colloidal Acheson graphite. The colloidal graphite was amorphous, consisting of particles of about 130 Å diameter (12). Both had dimensions 2.5 cm × 3.5 cm.

The diffracted beam was detected by a Geiger-Müller counter and the spectrum was scanned point by point by a fixed-time counting method. Each point was measured in total for 2 h, so that the statistical error in the region of the Raman effect was 1.3%, and in the region of the Rayleigh line 0.3%. In order to avoid any drift of the counting rate during the long scanning period, each point was measured only 100 s at a time and the spectrum was scanned 72 times. In the region of interest, the step of the scanning was 0.15° in the rotating angle of the analysing crystal, i.e., 2.68 eV.

The experimental data were computer fitted using the MINUIT program (13).

Figure 1 shows the whole spectrum of colloidal graphite for a 200 cm scatterer-crystal distance. The insert is a magnification of the Raman region after subtraction of the background by the computer. Figure 2 corresponds to polycrystalline graphite.

For the polycrystalline graphite, the fitting of the measurements showed that an additional anomaly probably exists in the low energy side of the Raman band. In order to confirm the existence of the above anomaly, the measurements were repeated for a scatterer-crystal distance 125 cm (Fig. 3).

Conclusions

From Fig. 1 it is concluded that for colloidal graphite, an energy shift is observed at $\Delta E = 288.3 \pm 0.6$ eV from the primary line. This peak is $\eta = 6 \pm 1$ counts/min above the background. From Fig. 2 an energy shift is observed for the polycrystalline graphite at $\Delta E = 284.9 \pm 0.5$ eV from the primary line. This peak is $\eta = 6 \pm 1$ counts/min. These energy shifts can be ascribed to the Raman effect.

For the polycrystalline graphite, the surface plasmon of 50 eV (14) is clearly observed at about 48 eV.

Although due to the localization of the final wave function in the amorphous form the peak intensity of the Raman band in the colloidal specimen is expected to be greater than that in the polycrystalline one, no difference between the two peaks was observed. This means that this difference, if it

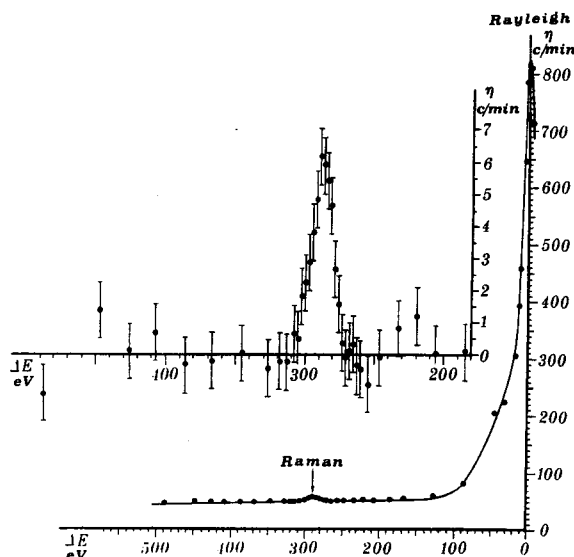


FIG. 1. The whole spectrum of colloidal graphite and the region of the Raman effect. Distance between scatterer and crystal is 200 cm.

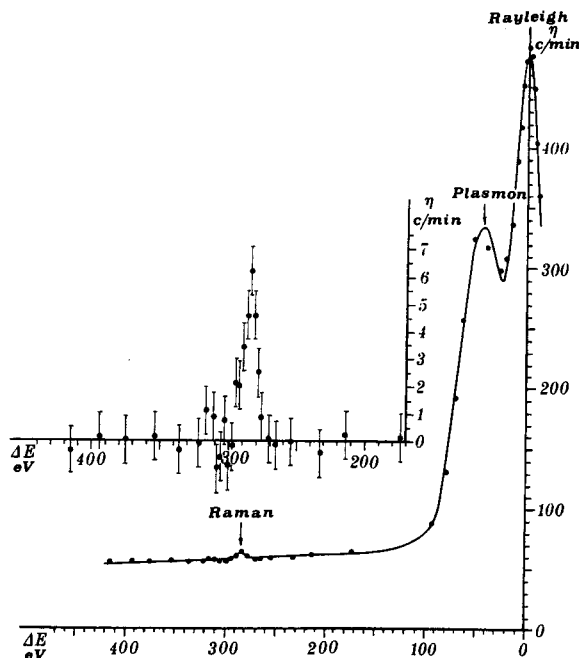


FIG. 2. The whole spectrum of polycrystalline graphite and the region of the Raman effect. Distance between scatterer and crystal is 200 cm.

exists, is smaller than $1/6 = 17\%$ except if a spurious difference in the intensities interfered.

For the polycrystalline graphite and for a 125 cm scatterer-crystal distance (Fig. 3), the Raman peak is about 9 counts/min and there is a strong indication of a second peak beyond the Raman band

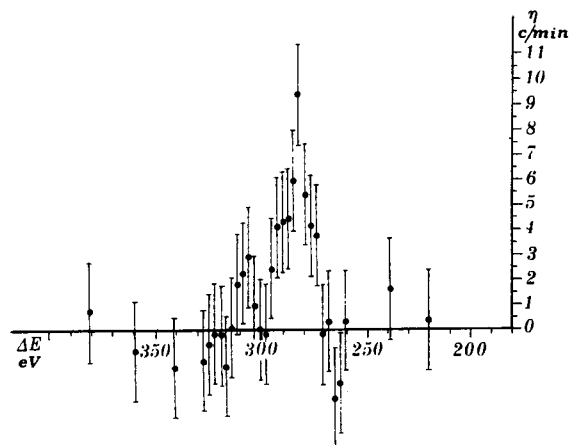


FIG. 3. The spectrum of polycrystalline graphite in the region of Raman effect, without background. Distance between scatterer and crystal is 125 cm.

towards the low energies. This was studied in detail (15) and the anomaly was found at 311 eV from the primary line. This anomaly was not observed in the colloidal graphite.

The gross features of the two spectra are generally the same, as is expected because the gross features of the density of states depend on the atomic properties and the short-range order in the material. On the other hand, the long-range order is responsible for the appearance of the fine structure in the spectrum (16). Using Zunger's data for the density of states of graphite (17), we have ascribed this anomaly to the transition of the core electrons to the anti-bonding band of graphite.

The electronic structure of materials is studied by optical absorption, photoelectron spectroscopy, photoemission, etc. The observation of fine structure in the X-ray Raman spectrum offers a new possibility for the study of the electronic structure. The advantage of this method is that we can have

direct information about the density of states, because the initial state $1s$ is completely determined. In the conventional optical absorption method, the initial state has a density of states, and consequently, the spectrum is the convolution of the initial and the final electron density of states. Thus, the X-ray spectra will be used successfully to test theories of disordered materials.

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