EUROPHYSICS LETTERS 10-20 August 1995

Europhys. Lett., **31** (5-6), pp. 299-303 (1995)

First Experimental Evidence of a C-1s Core Exciton in Amorphous Carbon Films.

A. GUTIÉRREZ (*) and M. F. LÓPEZ (*)

Institut für Experimentalphysik - Arnimallee 14, D-14195 Berlin, Germany

(received 10 March 1995; accepted in final form 7 July 1995)

PACS. 71.35+z – Excitons and related phenomena (including electron-hole drops).
PACS. 78.70Dm – X-ray absorption and absorption edges.
PACS. 71.25Mg – Electron energy states in amorphous and glassy solids.

Abstract. – Amorphous carbon films obtained by pulsed-laser ablation of graphite have been investigated by high-resolution X-ray absorption spectroscopy (XAS). The onset of the $1s \rightarrow \sigma^*$ transitions lies in the gap between π^* and σ^* states in graphite, indicating a high content of sp^3 hybridization in the films. A sharp peak similar to the core exciton in diamond is observed and assigned to a core exciton in sp^3-hybridized disordered C atoms. The observed binding-energy shift of ~ 0.5 eV with respect to the diamond core exciton can be explanined in terms of a higher localization of the excited state induced by disorder. This result supports a Frenkel model to describe the core exciton in sp^3-hybridized carbon.

The C-1s core exciton of diamond has attracted much interest since its first observation in 1985 by Morar *et al.* [1], and much theoretical and experimental work has been devoted to understand the processes involved in this electron-hole interaction. In particular the question whether it can be treated as a Wannier exciton or a more localized Frenkel exciton has led for long time to controversy. In their pioneer work, Morar *et al.* described it using the effective mass approximation, giving a Wannier exciton with a binding energy of 0.2 eV, in accordance with their experimental data. In the equivalent core approximation, however, the excited core is equivalent to a $Z + 1$ atom, *i.e.* nitrogen, which would give a much higher binding energy, of order 1.7 eV [2]. This model would support a more localized Frenkel exciton. Experimental results, both by X-ray absorption spectroscopy (XAS) [1] and by electron energy loss spectroscopy (EELS) [3], are more easily interpreted in the framework of a Wannier-like exciton, since the excitonic peak preceding the absorption edge seems to be only ~ 0.2 eV separated from it. Jackson and Pederson argued, however, that the observed exciton is a shallow exciton with $2p$ symmetry, whereas a deeper exciton with higher binding energy is dipole forbidden due to symmetry selection rules [2], and therefore cannot be observed experimentally. However, a recent symmetry-selected EELS scattering experiment has made it possible to determine the symmetry of the observed exciton [4], excluding the interpretation given in ref. [2]. Later on, Nithianandam [5] suggested that the diamond conduction minimum relative to the 1s core level might be as much as 1 eV higher than had

(*) Present address: CENIM - Avda. Gregorio del Amo 8, 28040 Madrid, Spain.

been thought previously. This would increase the observed binding energy of 0.2 eV to 1.2 eV, supporting the Frenkel exciton picture.

In a recent work, Ma *et al.* [6] have proposed a model, based on an X-ray absorption and emission study, which reconciles both the Wannier and the Frenkel approaches. According to this model, during the X-ray absorption process the excitonic final state is weakly bound in a symmetric state for about 10^{-14} s, a very short time relative to phonon processes which involve atomic motion, but long relative to the absorption timescale (10^{-16} s). This explains why a weakly bound Wannier exciton is observed in the absorption spectrum. Later, this exciton couples to lattice excitations causing Jahn-Teller distortions that lead to the Frenkel structure with $\simeq 1.5$ eV binding energy observed in the X-ray emission spectrum. Therefore, although the final picture is that described by the equivalent core approximation, an intermediate delocalized Wannier exciton is responsible for the spectral features observed in the X-ray absorption spectra.

In amorphous systems the screening of the core hole created after electronic excitation is not so effective as in crystalline systems due to the lack of long-range order. This causes the excited electron to be spatially localized near the core hole, and, consequently, increases the electron-hole interaction. Within this picture, the excitonic binding energy should increase for disordered systems with respect to crystalline materials. In the case of Si, Evangelisti *et al.* have reported an increase of more than 0.5 eV in the binding energy of the $2p$ core exciton when going from crystalline to amorphous samples [7]. In this letter we show, for the first time, experimental evidence of a core exciton in sp^3-hybridized disordered carbon atoms. Its binding energy shift of ~ 0.5 eV with respect to crystalline diamond suggests a higher localization of the excited electron.

Our initial interest in amorphous carbon films (a-C) with high sp^3 content aroused from their possible technologial applications based on properties like chemical inertness, good mechanical and thermal properties, wide band gap and possibility of doping [8-11]. These films are usually characterized by EELS [10] or XAS [12], though no exciton had been reported up to now, probably due to the poor resolution used in the characterization. In this work high-resolution XAS is used to investigate a-C films prepared by pulsed-laser evaporation of a graphite target onto a Si substrate. This method to prepare a-C samples is known to give ultrathin crystalline «diamond-like» films with a thickness below 10 Å [13]. Thicker films become amorphous and the ratio of sp^3 to sp^2 hybridization decreases [14]. Samples used in this experiment were ~ 2000 Å thick. More details about sample preparation and characterization can be found elsewhere [15]. XAS measurements were performed at the SX700/II monochromator of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) in total electron yield mode (TEY). The resolution was set to ~ 150 meV at the C-1s absorption edge. To avoid effects from the transmission function of the monochromator we normalized all spectra to the total yield spectrum of a scraped gold foil. In addition to the a-C films, a highly oriented pyrolytic graphite sample (HOPG) and a diamond film grown by chemical-vapour deposition (CVD) were measured as reference.

Figure 1 shows XAS spectra of the HOPG (a)) and CVD-diamond (b)) reference samples as well as two a-C films, labelled a-C(0) (c)) and a-C(45) (d)), prepared at different angles with respect to the graphite target. The film labelled a-C(0) was grown on a substrate facing the target whereas the film labelled a-C(45) was grown on a substrate 45° from normal to the target. The ratio of sp^3 hybridization is higher for the a-C(0) film, as is shown elsewhere [15]. Both the HOPG and the CVD spectra show well-defined features similar to spectra reported in the literature [16, 17]. In graphite, the onset of the $1s \rightarrow \pi^*$ transitions lies at ~ 285 eV while the $1s \rightarrow \sigma^*$ transitions start at ~ 291 eV. In diamond the onset of σ^* states lies in the gap between π^* and σ^* states in graphite, *i.e.* at ~ 289 eV. The core exciton in the CVD sample is clearly visible at 289.2 eV. The rest of the spectrum consists of the same structures

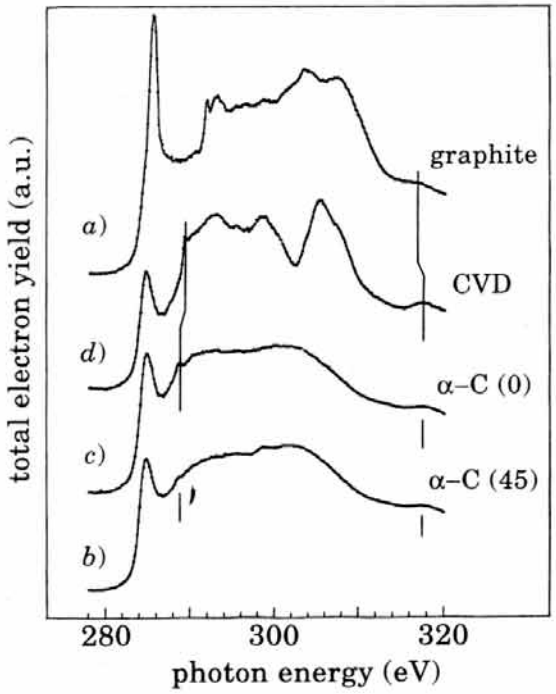

Fig. 1.

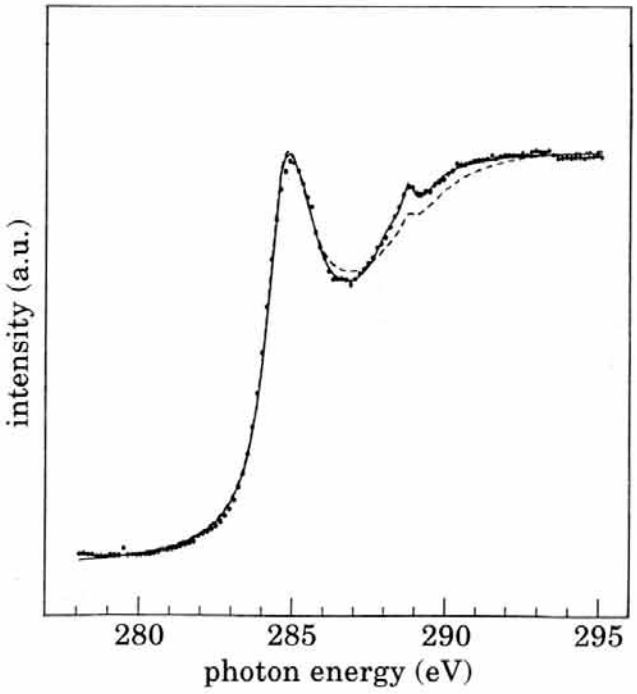

Fig. 2.

Fig. 1. – X-ray absorption spectra in TEY mode of a highly oriented pyrolytic graphite sample (*a*)), a CVD-diamond film (*b*)), and two a-C films with different sp^3 content (*c*), *d*)). The sample labelled C(0) was grown with the substrate placed in front of the graphite target, while in the sample labelled C(45) the angle between the normal to the target surface and the substrate position was 45°. This sample has a lower sp^3 content.

Fig. 2. – Comparison of the onset of σ^* transitions in the two a-C samples: —— a-C(0), – – – a-C(45). The dashed line corresponds to the C(45) sample and the points to the C(0) sample. The solid line across the data points is the result of a least-squares fit used to get the exact position and lineshape of the peak at 288.7 eV.

observed in pure diamond [1]. CVD-diamond films usually consist of small diamond crystallites embedded in an amorphous carbon matrix made of sp^2 hybridized atoms. The first broad peak at 284.6 eV in spectrum *b*) originates from $1s \rightarrow \pi^*$ transitions in the sp^2 hybridized atoms of this amorphous matrix. Note the asymmetry of this peak and its shift of ~ 0.7 eV to lower energies with respect to graphite. Similar shifts have been observed in other amorphous sp^2 carbon samples [18]. According to Mele and Ritsko [19], the lack of agreement between experimentally obtained $1s \rightarrow \pi^*$ transitions and calculations of the density of empty states in graphite can be removed by including an excitonic interaction into the description of the final states of the system. Their model, including excitonic effects, quite well describes experimental data on graphite. The shift of the π^* band in amorphous sp^2 carbon can be easily explained in this model by a poorer screening of the hole, induced by disorder, which results in higher localization of the excitonic state and increases its binding energy. A similar effect can be present in the diamond core exciton as will be shown below. Spectrum *c*) corresponds to the a-C film with higher sp^3 content. The first peak at 284.6 eV is assigned to π^* states from sp^2 hybridized atoms in an amorphous matrix, and has the same shape and energy position as that in spectrum *b*). The rest is almost featureless, except for a sharp feature at 288.7 eV and two broad bands centred at 293 eV and 302 eV. In the sample with lower sp^3 content (spectrum *d*)), the peak at 288.7 eV has a lower intensity and the broad band around 300 eV is splitted into a double structure. A similar splitting has been

observed in the graphitization process with temperature of a-C films [12]. The most striking feature of the spectrum is, however, the peak at 288.7 eV. A least-squares fit of the data, using Lorentz lines convoluted with a resolution function, gives a similar spectral line shape to the diamond core exciton, only 50 meV broader. We can exclude the possibility that this peak is caused by changes in the transmission function of the monochromator because all spectra were normalized to the incident photon flux and because this function is a much smoother function of the photon energy, not giving any feature with such a small width. There is also no systematic appearance of this peak in all samples and its intensity is different in both a-C samples. We can also exclude any contribution from C-H bonds because the samples were prepared under high-vacuum conditions and no hydrogen content has been found by other techniques, like XPS [20]. Therefore, the only possibility is that this peak is a core exciton from sp^3-coordinated disordered atoms.

One method to determine the sp^3 content of a-C films is to monitor the intensity ratio of the π^* and σ^* bands [10]. Such an analysis of our samples would give a low content of sp^3 hybridized atoms. Nevertheless, we find a significant contribution of sp^3 hybridization that can give rise to the observed excitonic peak. To illustrate it we show in fig. 2 the XAS spectra of the C(0) sample superimposed to the C(45) sample. There is clearly a decrease of the signal in the region of sp^3-σ^* states when going from the C(0) to the C(45) sample. This is expected, since the plume coming from the graphite target has a lower plasma content at higher angles from the normal [15]. The differences between both spectra in fig. 2 can be therefore regarded as a higher sp^3 content of the C(0) sample. Note that the intensity of the peak at 288.7 eV decreases for the C(45) samples, so it seems to be associated to the sp^3 content of the film. Another evidence is shown in fig. 1, where a peak at ~ 317 eV is observed in CVD diamond and shifted with respect to graphite. At this energy, the EXAFS region starts, and for a complete detailed analysis a much broader energy range is needed. However, since scattering amplitudes and phases are only element dependent and in both cases the only element is carbon, the difference between graphite and CVD diamond in the region around 317 eV may be due to differences in the bond length. In the a-C films the peak is at the same position as in the CVD sample indicating that the content of sp^3 in the a-C samples is appreciable. This, together with the spectral features observed in fig. 2, confirm the sp^3-excitonic character of the peak observed at 288.7 eV.

In amorphous silicon the core exciton has a binding energy 0.54 eV higher than in crystalline silicon, as shown by Evangelisti *et al.* [7], whereas in our a-C films this shift is 0.57 eV relative to the CVD sample. This value is obtained assuming no shift of the $1s \rightarrow \sigma^*$ absorption edge in the a-C sample with respect to the CVD sample, as has been observed in previous XAS and EELS studies of amorphous, diamond-like films [10, 12]. The shift of the binding energy of the $2p$-core exciton in amorphous Si can be explained by the higher localization of the excited state in disordered systems, as mentioned above. Evangelisti *et al.* also found that this shift increases for Si systems where the degree of disorder is higher, like hydrogenated amorphous Si or hydrogenated amorphous Si_xC_y [7]. Since a Wannier exciton involves spatially extended states, such shifts can only be explained if no long-range order is present around the excited atom. The smilarity between a-Si and tetrahedral a-C, as well as in the exciton binding-energy shift when going from the crystalline to the amorphous system, suggests that disorder is producing in a-C similar effects as in a-Si. In particular, the higher degree of localization in the amorphous systems should increase the excitonic binding energy in a similar way, as is indeed the case.

Some additional assumptions are needed in order to include this picture of the excitonic process in amorphous systems into the model of Ma *et al.* [6]. According to this model, the absorption process involves a transition from the symmetric C-1s state into an intermediate *non-totally symmetric* state, but, due to symmetry selection rules, the recombination

process is only possible from a non-symmetric, Jahn-Teller–distorted state into the 1*s* core level [6]. This explains the different width of the excitonic state observed by X-ray emission and X-ray absorption spectroscopies. In the case of a-C the situation is different because the delocalized state is no more symmetric due to distortions in bond angles and lengths. Transitions from the 1*s* core level are now allowed, and should give an excitonic peak much broader than in the crystalline sample. We indeed observe a broadening of the excitonic peak in a-C of (50 ± 10) meV with respect to the CVD sample, but, according to the model of Ma *et al.*, this broadening should be larger. A compromise between this model and our results is that while transitions to the delocalized state are now symmetry allowed, they are unfavoured with respect to transitions into the narrower non-totally-symmetric state proposed in ref. [6]. The mentioned distortion in bond angles and lengths would cause the observed small broadening of the excitonic peak.

In summary, using high-resolution XAS we have observed for the first time a 1*s* core exciton in disordered, sp^3-hybridized carbon atoms. Its larger binding energy with respect to the diamond core exciton can be explained in terms of a higher localization of the excited state caused by disorder. A small broadening of the excitonic peak with respect to diamond is also observed, and explained in terms of the asymmetry of the initial state induced by disortions in bond angle and length.

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Authors thank the Spanish Ministerio de Educación y Ciencia for financial support. Samples were kindly provided by J. DÍAZ, S. FERRER and F. COMIN. Critical reading of the manuscript by C. T. SIMMONS and E. NAVAS is greatly appreciated. Experimental assistance during the measurements by E. NAVAS and S. L. MOLODTSOV is also gratefully acknowledged. We also thank J. DÍAZ for helping in the interpretation of the absorption data.

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