

# K-EDGE RESONANT INELASTIC X-RAY SCATTERING IN GRAPHITE

**P. CARRA AND M. VAN VEENENDAAL\***

**ESRF, THEORY GROUP (\*PRESENT ADDRESS: ARGONNE NAT. LAB., USA)**

Recent numerical calculations have provided evidence of the presence of excitonic states in the K-edge emission spectra of graphite, thus identifying a major drawback in the use of resonant inelastic X-ray scattering as a probe of electron band structures.

**T**he scattering of X-rays by a crystal displays unusual anisotropy properties when the response of particular atoms or ions in the lattice is boosted by resonances. Such resonances occur when the X-ray photon energy approaches the value required to excite an inner-shell electron to an empty orbital near the Fermi surface of a solid. Disparate elements - the X-ray polarisation, magnetism of the resonant atoms, and lattice features - then combine to yield a sensitive anisotropy, reflecting lattice properties that otherwise fail to emerge. Electric dipolar transitions usually dominate the scattering process.

High brilliance, tunability and polarisation control, available at synchrotron radiation sources, have stimulated a wealth of experimental investigations using X-rays at resonance. In particular, in recent years, a number of experiments have been carried out to test the applicability of resonant inelastic X-ray scattering (RIXS) in determining electronic band structures. Data have been collected from diamond [1,2], B<sub>2</sub>O<sub>3</sub> [3], boron nitride [3,4], silicon [5], and graphite [6].

## RESONANT SCATTERING AND BAND STRUCTURE

RIXS probes inter-band (valence and conduction) electronic excitations of energy  $\omega = \omega_1 - \omega_2$  and momentum  $\mathbf{q} = \mathbf{q}_1 - \mathbf{q}_2$ , as allowed by the corresponding conservation laws. (The subscripts denote incoming and outgoing photons;  $\hbar = 1$ ). Data are recorded as a function of  $\omega_1$  and  $\omega_2$ , at a given  $\mathbf{q}$ ; usually, the emission spectrum is analysed for a discrete set of

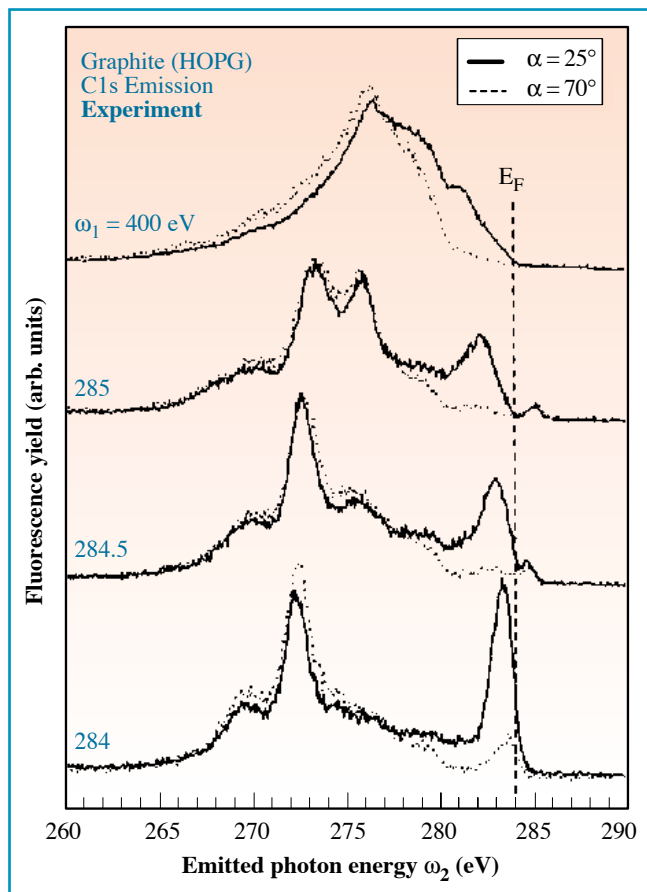
$\omega_1$  values, which are taken across an absorption threshold. A typical example, thoroughly discussed in the present report, is provided in Figure 1, where graphite emission profiles are plotted for a few values of the incoming photon energy near the carbon K edge (~284 eV). [The spectra are shown for two different experimental geometries:  $\alpha = 25^\circ$  and  $75^\circ$ , as described in the caption of Figure 1. This «angular» dependence will not be discussed here. The fluorescence spectrum recorded at  $\omega_1 = 400$  eV, that is way above the K edge, is also depicted in Figure 1. We will shortly come back to it.]

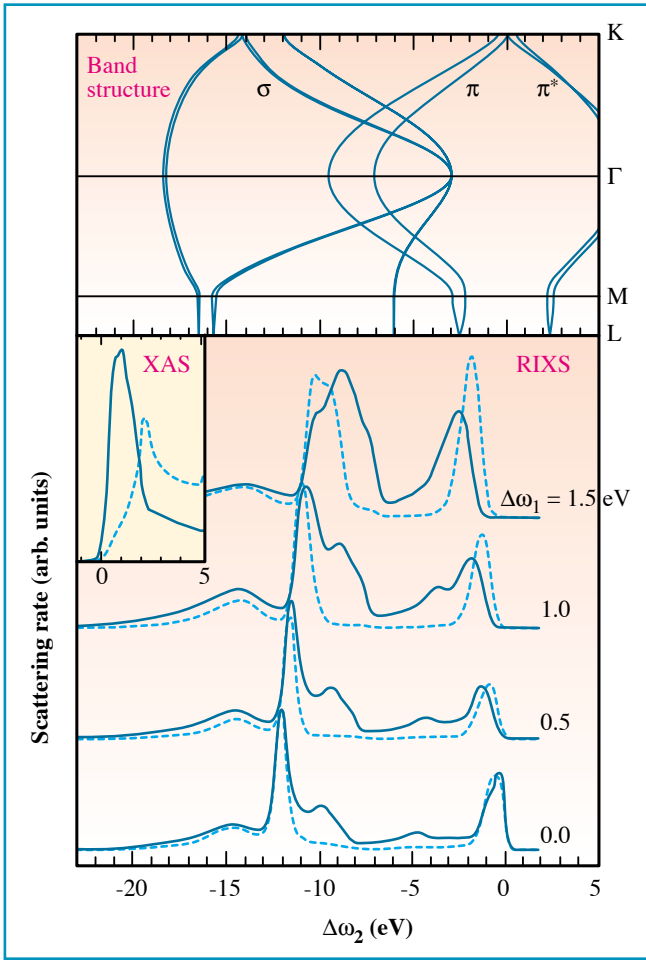
A correspondence (band mapping) between the dispersive spectral features of Figure 1 and the graphite band structure, which is depicted in Figure 2 (top panel), is established as follows.

RIXS is accurately described by the lowest Born approximation and proceeds through a core-hole excitation followed by an emission with, in general, an electron relaxation process in between. The total scattering rate (golden rule) reads

$$P_{\text{tot}}(\omega_1, \omega_2) = 2\pi \sum_f |U_{i \rightarrow f}|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

*Fig. 1: Graphite RIXS spectra obtained by Carlisle and co-workers, for two different photon take-off angles:  $\alpha = 25^\circ$  (solid lines), and  $\alpha = 70^\circ$  (dotted lines). Experimental geometry: the scattering plane is perpendicular to the graphite planes; the ingoing photon is linearly polarised in the scattering plane and the outgoing polarisation is not detected. The scattering angle is fixed at  $90^\circ$ . (Reproduced from [6]).*





**Fig. 2:** Upper panel: the band structure of graphite. Lower panel: numerical calculations of the graphite K-edge emission spectra for  $\alpha = 25^\circ$ , in the scattering geometry of Figure 1. The independent quasi-particle approximation is given by the dashed lines. The inclusion of a local  $U = -3$  eV core-hole potential is represented by the solid lines. The corresponding absorption (XAS) profiles are depicted in the inset. (Reproduced from [7]).

where  $U_{i \rightarrow f}$  denotes the resonant amplitude for a transition from the initial state  $i$  to a final state  $f$  of the scattering system. (The double-differential cross-section is obtained by multiplying  $P_{\text{tot}}$  by the density of states of the outgoing photon and dividing by the incoming-photon flux.) Now, assume that the electron states are properly described by a Slater's determinant of Bloch's wavefunctions, i.e. neglect the electron-electron interaction. This approximation, known as 'independent quasiparticle theory', leads to a particularly simple form for the transition amplitude  $U_{i \rightarrow f}$ , the simplifying features being

1. the absence of relaxation effects between absorption and emission,
2. the presence of a single electron-hole pair in the final state.

With reference to the band structure of Figure 2, in graphite the allowed single-pair final states are given by  $\pi^* \underline{\pi}$  and  $\pi^* \underline{\sigma}$ . (Hole states are underlined.)

To compare the data of Figure 1 with the predictions of the independent quasiparticle theory, the present authors have performed numerical calculations of  $P_{\text{tot}}(\Delta\omega_1, \Delta\omega_2)$  for  $\Delta\omega_1 = 0, 0.5, 1.0$  and  $1.5$  eV, neglecting electron-electron

interaction. ( $\Delta\omega_1$  and  $\Delta\omega_2$  refer to the threshold energy at 284 eV). Only vertical transitions have been considered, thus disregarding the effect of a small but finite photon wave vector. The results are shown in Figure 2 (lower panel, dashed lines). These emission spectra reflect a  $1s \rightarrow \pi^*$  absorption process, near the K symmetry point, followed by emission from the  $\pi$  and  $\sigma$  bands at about 0, -11, and -14 eV. The changes in the spectral profiles, as  $\omega_1$  is swept from threshold to 1.5 eV above, are readily explained by following the band structure in the  $K \rightarrow \Gamma$  direction. Notice that the independent quasiparticle approximation provides no explanation for the emission peak observed at -8 eV.

To overcome this mismatch, Carlisle and collaborators [6] included a fraction of the fluorescence spectrum ( $\omega_1 = 400$  eV) which, as clearly visible in Figure 1, happens to peak at about  $\omega_2 = 276$ . In our view, their procedure suffers from a twofold inadequacy. Firstly, it introduces a somewhat arbitrary superposition of events which are far removed in energy; and secondly, it relies on a conceptually ill-defined distinction between spatially coherent (near the edge) and incoherent (fluorescence) processes. In fact, it is

straightforward to prove that, for Bloch's electrons,  $P_{\text{tot}}(i \rightarrow f) \sim N$  with  $N$  the number of lattice sites, thus indicating a spatially incoherent process [ $P_{\text{tot}}(i \rightarrow i) \sim N^2$ , so that coherence is recovered in the elastic limit.]

## ELECTRONIC RELAXATION

To remove the discrepancy described previously, we have included intermediate state relaxation in the form of a screened Coulomb potential acting between the  $1s$  hole and the promoted  $\pi^*$  electron. As a result, three steps can be identified in the resonant process

1.  $1s \rightarrow \pi^*$  absorption exciting the system to its intermediate state;
2. action of the screened Coulomb potential (relaxation) with formation of excitonic states;
3.  $\pi \rightarrow 1s$  and  $\sigma \rightarrow 1s$  emission from the relaxed states.

The corresponding numerical emission spectra are shown in Figure 2 (lower panel, solid lines). Notice that an excitonic peak has appeared at about -8.0 eV, in satisfactory agreement with the observations. This excitonic peak is mainly a result of dipole transitions into the flat-band region between the L and M symmetry points. These states are pulled down by the core-hole Coulomb interaction; consequently, the absorption process is allowed closer to threshold. (We remind the reader that M is a saddle point in the  $\pi^*$  band, yielding therefore a large contribution to the graphite density of states.)

The screening of a carbon  $1s$  hole in graphite (a semimetal) has been a point of discussion for nearly twenty years. The lack of agreement between the one-electron density of states and absorption spectra (electron-energy-loss data) was interpreted by Mele and Ritsko [8] as a clear indication of a strong excitonic shift in the final state. Their findings were contradicted by several authors until the



Uppsala group provided unequivocal evidence that, near threshold, the excited electron is localised [9,10]; thus, excitons significantly contribute to electronic screening.

The model we have discussed contains one free parameter: the strength  $U$  of the screened Coulomb potential, and our emission spectra have been calculated assuming  $U = -3$  eV. The same potential strength determines the absorption-peak shift shown in Figure 2 (inset), in agreement with previous calculations and observations. ■

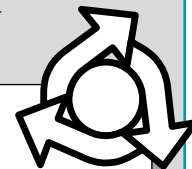
## References

- [1] J.-E. Rubensson, D. Mueller, R. Shuker, D.L. Ederer, C.H. Zhang, J. Jia, and T.A. Calcott, *Phys. Rev. Lett.* **64**, 1047 (1990).
- [2] Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P.D. Johnson, J.-E. Rubensson, T. Boske, W. Eberhardt, and S. Kevan, *Phys. Rev. Lett.* **69**, 2598 (1992);
- [3] W.L. O'Brien, J. Jia, Q.-Y. Dong, T.A. Calcott, K.E. Miyano, D.L. Ederer, D.R. Mueller, and C.-C. Kao, *Phys. Rev. Lett.* **70**, 238 (1993).
- [4] J. J. Jia, T.A. Calcott, E.L. Shirley, J.A. Carlisle, L.J. Terminello, A. Asfaw, D.L. Ederer, F.J. Himpsel, and R.C.C. Perera, *Phys. Rev. Lett.* **76**, 4054 (1996).
- [5] Y. Ma, K.E. Miyano, P.L. Cowan, Y. Aglitzkiy, and B.A. Karlin, [6] J. A. Carlisle, E.L. Shirley, E.A. Hudson, L.J. Terminello, T.A. Calcott, J.J. Jia, D.L. Ederer, R.C.C. Perera, and F.J. Himpsel, *Phys. Rev. Lett.* **74**, 1234 (1995).
- [7] M. van Veenendaal and P. Carra, *Phys. Rev. Lett.* **78**, 2839 (1997).
- [8] E. J. Mele and J. J. Ritsko, *Phys. Rev. Lett.* **43**, 68 (1979).
- [9] P.A. Brühwiler, A.J. Maxwell, C. Puglia, A. Nilsson, S. Andersson, and N. Mårtensson, *Phys. Rev. Lett.* **74**, 614 (1995).
- [10] R. Ahuja, P.A. Brühwiler, J.M. Wills, B. Johansson, N. Mårtensson, and O. Eriksson, *Phys. Rev. B* **54**, 14396 (1996).

## ACKNOWLEDGEMENT

We are grateful to Y. Petroff for his spirited resistance to the presence of mathematical expressions in the text. Two was the maximum number of equations he recommended ... one turned out to be sufficient.

## THE EUROPEAN SYNCHROTRON RADIATION SOCIETY



### ESRS

is the Society for you, working on your behalf by

### Running SUMMER SCHOOLS

introducing Synchrotron Radiation (SR) techniques to young scientists.

#### •Maratea, Italy:

1997 - SR in Life Sciences and Chemistry.

#### •Luso, Portugal:

1998 (6th - 14th May) SR in Materials Science and Physics. We hope to establish a series, e.g.

1999 Applications of SR in Biological Sciences.

2000 Applications of SR in Materials Sciences.

### Offering a PRIZE

for outstanding SR work by a young scientist.

The Prize is a massive 1500 ECU, to be presented at the Grenoble SR Jubilee conference in November. Details on the WWW at <http://fy.chalmers.se/esrs/>

### Publishing a NEWSLETTER

See the www page if you are a member and have not received yours.

### ESRS

needs your membership - otherwise next year will mark both the 10th anniversary of the founding of ESRS and its imminent demise! Use the accompanying form (or the one on the www) to renew or take out membership - PLEASE.

## ESRS: MEMBERSHIP FORM

### Membership fees

- Scientist 20 ECU - 1 year
  - Student 10 ECU - 1 year
  - Scientist 40 ECU - 3 years
  - Student 20 ECU - 3 years
- (1 ECU = 6.58 FF, £ 0.70, 1.96 DM on 18 April 1997)

### Eastern European countries:

- Scientist 4 ECU - 3 years
- Student 2 ECU - 3 years
- New Membership
- Renewal

Family name: \_\_\_\_\_ Title : \_\_\_\_\_

First name: \_\_\_\_\_

Address: \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Tel : \_\_\_\_\_ Fax : \_\_\_\_\_ E-mail: \_\_\_\_\_

Date : \_\_\_\_\_ Signature : \_\_\_\_\_

**France:** send with your fee in FFr or in ECUS by Eurocheque payable to «ESRS trésorier», to Dr M-Y Adam, ESRS Treasurer, Bat 209d LURE U-Paris Sud, 91405 Orsay Cedex, France.

**Germany:** Send with a DM cheque to «ESRS», to Dr R. Frahm, HASYLAB-DESY, Notkestieg 85, D-22603 Hamburg, DE. Germany.

**Italy:** Send with a Lire cheque payable to «ESRS», to Prof. A Mottana. Treasurer: Societa Italiana Luce di Sinchrotrone, via Segre Corrado 2, 00146 Roma, Italy.

**United Kingdom:** Send with a sterling cheque payable to «ESRS», to Dr Graham Bushnell-Wye, Daresbury Laboratory, Warrington WA4 4AD, UK.

For any queries about ESRS contact the Treasurer, Dr M-Y Adam (Fax: (33) 1 64464148, e-mail: [esrsmya@Lure.u-psud.fr](mailto:esrsmya@Lure.u-psud.fr)), or the secretary Prof. P-O Nilsson, Dept. of Physics, Chalmers Univ. of Tech., S-412 96 Göteborg, Sweden (Fax: (46) 31 165176, email: [flxpon@fy.chalmers.se](mailto:flxpon@fy.chalmers.se)).