JOURNAL OF
Materials
CHEMISTRY

Comparative performance of X-ray diffraction and Raman microprobe techniques for the study of carbon materials

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Received 27th July 1998, Accepted 25th September 1998

This paper compares the information provided by X-ray diffraction and Raman spectrometry in terms of the structural order in a wide set of carbon solids. A special emphasis is placed in checking the validity of the commonly used formula of Tuinstra and Koenig and establishing the magnitude of errors potentially derived from its application. For this, a total number of 45 carbon materials aiming to cover the whole spectrum of properties and applications of these solids were jointly characterised by X-ray diffraction and Raman microprobe spectrometry. The comparison of d_{002} interlayer spacing and the ratio of D to G Raman band intensities allows one to conclude that both techniques are complementary rather than equivalent. The different types of factors affecting the D and G band intensities and widths are discussed, it being concluded that their contributions are difficult to separate. The overall conclusion is that Tuinstra and Koenig's formula is valid only as a first approximation to L_a values, and that errors as high as 100% are possible, so that, whenever feasible, direct measurements by XRD are recommended.

Introduction

From its earliest applications to carbon materials,[1,2] Raman spectrometry has usually been considered as an alternative to X-ray diffraction (XRD), with respect to which it offers as main advantages a higher surface selectivity (with a sampling depth estimated[3] to be about 100 nm) and the possibility of sampling reduced areas of the surface. Both advantages have found applications in the study of carbons.[3–7]

Despite the very different physical phenomena involved in these two techniques, the structural information provided by XRD and Raman spectrometry has traditionally been assumed as equivalent. Tuinstra and Koenig, in the very first paper on the Raman spectrum of graphite,[1] already found a correlation between the $R=(I_D/I_G)$ ratio of intensities of the two main bands in the Raman spectra and the reciprocal of the crystallite size parameter along graphite basal planes ($1/L_a$) as measured from X-ray diffraction. This relationship was justified by assigning the D (after defects) Raman band at *ca.* 1360 cm^{-1} to the A_{1g} mode, forbidden in an hexagonal lattice and activated when symmetry rules relax owing to boundary discontinuities. The above correlation would be later used to estimate L_a parameters for carbons as different as carbon fibres,[8] hard carbon films,[9] pitches[10] and coals,[11] some of them widely departing from the pseudographitic order which originally gave raise to Tuinstra and Koenig's formula.

The applicability of such a formula to disordered carbons would be most desirable, since direct L_a measurement from their X-ray diffractograms is somehow hindered by the poor definition of the (10) band while indirect L_a measurement from the intensity of Raman D band should be easier provided that D band and G band do not overlap to a large extent (as is indeed the case for a few of the most disordered carbons); however, anomalies soon became evident. Fitzer *et al.*[12] found an analogous correlation between R and $1/L_a$ for a set of carbon fibres, but the slope measured by them was different from that reported by Tuinstra and Koenig, resulting in higher L_a values. They attributed this discrepancy to their XRD measurements being performed in bundles, which in case of a high preferred orientation of the fibres could render higher L_a values than if measured in powder. Zerda *et al.*[11] also reported higher L_a values for hard coals based on Raman measurements than when measured by XRD, which they attributed to a predominance of the aliphatic over the aromatic fraction in these particular carbons. On the other hand, there are also reports[13] of L_a values obtained from Raman measurements being up to an order of magnitude lower than those calculated from XRD. To complicate things further, Katagiri *et al.*[14] obtained the Raman spectrum of pure edge planes of graphite and found that the D band had a higher intensity than when measured on pure basal planes, whereas only an L_a value would obviously be applicable.

The idea started to emerge[15] that a small crystal size may not be the only cause for appearance of the D band in the Raman spectra of carbons. The difference between edge and basal plane spectra evidences that orientation has a large influence on the D band. While the powder method implies that XRD measurements come from a volume of randomly disposed particles, thus averaging any preferred orientation of the microcrystals, the Raman microprobe signal results from a limited volume (a few micrometers wide and not much more than 100 nm deep) of a particle surface. Even if a high number of signals from different particles are averaged, orientation effects cannot be entirely eliminated.

Still other factors seem to influence the way in which both R (Raman) and L_a (XRD) evolve as a result of increasing order/disorder. Benny-Bassez and Rouzaud[16] found that when carbons from different starting materials were treated to various high temperatures there was always a certain correlation between R and $1/L_a$ inside each series, but the validity range and the slope of such correlations varied from one starting material to the other. They rationalized their results in terms of the effect that removing different types of defects, all of them resulting in a decreased D band intensity, would have over the growing and coalescence of the crystallites, and so an increase in L_a.

All of the above arguments are evidence in support of the idea that Tuinstra and Koenig's formula should only be taken as a first approximation when direct L_a measurement is not available, and that the goodness of such estimation depends heavily on the type of carbon under study. Nevertheless, its use in recent years has by no means decreased, and it is often the case[17–19] that while XRD measurements are used in the same paper to report d_{002} and L_c parameters, L_a is separately estimated from a Raman spectrum without any attempt being made to check the agreement between this estimation and the values that would otherwise be obtained by XRD.

In the present paper, we make use of an array of XRD and Raman parameter values obtained for a wide set of different carbon materials[20,21] to compare the information provided by both techniques regarding the carbon's structural order. The focus is placed in checking the validity range for use of Tuinstra and Koenig's formula and the magnitude of the errors potentially derived from its application. Both are discussed in terms of the different subsets of carbons studied.

Experimental

Materials

A total number of 45 carbon materials, aiming to cover as far as possible the whole spectrum of properties and applications of carbons, have been included. Their classification and reference codes are given in Table 1. More details can be found elsewhere.[22]

Methods

X-Ray powder diffractograms were obtained in a Philips PW 1010 diffractometer using Ni-filtered Cu-Kα radiation. Silicon was used as a standard for peak position and broadening corrections. Interlayer spacing, d_{002}, and apparent crystallite size along the c axis, L_c, were obtained from the (002) peak. Apparent crystallite size along basal planes, L_a, was obtained from the (10) band except for the most crystalline solids, where the (100) peak was used. L_c and L_a parameters were calculated using Scherrer's formula, with values of $K=0.9$ and 1.84 respectively.

Raman spectra were obtained in an XY Raman microspectrometer (Dilor Co., France) using the green line of an argon laser ($\lambda=514.53$ nm) as excitation source. This laser wavelength has also been used in some of the papers reported in this work, although other wavelengths are also common. Five 5 s accumulations were taken, at a laser power of 100 mW, for the most crystalline samples. Less-ordered samples were damaged by the laser in these conditions, so ten 10 s accumulations at 20 mW were taken instead. The objective used was an 80× (laser spot size <3 μm), Raman light being collected in a backscattering geometry. Results were collected in reflection mode, with perpendicular polarisation to maximise intensity.

Table 1 Materials classification and codes

GRAPHITES			NATURAL	MICROCRYSTALLINE		GP1
				CONVENTIONAL		GC1
			SYNTHETIC			GC2-5
				EXFOLIATED		GE1
				HIGHLY ORIENTED		HOPG
				ACTIVATED		GA1-3
NON GRAPHITIC	GRAPHITIZABLE	COKES	PETROLEUM-BASED	SPONGE	GREEN	CVE
					CALCINED	CCE
				NEEDLE	GREEN	CVA
					CALCINED	CCA
			COAL - BASED			CS1
		MESOCARBON MICROBEADS				MM1
		PITCHES	PETROLEUM - BASED			BP1-2
			COAL TAR - BASED			BA4
			SYNTHETIC			BS1
		CARBON FIBRES	SHORT	PITCH-BASED	LOW MODULUS	FC1
			CONTINUOUS		ULTRAHIGH MOD.	FU1-2
	NON GRAPHITIZABLE			PAN-BASED	HIGH MODULUS	FM1
					HIGH STRENGTH	FT1-2
		CARBON BLACKS		LOW TEMPERATURE		NC1-2
				HIGH TEMPERATURE		NC5
		GLASSY CARBON				CTV1
		ACTIVATED CARBONS		FROM PINE WOOD		CA1-6,9
				FROM VEGETABLE DEBRIS		CA7
				FROM COAL		CA8
		CHARS		DEMINERALISED		CD1
				RAW		CB2
		COALS		ANTHRACITE		CM1
				SUBBITUMINOUS		CM2-3

Results and discussion

Table 2 lists XRD and Raman parameter values to be used in the following discussion. Further details concerning band deconvolution in Raman spectra can be found elsewhere.[20] While R has been traditionally expressed as the I_D/I_G ratio, the entirely equivalent $I_D/(I_D+I_G)$ index provides a more compact scale when considering highly disordered carbons and will be used here except when direct comparison with other works is needed.

From the various parameters proposed[3] as indicative of graphitization level in the Raman spectrum of carbons, the ratio of D/G band intensities (in any of its two analogous forms) is the most commonly used. This parameter is compared in Fig. 1 with the interlayer spacing, d_{002}, obtained from X-ray diffraction and traditionally used to calculate a graphitization degree. Two to three zones can be distinguished.

The first zone comprises all graphite samples (circles), which exhibit similar d_{002} values but for which R varies from 0–40%. Activated graphites (⊗) exhibit R values increasing along with their activation level (sequence GA1–3-2, see Table 2) while no significant change in d_{002} is observed. Consequently, the disorder induced upon activation is not reflected in the interlaying spacing although its effect on the Raman-based order degree is clearly appreciated. Gardner *et al.*[23] used neutron diffraction to structurally characterise microporous activated carbons and concluded that although the basic underlying atomic structure remained unchanged during the burnoff process the presence of micropores changed the structure in an intermediate range. So, it would appear that Raman parameter R is giving information about this intermediate range.

On the opposite side of Fig. 1, disordered materials ($d_{002}>0.35$ nm) exhibit highly dispersed R values (varying between 60 and 80%), so Raman spectrometry does not allow to position these solids in an order/disorder scale whereas XRD clearly serves to distinguish them on the basis of their d_{002} values.

GP1 microcrystalline graphite (○) lies at the intersection of the prolongations of both straight lines; thus, according to XRD it would fall among the most ordered studied materials, whereas according to Raman spectrometry it would be among the most disordered ones. Finally, there seems to be an intermediate zone where d_{002} (0.34–0.35 nm) and R (40–60%) increase in parallel. It would be legitimate to argue that the existence of this third zone is dubious and that Fig. 1 shows instead an inverted L. While this is open to interpretation, the information inferred would be virtually the same.

The main conclusion drawn from this figure is that although the general direction of growing disorder is reflected in increased values of both d_{002} and R, the weight of the different causes for disorder in both parameters is radically different, to the point that some disorder factors are reflected on d_{002} but not on R and *vice versa*. Therefore, the information provided by XRD and that provided by Raman must be considered complementary rather than equivalent. The suggestion of Lespade *et al.*[3] that the first order Raman spectrum of carbons relates to their in-plane or bidimensional order, as opposed to the tridimensional, stacking order that could be inferred from d_{002}, seems therefore backed by the results presented here.

When considering what (bidimensional) disorder factors are reflected in R, the main working hypotheses gathered from the literature are the finite domain size and the orientation. The first hypothesis is endorsed by Tuinstra and Koenig's formula,[1] and is reasonably easy to check on comparing R with the reciprocal of the XRD-based parameter L_a. Such comparison is made in Fig. 2.

Table 2 XRD and Raman parameters

Sample	d_{002}	L_c	L_a	I_G/I_{total}	I_D/I_{total}	W_{G_1}	W_{D_1}
GP1	0.3353	9.2	5.3	28.8	67.5	59.9	66.6
GC1	0.3370	39.9	56.0	77.8	21.0	17.3	43.1
GC2	0.3351	22.3	30.2	100.0	0.0	14.2	—
GC3	0.3355	36.5	47.6	82.6	17.4	23.5	58.6
GC4	0.3366	22.3	69.0	97.8	2.3	17.2	40.2
GC5	0.3353	22.3	30.0	93.7	6.4	16.4	32.3
GE1	0.3363	22.3	30.2	71.0	28.0	21.6	61.5
HOPG	0.3362	26.2	22.2	85.4	14.6	24.1	57.8
GA1	0.3358	17.2	6.3	86.3	12.7	22.6	55.0
GA2	0.3368	9.1	5.8	56.0	38.0	25.7	60.4
GA3	0.3355	19.2	5.5	74.3	21.9	19.5	49.3
CVE	0.349	2.7	2.3	29.0	65.6	47.2	279.3
CCE	0.351	2.7	5.3	30.9	67.3	87.6	238.8
CVA	0.351	2.2	3.2	16.6	76.8	58.8	313.9
CCA	0.350	3.5	5.8	32.1	57.3	79.0	146.1
CS1	0.349	2.0	6.0	18.2	63.8	65.3	163.3
MM1	0.347	2.6	2.3	32.1	59.1	79.0	170.1
BP1	0.378	1.3	2.5	18.4	81.6	69.9	350.8
BP2	0.366	1.4	2.8	36.6	63.4	66.0	216.8
BA4	0.371	1.2	2.3	24.2	75.8	62.4	295.1
BS1	0.362	2.0	—	39.2	47.7	83.2	147.4
FU1	0.339	16.5	22.0	56.2	40.7	25.0	52.7
FU2	0.343	13.0	14.5	55.4	41.7	28.1	50.3
FM1	0.347	3.1	7.6	46.2	48.2	55.9	58.4
FT1	0.359	1.5	4.6	33.6	65.9	112.8	247.7
FT2	0.353	1.6	4.3	20.7	75.6	105.8	264.1
FC1	0.389	0.9	3.8	22.3	67.2	70.9	237.4
NC1	0.368	1.3	3.5	27.8	69.6	106.1	251.7
NC2	0.368	1.4	3.5	24.5	68.7	81.4	252.8
NC5	0.359	1.7	4.4	24.1	57.7	59.2	167.5
CTV1	0.353	1.9	7.0	23.6	55.4	65.3	70.4
CA1	0.377	1.0	3.7	17.6	47.0	62.4	182.5
CA2	0.379	1.1	3.8	19.9	48.1	59.9	157.6
CA3	0.403	1.1	4.6	23.4	38.5	54.8	108.3
CA4	0.366	1.1	4.0	25.2	44.0	55.3	100.0
CA5	0.380	1.0	4.0	22.9	42.3	61.6	130.5
CA6	0.374	1.0	3.2	20.9	47.2	56.0	121.2
CA7	0.380	1.1	3.7	23.2	37.7	51.8	110.1
CA8	0.380	1.0	3.4	18.9	43.6	56.4	166.1
CA9	0.375	0.9	3.1	24.6	47.1	65.8	136.0
CD1	0.371	0.8	2.8	26.0	74.0	113.0	296.3
CB2	0.386	0.9	2.7	34.9	65.1	109.6	240.6
CM1	0.355	1.6	3.0	34.7	65.3	45.9	178.1
CM2	0.382	0.8	1.8	33.7	60.9	94.7	246.6
CM3	0.399	0.9	2.4	6.9	83.1	107.2	433.2

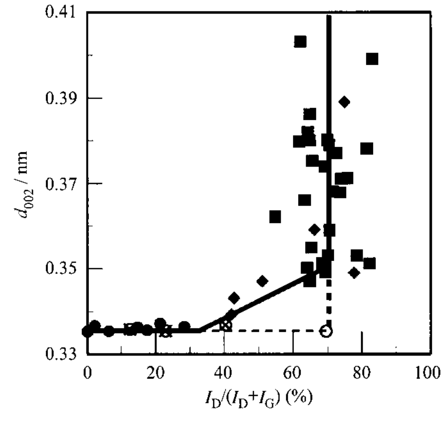

Fig. 1 Relationship between conventionally used order degrees from XRD (d_{002}) and Raman spectrometry $[I_D/(I_D+I_G)]$ techniques; (●) is used for conventional graphites, (⊗) for activated graphites, (○) for the microcrystalline graphite, (◆) for carbon fibres, and (■) for the rest of carbons.

Fig. 2(a) shows that a limit occurs such that for a given value of R there seems to be a maximum value for L_a rather than a single relationship. This is particularly true for disordered materials ($R > 50\%$), with a high level of dispersion towards lower L_a values. On the other hand, ordered materials ($R < 50\%$) seem to lie in a defined path with the exception of the three activated graphites (⊗), which exhibit lower L_a values than other carbons of similar R. It must be pointed here that activated graphites present a broad (10) band in their diffractograms instead of separated (100) and (101) peaks. All carbons for which L_a can be calculated from well defined (100) peaks (namely, conventional graphites, ●, and ultrahigh modulus carbon fibres, ◆) follow the solid line in Fig. 2(a), thus suggesting that there could actually be a single relationship between R and L_a which in turn would justify calculating L_a from the Raman spectra of these materials.

In order to be able to make a direct comparison with Tuinstra and Koenig's postulate, we need to represent this relationship in its traditional mode, as in Fig. 2(b). The solid line in this figure corresponds to Tuinstra and Koenig's formula. It is easy to see that while the line provides a reasonable average trend for XRD-measured values in the conventional graphites group, ● (although the dispersion is high even for this particular group, see below), the estimation soon tends to provide lower values for L_a than those calculated by XRD for less ordered carbons, and the magnitude of the discrepancy becomes more significant for highly disordered materials, with $I_D/I_G > 2$, for which Tuinstra and Koenig's formula predicts very low L_a values while XRD-based values rarely fall below 2 nm. While $I_D/I_G > 2$ values may seem somewhat too high, they have been reported before.[3,16] Let us

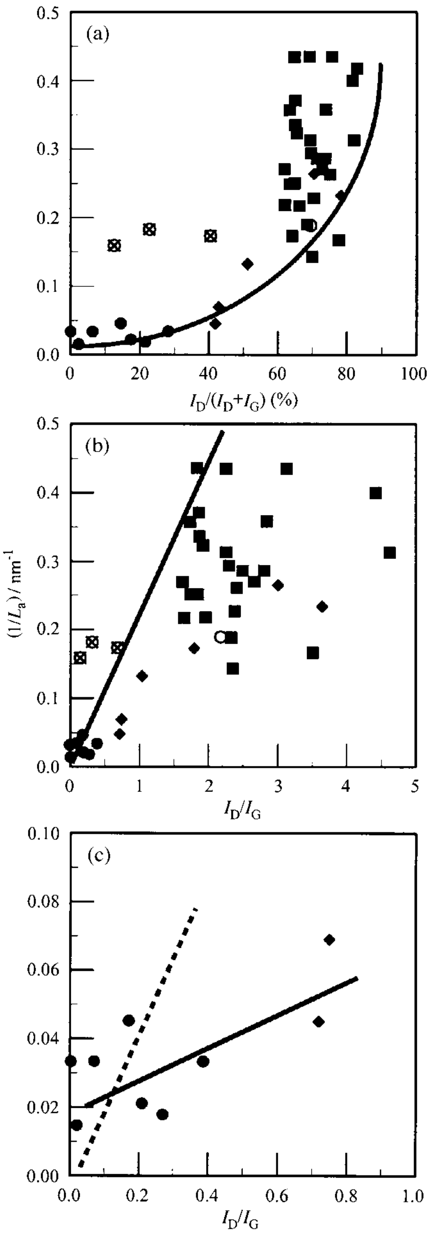

Fig. 2 Relationship between XRD-measured $1/L_a$ and the ratio of Raman band intensities, in two different forms; (●) is used for conventional graphites, (⊗) for activated graphites, (○) for the microcrystalline graphite, (◆) for carbon fibres, and (■) for the rest of carbons.

also remind here that the set of materials studied in this work includes a number of highly disordered carbons in comparison with many previous papers. The dispersion of the results in Fig. 2(b) is very high, both in general and for particular subsets of carbons, with the exception of carbon fibres (◆), for which a linear relationship ($r=0.9$) was observed although the slope is still different from Tuinstra and Koenig's one.

Of course, a part of the discrepancy might arise from the fact that for disordered carbons L_a must be measured on broad (10) bands which may be of questionable accuracy. To avoid this drawback, we show in Fig. 2(c) an extract of Fig. 2(b) including only those carbons presenting neat (100) peaks, namely conventional graphites (●) and ultrahigh modulus carbon fibres (◆). We had mentioned when discussing Fig. 2(a) that this subset of carbons actually seemed to present some unique relationship between R and $1/L_a$. This happens to be about linear ($r=0.7$), as suggested by Tuinstra and Koenig, although the slope (solid line) is different from theirs (shown by the dashed line). Nevertheless, the dispersion is very important among the graphites, where Tuinstra and Koenig's line would seem to be about as good a fit, although discrepancies between the so-fitted and the measured L_a values are of the order of $\pm 100\%$, with about equally likelihood for overestimation and underestimation. In practical terms, this means that of the seven graphites represented (excluding the activated graphites and the microcrystalline one) in all cases but one the calculated L_a values were either double or half the XRD-based ones.

Apart from numerical considerations, two conceptual problems arise with assuming that R comes from a finite L_a. The first one is that no D band ($R=0$) was found in this study for a graphite with an L_a value of just 30 nm. On the other hand, a synthetic pitch for which L_a is not measurable (the structure of this pitch is such that the stacking of layers resembles that of conventional carbons but the layers are made up of heavily hydrogenated rings joined by aliphatic chains instead of aromatic domains) presents a moderate I_D/I_G value of 1.22.

A point to take into account here, which was irrelevant to Tuinstra and Koenig's study, is the contribution from band broadening to the measured intensity. Both D and G bands widen appreciably for disordered materials, the effect being always higher for the D than for the G band (D band widths cover a scale three times that of G band widths). The ratio of widths for both D and G bands is plotted in Fig. 3 as a function of L_a. Far from W_D/W_G being constant, D tends to widen more than G for a given carbon, and the effect is more noticeable the lower the L_a values, which of course results in an increased R with decreasing L_a. This is not a direct cause–effect relationship, though. Knight and White[24] pointed out that while 'the intensity of the M-zone boundary line relates to particle size and would presumably appear in the spectra of small crystallites even if they were perfect crystals' … 'the line is narrow because the optic branch is very flat across the M point'. Benny-Bassez and Rouzaud[16] assimilate D band intensity at different wavelengths to different types of defects, whose removal always has an effect over L_a but the magnitude of which varies from one type of defect to another. Therefore, it is expectable that virtually all kinds of defects will contribute to widen D band and in turn increase R, their effect being added to that of finite domain size. This would explain that Tuinstra and Koenig's formula, which ascribes all R intensity to reduced domain size, tends to result in underestimated L_a values for disordered materials. It would also explain the measured dispersion of results.

As for orientation effects, they have certainly been proved by the spectra of Katagiri *et al.*[14] of edge graphite planes, and could represent an added contribution to R in so far as both basal and edge planes are exposed to the Raman laser in a typical experimental set-up. Only for a single crystal would we expect this effect to be absent, since the chance is very small of all microcrystals being perfectly orientated as to expose only basal planes to the laser. Actually, we can expect

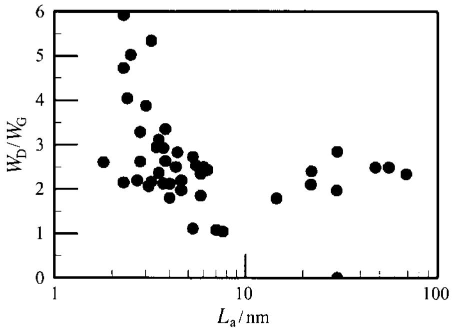

Fig. 3 Relationship between the ratio of Raman band widths (W_D/W_G) and XRD-measured L_a.

a certain relationship between the domain size (and more generally the order degree) and the orientation level of a carbon. In general, the more crystallites exposed (the lower L_a) the higher the chances of edge planes contribution to the Raman spectrum, thus rendering both effects difficult to differentiate. For disordered carbons, with a high number of crystallites being exposed and no reason for them to show a preferential orientation, we can expect a randomly average of orientations and thus a constant percentage of basal/edge planes, so a constant contribution to *R*. On the other hand, well ordered carbons, for which less crystallites are exposed to the laser and orientation effects are possible, are prone to be differentiated by their orientation level. This could explain some facts still unaccounted for in Fig. 1.

In principle, graphites could present different orientation levels, depending for example on their origin, and that could be the source of their different *R* values as highlighted by Raman spectrometry. Indeed, the graphites presenting the lowest *R* values in this study are all synthetic graphites (often prepared by deposition methods, which would favour a high degree of orientation). At the other end, the natural 'microcrystalline' graphite GP1, which possesses the peculiarity of being formed by a myriad of small intrinsically graphitic crystallites (randomly orientated), presents as high an *R* as disordered carbons of much lower L_a and structural order. On the other hand, activated graphites whose L_a has been greatly diminished upon activation, still present *R* values analogous to those of conventional graphites (except for the most activated one). A gradual increase of *R* upon activation of these graphites (in spite of their analogous values of L_a and band widths) would then imply that activation does change to a certain extent the orientation level of these graphites. Similarly, the fact that the 'highly orientated' HOPG sample presents a sizeable value of *R* would be justified by distortions introduced upon grinding this sample for uniformity with the other carbons. Also, the transitional third zone proposed in Fig. 1 is populated by high and ultrahigh modulus fibres, for which the orientation degree achieved depends directly on their structural order. And finally, the right-hand vertical band in Fig. 1 corresponds to disordered carbons for which orientation is expectedly random.

Conclusions

We have then to conclude that there are a number of factors responsible for D band intensity, whose contributions are often difficult to separate. Both the extent of preferred orientation and the presence of all kinds of disorder have a strong influence on the parameter *R*, the former predominating for well ordered graphites and the second for disordered carbons. While domain size has certainly an influence over D band intensity, this is modulated by the extent of orientation, and the contribution of band widening to disorder has to be considered as well. Tuinstra and Koenig's formula is then valid only as a first approximation to L_a values, it being highly advisable to use direct XRD methods whenever possible. If not available, it should be borne in mind that errors as high as $\pm 100\%$ are to be expected, and that these are likely to be underestimations rather than overestimations when considering highly disordered materials.

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Paper 8/05841E