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Laboratory experiments on cosmic dust analogues : the structure of small carbon grains

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Abstract. In this paper we present new results of our experiments aimed to study the internal structure of cosmic analogue carbon grains. The samples, produced by arc discharge between two carbon electrodes in an argon atmosphere, were annealed in the temperature range 250–780°C in order to produce modification of the internal grain structure. These changes were monitored by analysing the variations of the extinction profile between 190 and 2600 nm and of the optical gap as a function of the annealing temperature.

The shift of the UV peak position towards longer wavelengths, the overall increase of the extinction coefficient and the closing of the gap as the temperature increases are all consistent with the evolution of carbon grains outlined by Mennella *et al.* (*Astrophys. J.* **444,** 288, 1995; *Astrophys. J. Suppl. Ser.* **100,** 149, 1995). It provides a growth in number and size of the sp^2 clusters forming the grains during the annealing. The relevance of the electronic structure of the aromatic clusters in the extinction processes and the dependence of the energy π transitions on their size are confirmed by the present results.

These results may be relevant in the context of interstellar bump attribution, as they show that the internal structure of small carbon grains is dominant in extinction processes.

Introduction

It is well known that carbon grains represent an important component of interstellar and circumstellar dust. Many aspects of the nature of this component are not clear. A much debated question is the identification of the carriers of the strongest feature in the interstellar extinction curves, the bump at 217.5 nm.

Although several explanations involving the properties of grains in the interstellar medium have been proposed, the attribution of the bump still remains controversial. Among the alternative identifications, carbonaceous materials seem to be the most attractive, even if the exact nature of the carriers has not yet been identified. Several carbon-based materials, such as graphite, coals and polycyclic aromatic hydrocarbon molecules (PAHs), have been proposed (e.g. Gilra, 1972; Draine and Lee, 1984; Joblin *et al.,* 1992; Papoular *et al.,* 1993; Mathis, 1994). At the present time, the proposed interpretations should be considered to be to some degree unsatisfactory, either because they require very peculiar conditions of the carrier population, or because they do not satisfy observational constraints.

We recall that one of the main constraints posed by astronomical observations is the lack of correlation between the bump position, λ_0, and its width, γ. While λ_0 is very stable at 217.5 nm for different sight lines, γ is small in the diffuse cloud medium and large in dense quiescent regions (Fitzpatrick and Massa, 1986). For a review of other observational properties of the bump, see Draine (1989).

A significant contribution to the bump attribution may come from the study in the laboratory of cosmic analogue carbon grains. Such studies can reveal clues about the details of the interaction of electromagnetic radiation with carbon grains having sizes similar to those expected for the bump carrier. Recently, Mennella *et al.* (1995a, b) have demonstrated that the internal structure of single grains, with a size of about 10 nm, plays a determining role in extinction processes. In particular, the electronic structure of the sp^2 clusters forming the single grain controls the interaction with UV photons.

In this paper we report new results of our experiments aimed to probe the internal structure of small carbon

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grains. The samples were annealed in order to induce structural modifications. These changes were studied by analysing the extinction profiles in the UV–near-IR range as a function of the annealing temperature. The results obtained agree with our previous conclusion that the degree of sp^2 clustering determines the extinction properties of small carbon grains.

Experimental and results

Two kinds of amorphous carbon grains were produced by means of different techniques. The first one (ACAR) was produced by arc discharge between two amorphous carbon electrodes in an argon atmosphere, at a pressure of 10 mbar, and collected on UV grade fused silica substrates at a distance of 5 cm from the source. Field Emission Scanning Electron Microscopy (FE-SEM) measurements show that the particles have a spherical shape and are clustered together to form a fluffy structure. The diameter of the single grains is about 10–12 nm. A similar morphology is also shown by the other sample (BE), produced by burning benzene in air, although the average diameter of the grains is 30 nm.

The thermal annealing experiment is aimed to study the spectral and structural rearrangements of carbon grains produced by heat treatment. It can also be considered as a reasonable simulation of grain processing active in space, such as UV and cosmic ray irradiation of small carbon grains (Hecht, 1986 ; Sorrell, 1990). The thermal annealing of the ACAR samples was performed at a pressure less than 10^{-5} mbar in an isothermal stainless steel cavity. The samples were annealed for 3 h at a fixed temperature, T_a, in the range 250–780°C. The temperature, measured by means of a thermocouple, was controlled by a microprocessor to better than 1%. A freshly produced sample was used for each annealing temperature and an average heating rate of about 10°C min^{-1} was applied. In the following the samples will be identified with a label that refers to the actual T_a (see Table 1).

Extinction measurements were performed both before and after each annealing process in the range 190-2600
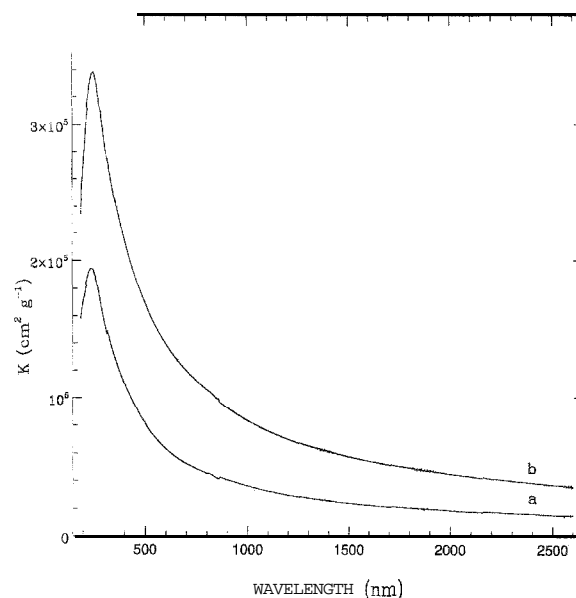

Fig. 1. Extinction coefficients of amorphous carbon grains as-produced (a) and annealed at 780°C (b)

nm, with a resolution of 2 nm, by using a dispersive double beam spectrophotometer (Perkin-Elmer model Lambda 9). Annealing processes and spectral measurements were repeated on several samples for each considered T_a. Since the results agree quite well, in the following we will refer to the averages of the obtained data.

Extinction variations

The extinction spectra of grains as produced and annealed at the highest considered temperature (780°C) are reported in Fig. 1. The curves are smooth except in the UV, where a broad band is observed at 242 and 253 nm for the ACAR and ACAR780 samples, respectively. We note that the extinction coefficient increases in the whole spectral range considered and the UV peak position, λ_p, shifts towards higher wavelengths as a result of the annealing : starting from 242 nm for the ACAR sample, the peak moves up to 253 nm in the case of the ACAR780 sample. The dependence of λ_p on T_a is reported in Table 1 and shown in Fig. 2. Here, the point relative to the BE sample and the thermal evolution of λ_p for hydrogenated amorphous carbon grains (ACH2) subject to a similar heat treatment [see Mennella et al. (1995a)] are also shown for comparison. We recall that, except for the gas used (H$_2$ instead of Ar), the production conditions of ACH2 and ACAR samples are the same.

The overall trend of λ_p as a function of T_a is different for the two kinds of carbon grains. However, at the highest temperatures considered, their peak positions tend to a value of 260 nm, where the peak of the as-produced BE sample falls. This wavelength can be considered as an asymptotic value for the λ_p thermal evolution (see below).

Optical gap variations

The structure of amorphous carbon is well characterized by the optical gap, E_g. In fact, it provides one of the most

Table 1. Optical and structural properties of the examined samples

Label	T_a* (°C)	λ_p† (nm)	E_g‡ (eV)	L_a§ (Å)
ACAR	—	242±2	0.52±0.05	15
ACAR250	250	242±2	0.53±0.05	15
ACAR325	325	241±2	0.52±0.05	15
ACAR415	415	243±2	0.50±0.05	15
ACAR515	515	244±2	0.37±0.05	21
ACAR700	700	250±2	0.07±0.05	
ACAR780	780	253±2	0.00±0.05	—
BE	—	260±2	0.15±0.05	51

* Annealing temperature.
† UV peak position.
‡ Optical gap.
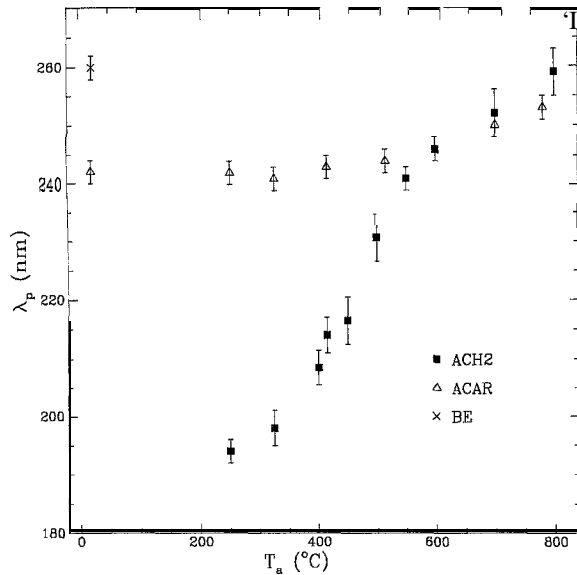§ Aromatic coherence length derived by the optical gap.

Fig. 2. The UV peak position of as-produced BE sample ACAR samples as a function of the annealing temperature. The values obtained by Mennella et al. (1995a) for anneal hydrogenated carbon grains are also reported for a comparison

Fig. 4. Tauc gaps of BE and ACAR samples as a function of the annealing temperature. The optical gaps determined by Mennella et al. (1995b) for as-produced and annealed hydrogenated carbon grains are also shown for comparison

valuable insights into the degree of clustering of sp^2 sites into the grains. To derive the optical gap from our optical data, we used the following "Tauc relation" between the absorption coefficient, α, and E_g (Tauc et al., 1966) :

$$(\alpha E)^{1/2} \propto (E-E,),\tag{1}$$

where E is the energy. The Tauc diagram for our samples shows a zone where equation (1) provides a good parametrization of the absorption edge. By extrapolating the linear slope to zero absorption in the Tauc diagram, it is possible to estimate the optical gap. The $(\alpha E)^{1/2}$ versus E plots of ACAR, ACAR780 and BE data are shown in Fig. 3, together with the linear fits obtained according to equation (1).
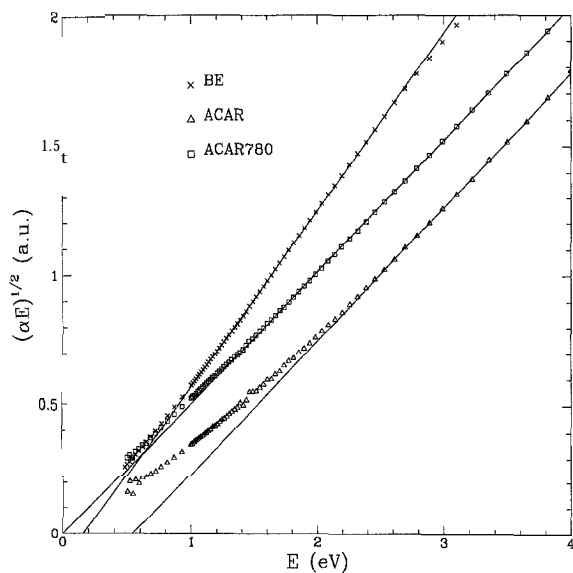

Fig. 3. Tauc diagram for ACAR, ACAR780 and BE samples. The fits obtained by means of the Tauc relation [equation (1) in the text] are also shown. The intersections of the fitting straight lines with the abscissa axis give the values of the optical gap
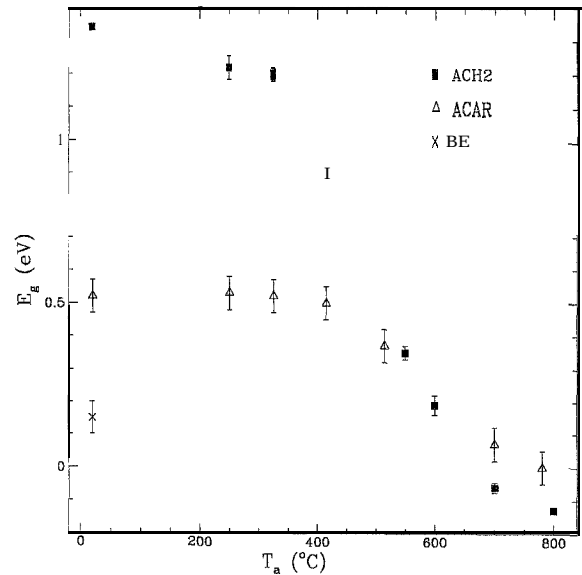
The optical gaps were obtained from spectral measurements repeated on several samples for each considered T_a. The average values, with the corresponding errors, are listed in Table 1. The dependence of E_g on T_a, together with that found by Mennella et al. (1995b) for as-produced and annealed hydrogenated carbon grains, is shown in Fig. 4. As in the case of the λ_p thermal evolution, the optical gap changes are less pronounced for ACAR than for ACH2 grains. Starting from a value of 0.52 eV for the ACAR sample, E_g remains constant up to 400°C and then slowly decreases until the closing of the gap at around 700°C. Despite a higher starting value, $E_g = 1.34$ eV, a faster decrease of the optical gap is observed for the hydrogenated grains during the annealing. This causes closing of the gap at a temperature slightly higher than 600°C. E_g is 0.15 eV for the as-produced BE sample.

Discussion and conclusions

The results reported in the previous section show that important modifications take place in the UV-near-IR spectrum of ACAR grains due to a heat treatment (see Figs 1 and 2) : (a) the extinction coefficient increases in the whole spectral range 190–2600 nm ; (b) the UV peak shifts towards longer wavelengths. As a counterpart to the spectral variations, changes of the optical gap, which show modifications of the structural properties of carbon grains, also occur. It is worth noting that electron microscopy shows that our samples have a complex morphology [see Colangeli et al. (1995)]. The single grains are aggregated in spherical structures formed by 3-5 grains. In turn, the aggregates are linked to each other in a chain-like structure and form the overall fluffy texture. Since the shape, the dimension of the particles and their degree of clustering can affect the optical properties of particulate materials (Huffman, 1989 ; Wright, 1989 ; Rouleau and

Martin, 1991), the observed spectral variations could be due to changes of these parameters during the annealing. So far, we have not carried out a morphological characterization of ACAR samples after the heat treatment. Nevertheless, electron microscopy results obtained for the ACH2 samples show that all the morphological properties do not change after the annealing process. Thus, we interpret the observed thermal evolution of the UV-near-IR spectrum of the carbon grains in terms of structural variations within the single grain.

We assign the UV band to $\pi-\pi^*$ electronic transitions of the sp^2 clusters forming the grains. Compact clusters of aromatic rings are indeed the most stable arrangement of the sp^2 sites in carbons (Robertson and O'Reilly, 1987). The shift of the UV peak is interpreted in terms of a dimensional growth of the graphitic islands. Moreover, we recall that all our carbonaceous materials studied in the extreme UV (Colangeli et al., 1993; Mennella et al., 1995a) are characterized by a second band falling at higher energy (II 13.5 eV) attributed to $\sigma-\sigma^*$ electronic transitions. Since the σ states form two very localized centre bonds which determine the short range order, they are less sensitive to structural variations than the π states. In fact, the delocalization of the π electrons of the sp^2 clusters introduces a medium range order and determines a strong link between electronic and structural properties in carbons. In order to understand this link we have to take into consideration that : (a) theoretical computations and experimental results obtained on amorphous carbon films indicate that in both hydrogenated and dehydrogenated carbons the edges of the electronic density of states (DOS) are π-like (Robertson, 1986, 1991) ; (b) the width of the π peaks in the electronic DOS, which in turn determines the optical gap (i.e. the energy spacing between valence and conduction bands), is correlated to the dimensions of graphitic islands, with the larger islands giving rise to smaller optical gaps (i.e. closer π and π^* bands). Robertson (199 1) found that the optical gap varies inversely with the aromatic coherence length, L_a, of the sp^2 clusters: $E_g \simeq 7.7/L_a$ (eV). The L_a values calculated by means of the previous relation are reported in Table 1. Of course, we cannot apply the Robertson relation for a null value of the Tauc gap ; moreover, this relation gives meaningless cluster sizes for very small values of E_g.

The closing of the optical gap, which indicates a complete delocalization of the π bonds, occurs at about 700°C. This result is in agreement with the thermal evolution of both ACH2 grains (see Fig. 4) and hydrogenated amorphous carbon films (i.e. Dischler et al., 1983; Fink et al., 1984; Smith, 1984).

The L_a values reported in Table 1 refer to the largest clusters present within the grains. In fact, when clusters of different sizes are present, each with its band gap, the observed gap is driven by the largest clusters (Robertson and O'Reilly, 1987).

The thermal evolution of the ACAR spectrum with annealing can be interpreted by taking into account the clustering degree variations within the grains. The absorption is determined by the number and the dimension of the sp^2 clusters. For ACAR grains, the largest clusters have a dimension of 15 A. However, as the broad absorption edge shows (see Fig. 1), a range of cluster sizes is

present within the grains. A single cluster size should produce a sharp absorption edge, as $\pi-\pi^*$ interband transitions only occur for photon energies greater than the optical gap. This explains why the ACH2 samples, and more generally hydrogenated carbons, which have large optical gaps, are transparent in the IR range, while they absorb weakly in the visible and strongly in the UV. The observed absorption edge corresponds to successive edges of a range of clusters. On the other hand, for the grains annealed at 780°C, the number of ringed carbon clusters and their average size are increased and the largest islands are able to close the gap. Therefore, their absorption is stronger and starts from lower energies.

Finally, we want to discuss the correlation between the λ_p and E_g. Mennella et al. (1995b) found a good correlation between these two parameters for the annealed ACH2 samples. Since E_g is inversely proportional to L_a, the previous result implies that the π energy transition depends on the sp^2 cluster size. Therefore, the correlation between λ_p and E_g is evidence of the dependence of the dipole matrix momentum of π transitions on the sp^2 cluster size : matrix element effects emphasize lower energy transitions in large clusters and higher energy transitions in small clusters. A plot of λ_p versus E_g for the samples studied in this work, together with the points obtained by Mennella et al. (1995b) for the annealed ACH2 samples, is reported in Fig. 5. The correlation coefficient for all the available data is -0.95. The best fit straight line, λ_p (nm) = $257.4 - 45.8 E_g$ (eV), is also shown in the figure. We note that a quite small difference exists between this fit and that obtained by considering only the annealed ACH2 samples [see Mennella et al. (1995b)].

However this result does not account for the empirical relation, found by Koike et al. (1994) for carbonaceous materials, between the UV peak position and the graphitic microcrystallite sizes determined by high resolution transmission electron microscopy : the UV peak position shifts
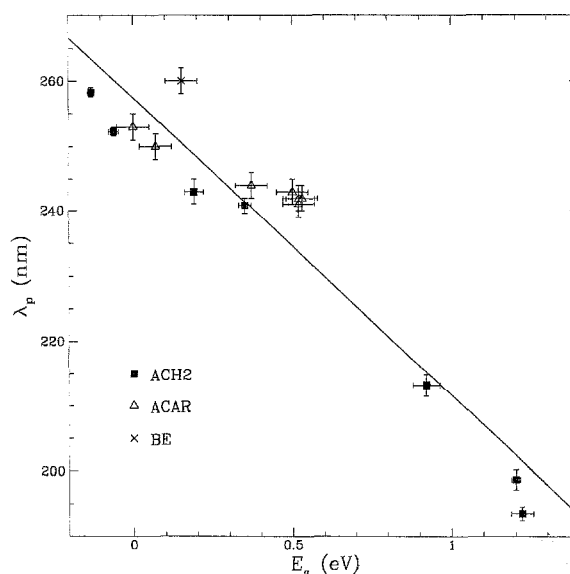

Fig. 5. The UV peak position versus the optical gap for as-produced BE and ACAR annealed up to 780°C. The values relative to ACH2 samples annealed up to 800°C are also reported (Mennella et al., 1995b). The straight line represents the best fit of the data

toward longer wavelengths as the microcrystallite size decreases.

The observed spectral changes of ACAR grains as a function of the annealing temperature, i.e. the increase of the extinction coefficient and the UV peak position shift towards longer wavelengths, are consistent with the thermal evolution of carbon grains, which implies a growth in number and size of the ringed carbon clusters forming the grains, as outlined by Mennella *et al.* (1995b). The differences in thermal behaviour up to 515°C of the UV peak and the optical gap between ACAR and ACH2 grains are due to the different starting hydrogen content. The presence of hydrogen in the ACH2 samples favours the sp^3 bonding hybridization of carbon so that the degree of sp^2 clustering is low and only very small clusters exist in hydrogenated carbon grains. At temperatures higher than 600°C, when hydrogen is completely removed from ACH2 samples, the thermal evolution of λ_p and E_g for the two kinds of grains is quite similar. On the other hand, the BE sample seems to be at the end of the thermal evolution, as it presents a small gap and a UV peak at 260 nm. This wavelength can be considered as the asymptotic value for λ_p, as it corresponds to that observed in the transmission spectrum of ultrathin flakes of single graphite crystals (Ergun and McCartney, 1963 ; Marchand, 1987).

According to Robertson (1986), we conclude that the observed structural changes correspond to the first two stages of a graphitization process : (1) the loss of volatile matter containing H, N and 0 up to 600°C (carbonization) ; (2) the growth in size and number of graphitic cluster (polymerization) at the highest temperatures considered in our experiments. Further evolution towards the three-dimensional graphite lattice should occur at higher temperatures (1200–3000°C). We note that structural changes in amorphous carbon grains, similar to those produced by thermal annealing, are also induced by high-energy particle irradiation (Ugarte, 1992).

The results obtained show that ACAR samples are not able to simulate the interstellar extinction bump at 217.5 nm. However, they provide a good match of the circumstellar bump position and profile (i.e. Muci *et al.,* 1994). On the other hand, only the ACH2 sample annealed at 450°C is able to match the interstellar bump position. This result would imply that our laboratory sample is a possible carrier of the interstellar feature only under strong constraints on the interstellar grain population. This appears a quite unlikely situation. Despite this, we believe that the results on the electronic and structural properties of small carbon grains presented in this work have a more general validity and may have implications on the interpretation of the interstellar extinction bump. They suggest that the interaction of UV photons with carbon grains is driven by their internal arrangement. Therefore, more attention should be given to the simulation of the 217.5 nm feature, not only by considering

shape, size, coating, etc. variations of homogeneous grains, as mainly done so far, but also taking into account the intimate nature of the carbonaceous carriers.

References

Colangeli, L., Mennella, V., Blanco, A., Fonti, S., Bussoletti, E., Gumlich, H. E., Mertins, H. C. and Jung, Ch., *Astrophys. J.* **418,** 435, 1993.

Colangeli, L., Mennella, V., Palumho, P., Rotundi, A. and Bussoletti, E., *Astron. Astrophys. Suppl. Ser.* **113,** 1, 1995.

Dischler, B., Bubenzer, A. and Koidl, P., *Solid State Commun.* 48, 105, 1983.

Draine, B. T., in *Znterstellur Dust* (edited by L. J. Allamandola and A. G. G. M. Tielens), p. 313. Kluwer, Dordrecht, 1989.

Draine, B. T. and Lee, H. M., *Astrophys. J. 285, 89, 1984.*

Ergun, S. and McCartney, J. T., in *Proceedings of the Fifth Conference on Carbon,* Vol. 2, p. 167. Pergamon Press, Oxford, 1963.

Fink, J., Müller-Heinzerling, T., Pflüger, J., Scheeler, B., Dischler, B., Koidl, P., Bubenzer, A. and Sab, R. E., *Phys. Rev. B* **30,** 4713, 1984.

Fitzpatrick, E. L. and Massa, D., *Astrophys. J. 307, 286,* 1986.

Gilra, D. P., in *Scientific Resultsfrom the Orbiting Astronomical Observatory OA02* (edited by A. D. Code), NASA SP-310, p. 295, 1972.

Hecht, J. H., *Astrophys. J. 305,* 817, 1986.

Huffman, D. R., in *Interstellar Dust* (edited by L. J. Allamandola and A. G. G. M. Tielens), p. 329. Kluwer, Dordrecht, 1989.

Joblin, C., Leger, A. and Martin, P., *Astrophys. J. 393,* L79, 1992.

Koike, C., Kaito, C. and Shibai, H., *Mon. Not. R. astron. Soc.* 268,321, 1994.

Marchand, A., in *Polycyclic Aromatic Hydrocarbons and Astrophysics* (edited by A. Leger, L. d'Hendecourt and N. Boccara), p. 31. Reidel, Dordrecht, 1987.

Mathis, J. S., *Astrophys. J. 422,* 176, 1994.

Mennella, V., Colangeli, L., Blanco, A., Bussoletti, E., Fonti, S., Palumbo, P. and Mertins, H. C., *Astrophys. J. 444,288,* 1995a.

Mennella, V., Colangeli, L., Bussoletti, E., Monaco, G., Palumbo, P. and Rotundi, A., *Astrophys. J. Suppl. Ser.* **100, 149,** 1995b.

Muci, A. M., Blanco, A., Fonti, S. and Orofino, V., *Astrophys. J.* 436,831, 1994.

Papoular, R., Breton, J., Gensterblum, G., Nenner, I., Papoular, R. J. and Pireaux, J. J., *Astron. Astrophys. 270,* L5, 1993.

Robertson, J., *Adv. Phys. 35, 317,* 1986.

Robertson, J., *Prog. Solid State Chem.* **21, 199,** 1991.

Robertson, J. and O'Reilly, E. P., *Phys. Rev. B 35, 2946,* 1987.

Rouleau, F. and Martin, P. G., *Astrophys. J. 377, 526,* 1991.

Smith, F. S. J., *Appl. Phys. 55, 764, 1984.*

Sorrell, W. H., *Mon. Not. R. astron. Soc. 243, 570, 1990.*

Tauc, J., Grigorovici, R. and Vancu, A., *Phys. Status Solidi* **15,** 627, 1966.

Ugarte, D., *Nature, 359, 707,* 1992.

Wright, E. L., *Astrophys. J. 346,* L89, 1989.