



Surface electronic states of meteoritic nanodiamonds

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Abstract—The C K edge of Orgueil nanodiamonds (C δ diamonds) was acquired by electron energy-loss spectroscopy (EELS), with an energy resolution of 300 meV. The spectra show peaks at 282.5, 284.7, and 286.4 eV, which occur in the band gap below the main diamond edge and are absent from the bulk diamond spectrum. These peaks are attributed to transitions from C 1s surface core levels to unoccupied surface states, and arise from single and π -bonded dangling bonds and C-H bonds. A shoulder to the main absorption edge at 287.8 eV may correspond to hydrocarbon adsorbates. These results can be used to further our understanding of C δ diamond structure and may reveal the presence of a fullerene-like surface. The unique surface electronic states of the C δ diamond surfaces are expected to affect their optical properties, which are dependent on features such as extent of H coverage, particle size, and surface structure.

INTRODUCTION

Nanodiamonds in meteorites (called C δ diamonds) occur in relatively unprocessed carbonaceous chondrites, such as the CIs and CMs, where they are present at concentrations up to 0.1 wt% and can account for up to 3 wt% of the total C (Cody and Alexander 2005; Huss and Lewis 1995; Lewis et al. 1987). A characteristic feature of C δ diamonds is their uniform size distribution with a mean diameter near 2 nm (Daulton et al. 1996; Fraundorf et al. 1989). At least some of the C δ diamonds are believed to be presolar, based on their anomalous Xe and Te isotopic ratios (Huss and Lewis 1994; Richter et al. 1998).

A host of mechanisms have been proposed for the formation of C δ diamonds (e.g., see Heymann 2001), including formation in supernovae outflows (Tielens et al. 1987), direct condensation of C gas (Nuth 1987), in a process akin to chemical vapor deposition (Joergensen 1988), grain-grain collisions in the interstellar medium (Tielens et al. 1987), high-energy irradiation of graphitic materials (Daulton et al. 2001), and by UV irradiation of C-rich ice mixtures (Kouchi et al. 2005). The presolar nature of C δ diamonds is not universally accepted since their paucity in interplanetary dust particles, which are derived from comets and asteroids, are thought to argue against a presolar origin (Dai et al. 2002).

There is observational evidence for diamonds outside the solar system in circumstellar regions of the pre-main sequence stars HD 97048 and Elias 1 (Habart et al. 2004; van Kerckhoven et al. 2002). This identification is based on

similarities between laboratory spectra of H-terminated diamond and IR emission bands for diamonds. The diamonds around the pre-main sequence stars differ spectroscopically from C δ diamonds since their emission bands around 3.41 and 3.50 μm match particles larger than 50 nm, i.e., an order of magnitude larger than the typical C δ diamonds (Jones et al. 2004). Thus, the identification of C δ diamonds outside the solar system is still open to debate.

It is because of the small sizes of C δ diamonds that their surfaces contribute significantly to their chemical and physical properties, since ~25% of the C atoms belong to the surface (Jones and d'Hendecourt 2000). These surface atoms exhibit bonding states that differ from the bulk and impart chemical and physical properties not present in the bulk (Jones and d'Hendecourt 2000; Jones et al. 2004; Mutschke et al. 2004; Peng et al. 2001). The C K edge of C δ diamonds acquired with an energy resolution of ~1 eV shows a peak near 285 eV that is attributed to sp²-bonded C at the surfaces of the diamond particles (Bernatowicz et al. 1990; Blake et al. 1988; Mykhaylyk et al. 2005). Further, high spatial resolution scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopic (EELS) measurements confirm the bonding differences between bulk and surface states of nanodiamonds (Belobrov et al. 2003; Peng et al. 2001).

Here we provide high-resolution EELS data at the C K edge of C δ diamonds extracted from the Orgueil meteorite. These data are compared with those of natural single-crystal diamond and crystalline and poorly ordered C and the spectral

differences discussed in terms of bonding and structure. Revealing the unique structure and electronic properties of these presolar meteorite grains can provide an important complement to astronomical observations.

EXPERIMENTAL METHODS

EELS data were acquired with a VG HB5 STEM operating at 100 keV and equipped with a cold-field-emission gun (FEG). The energy resolution was ~ 300 meV, as measured by the FWHM of the zero-loss peak. A probe size of ~ 1 nm diameter was scanned over the sample. The microscope was operated with a probe semi-angle of 11 mrad, a collection angle of 12.5 mrad, and a probe current of ~ 0.5 nA. Spectra were recorded with a Gatan 666 electron energy-loss spectrometer attached to the top of the microscope column. The spectrometer was calibrated against the Ni L_3 -edge of NiO that has a peak maximum at 853.2 eV. The diamond spectra were further calibrated during processing by assigning the excitonic diamond peak to 289.2 eV (Morar et al. 1985).

The EELS spectra were acquired with a dispersion of 0.1 eV per channel. The EELS data were obtained from areas 10×10 nm, with acquisition times ranging from 2 to 8 s. For each core-loss edge recorded, three additional spectra were collected: the dark current for the core-loss edge, the low-loss region, and its corresponding dark current. Before presenting the core-loss edges, the following processing was performed: dark current subtraction, removal of an AE^{-1} background from beneath the edge, deconvolution of multiple scattering effects, and deconvolution of the point spread function (Egerton 1996).

High-resolution TEM (HRTEM) images were acquired with a 200 keV Tecnai F20, with a Schotkey field-emission source and a point-to-point resolution of 0.24 nm. Images were captured on a 1K CCD GIF camera, with an electron optical magnification of 1.4–1.6 Mx. The HRTEM images were recorded near Scherzer defocus without an objective aperture.

The diamond-containing residues were obtained from the Orgueil meteorite through a combination of HF/HCl digestion and chromate and perchloric acid oxidation followed by centrifugation. The dried residues were redispersed in an isopropanol/water mixture and a small drop of the C δ diamonds in suspension was deposited onto a Cu TEM grid coated with lacey C film. Images and spectra were acquired from thin aggregates overhanging the holes of the lacey C film. Samples of the unprocessed, disaggregated meteorite and the residue after HF/HCl digestion but prior to the chromate and perchloric acid oxidation were also examined.

RESULTS

A typical thin area of the C δ diamond residue shows grains in the 1–10 nm size range aggregated together with a

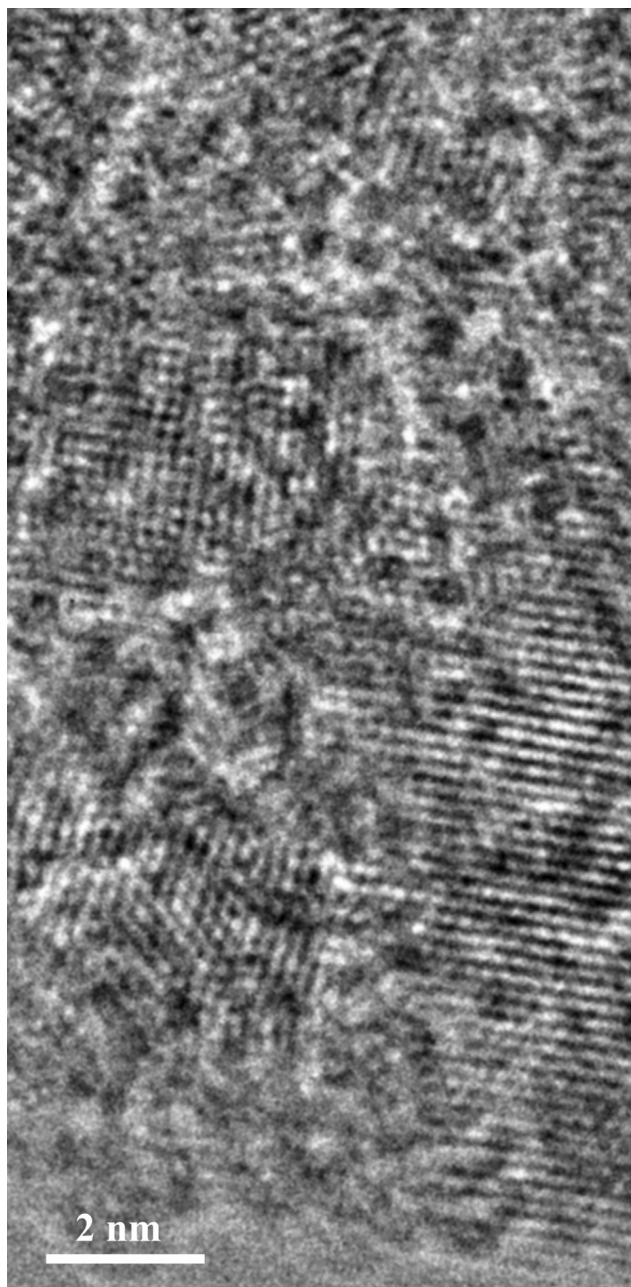


Fig. 1. An HRTEM image of a thin area of C δ diamond extract.

minor amount of disordered intergranular material (Fig. 1). Occasional crystals of SiC are also encountered. Individual diamonds are visible by their prominent 0.206 nm (111) lattice spacing. Occasional crystals in the $\langle 110 \rangle$ zone axis orientation show the cross-lattice fringes. Some crystals show a cross-hatched pattern with a 0.202 nm spacing, which were identified as the hexagonal C allotrope lonsdaleite (Daulton et al. 1996).

The core-loss EELS spectrum of the C δ diamond is dominated by the C K edge, with weak spectral intensity from N and O K edges. Spectra acquired from separate $\sim 10 \times 10$ nm regions show no discernable spectral differences. The

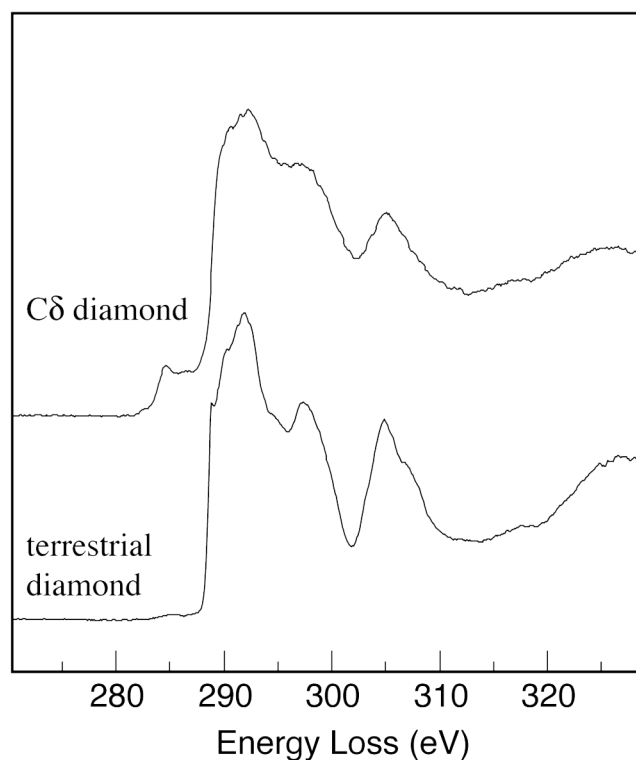


Fig. 2. The C K edges of C δ diamond and terrestrial single-crystal diamond.

C K edge of C δ diamond can be divided into the weak spectral intensity below 288 eV and the main edge above (Fig. 2). The spectra of C δ and terrestrial diamond show differences and the reasons are discussed below. The spectra of the synthetic and terrestrial sp²- and sp³-bonded materials are described first in order to understand the origins of their spectral features. The spectrum from C δ diamond is then described and compared with the spectra from the terrestrial samples.

Spectra of C₆₀, amorphous C, and graphite have a sharp peak near 285 eV (Fig. 3), which is attributed to transitions from the C 1s core level to π^* -antibonding states and is indicative of sp²-bonded C. Transitions above 290 eV are assigned dominantly to σ^* states (Martins et al. 1991). The more complex spectrum from C₆₀ compared to graphite reflects transitions to the unoccupied molecular orbital-like states of the C₆₀ molecules (Terminello et al. 1991). These spectra represent transitions for the bulk material, with only minor contributions from surface states.

In contrast to the dominantly sp²-bonded C-rich materials, the spectrum from the terrestrial single-crystal diamond exhibits minimal spectral intensity below 288 eV. The spectrum is similar to that from clean diamond acquired by X-ray absorption spectroscopy (XAS) (Morar et al. 1986) and EELS (Bernatowicz et al. 1990; Blake et al. 1988). This spectrum is explained by transitions to unoccupied σ^* and π^* states, with the lowest lying states of σ^* character. The sharp feature at 289.2 eV is caused by transitions to the C 1s

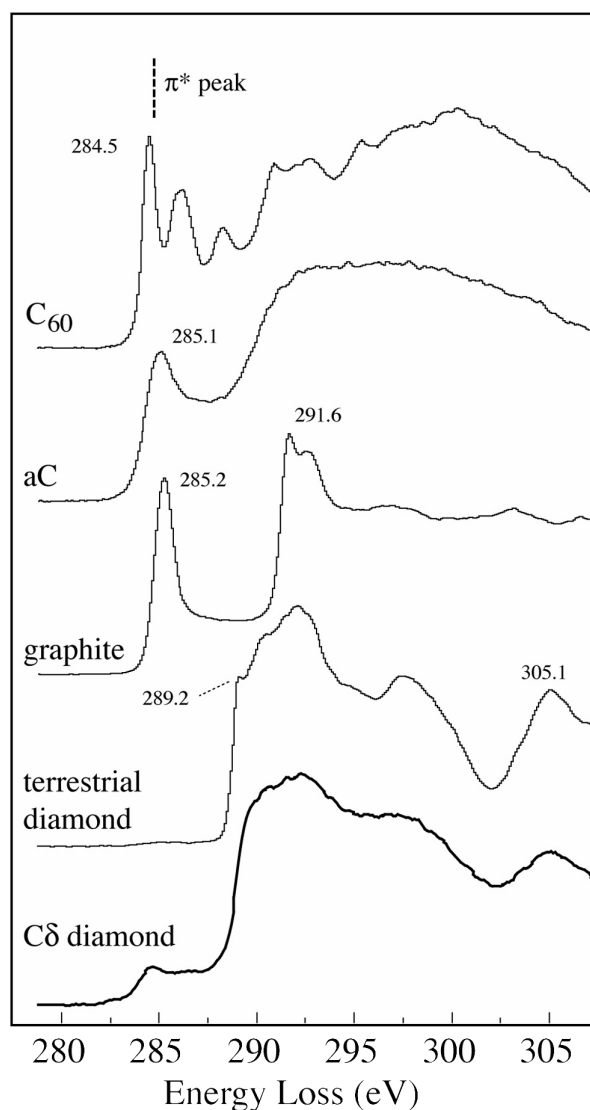


Fig. 3. C K edges of C δ diamond, single-crystal terrestrial diamond, graphite, arc-deposited amorphous C (aC), and C₆₀.

bulk core exciton (Morar et al. 1985), which is 0.25 eV below the conduction band minimum (Graupner et al. 1999).

The C K edge of the C δ diamond has the same overall shape as the spectrum from the single-crystal terrestrial diamond but with significant spectral intensity below 288 eV and broadened spectral features above. Similar spectral intensity below 288 eV has been recorded for C δ diamonds from a range of carbonaceous chondrites (Bernatowicz et al. 1990; Blake et al. 1988; Mutschke et al. 2004) and from synthetic nanodiamonds (Belobrov et al. 2003; Peng et al. 2001). The C 1s bulk core exciton peak is not visible in our C δ diamond spectra, consistent with its broadening in nanodiamonds (Raty et al. 2003). The high-energy resolution resolves the spectral intensity near 285 eV into three distinct features E₁ to E₃ and a partially resolved feature E₄ that sits on the tail of the main diamond ionization edge (Fig. 4). The

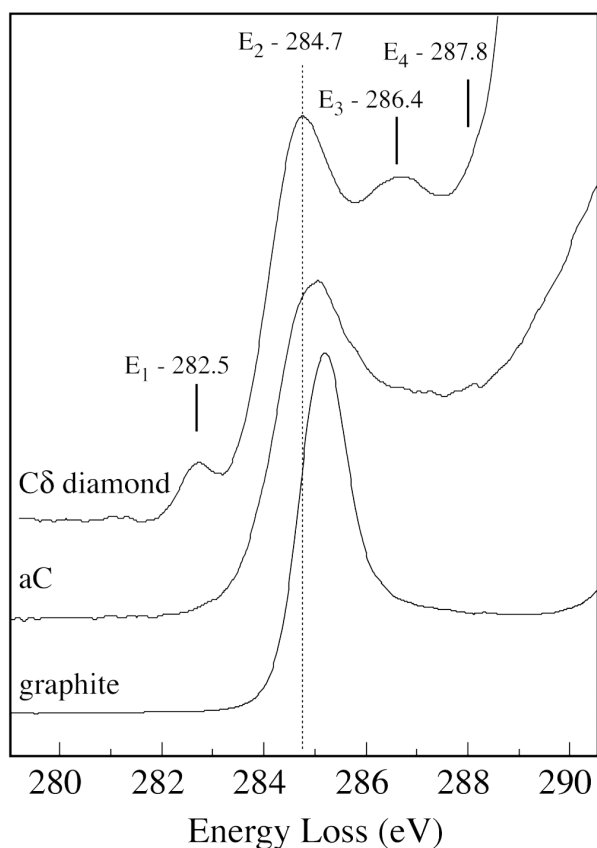


Fig. 4. Spectral intensity below 290 eV from C δ diamond, amorphous C (aC), and graphite. E₁ to E₄ refer to features described in the text.

sharp feature E₂ is at a lower energy than the π^* peak of graphite and aC. The π^* peak of graphite is narrow and symmetrical, whereas that of aC is broad, asymmetrical, with a partially resolved feature near 284.7 eV. There are no spectral features in aC or graphite corresponding to E₁, E₃, or E₄ from the C δ diamonds (Fig. 4).

Spectra of C δ diamonds were also acquired from the unprocessed meteorite and the HF/HCl acid residues. In the raw meteorite, the C δ diamonds are embedded in small, discrete patches of poorly ordered, dominantly sp²-bonded C. This C δ -bearing C is commonly N-rich. The EELS spectrum from the poorly ordered C shows a sharp peak at 285 eV, which is attributed to transitions to unoccupied π^* states of sp²-bonded C (Fig. 5). The intense peak at 285 eV from the poorly-ordered C masks the relatively weak intensity peaks below 288 eV from the C δ diamonds. A similar situation was encountered with the C δ diamonds in the HF/HCl residue, which is dominated by an insoluble organic material (IOM), which has a high degree of aromaticity (e.g., Cody and Alexander 2005; Garvie and Buseck 2006). The C δ diamonds are embedded in the poorly ordered C of the residue. It is therefore not possible to identify the spectroscopic features below 288 eV from the C δ diamonds because of the interference from the surrounding sp²-bonded C.

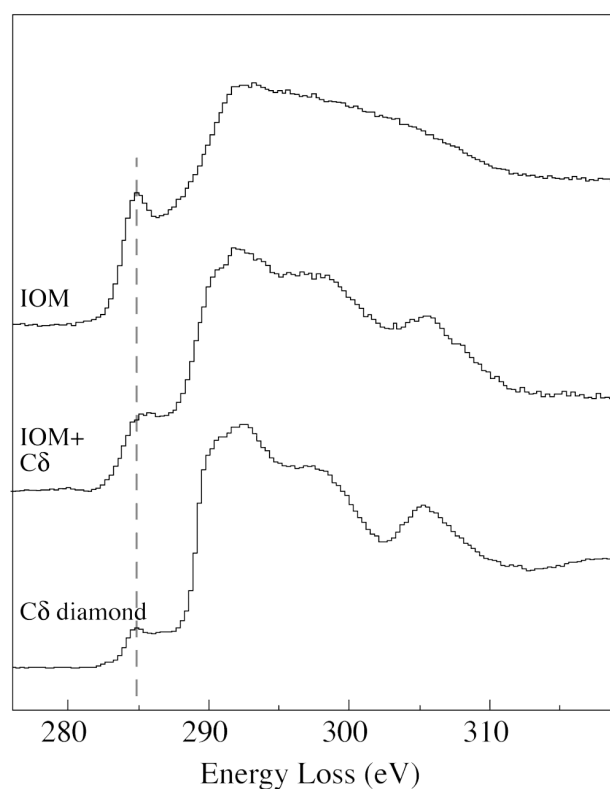


Fig. 5. Comparison of the C K edge from C δ diamond with spectra from diamond-free poorly-ordered C (IOM) and IOM with relatively high numbers of C δ diamond particles (IOM + C δ).

DISCUSSION

The high-resolution EELS spectra of the C δ diamonds reveal near-edge structure not present from the bulk terrestrial single-crystal diamond (Figs. 2 and 5). The peaks below 288 eV are attributed to transitions from the C 1s surface core level to unoccupied surface states (Morar et al. 1986). XAS spectra of diamond and diamond-like surfaces show a wealth of spectral features not present in the bulk, the energies and intensities of which depend on surface chemistry and structure (Bobrov et al. 2001; Graupner et al. 1997; Graupner et al. 1998; Graupner et al. 1999; Kono et al. 2005; Morar et al. 1986). Nanodiamond surfaces contain locally reconstructed superstructures on (111) and (100) facets, together with chemisorbed species, primarily H (Peng et al. 2001). The surface may also restructure to a fullerene-like configuration (Raty et al. 2003).

Determining the origin of the C δ diamond spectral features below 288 eV depends on knowing the position of the Fermi level (E_F) relative to the valence band maximum (E_{VBM}) and the conduction band minimum (E_{CBM}). Peaks below E_F are interpreted as surface core excitons whose energies are influenced by strong electron-hole interactions (Morar et al. 1986). States above E_F are assigned to unoccupied dangling-bond surface states (Morar et al. 1986).

The E_{CBM} for diamond is 0.25 eV above the C 1s bulk

core exciton energy (Graupner et al. 1999) and E_{VBM} is 5.47 eV below E_{CBM} . Hence, $E_{\text{CBM}} = 289.45$ eV and $E_{\text{VBM}} = 283.98$ eV. Since E_{F} has not been measured for C δ diamonds, we use a value determined for the hydrogenated diamond surface (Bobrov et al. 2001), given the evidence for C-H bonding (see below). The E_{F} is 0.42 eV above E_{VBM} giving $E_{\text{F}} = 284.4$ eV (Bobrov et al. 2001).

Peak E_1 is equivalent to the 282.5 eV peak from the diamond C(100)–(2 × 1) surface, and is assigned to a surface core-exciton state arising from single dangling bonds of a partially hydrogenated surface (Bobrov et al. 2001). It is absent on the H-free as well as fully hydrogenated diamond surfaces. This peak was also recorded from the diamond (111) surface (Morar et al. 1986).

Interpretation of E_2 is complicated by its proximity to E_{F} and also by its similar energy to the π^* -peak of sp^2 -bonded C. In the discussion above the value for $E_{\text{VBM}}-E_{\text{F}}$ is taken as 0.42 eV as measured by Bobrov et al. (2001). Since the energy of E_2 is greater than E_{F} this feature is assigned to an unoccupied surface state with C-H bonding. On the other hand, $E_{\text{VBM}}-E_{\text{F}}$ has been measured between 0.5 and 1.3 eV (Kono et al. 2005 and references therein). If E_{F} is greater than E_2 , then the origin of this feature can be described as a surface core exciton state. This peak may also correspond to sp^2 -bonded C of a fullerene-like surface (Barnard et al. 2003; Raty et al. 2003).

Feature E_3 corresponds to transitions to unoccupied π^* -antibonding states of surface π -bonded dimers (Bobrov et al. 2001; Graupner et al. 1999). A similar peak from nanodiamonds was explained as arising from a C-bonded surface reconstruction to a fullerene-like surface (Raty et al. 2003).

The shoulder, E_4 , is attributed to transitions from the C 1s level to unoccupied σ^* antibonding states of H bonded to a diamond-like C atom and to hydrocarbon adsorbates (Graupner et al. 1999; Laikhtman and Hoffman 2003; Ray et al. 2004). A large variety of saturated hydrocarbons exhibit an ionization feature around 287.5 ± 0.3 eV (Graupner et al. 1999 and references therein).

The C δ diamonds have experienced a long and complex history starting with their formation in circumstellar environments, irradiation in interstellar space, aqueous alteration in asteroidal parent bodies, and finally laboratory HF/HCl acid dissolution. Some of the post-formation processes may have affected the surface bonding characteristics, although it is impossible to know to what extent. The EELS measurements on residues from Orgueil and a range of CC meteorites (Garvie, unpublished data) including Murchison (CM2), Tagish Lake, and Acfer 214 (CH) show that C δ diamonds are heterogeneously distributed in the residue particles, where they are usually embedded in a poorly ordered, N-rich carbonaceous material. The C δ diamonds are also found in the poorly ordered, N-rich carbonaceous material from the untreated, disaggregated Orgueil meteorite, showing that this association is not an

artifact of the acid dissolution process. It is unknown whether the surface electronic states measured from the C δ diamonds in the residue also occur for the diamonds in the C in the unprocessed meteorites since the intense π^* peak of the amorphous C masks the weak spectral features associated with the surface electronic states of the C δ diamonds.

Given the uncertainties on where and how the measured C δ diamond surface electronic states originated care is needed in interpreting particular spectral features to specific astrophysical phenomena. The interpretations of the spectral features of the C δ diamonds in the band gap below the main diamond edge show the presence of C-H bonding on the C δ diamond surfaces. This interpretation is in accordance with IR measurements that show a variety of surface-bonded O, H, and N groups (Andersen et al. 1998; Braatz et al. 2000). The high-energy resolution EELS spectra are necessary to resolve the spectral features. The surface-related spectral features are of weak intensity compared to the main diamond C K edge requiring data with a high signal-to-noise ratio.

CONCLUSIONS

The C K edge of C δ diamonds from the Orgueil meteorite show a wealth of spectral structure that is interpreted as arising from surface electronic states. These states are absent from bulk diamond. The C K edge shows spectral features that are attributed to C-H bonding, and may also suggest a particular surface structure corresponding to the recently described fullerene-like surface reconstruction of bucky diamonds (Barnard et al. 2003; Raty et al. 2003). These results can be used to further our understanding of C δ diamond structure, chemistry, and electronic states. These surface electronic states are expected to affect the optical properties, which are dependent on features such as extent of H coverage, particle size, and surface structure.

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