Abstract. We performed ion irradiation experiments on diamond samples at room temperature, probed by in-situ Raman spectroscopy. Different ions are used with energies of 200 or 400 keV. The intensity of diamond Raman band (at 1332 cm⁻¹) decreases exponentially as the ion fluence increases. Results from different ions demonstrate that this effect is due to changes in the optical properties of the damaged samples and is correlated with the energy lost by ions through elastic collisions with target nuclei. Amorphous carbon (sp²) is formed after a threshold of about 2x10²² vacancies/cm³, or about 16 eV/C-atom deposited by elastic collisions. The peak position and full width at half maximum of the D-line and G-line of the synthesized amorphous carbon are studied. A comparison is made between the amorphization of diamond and that of graphite, forsterite, and water ice crystals. A linear relationship is found between the amorphization dose and the displacement energy. The results are discussed in view of their relevance in astrophysics.

1. Introduction
Several ion implantation studies on diamond have been performed for over 30 years, mainly for the purpose of doping diamond (with many applications to electronics) [1, 2], and focusing also on the transformation of diamond (sp³ hybridization) into a graphite-like sp² bonded carbon, sometimes referred to as amorphous carbon (aC) [2, 3, 4]. It was found that damage beyond the amorphization threshold leads, upon thermal annealing, to relaxation of the diamond structure to graphite for sub-MeV ion irradiation, while for MeV alpha particles irradiation annealing restores the original diamond structure [2]. The threshold for the sp³-sp² conversion and the resulting aC properties strongly depend on the implantation temperature [4, 5].

Also in astrophysics there is interest in diamonds, since nano-sized diamond grains (also called nanodiamonds) have been found in carbon-rich meteorites [6, 7] (carbonaceous chondrites) and diamond-like carbon absorption [8] and emission [9] features were observed in the infrared spectra of protostars and dusty envelopes surrounding stars. Several mechanisms for nanodiamonds formation have been proposed [10, 11]. It has been also suggested that ion implantation could explain the presence of trapped noble gas observed in meteoritic nanodiamonds [12].

Furthermore the interaction between diamonds and fast ions is part of the more general issue regarding ion irradiation processing of solids, and its application to astrophysics [13, 14]. In our Laboratory of Experimental Astrophysics, several ion irradiation experiments have been performed on silicates, frozen gases and carbons; in particular different carbonaceous materials have been irradiated [15, 16].
Raman spectroscopy is a useful technique in studying structural properties and damage effects, in particular that of carbonaceous materials, and thus it can be used to gain insight into the structural damage of solid materials resulting from ion bombardment, as in the case of implanted diamond [2].

2. Experimental details
Ion irradiation effects on diamonds at room temperature are here studied using in-situ Raman spectroscopy. Diamond samples are obtained with the chemical vapor deposition technique (from the Fraunhofer Institute, Germany); our samples have an area of 1 cm\(^2\) and a thickness of 100 ± 15 µm. The analyses are performed in a stainless steel vacuum chamber facing a Raman spectrometer. Depending on the wavelength of the exciting laser radiation, Raman spectroscopy is much more sensitive to the sp\(^2\) with respect to the sp\(^3\) hybridization [17], as it is in our case where a visible laser is used. Indeed, a continuous Ar ion laser beam (514.5 nm) is used as exciting radiation (power of about 15 mW on the sample). Since the virgin diamond is transparent at 514.5 nm, the laser radiation penetrates the whole sample thickness. A CCD camera is used as detector and the spectral resolution is about 3 cm\(^{-1}\). Further details of the experimental arrangement used for Raman spectroscopy can be found elsewhere [18].

Inside the stainless steel vacuum chamber the pressure is kept below 10\(^{-7}\) mbar and the diamond samples are in contact with a silicon substrate. The vacuum chamber is interfaced to an ion implanter (Danfysik 1080-200) from which ions with energy from 30 keV up to 200 keV (400 keV for double ionization) can be obtained; the ion beam produces a circular (1.5 cm in diameter) spot on the target. Ion currents are lower than 2 µA cm\(^{-2}\) to avoid macroscopic heating of the sample. The sample holder is mounted at an angle of 45° both with the ion beam and with the incoming Raman laser beam, so that spectra can be easily taken in-situ, even during ion irradiation, without tilting the sample. UV-Vis transmittance spectra of the samples are collected ex-situ.

Table 1. The ions used in the experiments, with the energy, maximum fluence, and mean penetration depth in the diamond target.

| Ion     | Max fluence (10\(^{16}\) ions/cm\(^2\)) | Mean penetration depth (nm) |
|---------|----------------------------------------|-----------------------------|
| H\(^+\) (200) | 1.4                                    | 620                         |
| He\(^+\) (200) | 2.1                                    | 370                         |
| Ar\(^{++}\) (400) | 0.17                                   | 140                         |
| Ar\(^+\) (200) | 4.2                                    | 72                          |

Diamond samples have been irradiated with ions and maximum fluences as given in Table 1. The ion mean penetration depth (R\(_p\)) is a function of the ion energy, ion mass, and of the properties of the target (see Table 1); it can be estimated by simulation programs such as the SRIM code. The stopping power (energy deposited per unit path length) is also a function of the ion energy and mass; ions release energy to the target atoms by elastic and inelastic collisions. The amount of elastic vs inelastic energy loss is as well a function of ion energy and mass, and slightly depends on the target material. In order to compare the effects of different ions we evaluate the number of displacements/cm\(^2\) and the number of displacements/cm\(^3\), that are: displ/cm\(^2\) = (displ/ion)(ions/cm\(^3\)); displ/cm\(^3\) = (displ/cm\(^2\))/R\(_p\). These two parameters are sensitive to the amount of energy released by elastic collisions to the target nuclei. The number of displ/ion can be evaluated by using the SRIM code [19].
3. Results

The diamond Raman spectra have been collected with increasing ion fluence, as shown in Figure 1. The three panels focus on the first order diamond Raman band and the aC band spectral region; the diamond band is seen at 1332 cm\(^{-1}\) with a FWHM (Full Width at Half Maximum) of about 4 cm\(^{-1}\) and no variations are observed in peak position and FWHM of the band during irradiation.

In all of the experiments the first order diamond Raman band area decreases progressively to zero as the ion fluence increases, as shown in Figure 2, where the normalized band area is plotted versus the number of displ./cm\(^2\). The behavior is that of an exponential decrease that we fit by: area = \(\exp[-A(d+d_0)]\), where \(d\) is the number of displ./cm\(^2\) and the cross section is \(A = (4.0 \pm 0.5) \times 10^{-18} \text{ cm}^2\). The parameter \(d_0\) takes into account the effects of uncertainties (of the order of a few percent) mainly due to the measurement of the ion fluences, and it is the same for all the implant species. The results clearly support the dependence of the effects on the energy released by elastic collisions.

The elastic collisions between ions and target nuclei cause a change of the optical properties, the diamond sample gets darker in the UV-Vis range, and the incoming laser radiation at 514.5 nm is absorbed in the damaged layer; the laser radiation penetrates the whole sample thickness (about 100 \(\mu\)m) in the undamaged diamond lattice, while it is more absorbed after progressive ion fluences, so the diamond band area decreases as the damage increases. This implies that the fraction of the signal in Figure 1 that comes from the unmodified target decreases following the curve in Figure 2, while the fraction of the signal coming from the damaged volume, whose depth is in the order of 0.5-1 \(\mu\)m, increases in the inverse proportion. The band at 1332 cm\(^{-1}\) of Raman shift corresponds to a wavelength of about 550 nm under the excitation of the 514.5 nm laser. We have then verified that the diamond transmittance at 514.5 and 550 nm decreases as the damage increases [18].

Amorphous carbon (sp\(^2\) hybridization) is formed during He\(^+\) and Ar\(^{++}\) ion irradiation, while it is not formed with H\(^+\) ions, because the displ./cm\(^3\) for the highest H\(^+\) dose are below the amorphization threshold. A broad band is observed in the Raman spectra at about 1550 cm\(^{-1}\) (Figure 1), typical of highly disordered sp\(^2\) layer. The spectra have been compared with those of interplanetary dust particles (IDPs) and meteorites and with other ion irradiation experiments of carbonaceous materials [16].
Figure 2. The normalized diamond band area versus the number of displacements $\text{cm}^{-2}$ in the four irradiation experiments; an exponential fit is also shown.

Figure 3. The dose $D_A$ needed to reach 80% of amorphous versus the displacement energy, for the four given material. For water ice we use the value of the O-H bonding energy and the total dose. A linear fit is shown.

An example of the resulting Raman spectra of the irradiated volume is reported in the right panel of Figure 1, showing also that G-line and D-line peak position and FWHM are calculated by a two peaks Lorentzian fit. G-line and D-line values lie in the range of respectively:

- G-peak pos. = 1515-1550 cm$^{-1}$, G-FWHM = 200-250 cm$^{-1}$;
- D-peak pos. = 1300-1330 cm$^{-1}$, D-FWHM = 300-500 cm$^{-1}$.

The previous values are typical of highly disordered aC. The peak intensity of the aC band has been studied as a function of the ion fluence, i.e. as a function of the number of displ./cm$^3$. We found that aC is formed beyond a threshold of about $D_c = 2.5 \times 10^{22}$ displ./cm$^3$, with about $2 \times 10^{22}$ vacancies/cm$^3$; this is close to what reported by other authors [1, 2, 5]. We can also estimate the mean energy deposited per ion in elastic collisions; we obtain $\epsilon = 16 \text{ eV/C-atom}$ from our data, and $\epsilon = 12 \text{ eV/C-atom}$ and $\epsilon = 15 \text{ eV/C-atom}$ from the data of Prawer and Kalish [4] at room temperature for C 100 keV and Xe 320 keV respectively.

The volume density of displacements is relevant: when the damaged regions in the lattice at certain critical doses overlap, the whole implanted volume changes into an sp$^3$ rich carbon.

We studied the aC peak position versus the number of displ./cm$^3$. At first the peak position, which is essentially the G-line peak position, is 1545 cm$^{-1}$, then shifting toward 1515 cm$^{-1}$ at the higher doses. This shift is also observed in several ion irradiation experiments of different carbonaceous materials (graphite, hydrogenated amorphous carbon grains, C-rich frozen mixtures, etc.) [16] and is indicative of an evolution toward an highly disordered material, as already remarked.

A comparison can be made between the amorphization doses of four different solid material relevant to astrophysics: water ice, forsterite, graphite, and diamond. Using the experimental data reported elsewhere [14, 16, 18, 20] we have calculated the doses $D_A$ needed to reach about 80% of amorphous material, in the four cases. Those values are reported in Table 2.

The amorphization mechanisms are different: diamond, graphite, and forsterite amorphize under the effects of the elastic dose released by the ions to the sample, while water ice is amorphized by the
effects of the total dose, i.e. both the contribution of the elastic and inelastic energy loss. Among these four materials, diamond is the hardest to be amorphized.

We have then plotted the experimental values of Table 2 versus the values of the displacement energy for the considered materials. For water ice we used the value of the O-H bonding energy. The resulting plot is given in Figure 3, with a linear fit of the data: \[ D_A (\text{eV/amu}) = a + m E_D (\text{eV}) \], where \( a = -0.03 \pm 0.05 \) and \( m = 0.022 \pm 0.003 \). The fit is good (\( r = 0.98 \)), confirming that the mechanisms of amorphization for these four materials have been rightly understood. Furthermore, since the linear trend shown in Figure 3 is valid for such different materials (ices, silicates, carbons), it may also act as a prediction for other species and compounds.

**Table 2.** The doses \( D_A \) needed to reach about 80% of amorphous material as derived from four different ion irradiation experiments.

| Irradiated material | \( D_A \) dose to reach 80% of amorphous (eV/amu) | Derived from the data in ref. |
|---------------------|-------------------------------------------------|------------------------------|
| Water ice           | 0.095\( \pm \)0.02 (total dose)                 | Leto and Baratta [20]        |
| Forsterite          | 0.45\( \pm \)0.05 (elastic dose)                | Brucato et al. [14]          |
| Graphite            | 0.55\( \pm \)0.05 (elastic dose)                | Baratta et al. [16]          |
| Diamond             | 1.29\( \pm \)0.04 (elastic dose)                | Brunetto et al. [18]         |

4. Astrophysical implications

Dust grains form in stellar outflows and in supernova ejecta. It is known that a number of these grains, often referred to as pre-solar grains, are included in primitive meteorites. These grains, mainly made of diamond, silicon carbide, graphite, corundum, and silicon nitride, are studied in the laboratory and detected by their isotopically anomalous composition [21].

It is generally accepted that pre-solar nanodiamonds are formed in circumstellar environments, expelled in the cold interstellar medium (ISM) and eventually included into solid objects in the Solar System (asteroids and/or comets) that are the parent bodies of the meteorites. Newly formed nanodiamonds can be exposed to ion irradiation during their stay in circumstellar environments, such as the ISM, or in the solid objects in the Solar System. As suggested by our experiments, ion processing modifies the grains which in some instances are converted into aC. A fraction of diamonds are not amorphized, probably buried deep inside the rocky body, or because they have not been exposed to high enough damage by cosmic ions.

Laboratory results obtained after ion irradiation experiments can be extrapolated to the astrophysical environment if we understand the physical mechanism which causes the observed effect. Solid state effects as those here studied are caused by particles with high L.E.T. (Linear Energy Transfer) i.e. having energies in the keV-MeV range. The energies of cosmic ray and stellar wind particles span a range larger than that used in laboratory experiments. In the present case we focus on the result that the amorphization of irradiated diamond depends on the energy released by elastic collisions, whatever is the colliding ion. Thus a comparison of laboratory results is possible if cosmic particle fluxes are known and the energy fraction lost by elastic collision is estimated.

As discussed by Brucato et al. [14] dust particles exposed to a supernova shock (average ion energies of a few keV) suffer, in the low density ISM, a dose of at least 200 eV/C-atom due to elastic collisions. This dose is higher than the laboratory threshold value (16 eV/C-atom) needed to cause the amorphization of bare diamond grains (i.e. not covered by other materials such as silicates, carbons and ices). This would imply that diamond nanocrystals observed in meteorites have not been exposed to a supernova shock.

As stated above, it is believed that comets are rich of pre-solar grains, such as nanodiamonds. Using the threshold value (16 eV/C-atom) here reported and the estimated values of ion fluxes and energy deposition of cosmic ions in the Oort Cloud [22], we estimate that in 10^7 years (lower than the age of the Solar System) cosmic ions can convert nanodiamonds into aC down to a surface depth of
about 10 µm. Below 10 µm the nanodiamonds should remain unaltered, and eventually be observed in meteorites. Thus the only diamond grains that survive are those unexposed to supernova shocks and then protected inside comets, below a depth of about 10 µm.

Amorphous carbon has been observed in carbonaceous chondrites and IDPs. A comparison of the profile of the aC feature observed in IDPs and meteorites [16] with that formed after ion irradiation of diamond shows that in the latter case aC is more disordered. Our results confirm that increasing the ion fluence the FWHM of G-line and D-line of the aC feature increases, and the peak position of G-line shifts toward lower wavenumbers. This could partially explain why Raman spectra of meteorites and IDPs show a large spread of the peak position and FWHM values of their aC feature [16].

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