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Neutron irradiation effects in quartz: optical absorption and electron paramagnetic resonance

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Abstract. Optical absorption measurements in the 3–9 eV energy range and electron paramagnetic resonance (EPR) have been performed at 300 K and at 80 K on Sawyer PQ quartz. Both as-received and neutron-irradiated samples (neutron fluences up to 3×10^{18} neutrons cm^{-2}) have been studied. The absorption spectra have been analysed in terms of a sum of elementary Gaussian components.

The effect of the neutron irradiations is to induce the presence of absorption bands at 7.6 eV (E band), at 7.1 eV (D band) and at 6 eV (E' region).

The most intense peak of all the spectra is the E band (7.6 eV); its shape is complex and the existence of a double structure can be suggested.

The D band is evidenced for the first time in neutron-irradiated synthetic quartz; our measurements show that this structure is correlated with the 6.0 eV band.

The 'E' region is complex; in fact, at the highest neutron fluence the optical absorption spectrum reveals the existence of four structures, at 4.7, 5.2, 5.6 and 6.0 eV, where the 4.7 eV band has the same characteristics as the D_0 band, which is present in amorphous silica. The comparison between the results of EPR measurements and the analysis of the complex structure of this absorption indicates that the correlation between optical absorption bands in this region and the EPR E'-centre signals suggested previously must be re-examined.

1. Introduction

Quartz, the crystalline form of silicon dioxide, is transparent over a wide frequency region, its absorption edge being approximately at 8.5 eV at room temperature (RT) [1]. Ionizing irradiations greatly affect the absorption spectrum of this material, giving rise to several bands in the 2–8.5 eV region. These bands are related to optically active point defects, produced by ionization (as in x-ray and γ -ray and electron irradiations) as well as by displacement events (present in neutron or ion bombardments).

This study has been undertaken in order to clarify the features of the optical absorption in crystalline SiO_2 , and to verify the correlations with EPR data already proposed. Good knowledge of the structure of the optically active defects which are responsible for the near-ultraviolet absorption bands induced in quartz by radiation damage is far from being reached; the data in the literature, mostly belonging to

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papers published several years ago, have been obtained on samples of different (natural or synthetic) or even unspecified origin and are thus difficult to compare.

The most prominent optical absorption structure of irradiated samples is the E band at 7.6 eV, in the vacuum-ultraviolet (VUV) region, observed in both crystalline and amorphous SiO₂. In silica, several workers [2–4] suggested a relation with the peroxy radical defect while, more recently, both the silicon vacancy [5] and the oxygen vacancy [6] have been proposed. This band has a double structure in thermally and optically bleached γ -irradiated quartz and silica [7].

A band at 7.1 eV (called the D band) has been observed, up to now, only in x-ray-irradiated natural quartz [2]. No hypotheses have been made until now on the nature of this band which has also been detected in amorphous SiO₂ irradiated by heavy ions [8].

Finally, in the region of 6 eV, two radiation-induced absorption bands, at 6.2 and 5.4 eV, were detected in early optical absorption measurements [9], but they are not systematically observed in the absorption studies performed up to now; in the earlier work of Mitchell and Paige [2], only one very broad structure centred at 5.7 eV was detected, whose half-width remained constant by lowering the temperature. Later, in addition to the work of Nelson and Weeks [9], other studies showed complex structures, involving additional maxima at 5.6, 5.9 and 6.1 eV. The crystal orientation, type and temperature of the irradiations have been found to affect the spectra [10–12]. All these bands still lack specific attributions, and the structural models pertaining to the defects responsible for their presence in the optical absorption spectrum are unknown. Most of the existing information is related to the paramagnetic point defects and has been reached by EPR spectroscopy studies.

Among the numerous intrinsic defects of quartz, the E' centres are of the utmost importance. These centres are common to both crystalline and amorphous SiO₂ and are related to oxygen vacancies. In quartz, at least three variants of the E' centre, namely E'₁, E'₂ and E'₄, are known to exist, for which reliable models have been suggested on the basis of EPR measurements [13–18]: the E'₁ centre comprises an unpaired electron spin highly localized in an sp³ hybrid orbital of a single silicon located at a normal crystallographic site; the E'₂ and E'₄ centres are variants of the E' centre whose EPR spectra show a hyperfine interaction with a substitutional hydrogen ion in two different configurations [17].

In connection with EPR data [9], an association was suggested between the two absorption bands at 6.2 and 5.4 eV, and the EPR signals due to the E'₁ and E'₂ variants of the E' centre, but this correlation was not confirmed in later work [19].

In order to disentangle the situation which arises from all the heterogeneous results and proposals present in the literature, we performed a systematic set of measurements of optical absorption electron paramagnetic resonance. In particular:

- (i) we carried out the detailed spectral analysis of the near-ultraviolet absorption region,
- (ii) we studied the fluence dependence of the components of the optical spectrum, in order to demonstrate the correlations eventually existing between different optical bands characterized by similar intensity growth versus neutron fluence and
- (iii) finally, we compared the optical absorption data with EPR data on E'-type centres to verify the attribution of the 6 eV absorption region.

Highly pure synthetic quartz was chosen for this study to focus on the intrinsic defect effects on the absorption spectrum. Neutron irradiations were preferred to

simple ionizing treatments because of their higher defect creation yield. Also, a better comparison can be performed with results in the optical literature obtained mainly on samples submitted to this type of irradiation. In the case of EPR spectra, the analysis of the effects of neutron irradiation has been compared with those due to x-rays.

2. Experimental techniques and numerical analysis

2.1. Samples and treatments

The crystalline SiO_2 used in this work was Sawyer PQ, highly controlled synthetic quartz, its aluminium content being less than 13 ppm; samples for the optical measurements were in the form of discs ($d = 10$ mm) cut perpendicular to the optical axis, the two surfaces being polished to an optical grade. The sample thicknesses were 0.3, 1.0 and 4.0 mm depending on the irradiation fluence (see below); the higher the fluence, the thinner the sample used. Samples for EPR measurements were cut into bars (2 mm \times 2 mm \times 2 mm) with an edge parallel to the z crystal axis.

The samples were neutron irradiated with fluences ϕ_n ranging from 3×10^{15} to 3×10^{18} neutrons cm^{-2} at the TRIGA reactor of the Comitato Nazionale per la Ricerca e lo Sviluppo dell' Energia Nucleare e delle Energie Alternative laboratories (Casaccia, Roma). The above mentioned fluences refer to neutrons whose energies are lower than 22.6 eV; these are 68.5% of the total. The sample temperature during the irradiation was $65 \pm 2^\circ\text{C}$.

After the samples had been placed in the reactor, they were exposed also to γ -radiation with doses ranging from 10^1 to 10^4 kGy; however, we rule out any effect of the γ -radiation on our spectra. In fact, Nelson and Crawford [12] have already observed that a neutron fluence of 10^{17} neutrons cm^{-2} induces an absorption spectrum with a similar shape but with much higher strength than a dose of 10^4 kGy γ -rays (which in our irradiation conditions is associated with $\phi_n = 3 \times 10^{18}$ neutrons cm^{-2}).

2.2. Experimental techniques

The relevant information for this work is the variation in the absorption coefficient induced by neutron irradiation; therefore, unless otherwise specified, only the difference between the absorption spectrum of the irradiated samples and the spectrum of a non-irradiated sample of equal thickness will be considered; in this way, we correct also for the reflection losses of the samples.

We measured transmission spectra at 300 K (RT) and 80 K (liquid-nitrogen temperature (LNT)) in a wide spectral range (0.4–9.0 eV). In the 3.5–9.0 eV range a home-made double-beam VUV system was used; spectra between 0.4 and 6.2 eV were measured using a Varian 2300 spectrophotometer. The two systems have different characteristics and performances. The useful optical densities (OD) range and the corresponding precision of the VUV apparatus are 0.0–2.2 and $\pm 1 \times 10^{-2}$. The corresponding features for the Varian spectrophotometer are 0.0–4.0 and $\pm 1 \times 10^{-3}$, respectively. The absolute value of the optical density, which also depends on other operative parameters (such as, for instance, sample alignment), has been estimated to be better than 5×10^{-2} for the two systems.

For the EPR measurements, the samples were mounted on a goniometer in order to change their orientation with respect to the magnetic field direction. The EPR

spectra were detected in the X band (about 9.13 GHz) at RT. Different microwave powers ranging from 10^{-6} to 10^{-1} W were employed to obtain eventual saturation effects; the modulation intensity was kept at about $3 \mu\text{T}$. The estimated sensitivity is about $10^{13} \text{ cm}^{-3} \text{ mT}^{-1}$ which results in a minimum detectable centre density of 10^9 cm^{-3} for the observed linewidths of the signals ($10 \mu\text{T}$).

2.3. Numerical analysis

All the optical spectra have been analysed as a sum of elementary bands that have been assumed to be of Gaussian shape; the limits and the validity of this assumption will be discussed below. Since the number of free parameters is high (typically more than ten), much care had to be paid to the fitting procedure, in order to avoid non-physical solutions of the minimization algorithm. With regard to this problem the following criteria have been followed.

(i) The number of bands for each fit was limited as much as possible; only the bands that are clearly present in the spectra have been considered first. When a poor spectrum reconstruction was obtained, other bands were included in the fits; in these cases, we considered only the bands whose existence had already been reported in the literature from absorption or photoluminescence excitation studies.

(ii) As input values for the peak energies and half-widths we chose the mean of the values in the literature; for the minimization procedure the parameter variation has been limited by taking into account the spread of the data in the literature.

3. Results

3.1. Electron paramagnetic resonance

The EPR spectra of neutron-irradiated crystals show a large number of lines, all induced by irradiation since the spectrum of unirradiated samples is completely flat (figure 1, curves a and b). In order to demonstrate the presence of E' -like centres, EPR spectra have been detected at a low power; in these conditions the signals of the E' -like centres dominate the spectra owing to the long spin-lattice relaxation times of these defects (about 10^{-4} s at room temperature [20]). In particular, the spectrum of the neutron-irradiated samples, with the magnetic field directed along the crystal z axis, shows a strong and narrow line with $g_z = 2.0008$. This line corresponds to the EPR signal of the E'_1 centre†; this defect is present in six inequivalent sites in the quartz structure but, for $B \parallel z$, it gives rise to a single intense line with $g_z = 2.0007 \pm 0.0001$ [16]. For this orientation, the E'_2 centre, characterized by the hyperfine interaction with a hydrogen ion [15, 17], should give rise to a doublet with $g_z = 2.0009$ a.u.¹ HF separation of 0.04 mT [16]‡. Really, weak evidence of this signal may be found in some features at the sides of the main signal of the E'_1 centre; see the arrows in the inset of figure 1, where the restricted spectral region of the E'_1 centre is shown

† The principal values of the g -tensor of the E'_1 centre are 2.0018, 2.0005 and 2.0003 along the directions (specified by the two angles (ϑ, φ) measured with respect to the z and x axes) given by $(114^\circ, 48^\circ)$, $(47^\circ, 343^\circ)$ and $(53^\circ, 118^\circ)$, respectively.

‡ The principal values of the g -tensor of the E'_2 centre are 2.0020, 2.0007 and 2.0005 along the directions $(120^\circ, 208^\circ)$, $(67^\circ, 133^\circ)$ and $(39^\circ, 253^\circ)$ while the principal values of the hyperfine (HF) tensor are $1.5 \times 10^{-4} \text{ cm}^{-1}$, $-0.2 \times 10^{-4} \text{ cm}^{-1}$ and $-0.1 \times 10^{-4} \text{ cm}^{-1}$ along the directions $(126^\circ, 215^\circ)$, $(70^\circ, 140^\circ)$ and $(44^\circ, 257^\circ)$, respectively.

at a lower microwave power. These features have been reproduced in a simulation featuring in addition to the E'_1 signal a double structure which is less intense by a factor of ten and with a doublet separation of 0.04 mT, corresponding to that of the E'_2 centre. No evidence of E'_4 centres, characterized by four lines centred at $g_z = 2.0012$ and separated by 0.48 mT (for $B \parallel z$ and microwave frequency in the X band), [18] has been observed in the neutron irradiated samples analysed. The values of the E'_1 -centre density have been evaluated for different neutron fluences and will be discussed below.

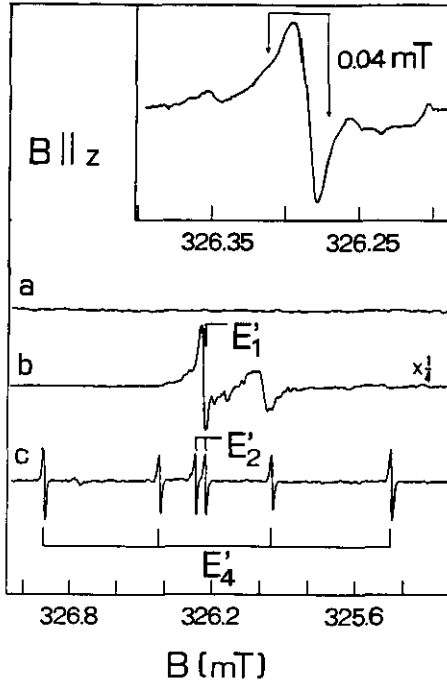


Figure 1. EPR derivative signals of unirradiated (curve a), neutron-irradiated ($\phi_n = 3 \times 10^{17}$ neutrons cm^{-2}) (curve b) and x-ray irradiated (about 10^6 Gy) (curve c) Sawyer PQ crystalline quartz samples; the spectra are detected with the magnetic field parallel to the z -crystal axis. The E'_1 centre line position and the hyperfine structures of E'_2 and E'_4 centres are indicated. In the inset the restricted spectral region of the E'_1 centre signal at slightly different experimental conditions is shown with the features at the sides of the main signal (arrows) suggesting the presence of a weak E'_2 signal.

The predominance of E'_1 centres over the other E' variants seems a peculiar feature of the neutron irradiation; other workers [19–21] failed to detect relevant concentrations of E'_1 centres after x-ray, γ -ray and electron irradiations. In order to obtain a direct comparison between neutron- and x-ray-irradiated crystals, one of the samples was x-ray irradiated at a dose of 10^6 Gy and measured in the same experimental configuration used for neutron-irradiated samples. In fact (see figure 1, curve c), x-ray irradiation gives rise to only E'_2 and E'_4 centres. After a thermal treatment of only 10 min at 300°C , the x-ray-irradiated sample shows the signal of the E'_1 centres, as already observed [9, 22].

3.2. Optical absorption

Measurements performed on both unirradiated and neutron-irradiated samples in the 1.5–3.5 eV region did not allow us to detect the A-band structure associated with substitutional aluminium [23, 24], the most important extrinsic defect in quartz, thus confirming the low impurity content of the material that we studied.

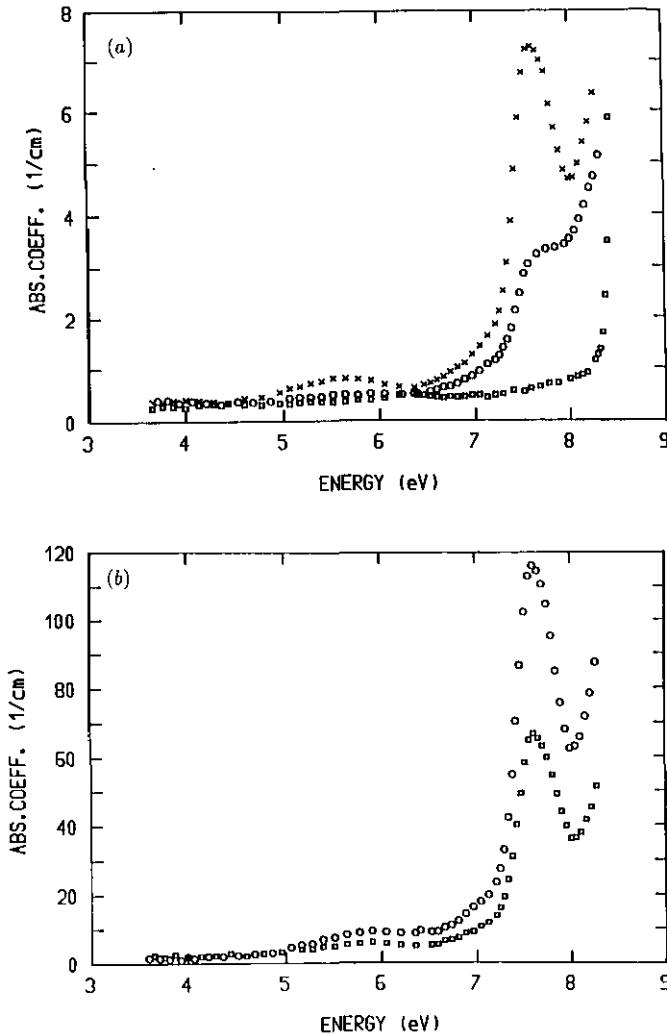


Figure 2. Optical absorption spectra measured at $T = 300$ K (absolute values) of Sawyer PQ crystalline quartz samples irradiated with different neutron fluences: (a) \square , unirradiated; \circ , $\phi_n = 1 \times 10^{16}$ neutrons cm^{-2} ; \times , $\phi_n = 3 \times 10^{16}$ neutrons cm^{-2} ; (b) \square , $\phi_n = 3 \times 10^{17}$ neutrons cm^{-2} ; \circ , $\phi_n = 5 \times 10^{17}$ neutrons cm^{-2} .

In figure 2 we show several spectra at 300 K of specimens irradiated at different fluences; in this case, the absolute value of the absorption coefficients are reported. The following features were found.

(i) The absorption edge, situated in unirradiated samples at 8.5 eV, does not have a well defined shape in the irradiated samples.

(ii) In all the spectra, two main absorptions are present: the first, situated at 7.6 eV, is the well known E band [2, 7] while the second is a very broad band at approximately 5.9 eV, tentatively identified with E'_1 [10, 12].

(iii) Besides these two major structures, a shoulder is present at 7 eV, at the same energy where the so-called D band has been observed in x-ray-irradiated quartz [2].

(iv) All the bands show a significant growth, about two orders of magnitude, when ϕ_n increases from 3×10^{15} to 3×10^{18} neutrons cm^{-2} .

As already pointed out in the previous section, all the spectra have been analysed in terms of Gaussian components and a first choice has been to consider only those bands that are either clearly present in the spectra (E and D) or suggested from the data in the literature (E'_1 and E'_2) [9]; because of its complex shape, the region of the absorption edge has been simulated by two components, namely one exponential tail and one Gaussian band peaking at 8.3–8.6 eV.

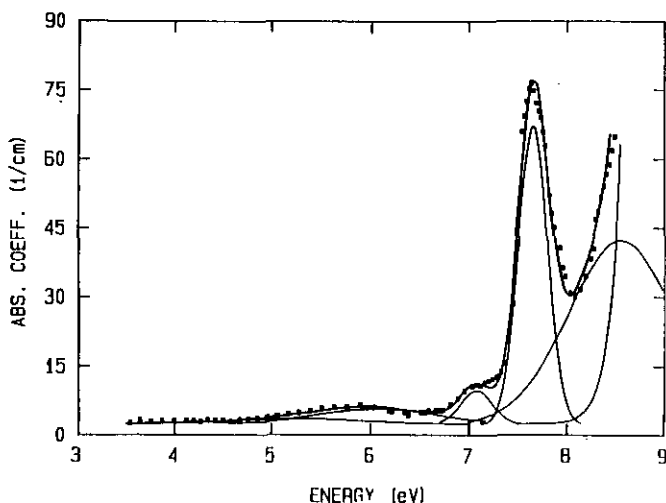


Figure 3. Optical absorption spectrum induced by neutron irradiation ($\phi_n = 3 \times 10^{17}$ neutrons cm^{-2}) measured at 80 K, where the decomposition into Gaussian components is also shown: ■, experimental data; —, Gaussian components; —, calculated spectrum. The peak energies E_m and half-widths ΔE used in the fit are reported in table 1.

Figure 3 shows an example of this kind of decomposition for a spectrum measured at 80 K of a sample irradiated with $\phi_n = 3 \times 10^{17}$ neutrons cm^{-2} . The peak energies and half-widths do not appear to be fluence dependent and so in table 1 we list their mean values. In figure 4 the values of the absorption coefficients of the E and D bands at 80 and 300 K versus neutron fluence are reported. No relevant difference between the data taken at the two different temperatures resulted. Both the bands show a nearly linear behaviour up to neutron fluences of about 10^{18} cm^{-2} .

In figure 5 the values measured at RT of the absorption coefficient of the E'_1 and E'_2 bands are reported as a function of the neutron fluence, together with the EPR data of the paramagnetic E'_1 centre. From these data, one might find a possible confirmation

Table 1. Peak energies E_m and half-widths ΔE of the components obtained from the spectral decompositions. The parameters reported are the mean values and the uncertainties calculated in all the measured spectra, at 300 K and at 80 K. An example of these decompositions is reported in figure 3.

	E_m (eV)		ΔE (eV)	
	RT	LNT	RT	LNT
E'_2	5.35 ± 0.16	5.20	1.49 ± 0.26	1.60
E'_1	5.92 ± 0.10	6.08 ± 0.02	1.07 ± 0.30	1.44 ± 0.22
D	7.06 ± 0.08	7.07 ± 0.08	0.67 ± 0.34	0.56 ± 0.24
E	7.64 ± 0.05	7.65 ± 0.04	0.50 ± 0.06	0.36 ± 0.03

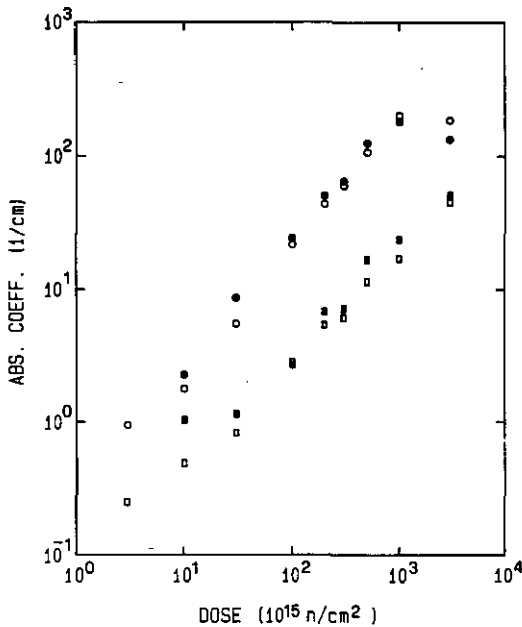


Figure 4. Fluence dependence of the absorption coefficient of the E (O, ●) and D (□, ■) optical bands: □, □, RT measurements; ●, ■, LNT measurements.

of the correlation between optical and EPR data already proposed. However, we shall show that the decomposition of the 6 eV absorption in two bands (E'_1 and E'_2) is not correct and this may affect the reliability of the apparent correlation shown in figure 5.

Actually, this preliminary decomposition of the optical spectra is affected by several discrepancies which are considered in more detail in the following: we shall discuss separately the fits in the high-energy (6.5–9 eV) and in the low-energy (4.0–6.5 eV) region.

It can be noted from figure 3 that the E band is not correctly reproduced by one Gaussian component; its shape appears composite, as figure 6 shows better. In the latter figure, the spectrum from 6 to 9 eV of the same sample reported in figure 3 is analysed by considering two components in the E region. The quality of the fit is definitely better than the corresponding fit in figure 3; an analogous situation has

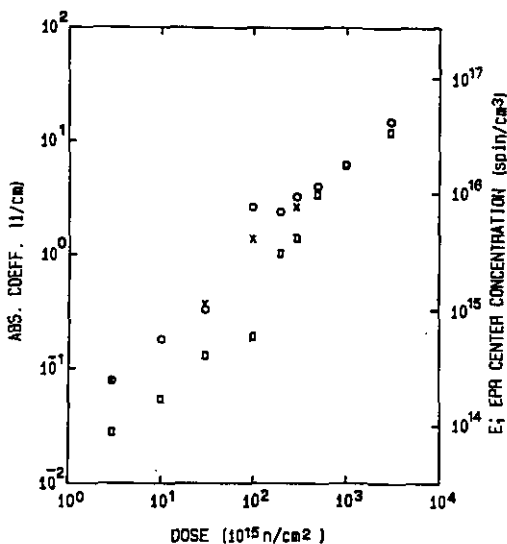


Figure 5. Fluence dependences of the E_1' EPR centre concentration (\times), from EPR measurements and of the absorption coefficient of the ' E_1' ' (\circ) and ' E_2' ' (\square) optical bands. The concentration of the E_2' EPR centre is not shown because the intensity of its signal, which is very weak and superimposed on that of the E_1' centre, is not measurable with sufficient accuracy.

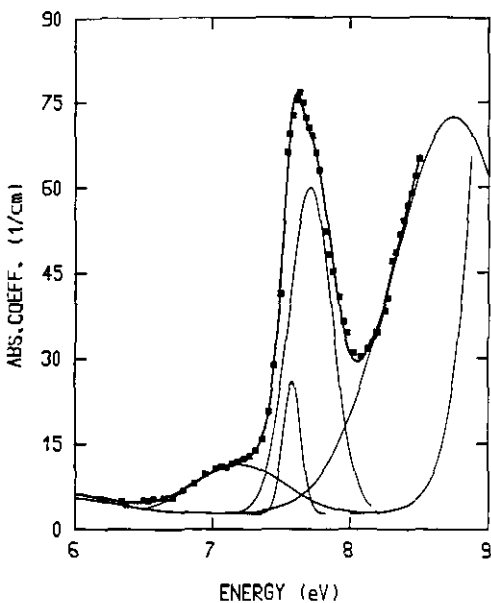


Figure 6. Analysis in Gaussian components in the 6-9 eV region of the same absorption spectrum reported in figure 4, where two Gaussian components in the region of the E absorption band are considered: \blacksquare , experimental data; —, Gaussian components; ---, calculated spectrum.

been found for all the samples that we analysed. We feel that this indicates that different components are present in the spectral region of the E band, in agreement with some data in the literature [7].

However, the dependence of the fitting parameters obtained on the neutron fluence is not regular and the analysis of samples of different thicknesses but irradiated with the same fluences does not give the same ratio of intensities of the two components; this could be due to the difficulty of taking into account the influence of the nearby absorption edge. The choice that we used to fit the edge with the sum of one exponential and one Gaussian band is rather arbitrary and can be tested only when absorption data at higher energies and at higher absorption coefficients are available.

Problems are also present in the E' region: as reported in table 1, the half-widths of the E'₁ and E'₂ components are very large, greater than 1 eV both at 300 K and at 80 K; in particular, the half-width of E'₂ is obtained at the upper limit of the parameter variability range (1.6 eV) and for this reason in table 1 we do not report the errors relative to this band. This result, although in agreement with earlier studies on crystalline quartz [2, 25], is unsatisfactory when compared with analogous data on fused quartz [8, 26] which report half-widths of the corresponding bands lower than 1 eV; in fact, this behaviour is contrary to the expectation of broader bands in vitreous materials because of inhomogeneous broadening effects.

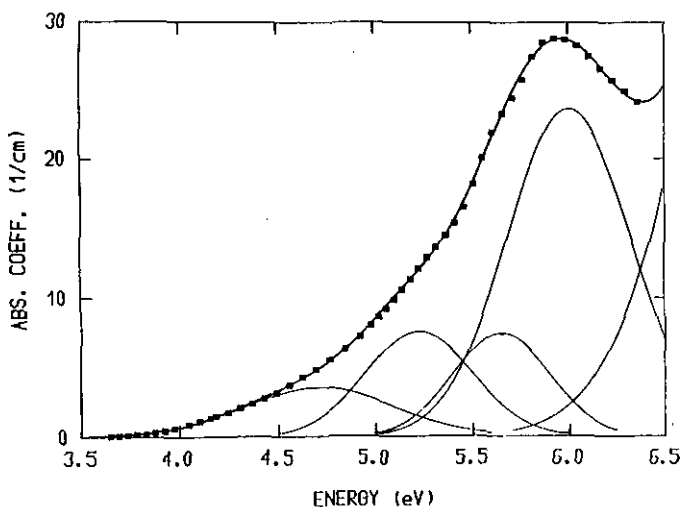


Figure 7. Analysis in Gaussian components in the 3.5–6.5 eV region of the optical absorption spectrum induced by neutron irradiation ($\phi_n = 3 \times 10^{18}$ neutrons cm^{-2}), where four Gaussian components in the region of the E' absorption are considered (the fitting parameters are reported in the text); ■, experimental data; —, Gaussian components; —, calculated spectrum.

It can also be noted that the E'₂ component shifts to a lower energy on going from RT (5.34 eV) to LNT (5.2 eV), while data in the literature indicate that the maximum of the E'₂ band is at 5.4 eV also for 80 K [9]. In view of these controversial results, we carefully considered the low-temperature ($T = 80$ K) spectrum of the most heavily irradiated sample. The spectrum, measured with the Varian spectrophotometer, is

reported in figure 7; besides the maximum peaked at 6 eV, two other shoulders are visible at 5.6 eV and at 5.2–5.3 eV. We then fitted the spectrum between 3.5 and 6.5 eV using four Gaussian components; we added to the three structures clearly evidenced by the spectrum a fourth low-energy band (4.7 eV) in order to account for the long-wavelength absorption tail. The result of the fit is very good; the peak energies of the four bands, as deduced from the fits, are 6.0 eV, 5.6 eV, 5.2 eV and 4.7 eV; the corresponding half-widths are 0.75 eV, 0.58 eV, 0.65 eV and 0.90 eV, respectively. We observe that the 6.0 eV band remains the dominant component in the spectrum and that its peak intensity ($\alpha_m = 23.6 \text{ cm}^{-1}$) nearly coincides with that calculated considering only the E'_1 and E'_2 components: $\alpha_m = 23.2 \text{ cm}^{-1}$.

Unfortunately, it has not been possible to perform this kind of fit in the case of weakly irradiated samples, because of the low absorption in this energy region, which would give rise to too large an error in the parameters; however, it is reasonable to think that this kind of calculation is more correct than that previously described.

In summary, we can say that new bands, which have not been identified until now, appear in the spectrum for neutron-irradiated crystalline SiO_2 .

4. Discussion

The point defects responsible for absorption in the energy range considered in this work are quite probably of intrinsic origin; in fact, the quartz used in this study is of high purity and, in spite of the high neutron fluences to which our samples have been submitted, no bands typically attributed to radiation-induced aluminium impurity centres (the A bands) have been detected.

In the following, the individual structures induced by neutron irradiation will be considered and discussed separately.

4.1. Vacuum-ultraviolet region

In unirradiated samples, our data on the position of the absorption edge (located at 8.5 eV) substantially confirm results already published [1]; upon irradiation, the shape of the edge does not appear to be a simple exponential; a further band at 8.3–8.6 eV may be present. Our choice to fit the edge region by one Gaussian band and one exponential tail could be considered rather arbitrary, because of the lack of experimental data for $E > 8.5$ eV, but it was also supported by previous observations of an absorption band in this energy region [7]. Obviously our choice for the fit of the absorption edge has some influence on that of the E band.

As already described in the previous section, two main structures are present at $E > 6.5$ eV: the D band (7.15 eV) and the E band (7.6 eV).

In the past, the D band has been detected in both x-ray- and heavy-ion-irradiated amorphous silica [2, 8] whereas previously only x-ray-irradiated crystalline quartz samples have shown its presence [2]. The structure of the point defect related to this optical transition is as yet unknown; however, interesting observations can be made on the basis of our data.

Figure 8 shows the peak absorption coefficient of the 6.0 eV band versus that of the D band; the experimental points refer to the whole range of neutron fluences; data measured at RT as well as at LNT are reported. The linear relation that exists between the absorption coefficients of the two bands suggests a possible correlation between them, whose nature, however, remains a matter of debate. It must be noted

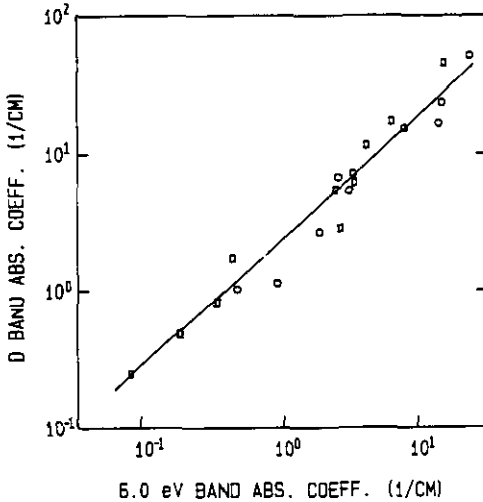


Figure 8. Peak absorption coefficient of the D band versus peak absorption coefficient of the 6.0 eV band: \square , data measured at 300 K; \circ , data measured at 80 K.

that the values shown in figure 8 are those of the band labelled E'_1 in the preliminary decomposition. However, a very similar peak intensity of the 6.0 eV structure is obtained from the second and more trustworthy calculation performed on the most highly irradiated specimen from 3.5 to 6.5 eV (see figure 7). The reliability of this correlation is further confirmed by analogous results that we have recently obtained on optical absorption in amorphous SiO_2 [27].

The E band is the most intense structure of all the spectra; two components are evident, at approximately 7.6 and 7.8 eV. This band has been more extensively studied in silica, and several models have also been proposed concerning the nature of the intrinsic defect responsible for this optical transition in amorphous SiO_2 ; as already mentioned, the various attributions refer to a peroxy radical defect [2-4], to the silicon vacancy [5] or to the oxygen vacancy [6]. Future interpretations of the absorption spectra in this region should consider that in the crystalline material the structure of this band appears to be complex and, however, it has not been clear until now whether the absorptions at 7.6 and 7.8 eV pertain to the same defect centre.

4.2. E' region

It has been proposed that, in irradiated crystalline quartz, two absorption bands, namely E'_1 and E'_2 , are present in the 5.3-6.2 eV region [9]. Our results lead us to disagree; in fact, the absorption spectra decomposition performed by considering only ' E'_1 ' and ' E'_2 ' contributions gave unsatisfactory results; the data in table 1 show that the energy of E'_2 at $T = 80$ K is systematically lower than the value reported in the literature (5.4 eV) and that the half-widths of both structures are exceedingly large. The latter result and a careful consideration of the spectra relative to the most heavily irradiated specimen (figure 7) suggested that the presence of additional components should be considered. The numerical analysis of the absorption spectrum of this sample indicates the presence of four components. The peak positions are at 4.7, 5.2, 5.6 and 6.0 eV, the latter band corresponding substantially to E'_1 of the previous fit. In fact, the large half-widths of the E'_1 and E'_2 components reported

in the literature indicate the existence of a more complex structure and our analysis brings the half-widths of the bands to more acceptable values.

The 4.7 eV band is responsible for the long-wavelength tail of the spectrum (see figure 7); in the past, a weak band at a slightly lower energy (4.6 eV) has been detected only in γ - and electron-irradiated crystalline SiO_2 [9, 11]. On the contrary, in amorphous SiO_2 a band at 4.7–4.8 eV, named D_0 has been studied in detail [11, 12, 28]; excitation in this band gives rise to the 1.9 eV emission, which is attributed to non-bridging oxygen hole centres [29]. Recent photoluminescence results obtained on various types of silica in our laboratories [30] revealed the occurrence of emissions not only at 1.9 eV but also at 2.2 eV with distinct excitation spectra at 4.8 and 4.7 eV, thus suggesting the existence of an even more complex absorption structure. In crystalline quartz, photoluminescence emission bands at 1.9 and 2.2 eV have also been detected under excitation in the same energy region, although with a lower intensity with respect to silica [30]; because of the similarities of their characteristics, we propose to identify the 4.7 eV absorption in quartz with the better studied (and perhaps complex) D_0 band of amorphous SiO_2 .

The 5.2 eV band has an energy similar to that of the widely studied B_2 band of silica [8].

We now discuss the relation between the absorption and EPR data; Nelson and Weeks [9], in their study of γ -irradiated quartz, proposed a correlation between the E'_1 and E'_2 EPR signals and the two absorption bands at 6.2 eV and at 5.4 eV respectively. We observe the same EPR signals in our quartz samples, but no absorption bands at 5.4 and 6.2 eV were found; instead, our optical spectra showed the existence of structures peaking at 5.2, 5.65 and 6.0 eV; thus, we cannot confirm the correlation between paramagnetic defects and absorption in this energy region, as proposed in [7]. This is in agreement with [19]. The identification of defects responsible for the absorption bands in the 6 eV region is considered to be still an open problem; in fact our data show that E'_1 and E'_2 centres cannot completely account for this structured absorption. However, from the comparison between the absorption and EPR data, we do not rule out that the E' -type defects play a role in the origin of these optical transitions.

In the picture just described, the broad 3.5–6.5 eV absorption is shown to be mainly due to the superposition of four different bands; two of these, at 4.7 and 5.2 eV, have a corresponding band in amorphous SiO_2 and so one might think that their presence is bound to partial amorphization, since the structural disorder induced by neutrons may be relevant [31]. However, the EPR spectrum induced by neutron irradiation shows the typical features of a single-crystal signal, without broadening or lineshape distortions which might be consequent to amorphization.

5. Conclusions

Our results update the phenomenology of the optical absorption features of neutron-induced intrinsic point defects in crystalline quartz; the effects of the neutron irradiations have also been studied in detail by means of EPR.

In the VUV region, two absorption structures have been studied: the D and the E bands at 7.15 eV and at 7.6 eV, respectively. A correlation between the D band and the 6.0 eV band has been found, while a double structure of the E band has been suggested. These features should be considered in future studies concerning the structure of the point defects responsible for the absorption in the VUV region.

A new picture of the 3.5–6.5 eV region emerged from careful consideration of our data; this required us to discuss the correlation between optical absorption in that region and 'E' EPR signals already proposed. Our description gives a more complex view of the optical absorption in this energy region and removes some discrepancies which arose from the previous and too-simplified picture.

Also, our results demonstrate the existence of analogies between the optical features of crystalline quartz and those of amorphous silica, suggesting once more that the point defects are similar in both types of SiO₂, in spite of the structural differences of the materials.

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