The shape of the boson peak in neutron-irradiated quartz crystals

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Abstract. We have studied the shape of the boson peak observed in neutron-irradiated crystalline quartz at different irradiation doses. This shape has a universal character and can be described by the soft potential model.

1. Introduction
The boson peak observed in Raman and inelastic neutron scattering in the frequency range of 1—3 THz is a universal feature of amorphous and disordered solids [1, 2, 3]. Different theories were proposed to explain this phenomenon [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. However, the nature of the boson peak is still under debate.

Measurements of the boson peak in partly disordered crystals, such as neutron-irradiated quartz, can help us understand the universality of the boson peak and test the proposed theories.

The phenomenological soft-potential model [15, 16, 17] have proposed that quasilocal vibrations exist in amorphous and disordered solids. These vibrations and two-level systems have a common origin — soft potentials. Such universal feature of amorphous solids as a plateau in the thermal conductivity at temperatures 5 — 20 K was quantitatively explained in the framework of this model [18] as a result of the resonance scattering of acoustic phonons on these soft modes. An analysis of the low-frequency Raman scattering performed in the framework of the soft potential model [7, 8] has shown that the elastic interaction between quasilocal vibrations produces a peak in the reduced density of vibrational states, $g(\omega)/\omega^2$, and can explain the universal character of the boson peak in different amorphous solids. The peak position corresponds to the Ioffe-Regel limit for acoustical phonons and can be calculated from known tunneling parameters [19].

The detailed study of the boson peak in neutron-irradiated quartz crystals [20] with different irradiation doses and known tunneling parameters has confirmed this relation. It was proposed also that the origin of the boson peak in neutron-irradiated quartz and vitreous silica can be attributed to quasilocal soft optic modes, which are analogous to the soft optic mode that drives the $\alpha$ — $\beta$ transition in quartz.

In the present work we study a shape of the boson peak in neutron-irradiated quartz crystals with two different irradiation doses, which corresponds to different degrees of disorder, and compare it with a material independent shape predicted by the soft potential model [8].
2. Experimental details

Two x-cut synthetic α-quartz samples of high purity [21] were shaped into a cylindrical rod with 8 mm length and 3 mm diameter and were irradiated in the same reactor at SCK (Mol, Belgium). The irradiation doses (for energy of neutrons above 0.3 MeV), mass densities and the value of the amorphous fraction for these samples are given in Table 1. We have chosen for the analysis these two quartz samples, because there are quite remarkable: the N6 sample is mainly crystalline (35% of amorphous phase) and N8 sample is mainly amorphous (70% of amorphous phase). The details of the amorphous fraction calculation were reported in previous publication [20]. The irradiation doses for the samples N6 and N8 are below and above of the threshold value $6 \times 10^{19}$ n/cm$^2$, respectively. Previous studies have shown that this threshold irradiation leads to significant irreversible structural changes in quartz crystals. Crystalline structure of quartz irradiated with a dose below this threshold value can be recovered after heat treatment at 700 - 800 °C, whereas quartz irradiated with a dose above the threshold value evolves after the same heat treatment to the vitreous silica phase [22].

The Raman spectra were excited by the 488 nm line of an argon-ion laser with the power on the sample 120 mW. Stokes and anti-Stokes spectra were recorded at room temperature in the low frequency range - from 15 cm$^{-1}$ to 150 cm$^{-1}$ for VV polarisation with a double monochromator Ramanor U-1000 equipped with the photon-counting system. The resolution was 2.5 cm$^{-1}$. The experiments were performed in the 90° geometry so that the scattered light propagated along the x-axis in the quartz samples. To eliminate the parasitic luminescence background observed in the Raman spectra of irradiated quartz samples these samples were heat-treated for several hours at 400 °C in a hydrogen atmosphere.

3. Results and Discussion

As was argued in the framework of the soft potential model [7] the quasilocal optic-like vibrations provide the dominant contribution to the low-frequency inelastic Raman scattering in amorphous and disordered solids and are responsible for the boson peak. The intensity of the first order Raman scattering by these vibrations is given by: $I_S(\omega, T) = C g(\omega) \frac{n(\omega, T)+1}{\omega}$ for the Stokes part, and

$$I_A(\omega, T) = C g(\omega) \frac{n(\omega, T)}{\omega}$$

for the anti-Stokes part, where $g(\omega)$ is the density of vibrational states, $C$ is the coupling constant (independent of frequency), and $n(\omega, T)$ is the Bose factor at equilibrium temperature T. Numerous studies devoted to the comparison of Raman spectra with neutron inelastic scattering data in vitreous silica (see for example [2, 23]) have shown that the coupling constant $C$ must vary linearly with frequency. However, in such analysis the important assumption was made that the vibrational densities of states obtained from neutron and Raman data are the same. Hyper-Raman measurements in vitreous silica [24] have demonstrated that additional vibrational modes give the main contribution to the boson peak observed in hyper-Raman spectra and these vibrations are silent in the first-order Raman scattering due to selection rules. These results
support the original idea of Shuker and Gammon [4] that the Raman intensity is given by a sum over all the vibration bands. The coupling constant is independent of frequency for each vibration band including the normal vibrations with similar microscopic motion. A value of the coupling constant depends on the local symmetry of the vibrational mode. As we mention in introduction, the origin of the boson peak in neutron-irradiated quartz and vitreous silica can be attributed to quasilocal soft optic modes, which are analogous to the soft optic mode that drives the $\alpha - \beta$ transition in quartz (for details see [20]). The coupling constant of this mode is independent of frequency.

According to the soft potential model [7, 8], the boson peak is a peak in the reduced density of vibrational states, $g(\omega)/\omega^2$. It appears as a result of the elastic interaction between different quasilocal vibrations. The interaction is due to the bilinear coupling between these vibrations and acoustical phonons. This interaction produces an instability in the spectrum of interacting quasilocal harmonic modes. As a result, for small interaction the rapidly growing density of states of quasilocal vibrations, $g(\omega) \propto \omega^4$, is transformed to a linear function of $\omega$, $g(\omega) \propto \omega$, above the boson peak frequency $\omega_b$. The boson peak in $g(\omega)/\omega^2$ appears as a result of this transformation. It has a material independent shape, which is given by [8]

$$
g(\omega)/\omega^2 = \frac{3B}{\pi \omega^*} \left(\frac{\omega^*}{\omega}\right)^4 \left[ z_1^2(\omega) + z_2^2(\omega) \right]^{-1} \times \left[ \frac{1}{2z_1(\omega)} \ln \frac{z_1(\omega)}{z_1(\omega) - 1} + \frac{1}{z_2(\omega)} \tan^{-1} \frac{1}{z_2(\omega)} \right]$$

(2)

where $B$ is a constant and

$$z_{1,2}(\omega) = \frac{1}{2} \sqrt{9 + 8(\omega^*/\omega)^6} \pm 3.$$  

(3)

The function $g(\omega)/\omega^2$ depends on a single parameter, $\omega^*$ characterizing the position of the boson peak. The maximum of $g(\omega)/\omega^2$, the boson peak, is at $\omega_b \approx 1.08 \omega^*$. For small frequencies, $\omega \ll \omega_b$, $g(\omega) \propto \omega^4$. For large frequencies, $\omega \gg \omega_b$, $g(\omega) \propto \omega$.

In Fig. 1 we compare our experimental data for sample N6 with theoretical predictions based on the soft potential model and described by Eqs. (2,3). For this comparison we have used reduced Raman intensity calculated from anti-Stokes part (Eq. (1)): $I_{\text{red}} = \frac{I_{\text{red}}}{n w(T) \omega} = C \frac{\sigma^2}{\omega^2}$.

One can see that the dashed line given by Eqs. (2,3) with $\omega_b = 60 \text{ cm}^{-1}$ describes very well the shape of the boson peak. To fit the broadened crystalline line at $120 \text{ cm}^{-1}$ we add to the function given by Eqs. (2,3) a Gaussian shown by the dot-dashed line. The resulting theoretical fit is shown by the solid line.

The reduced Raman intensity and the theoretical fit for sample N8 are shown in Fig. 2. The dashed line given by Eqs. (2,3) describes quite well the frequency dependence below the boson peak. However, to fit the whole frequency range we have used the same Gaussian as for sample N6 but with smaller amplitude and higher standard deviation. The total number of vibrational modes in this Gaussian is reduced to 30% in comparison with the previous case. From the

![Figure 1. Reduced Raman spectrum for the neutron-irradiated quartz sample N6. The solid line is a theoretical fit. It is a sum of two contributions. One (dashed line) is given by Eqs. (2,3) with $\omega_b = 60 \text{ cm}^{-1}$. The second (dot-dashed line) is a Gaussian centered at $120 \text{ cm}^{-1}$ with a width of $26 \text{ cm}^{-1}$ (the standard deviation $\sigma = 9.2 \text{ cm}^{-1}$).](image)
last fit it follows that the contribution of the strongly broadened crystalline line at 120 cm$^{-1}$ is still essential for explaining the slope above the boson peak. The study of the boson peak in neutron-irradiated quartz with higher doses than for sample N8 have shown [20] that the peak has the same shape as in Fig. 2. It means that relative contribution for the quartz mode is saturated on some level about 30% from the boson peak value.

4. Conclusion

We conclude that the shape of the boson peak observed in neutron-irradiated quartz crystals can be described in the framework of the soft potential model. However, we need to mention that a frequency range of a universal behavior in the region of the boson peak given by the soft potential model is rather narrow in neutron-irradiated quartz in comparison with lithium borate glasses considered in Ref. [8]. It was shown that this universal behavior covers a broad frequency range in lithium borate glasses: up to 5$\omega_b$. The possible explanation of this difference is the presence of the low-lying optic band in $\alpha$-quartz around 120 cm$^{-1}$, which provides additional contribution to the vibrational density of states above the boson peak. Such situation can be characteristic for strong glasses.

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