Neutron-irradiated crystalline quartz

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Neutron irradiation of crystalline SiO_2 creates two-level-state (TLS) excitations similar to those found in vitreous SiO_2. Using evidence obtained from x-ray and mass-density measurements, we conclude that the TLS excitations in damaged crystals need not reside in regions of material made amorphous.

In an attempt to gain some insight into the localized TLS (two-level-state) excitations found in vitreous silica and other amorphous materials, several recent measurements have been made on single-crystal quartz damaged through exposure to fast neutrons.[1] Gardner[2] measured the specific heat and thermal conductivity of irradiated crystals and concluded that the TLS excitations probably occur in clusters which are not amorphous. On the other hand, Grasse *et al.*[3] studied the damage created by neutrons using x-ray scattering and concluded that the TLS excitations reside in amorphized clusters, since the decreased density of the irradiated crystal and the total number of excitations were both consistent with this interpretation. Whether or not the clusters are amorphous is an important point. If amorphous, then one is studying only bits of vitreous silica and the neutron-irradiation studies add little new information about the TLS excitations. If the clusters are not amorphous, the TLS excitations must exist in a defective but otherwise highly crystalline local environment. The present Communication provides additional evidence that the clusters need not be bits of vitreous silica.

The 27-h sample of Gardner had about the same neutron exposure as the sample used by Grasse *et al.*, namely, $\approx 3\times10^{18}$ fast neutrons per cm^2. Indeed, the change in density ρ was about the same, $\Delta\rho/\rho \simeq 4\times10^{-3}$. The average density of TLS excitations, relative to that found in vitreous silica, was $x_{TLS}\simeq 0.03$ as measured by Gardner. This is close to the ratio $x_{TLS}\approx 0.04$ estimated by Grasse *et al.* In brief, the two samples were very similar. At this point, both $\Delta\rho$ and x_{TLS} are consistent with a $\approx$3–4% content of vitreous silica within the neutron-damaged crystal,[2,3] and the data of Gardner and of Grasse *et al.* are in agreement. The TLS excitations could exist in bits of vitreous silica. This statement is true *prior* to heat treatment.

In order to observe clearly the TLS excitations in specific heat and thermal conductivity, Gardner had to heat treat his samples to remove other excitations. There was no evidence that this heating significantly reduced the average density of TLS excitations; however, the heat treatment did increase the mass density ρ_t of the samples. Ratios of densities can be measured with high precision, and for the 27-h sample we find $\rho_t/\rho_c = 1.0000\pm0.0005$, where ρ_c is the density of a sample of the *same* crystal but not irradiated. The irradiated crystal now has the same mass density as the original crystal of α-quartz. Our x-ray studies showed the crystal structure to be α-quartz, the same as the unirradiated sample. The volume fraction x_{vs} of vitreous silica contained within the sample would be, for small x_{vs},

$$x_{vs} = [1-(\rho_t/\rho_c)][1-(\rho_g/\rho_c)]^{-1} ,$$

where ρ_g is the density of vitreous silica and need not be known precisely. Substituting measured values gives $x_{vs}=0.000\pm0.003$. This implies that inclusions of vitreous silica could contribute no more than 10% of the TLS excitations actually present in this sample. (It seems unlikely that annealing would increase the pressure on an amorphous cluster sufficiently to increase its mass density by a factor of ≥ 10.) We therefore conclude that the TLS excitations need not reside in clusters which are simply bits of vitreous silica.

Gardner also studied a sample, 270 h, having a factor of 10 longer exposure to fast neutrons. Our x-ray studies show this 270-h sample to be composed of the high-temperature β phase stablized at room temperature by inclusions of the cubic melanophlogite phase of quartz.[4] The volume of the melanophlogite phase is at least 1% that of the β phase. Using the x-ray densities[5] of both phases and the measured density ratio of the 270-h sample to the unirradiated sample[4] gives a glassy fraction $x_{vs}\lesssim 0.1$. The average density of TLS excitations, relative to that found in vitreous silica, is $x_{TLS}\approx 0.6$. Thus for the β phase, as for the α phase, the TLS excitations appear not to reside in bits of vitreous silica.

Grasse *et al.* state that a heat treatment of their samples to 500 °C reduced the concentration of clusters, observed by x-ray scattering, by a factor of ≈ 2. The strength and symmetry of the remaining clusters did not change. An anneal at 1000 °C removed all defects. The treatment temperature used by Gardner was 840 °C; so it is difficult to make a direct comparison. Nevertheless, it would appear that the defects detected by x rays anneal out at a faster rate than the TLS excitations. Certainly the x-ray data of Grasse *et al.* argue against the possibility of individual clusters simply shrinking in diameter by a factor of 2 or 3 with heat treatment. Hence the defects detected by x-ray scattering could be in close proximity to the TLS excitations, but they may not be necessary for the existence of those excitations.[6]

In summary, we find that TLS excitations in neutron-damaged crystalline quartz do not necessarily exist within bits of amorphized quartz. Further, we suggest that the clusters detected by x-ray scattering in neutron-damaged crystalline quartz may not be responsible for the existence of TLS excitations.

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[1]J. W. Gardner and A. C. Anderson, Phys. Rev. B 23, 474 (1981); D. Grasse, O. Kocar, H. Peisl, S. C. Moss, and B. Golding, Phys. Rev. Lett. 46, 261 (1981).

[2]Gardner and Anderson, Ref. 1.

[3]Grasse, Kocar, Peisl, Moss, and Golding, Ref. 1.

[4]The melanophlogite inclusions were larger than 1000 Å, and were highly oriented with a [110] cubic direction parallel to the [100] hexagonal direction of β-quartz. This caused some line broadening of $(h00)$ peaks due to strain in the $(hh0)$ planes, but there was no line broadening in the [001] direction. Additional details are planned to be published by J. A. McMillan.

[5]The ratio of the mass density of the 270-h sample to that of α-quartz was 0.952 ± 0.001. The x-ray density for the high-temperature β phase at room temperature was 2562 ± 5 kg/m^3; for the cubic melanophlogite phase, 1940 ± 7 kg/m^3.

[6]Reference 3 concludes that the size of the clusters is ≈ 20 Å, and hence that TLS excitations must be ≤ 20 Å in size. This statement is not valid if the defects detected by x rays are not responsible for TLS excitations. However, M. V. Shickfus and S. Hunklinger also deduced a maximum size of ≤ 20 Å [J. Phys. C 9, L439 (1976)].