Diffuse X-Ray Scattering and Phonon Echoes from Neutron-Irradiated Crystalline Quartz

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Measurements of diffuse x-ray scattering from α-quartz single crystals after irradiation with 3×10^{18} fast neutrons per square centimeter are reported. The neutrons create defective regions of mean radius 10 Å, concentration 13.6×10^{-5}, and a volume change per region of 29 mean atomic volumes. The crystalline matrix is heavily strained by the defective regions and the symmetry and magnitude of the strain field is determined. These regions, which are most likely amorphous, contain the tunneling centers responsible for the recently observed phonon echoes.

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It is well known that many of the low-temperature properties of glasses may be strongly influenced by the presence of low-energy atomic tunneling systems.[1,2] These centers couple to phonons by means of a strong resonant interaction and are responsible for the low phonon thermal conductivity,[3] nonlinear acoustic absorption,[4] and coherent phenomena such as phonon echoes,[5] which are observed in glasses. Recently, acoustic saturation was seen in crystalline quartz[6] after light irradiation with fast neutrons, illustrating a qualitative similarity to the behavior of SiO_2 glass. The very recent observation of phonon echoes in this system[7,8] showed that the phonon couplings to the centers were equivalent in glass and irradiated crystal, thus indicating that the tunneling systems were the same in both substances.

In this Letter we report measurements of the diffuse x-ray scattering (Huang scattering and asymptotic scattering) from neutron-irradiated quartz single crystals. This method is a powerful tool to study the strength and symmetry of strain defects and their local correlations.[9-12] We are thus able for the first time to discuss the nature of lightly irradiated quartz in a regime of dosage which has heretofore not been characterized, and relate this to the relevant low-energy tunneling excitations. We show that the disordered clusters created by the neutrons are the locations of the tunneling centers and are most likely amorphous (glasslike) in nature. Single-crystal cubes of natural quartz of dimensions $6\times6\times6$ mm^3 with faces parallel to $(11\bar{2}0)$, $(1\bar{1}00)$, and (0001) prepared for ultrasonic studies were irradiated at ambient temperature (80 °C) in the Munich research reactor (Forschungs Reactor Munich) with a total dose of 3×10^{18} n/cm^2 ($E>0.1$ MeV). The intensity distribution of scattered Cu $K\alpha_1$ x rays reflected from a bent quartz monochromator was measured for various settings of crystal and detector angle from each face. The primary intensity from a stabilized 6-kW rotating-anode x-ray generator was monitored by a second counter.[12] The scattered intensity was put on an absolute scale in the usual way by a polystyrene scatterer. During the measurements the crystals were kept near 80 K in order to minimize thermal diffuse scattering. The defect-induced diffuse intensity was obtained as the difference between scattered intensity from the crystal after irradiation and after complete thermal annealing of the defects at 1000 °C. There was no evidence that crossing the α-β phase transition at $T_c=573$ °C damaged the initial perfection of the single crystal. It was, however, necessary to heat above T_c to remove the radiation-induced effects. Figure 1 shows a typical result. The scattering intensity close to a $(22\bar{4}0)$ Bragg reflection measured in $[11\bar{2}0]$ and $[1\bar{1}00]$ direction is given for a quartz crystal after irradiation with 3×10^{18} n/cm^2 and after anneals below and above T_c. The scattering distributions have been translated to make the positions of the

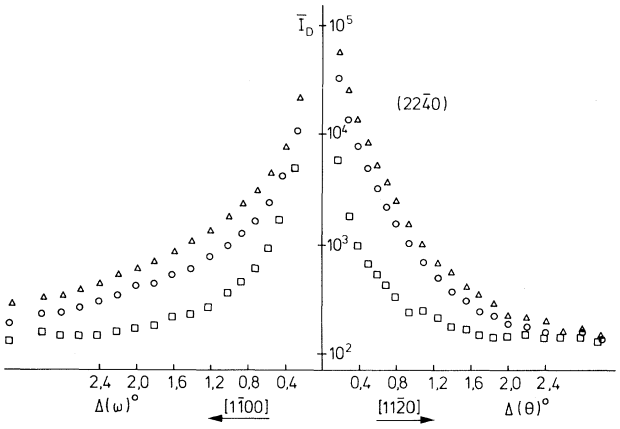

FIG. 1. Diffuse scattered x-ray intensity at liquid-nitrogen temperature from quartz single crystal near (22$\bar{4}$0) reflection in [11$\bar{2}$0] and [1$\bar{1}$00] directions. Triangles, after irradiation at 80° with 3×10^{18} n/cm^2; circles, after thermal annealing at 500 °C; squares, after complete annealing at 1000 °C.

Bragg peaks, which had been shifted because of the lattice expansion on irradiation, coincide. The relative lattice-parameter changes $\Delta a/a$ and $\Delta c/c$ were measured on each sample by the Bond method, with use of a different diffractometer especially designed for high-precision lattice-parameter measurements. The accuracy in $\Delta a/a$ is $\pm5\times10^{-5}$ and comes from variations due to repeated sample adjustment. We observed an asymmetry of the defect-induced scattering intensity about the Bragg peaks, not to be confused with the two directions shown in Fig. 1. This indicates that the distortion field is dominated by defects which expand the lattice. For the neutron dose used here the statement that "no distortion in the x-ray diffraction pattern is observed"[13] maintains in the usual sense. The line shape and the full width at half maximum are not changed within "usual" experimental error, and, in fact, the maximum intensity is increased due to loss of primary extinction. The present diffuse scattering close to the Bragg peaks is only about 10^{-4} of the intensity of a Bragg peak and has not been considered in the previous x-ray studies on irradiated quartz single crystals, although Wittles[13] photographs clearly reveal it at higher dosage.

For each Bragg reflection and each measuring direction the radiation-induced additional intensity from both sides of the Bragg maximum has to be averaged to give the appropriate diffuse scattered intensity.[12] This is plotted in Fig. 2(a) and (b) on a double-logarithmic scale versus the

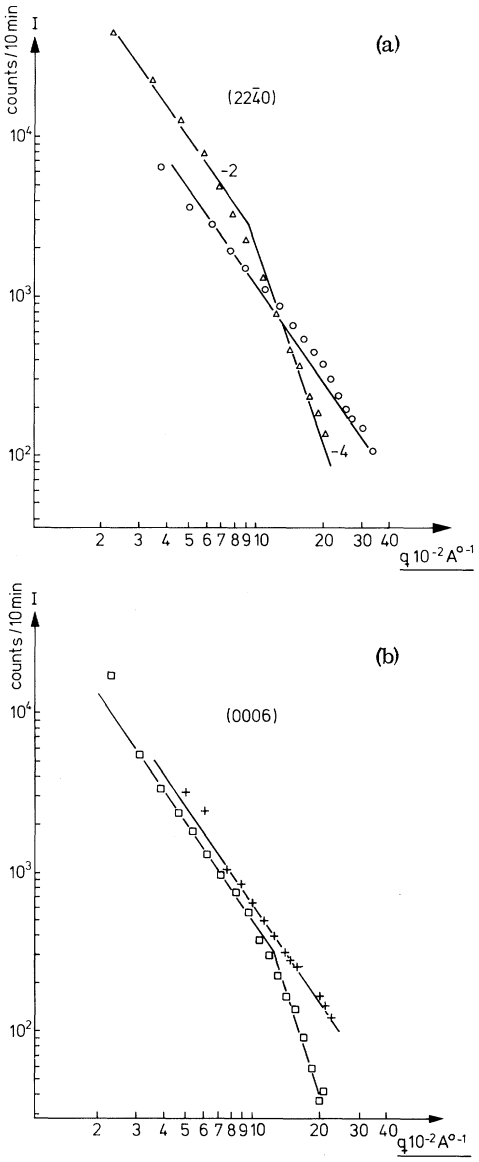

FIG. 2. Defect-induced scattering intensity from crystalline quartz. (a) Near (22$\bar{4}$0): triangles, in [11$\bar{2}$0] direction (radial); circles, in [1$\bar{1}$00] direction (angular). (b) Near (0006): squares, in [0001] direction (radial); crosses, in [1$\bar{1}$00] direction (angular).

distance $\vec{q}$ from the corresponding reciprocal-lattice point $\vec{G}$, where $\vec{q}=\vec{K}-\vec{G}$ is the difference between the scattering vector $\vec{K}$ and $\vec{G}$. The characteristic q^{-2} (Huang scattering) and q^{-4} (Stokes-Wilson or asymptotic scattering) dependence is observed.

The two parts of the diffuse scattering distribution are usually treated separately. For a small concentration of randomly distributed defects the

diffuse scattering intensity close to the Bragg peak (Huang diffuse scattering) is determined by the defect concentration c and the Fourier transform $\tilde{u}$ of the long-range displacement field $\vec{u}_m^n$ of the individual defect. By individual defect it should be clearly understood that the long-range part of the displacement field does not uncover the detailed internal structure of this defect or strain center. It may in fact be a point defect, an agglomerate of point defects, or, generally, a larger defective region. The Huang scattering intensity may be written generally as[10,11]

$$I_{\mathrm{HDS}} \sim F^2 c |\vec{K}\cdot\tilde{\vec{u}}|^2 \simeq c\Pi(\vec{G},\vec{q})/q^2, \quad (1)$$

where F is the structure factor, including a thermal and a static Debye-Waller factor. For small $\vec{q}$ the Fourier transform $\tilde{\vec{u}}(\vec{K})$ is given in terms of the double force tensor P_{ij}, which describes the strength and symmetry of the defect, and the elastic constants of the host lattice, which reflect its symmetry. These are incorporated into $\Pi(\vec{G},\vec{q})$ in Eq. (1), which contains quadratic combinations of the tensor components, depending on the reciprocal-lattice vector $\vec{G}$ and the measuring direction $\vec{q}$.

For example, if the symmetry of the distortion field of the defect is the same as the crystal symmetry there will be planes of zero scattering intensity normal to each reciprocal-lattice vector. Lower distortion-field symmetry extends intensity into these null planes. Whereas the Huang scattering intensity depends on P_{ij} quadratically, the relative lattice-parameter change depends on linear combinations of P_{ij}. Thus from the absolute diffuse scattering intensity and the measured lattice-parameter changes, the defect concentration c and selected combinations of the elastic double force tensor P_{ij} can be determined.

The symmetry of P_{ij} and the combination of tensor components given below are obtained from the measurements in various directions in reciprocal-lattice space. The tensor components are given in orthogonal coordinates where the x axis coincides with the twofold axis of the crystal, i.e., $(11\bar{2}0)$. From two sets of crystals irradiated with the same dose the following results have been obtained: $T_{\mathrm{irr}} \approx 80\,^{\circ}\mathrm{C}$, $\varphi t = 3\times10^{18}\, n/\mathrm{cm}^2$, $E > 0.1$ MeV, $\Delta a/a = (17.38\pm0.5)\times10^{-4}$, $\Delta c/c = (4.62\pm0.3)\times10^{-4}$; $P_{11}+P_{12} = 197\pm29$ eV, $P_{33} = 55\pm10$ eV; $P_{11}^2+P_{22}^2+2P_{12}^2 = 22\,160\pm2676$ eV^2; $(P_{23}^2+P_{13}^2) = 2816\pm375$ eV^2; $c = 13.6\times10^{-5}$, $\Delta v/\Omega = 29$. The defect concentration c is related to the number of atoms. Ω is the mean atomic volume, with $\Omega = a^2c\sqrt{3}/18 = 12.5$ Å^3. Upon annealing at 500 °C the defect concentration changes to $c = 7.4\times10^{-5}$, whereas the double force tensor P_{ij} of the defect does not change. The anisotropy of the lattice-parameter change $(\Delta a/a)(\Delta c/c)^{-1} = 3.8$ stays also the same within error bars after irradiation.

For large displacements $\vec{u}_m$, as they may occur close to our defect agglomerates, the product $\vec{K}\cdot\vec{u}_m > 1$ and the asymptotic or Stokes-Wilson scattering is observed farther away from the Bragg peak:

$$I_{\mathrm{as}} \sim c|\Delta v/\Omega|/q^4 \quad (2)$$

At the q values where the $1/q^2$ dependence changes to $1/q^4$ the lattice is so heavily strained ($\vec{K}\cdot\vec{u}_m = 1$) that the scattered x-ray wave comes out of phase. For directions $\vec{q}\parallel\vec{G}$ this can be used as an approximate measure of the size of the defective region $r_c = 1/q$. By definition such a cluster radius must lie within the (heavily strained) crystalline matrix. A value of $r_c \approx 10$ Å is an averaged one from various measurements ($r_c([0006]) = 8$ Å, $r_c([22\bar{4}0]) = 11$ Å, and $r_c([4\bar{4}00]) = 11$ Å). The above experimental results are consistent with a strain defect that is a rather defective region in the crystal. The average size is given by $r_c \approx 10$ Å or, under the assumption of a spherical cluster, $v_c = 335\Omega = 4190$ Å^3. The magnitude of P_{ij} and $\Delta v/\Omega$ also clearly indicate that many atoms contribute to the defect. [For point defects (interstitials or vacancies) one expects a $\Delta v/\Omega \approx \pm 1$.] The total defective volume in the crystal amounts to $V_c/V = 0.045$. Comparing the concentration of these defective regions with the neutron dose we note that each neutron gives rise effectively to about ten such clusters.

Let us assume for the moment that the defective region or cluster has become amorphous due to irradiation either through a high defect density or through heating by a thermal spike and consecutive quenching. From the fractional density of α-quartz on irradiation at $3\times10^{18}\, n/\mathrm{cm}^2$, $-\Delta\rho/\rho = 2\Delta a/a + \Delta c/c = 3.9\times10^{-3}$, and the volume fraction of disordered clusters, $V_c/V = 0.045$, the density of the amorphized regions can be calculated. We find a cluster density which is 9% smaller than density of α-quartz. This is to be contrasted with a density change for fully irradiated ($\gtrsim 10^{20}\, n/\mathrm{cm}^2$) quartz or silica glass[14,15] which is 14.5% smaller than α-quartz. Therefore, the amorphous clusters represent a highly compressed, or densified, state of disordered SiO_2.

Assuming the internal structure of the defective region to be truly amorphous or glassy, we may

scan the appropriate region in K space to detect the first strong amorphous halo at about $K \approx 1.5$ Å^{-1}. For the sample irradiated to 3×10^{18} n/cm^2 this search yielded hardly any intensity above background. We do, however, have results for crystals irradiated at 8×10^{18} n/cm^2 and 16×10^{18} n/cm^2 in which a pronounced amorphous peak is clearly developing at the correct angle for irradiated glass. While these results are part of a much more extended study,[16] we note here that the double force tensor, cluster size, and principal displacement axis do not change significantly with increasing dosage. We are therefore led to the conclusion that the defective regions in the present experiment are glasslike in nature. While we do not yet have a complete picture, it is our feeling that the structural damage on light irradiation reported here develops continuously towards the fully amorphized state[17] via the overlap of these defective regions. As noted earlier, the present damage can be annealed completely at 1000 °C. This seems to be true as well for the two other doses noted above.

This existence of amorphous defective clusters in neutron-irradiated quartz suggests that they may be the location of the tunneling centers detected by acoustic experiments. Velocity of sound measurements below 1 K[7,8] have yielded $\bar{P}M_l^2 = 1.3\times10^7$ ergs cm^{-3} for a 6×10^{18} n/cm^2 quartz sample, where $\bar{P}$ is the tunneling density of states and M_l is the longitudinal phonon deformation potential. Phonon echoes have shown[5,8] that M_l is the same for the defect centers in irradiated quartz and in nonirradiated silica glass. For silica glass,[4] $\bar{P}M_l^2 = 2\times10^8$ ergs cm^{-3} so that $\bar{P}$(irradiated quartz)/$\bar{P}$(silica glass) = 0.08. In the present dilute regime, the clusters are noninteracting, so that $\bar{P}$ should scale linearly with irradiation dose.[18] Thus at 3×10^{18} n/cm^2 we find the above density of states ratio to be 0.04. This is in good agreement with the volume fraction of clusters, 0.045, discussed above. Since it has been shown that the tunneling centers do not exist in nonirradiated quartz,[19] we infer that the amorphized clusters contain the tunneling centers in the neutron-irradiated material. This identification allows us to place an upper limit of 20 Å on the size of a tunneling system in amorphous SiO_2.

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