

domains. H adsorption (or cooling) increases the long-range order giving sharper spots. At the same time a change in displacement may occur to account for the higher intensity in the half-order spots. Another consideration involves the charge-density-wave mechanism originally proposed by Felter, Barker, and Estrup² for the clean surface and discussed recently by Tosatti.¹³ It is possible that the hydrogen coverage induces changes on the two-dimensional Fermi surface yielding initially a change in the first monolayer distortion pattern from an incommensurate to a commensurate structure corresponding to the sharp $c(2 \times 2)$ pattern, and then finally to the $p(1 \times 1)$ pattern.^{13,14}

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⁸The unit atoms per row is convenient for comparison to calculations. Consider, for example, normal incidence on W(001). Of the $\langle 001 \rangle$ rows half have their first atom in the surface layer, and half in the second layer, each layer having a density of 1×10^{15} atoms/cm². In this case 1 atom/row is therefore 2×10^{15} atoms/cm².

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¹²A comparison in Ref. 8 showed that measured surface-peak intensities are in general slightly higher than calculated values. The higher scattering yield has been explained by enhanced surface-vibration amplitudes. The present work indicates that in one case (Ref. 6) at least part of the reason is the reconstructed surface phase. Existing data are insufficient to conclude that the ion-scattering results should always show an excess. Although the influence of the adsorbed H on the surface vibrational amplitude is assumed small, it is conceivable that adsorption removes some soft-phonon modes parallel to the surface, bringing the experimental value closer to the calculation.

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Saturation of the 9.4-GHz Hypersonic Attenuation in Fast-Neutron-Irradiated Crystalline Quartz

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Saturation of the 9.4-GHz hypersonic attenuation was observed in crystalline quartz after fast-neutron irradiation. The sample, which exhibits long-range order, shows a low-temperature acoustic behavior similar to that observed in amorphous materials. As in glasses, the results can be explained by the existence of configurational low-energy excitations, with a two-state nature, which were put forward as intrinsic to the amorphous state.

In this Letter, I report observations¹ of the saturation of the high-frequency acoustic attenuation in a crystal, possessing long-range order, which are similar to the acoustic anomalies in glasses.²⁻⁶ A quartz crystal was neutron irradiated, producing localized defects which we be-

lieve to be the elusive two-level systems (2LS) hypothesized for glasses.^{7,8} Furthermore, I present additional evidence for a certain microscopic picture for the localized low-energy excitations which cause the anomalies: The elongated Si-O-Si bond with two equilibrium positions

for the bridging oxygen atom, introduced by Strakna,⁹ is consistent with our hypersonic attenuation measurements and the studies on neutron damage in crystalline quartz and vitreous silica. The measurement of the low-temperature ultrasonic properties of a crystal in which a small amount of disorder is introduced by high-energy-particle irradiation turns out to be an important means for the understanding of the anomalous dynamic properties of amorphous materials.

The single-crystalline quartz sample of natural Brazilian quartz was irradiated in a uniform flux in the reactor-centrum Studiecentrum voor Kernenergie (SCK) in Mol, Belgium. The integrated flux density of the fast neutrons (energy ≈ 1 MeV) was about 6×10^{18} neutrons/cm², and the ambient temperature during the irradiation was about 60°C (the sample was put in an aluminum holder which was water cooled). The atomic impurity content of the quartz is less than 100 ppm. After the irradiation the quartz crystal showed a smoky color which is known to be due to the color center created at the aluminum substitutional impurities, after irradiation.¹⁰ (Most quartz crystals contain a small amount of aluminum.) Magnetic susceptibility measurements were carried out in a small quartz disk, cut from the same single crystal as the one used in our hypersonic experiments and irradiated at the same time and reveal an unpaired-electron density of about 5×10^{19} /cm³.¹¹ The specimen was finished, according to the requirements for 9-GHz hypersonic experiments, prior to the irradiation, and it was not necessary to refinish the surfaces after the irradiation.

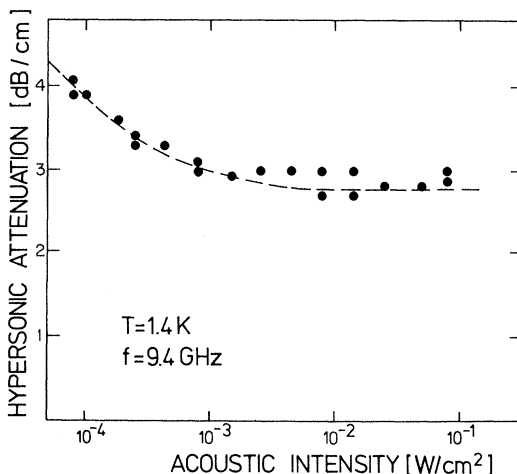


FIG. 1. Hypersonic attenuation as a function of the acoustic intensity.

The electroacoustic conversion efficiency for the surface excitation in the sample, the technique which was used for the generation of the hypersonic waves, was measured and there was no observable difference with a nonirradiated crystal. This shows, considering the piezoelectric conversion process in x -cut quartz at these frequencies, that the quartz sample is still crystalline and that long-range order was conserved. This is not surprising since it is known that for the used fast-neutron dose no distortion is observed in x-ray diffraction patterns.¹²

We have measured the 9.4-GHz hypersonic attenuation for the longitudinal mode as a function of the acoustic intensity at 1.4 K and as a function of temperature between 1.4 and 4.2 K. A pulse-echo method was used in a single-ended reentrant cavity setup. Electromagnetic pulse lengths of 1 μ s were used. Great care was taken to prevent the effect of any nonlinearity in the receiving system. Figure 1 shows the attenuation as a function of the acoustic intensity and it is seen that at lower intensities the attenuation increases with decreasing intensity which is typical for a saturation behavior. If the constant attenuation at high power levels is subtracted, Fig. 2 is obtained. Figure 3 shows the hypersonic attenuation as a function of temperature at high acoustic intensities. The temperature-independent part of this attenuation has first been subtracted. This plot shows a behavior which is completely different from that of a pure nonirradiated sample. Attenuation measurements on a nonirradiated sample cut of the same crystal did not reveal any temperature dependence in this temperature region.¹³

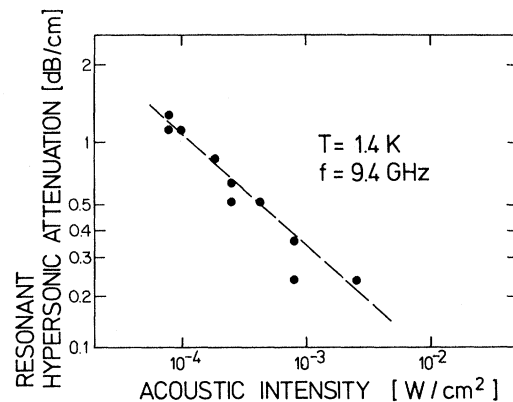


FIG. 2. Resonant attenuation as a function of acoustic intensity. The broken line represents $1/\sqrt{J}$.

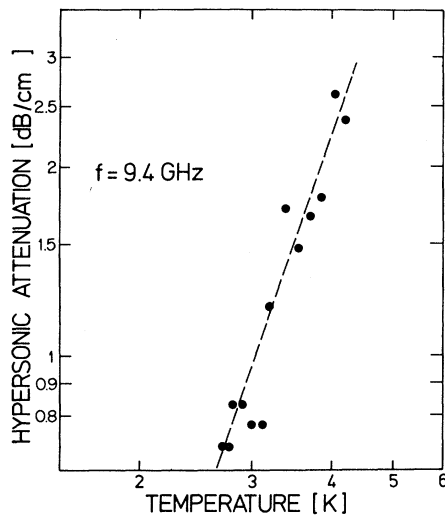


FIG. 3. Attenuation as a function of temperature. The temperature-independent part has first been subtracted (2.6 dB/cm). The broken line represents T^3 .

The similarity to an experiment in an amorphous material is apparent. In glasses, such a behavior is ascribed to the interaction between the acoustic wave and a low-energy tunneling state. The existence of such states not only explains the acoustic properties of the glasses at low temperature but various other anomalies observed until now.¹⁴⁻¹⁹ The interaction of an acoustic wave and a 2LS is twofold: the direct interaction between the 2LS and a resonant phonon, which leads to the saturation of the ultrasonic absorption at high power levels, and the relaxation attenuation due to the relaxation of the 2LS after their thermal equilibrium has been disturbed by the traveling acoustic wave.²⁰ For high intensities, the attenuation due to the resonant interaction is given by³

$$\alpha_{\text{res}} \propto n_0 M^2 (J_c/J)^{1/2}.$$

In this expression the factor $(J_c/J)^{1/2}$ represents the intensity dependence of the acoustic attenuation, J_c being the critical intensity at which saturation effects become noticeable. The coupling between a 2LS and the elastic perturbation for the resonant interaction is given by the coupling constant M and n_0 is the density of states of those 2LS. Comparing with our experimental results for the intensity-dependent attenuation in Fig. 2, it is seen that they can be described by the $1/\sqrt{J}$ behavior, according to this model. For the relaxation attenuation one finds¹⁴

$$\alpha_{\text{rel}} \propto n_0 M^2 D^2 T^3$$

in which D is the coupling constant for the relaxation process. In Fig. 3, it can be seen that our experimental results for the temperature dependence of the attenuation can be described by this expression. Therefore, from our measurements there is strong evidence that also in the neutron-irradiated crystalline quartz there may exist extralocalized excitations similar to those found in a variety of glasses. Furthermore, they support the idea that the "glassy" behavior is not due to the absence of long-range order, but to localized disorder, an idea which was explicitly put forward by Phillips²¹ and which was already implicitly present in the earliest papers.^{7,8} They also agree with the thermal measurements in Nb-Zr alloys²²: Although crystalline, this material shows a glassy behavior for the heat capacity and the thermal conductivity; the specimen, however, contains small amounts of the ω phase in a matrix of the β phase, which form in the 20% Nb sample isolated regions of about 5 Å in diameter with a concentration of about $10^{19}/\text{cm}^3$.

What the exact nature is of the local disorder, which causes the anomalies, is, however, not clear. An extended literature on the neutron-irradiation damage in crystalline quartz is available.²³ According to Wittels and Sherril,²⁴ during fast-neutron irradiation, long-range order is maintained in single crystals but is gradually diminished until they have suffered a bombardment of approximately 1.2×10^{20} neutrons/cm². In crystals irradiated with less than 3×10^{19} neutrons/cm² the structural effects are, according to Wittels,¹² point-defects and slightly disordered regions. Paramagnetic resonance experiments by Weeks²⁵ show that the irradiation causes mainly oxygen vacancies and interstitials; many broken bonds are created and all the defects are generated in the basic SiO_4 tetrahedra. It follows that rearrangements of the basic SiO_4 tetrahedra take place.

An important question is whether our observations are due to a structural defect or to an electronic center. There is strong evidence that in the neutron-irradiated sample a structural defect causes the anomalies. For example measurements of the ultrasonic attenuation in γ -irradiated quartz^{26,27} at liquid helium temperatures do not show any temperature dependence; the absorption is constant, while we observed a strong temperature dependence, almost as T^3 . On the other hand, it is known that in quartz, which is partly covalently bonded, γ irradiation, as other types of electromagnetic irradiation, results primarily

in electronic changes, while high-energy-particle bombardment causes structural changes in addition to electronic changes.²⁸ This shows that I have to attribute our observations to structural changes.

Furthermore, there is additional evidence for a certain structural defect: the elongated Si-O-Si bond with two equilibrium positions for the bridging oxygen atom, put forward by Strakna⁹ to explain his ultrasonic and the thermal measurements by Clark and himself²⁹ in neutron-irradiated vitreous silica. Comparing studies of x-ray radial distribution curves with his ultrasonic studies in vitreous silica Strakna found that the decrease of the ultrasonic absorption corresponds to a decrease of "anomalous" Si-O distances observed in x-ray measurements. This is also consistent with thermal measurements on neutron-irradiated vitreous silica²⁹ and more recent ultrasonic studies at lower temperatures.⁶ In pure crystalline quartz, at the other hand, this defect is not present; however, it is gradually introduced, according to Clark and Strakna²⁹ upon neutron irradiation. Both the crystalline and the vitreous phase of quartz seem to evolve to the same modified glass upon increasing the dose. Measurements of the excess specific heat in the irradiated crystal are consistent with that,²⁹ and now my observations of the hypersonic saturation are. Therefore I think that our measurements present additional evidence for the elongated Si-O-Si bond defect.

If the hypersonic wave couples to two-level systems in the neutron-irradiated quartz it would be interesting to compare the coupling strength of the acoustic phonons to such systems in the quartz with the in vitreous silica. Since there is some discrepancy between the 9-GHz data³⁰ for the resonant attenuation and the data at lower frequencies³¹ in the regime $J > J_c$, I compared our data with the high-frequency data of Bachelier³⁰ which were taken at almost the same frequency and temperature as in our experiment. He measured the hypersonic attenuation as a function of the acoustic intensity in vitreous silica Suprasil W at 9.4 GHz and 1.46 K. Comparing $\alpha_{res}(J > J_c)$, for the same acoustic beam intensity, we see that it is about 4 times smaller in the neutron-irradiated quartz than in vitreous silica. This, however, gives not an exact value for the coupling strength n_0M since J_c enters in the expression for the resonant absorption for $J > J_c$. On the other hand, it does give the order of magnitude of the coupling strength compared to vitreous

silica. Furthermore, it is remarkable that the little disorder, which has been created in the quartz crystal by the neutron irradiation, gives rise to such a large effect.

In summary, I have observed a nonlinear behavior of the hypersonic attenuation in a crystalline quartz sample after a fast-neutron dose of about 6×10^{18} neutrons/cm², a dose for which it is known that the crystal still exhibits long-range order. The saturation of the acoustic absorption and the temperature dependence are consistent with the two-level system model which was developed to describe the anomalous dynamic behavior of amorphous materials.

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Spectra of Ternary Alloys

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The vibrational frequency-distribution spectra of the random one-dimensional ternary alloy $A_cB_{1-c}C$ are accurately predicted for the first time by a statistical theory of small clusters embedded in a coherent-potential-approximation effective medium. The theory can be applied practically to real three-dimensional alloys.

By treating small clusters embedded in an effective medium (described here by the coherent-potential approximation), we are able to reproduce the "exact" numerical frequency-distribution spectra of the vibrating, mass-disordered, random, one-dimensional (1D) alloy $A_cB_{1-c}C$. The atoms of this linear ternary alloy are coupled by nearest-neighbor harmonic forces with force constants φ , and execute only longitudinal vibrations. The present theory is valid for all concentrations and is especially applicable to concentrations $0.05 \leq c \leq 0.95$ throughout the alloy regime. We believe it to be the first statistical theory to reproduce the exact numerical vibrational state densities for the 1D ternary alloy. The theory can be applied to alloys of arbitrary mass ratios m_A/m_B and m_B/m_C ; it satisfies the oscillator strength sum rule; and it correctly reproduces the exact spectra in the limits $c \rightarrow 0$ and $c \rightarrow 1$. By far the greatest virtue of this theoretical method is that it is computationally efficient, and, unlike direct numerical calculations^{1,2} and cluster gen-

eralizations of the coherent-potential approximation,³⁻⁷ can be practically applied to real 3D alloys.

The basis of the computations is the coherent-potential approximation (CPA) originally invented by Taylor,⁸ Soven,⁹ and Velický, Kirkpatrick, and Ehrenreich,¹⁰ and subsequently adapted for ternary alloys by Taylor¹¹ and by Sen and Hartmann.¹² By itself, the CPA does not give a successful quantitative description of the alloy vibrational spectra; but when a relatively small random cluster is embedded in the CPA effective medium, the resulting cluster density of states accurately mimics the density of states of the random alloy.

To our knowledge, the first authors to publish the suggestion that effective-medium and cluster methods be merged were Gonis and Garland,¹³ whose suggestion dealt only with binary alloys; however, the general idea of treating a cluster embedded in a medium has been advanced independently by numerous authors^{7,14} and we were led to the CPA as an optimal medium by our syste-