# Low-temperature ultrasonic attenuation by strongly dispersive transverse-acoustic phonons in $\alpha$-quartz

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Measurements of the ultrasonic absorption in synthetic and natural quartz crystals below 20 K at frequencies less than 1 GHz show that the temperature dependence of the intrinsic attenuation coefficient departs from the power law predicted by theory. The deviations are explained in terms of anharmonic interactions of the ultrasonic waves with superthermal phonons of the strongly dispersive transverse-acoustic mode in quartz whose lifetimes are limited by point-defect scattering. The attenuation is independent of frequency and its magnitude falls below $2\times10^{-5}$ dB/$\mu$s at about 8 K.

## INTRODUCTION

Recent measurements of the ultrasonic attenuation in some dielectrics for $\Omega\tau \gg 1$ ($\Omega$ is the sound-wave frequency and $\tau$ is the phonon relaxation time) show a fast temperature dependence of the absorption at helium temperatures that strongly deviates from the power-law predictions of the usual theories of sound attenuation by three-phonon anharmonic interactions.[1] Experimental results in rutile[2] at 3 and 9 GHz below 30 K show an intrinsic attenuation coefficient as steep as $T^{15\pm5}$ which is far greater than the maximum of $T^{9}$ predicted by theory. Including (linear-chain) dispersion to higher order than is customary does not satisfactorily account for the very rapid experimental temperature dependence.[3] Preliminary studies below 1 GHz in synthetic and natural $\alpha$-quartz tentatively report a temperature dependence faster than $T^{10}$ for the intrinsic attenuation.[4] Attempts to explain this latter result by invoking the breakdown of the contact of the energy-conservation surfaces for the allowed three-phonon interactions,[5] which is expected for extremely long thermal phonon lifetimes,[6] fail to account for the magnitude or the frequency independence of the experimental attenuation. Both rutile and quartz have strongly dispersive low-frequency phonon branches[7,8] which make a continuum or a linear-chain dispersion model inadequate to explain some of their low-temperature properties. Rutile has a soft optic mode of reduced frequency $\hbar\omega/k \simeq 100$ K. Interactions of the sound wave with phonons of this mode predict an attenuation coefficient exponentially dependent on the inverse temperature[9] which is consistent with the experimental attenuation below 20 K. $\alpha$-quartz has, in common with other solids such as Ge and Se, a strongly dispersive transverse-acoustic (SDTA) mode with a zone-boundary reduced frequency of about 80 K, which is flat over a considerable extent ($q/q_{\max} > 0.3$) of the Brillouin zone. As a consequence of the SDTA modes all these solids present, for $0.01 < T/T_D < 0.1$, a deviation of the low-temperature specific heat from the Debye prediction.[10] The combination of the low frequency and extended flatness of these "soft" modes produces a pronounced peak in the phonon density of states. Consequently, an enhancement of the probability of interaction of ultrasonic waves with $\hbar\omega > kT$ SDTA phonons in these solids is to be expected at low temperatures.

In this work we present new accurate and more reproducible results of the ultrasonic attenuation below 20 K in synthetic and natural quartz crystals which definitely confirm a deviation of the temperature dependence of the intrinsic attenuation coefficient from the power-law predictions of normal-dispersion three-phonon anharmonic interactions. The results are consistently analyzed in terms of the SDTA model used by Leadbetter, Phillips, and co-workers[11,12] to explain the excess specific heat in crystalline quartz at low temperatures. The present analysis implies that the slowly propagating large-wave-vector SDTA phonons have their lifetime at liquid helium temperatures limited by point-defect scattering.

## EXPERIMENTAL PART

Samples were quartz rods cut and polished to hypersonic specifications of synthetic premium $Q$-grade and natural Brazilian quartz of best available quality.[13] Their axes were aligned parallel with the $x$, $ac$, and $z$ crystallographic directions. Longitudinal and shear waves in the range from 200 to 1000 MHz were surface excited in broadband nonresonant ultrasonic holders.[14] For propagation of longitudinal waves along the $z$ axis of natural quartz, 10-MHz unplated quartz transducers were glued to the samples by No-Naq vacuum grease. The attenuation at each frequency in the as-received samples was measured by the single-ended pulse-echo technique with a Matec automatic attenuation recorder (AAR) capable of a resolution of 0.01 dB. All samples showed echo patterns at helium temperatures that were at least a millisecond long. The patterns were reproducible with thermal cycling and its temperature independence below 4 K was carefully checked by repeated cycles between 4 and 1 K. Some synthetic quartz rods showed irregular nonexponential echo patterns at the higher frequencies. This favors the detection of very small changes of the attenuation with temperature since two echoes of similar magnitude and very long temporal separation could be selected for measuring in the most sensitive range of the AAR. Our technique allows reproducible measurements below 10 K and the detection of attenuation changes as small as $2\times10^{-5}$ dB/$\mu$s for longitudinal and shear waves. Any possible electronic nonlinearities due to the limited dynamic range of the video stages of the i.f. amplifiers were minimized be selecting two echos whose relative magnitude was never allowed to become greater than 4 dB. Such nonlinearities, if undetected, may yield an artificially smaller temperature dependence of the attenuation coefficient. The separation between the AAR's selecting gates was monitored by a sensitive electronic counter. The sample holder was placed inside a radiation-shielded vacuum can and thermally shunted to a massive copper block in good thermal contact with the liquid-He bath. The crystal temperature was determined by calibrated Ge thermometers soldered to one leg of a copper-beryllium torsion spring. The spring coils firmly embraced greased gold leaves which surrounded the side surfaces of the quartz rods. The temperature of the samples was thus measured to better than 0.05 K. Commercial wire resistors in thermal contact with the sample stage and a calibrated temperature controller were used to raise the temperature of the sample above that of the bath in 0.2-K steps. The attenuation data was recorded at fixed temperatures from 4 to 20 K. This experimental procedure yielded a reproducibility of the attenuation versus temperature curves better than 10% for successive experimental runs.

## RESULTS AND DISCUSSION

The measured attenuation relative to its constant low-temperature residual value is shown as a function of temperature in the conventional log-log graphs of Figs. 1 and 2. The points represent the result of three or more reproducible runs for each frequency and show that the relative attenuation $\alpha_j$ in good quartz crystals at temperatures below 10 K may be as small as $10^{-5}$ dB/$\mu$s. The line segments alongside of the data points in Fig. 1 are drawn to emphasize deviations from power-law predictions of the usual theories for quartz.[15] As can be seen from the log-log plots of Fig. 1, there is a pronounced and monotonic decrease of the attenuation as well as an increase of its temperature dependence beyond $T^9$ as the temperature is decreased. The extrapolated temperature dependence of the attenuation at the lowest temperatures is greater than $T^{11}$ and it becomes independent of frequency.

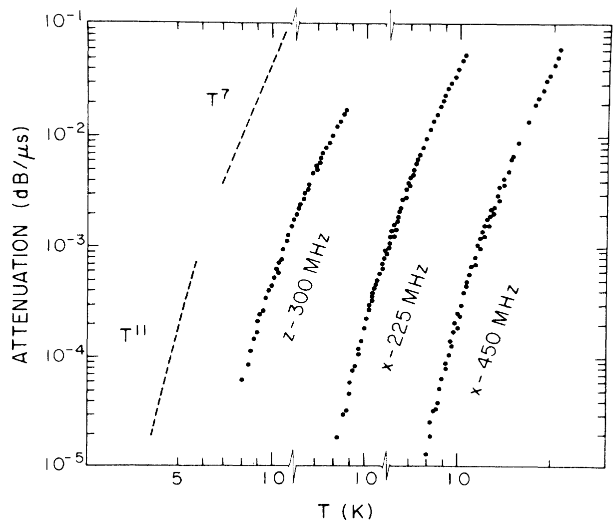


FIG. 1. Temperature dependence of the ultrasonic attenuation of longitudinal waves in natural $z$-cut and synthetic $x$-cut quartz crystals.

A clearly discernible "bump" around 7 K is observed in Fig. 2 for shear waves in our premium $Q$-grade, nominally of better quality, $ac$-cut cultured quartz samples. Such anomalies have been reported for imperfect natural and synthetic quartz crystals and attributed to residual impurities or imperfections.[16,17] Such is most likely the present case since preliminary measurements for $E$-grade $ac$-cut synthetic samples displayed a continuously increasing temperature dependence below 20 K as for longitudinal waves.[4] It has also been reported that the aluminum content in $Q$- and $E$-grade cultured quartz varies from

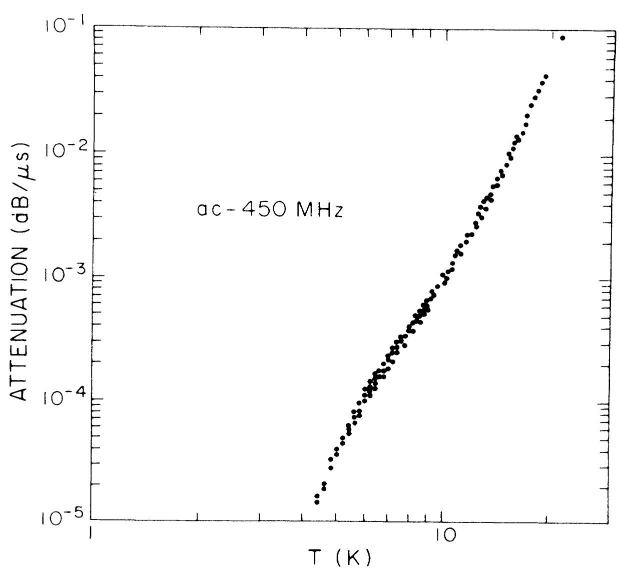


FIG. 2. Temperature dependence of the ultrasonic attenuation of shear waves in an imperfect Premium $Q$-grade synthetic quartz sample.

sample to sample.[18] It is thus also possible that the as-received $Q$-grade samples contain uncompensated Al-hole centers which are known to produce low-temperature ultrasonic relaxation peaks.[19]

A very good representation of the experimental data throughout the explored temperature range is obtained by plotting the value of $\alpha_j T$ versus $100/T$ in the semilog graphs of Figs. 3 and 4. Best least-squares fits of the data to the expression $\alpha_j T = B_j(n)\exp(-T_m/T)$ yield the following values for the adjustable parameters for longitudinal waves ($j$ and $n$ identify, respectively, the polarization and propagation direction of the sound waves): $B_L(x)=287.2$, $T_m(x)=119$ K, and $B_L(z)=90$, $T_m(z)=99$ K for the $x$- and $z$-cut samples, respectively. We note that the above given expression for $\alpha_j T$ produced the least mean-squared error (or best linear correlation factor) compared to other trial functions which were tried of the form $\alpha_j T^b$, $b>1$.

### Attenuation by SDTA phonons

In view of the observed temperature dependence of the different three-phonon interactions which may attenuate the sound waves, we need only consider processes such as $L+T'=T''$ (or $T+T'=T''$ for shear waves). $L$ and $T$ indicate longitudinal and transverse polarizations and the primed symbols correspond to thermal phonons of the SDTA mode. It has been argued that for this process the longitudinal attenuation is dominated by large-wave-vector phonons.[20] Also, as a consequence of the enhanced density of states for small phonon propagation velocity the interaction will be most effective along directions of greatest dispersion.

Under the assumption that nonlinear elasticity is adequate to treat anharmonic interactions of a sound wave of frequency $\Omega \ll kT/\hbar$ with long-wave-vector phonons of the SDTA branch, it is straightforward to calculate the corresponding lifetime-dependent attenuation coefficient.

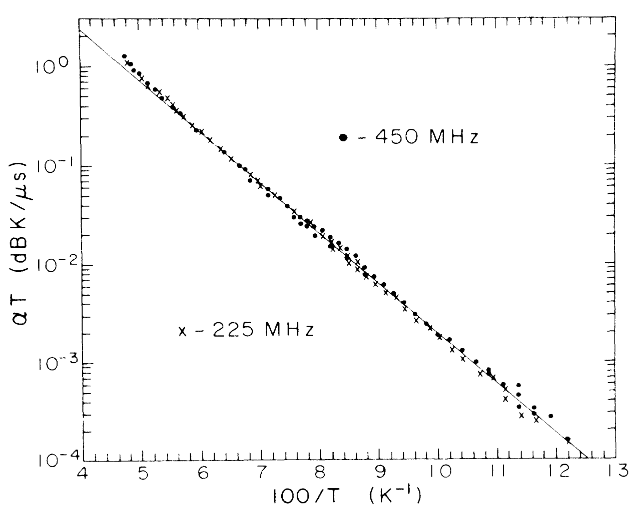


FIG. 3. Exponentially dependent longitudinal ultrasonic attenuation in $x$-cut cultured quartz samples. Continuous line represents $\alpha T = 287.2\exp(-119/T)$.

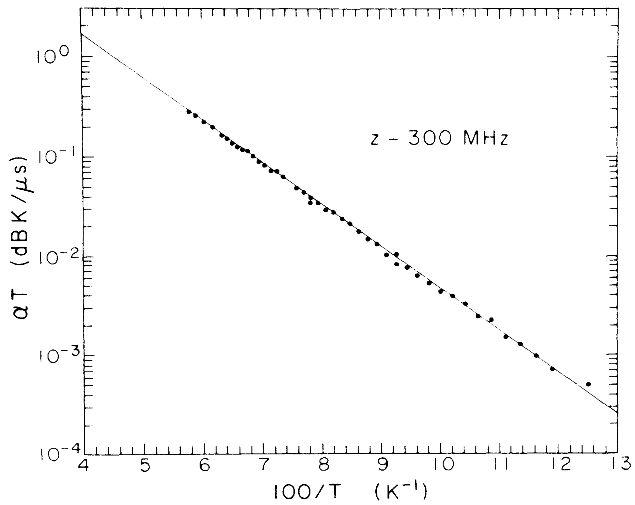


FIG. 4. Exponentially dependent longitudinal ultrasonic attenuation in $z$-cut natural quartz samples. Continuous line represents $\alpha T = 90\exp(-99/T)$.

For a wave of polarization $j$ and propagation velocity $c_j$ in anharmonic interaction with thermal phonons of frequency $\omega$, wave vector $\mathbf{q}$, polarization $i$, and group velocity $\mathbf{v}_i$, a linearized Boltzmann-equation treatment for the anisotropic dispersive continuum will yield a low-temperature attenuation coefficient given in Np/cm by

$$\alpha_j = \frac{\Omega T}{\rho c_j^3} \sum_{q,i} C_{q,i}\gamma_{ij}^2 \frac{\Omega\tau_i}{1+(1-\beta_i)^2\Omega^2\tau_i^2} \ . \tag{1}$$

Here $\rho$ is the mass density, $\beta_i = \mathbf{v}_i \cdot \hat{\mathbf{k}}/c_j$ where $\mathbf{k}$ is the sound-wave vector, $C_{q,i}$ is the phonon-mode specific heat, and $\gamma_{ij}$ is the generalized Grüneisen parameter for the interaction. Equation (1) can be simplified by restricting the interaction to a single SDTA mode whose dispersion is represented by Fig. 5. The values of the parameters given in the figure have been deduced from the experimental dispersion curve for quartz along the $z$ axis.[8] We have confirmed by calculations that for temperatures above 4 K the contribution to the attenuation for $q > q_1 \simeq 0.3 q_m$

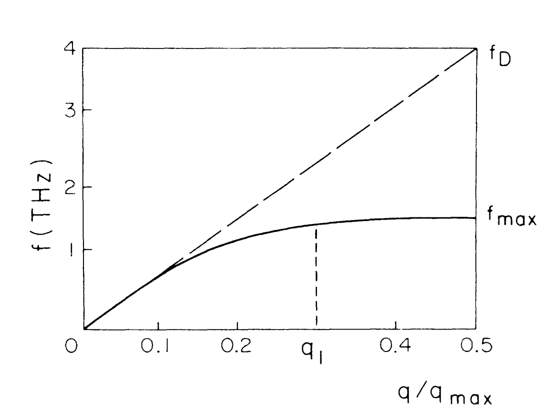


FIG. 5. Strongly dispersive transverse-acoustic-mode model for the lowest TA branch in the $z$ direction of $\alpha$-quartz. Frequency and reduced wave-vector values taken from Ref. 8.

greatly exceeds that from the more normally dispersive part of the SDTA branch. Thus we may take $\beta_i \approx 0$, $\omega = \omega_m > kT/\hbar$, and integrate Eq. (1) over $q$ space from $q_1$ to the zone boundary to obtain, in the limit $\Omega^2\tau^2 \gg 1$, the final expression

$$\alpha_j T \simeq \frac{\gamma_j^2 k}{6\pi^2 \rho c_j^2} \left[\frac{kT_D}{\hbar c_T}\right]^3 T_m^2 \exp(-T_m/T)\tau_m^{-1} . \quad (2)$$

Here $\gamma_j$ stands for an average Grüneisen parameter $T_m = \hbar\omega_m/k$, $c_T$ and $T_D$ are, respectively, the phase velocity and Debye temperature of the SDTA mode in the long-wavelength limit (4.68 km/s and 596 K), and $m$ labels the parameters of the zone-boundary phonons. An expression somewhat similar to Eq. (2) was derived in Ref. 20 for $\hbar\omega_m \lesssim 5kT$ to account for a $T^6$ temperature dependence of the longitudinal attenuation in $x$-cut quartz in the range from 15 to 30 K.

Although Eq. (2) predicts a temperature and frequency dependence of $\alpha_j T$ like that observed experimentally, its exact functional form will in turn depend on how the phonon relaxation rate $\tau_m^{-1}$ varies with temperature. The available calculation of the lifetime of high-frequency transverse phonons is due to Orbach[21] and is limited to an elastic continuum or a normally dispersive solid. This calculation predicts a phonon lifetime at He temperatures of a few milliseconds, a value far too long for a fit of Eq. (2) to our experimental results which require a $\tau_m$ in the picosecond range. It appears unlikely that an extension of Orbach's calculation to the case of strongly dispersive phonons may compensate for such enormous difference in relaxation rates since the phase velocity of SDTA phonons in dispersive dielectrics is not smaller than one-half to one-quarter of the long-wavelength limit $c_T$. On the other hand, recent experimental studies of the propagation of near-zone-boundary TA phonons in GaAs yield values of $\tau_m$ in the microsecond range.[22] Since large-wave-vector TA phonons appear to possess a long lifetime against anharmonic interactions, it follows that $\tau_m$ should be limited by point-defect (impurities or isotopes) scattering as discussed by Lax *et al.*[23] Substituting for the relaxation rate the usual expression $\tau_m^{-1} = A\omega_m^4$, we can finally calculate the attenuation by SDTA modes through Eq. (2).

Good agreement of Eq. (2) to the best fits to our experimental results requires $\gamma_j^2 A$ values of 3 and $1\times 10^{-45}$ s$^3$ for longitudinal waves in $x$- and $z$-cut samples, respectively. Taking the point-defect term from measurements of the thermal conductivity of natural[24] and synthetic[25] $\alpha$-quartz as $A \simeq 2\times 10^{-45}$ and $7\times 10^{-45}$ s$^3$, we deduced values for $\gamma_j$ of $\pm 0.65$ and $\pm 0.70$ for the $x$ and $z$ directions, respectively. These values of $\gamma_j$ appear reasonable considering the overly simplified dispersion of the SDTA model. A slight (17%) difference in the values of $T_m$ exists for waves propagating along the two crystallographic directions. We feel that this variation cannot be meaningfully discussed in the present context that disregards full elastic anisotropy.[26] We note, however, that the experimental values of $T_m$ are within the range of the observed variation in the frequency of the SDTA mode in quartz for different directions in $q$ space.[27]

## CONCLUSIONS

Most measurements of the low-temperature ultrasonic absorption in pure dielectrics are limited to attenuation changes in excess of $10^{-3}$ dB/$\mu$s and can be fitted by a power law in temperature as predicted by three-phonon anharmonic interaction theories. Piezoelectric quartz has been extensively used, because of its freedom from transducer and bonds effects, to put such theories to test with apparently good results above 10 K. We have presented evidence to show that improving the precision and reproducibility of the measurements reveals marked deviations from predictions that require the introduction of real solid features in the theory. Important in the present case has been the inclusion of the strongly dispersive transverse-acoustic mode to explain a dependence of the attenuation as $T^{-1}\exp(-T_m/T)$ below 20 K. One expects similar deviations in other solids with soft acoustic modes where precise low-temperature ultrasonic measurements could provide additional information on the lifetimes of superthermal phonons of SDTA modes.

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[1]For a review, see, H. J. Maris in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1971), Vol. VIII.
[2]M. Pomerantz, S. Grossman, and J. Koo, Phys. Rev. B **8**, 5828 (1973).
[3]M. Pomerantz and N. S. Shiren, Phys. Lett. **45A**, 209 (1973).
[4]R. Nava and M. Rodríguez, in *1982 IEEE Ultrasonics Symposium Proceedings,* San Diego, edited by B. R. McAvoy (IEEE, New York, 1982), p. 1013.
[5]R. Nava, Phys. Status Solidi B **133**, K81 (1986).
[6]H. Maris, Philos Mag. **9**, 901 (1964).
[7]J. G. Traylor, N. G. Smith, R. M. Nickow, and M. K. Wilkinson, Phys. Rev. B **3**, 3457 (1971).
[8]M. M. Elcombe, Proc. Phys. Soc. London **91**, 947 (1967).
[9]R. Nava, in *1974 IEEE Ultrasonics Symposium Proceedings,* Milwaukee, edited by J. de Klerk (IEEE, New York, 1974) p. 514.
[10]R. O. Pohl, in *Amorphous Solids,* edited by W. A. Phillips (Springer-Verlag, New York, 1981).
[11]A. J. Leadbetter and J. A. Morrison, Phys. Chem. Glasses **4**, 188 (1963); A. J. Leadbetter, *ibid.* **9**, 1 (1968).
[12]N. Bilir and W. A. Phillips, Philos. Mag. **32**, 113 (1975).
[13]Unswept Sawyer quartz, cut and polished by Valpey-Fisher Corp., Holliston, Mass.
[14]J. Baumann, W. A. Arnold, and R. Nava, Appl. Phys. **5**, 281

(1974).
[15]G. P. Barton and W. G. B. Britton, Acoust. **41**, 207 (1974).
[16]R. Nava, R. Arzt, I. Ciccarello, and K. Dransfeld, Phys. Rev. **134**, A581 (1964).
[17]M. F. Lewis and E. Patterson, Phys. Rev. **159**, 703 (1967).
[18]M. E. Markes and L. E. Halliburton, J. Appl. Phys. **50**, 8172 (1979).
[19]M. Saint-Paul and R. Nava, J. Phys. **39**, 786 (1978).
[20]R. C. Purdom and E. W. Prohofsky, Phys. Rev. B **2**, 551 (1970).
[21]R. Orbach and L. A. Vredevoe, Physics (N.Y.) **1**, 91 (1964).
[22]R. G. Ulbrich, V. Narayanamurti, and M. A. Chin, Phys. Rev. Lett. **45**, 1432 (1980).
[23]M. Lax, P. Hu, and V. Narayanamurti, Phys. Rev. B **23**, 3095 (1981).
[24]S. Wasin and R. Nava, Phys. Status Solidi A **51**, 359 (1979).
[25]M. Jalilian-Nosraty and J. J. Martin, J. Appl. Phys. **52**, 785 (1981).
[26]I. C. Simpson, Philos. Mag. **32**, 293 (1975).
[27]T. H. K. Barron, C. C. Huang, and A. Pasternak, J. Phys. C **9**, 3925 (1976).