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X-ray evidence of direct generation of nonequilibrium phonons in quartz by infrared radiation

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Direct electromagnetic stimulation of transverse-optical phonons in quartz has been accomplished by irradiation with a CO_2 laser, and experimentally observed through enhancement of x-ray diffuse scattering due to zone-center and zone-boundary phonons.

Generation of nonequilibrium high-frequency phonons and their subsequent decay to thermal equilibrium by anharmonic processes offers a clean and powerful probe for observing and characterizing anharmonic effects in crystals, and has received considerable attention recently.[1-3]

We describe in this paper an experiment in which nonequilibrium phonons have been generated in α quartz by direct action of the electromagnetic field of CO_2 laser light on the polar SiO_2 molecules, and detected through the consequent enhancement of thermal diffuse scattering of x rays. Use of x rays as a probe has the obvious advantage that large phonon wave vectors, comparable to the size of the Brillouin zone, are accessible.

It is known that quartz has a strong absorption band centered at 9 μm,[4] most likely due to resonance with a TO optical phonon with $\lambda = 9.3$ μm at $k = 0$.[5] Several lines are present between 9.2 and 9.6 μm in the spectrum of the CO_2 laser light, and a strong enhancement of the occupation number density of the pumped phonon is expected to take place.[6] As a consequence of energy and momentum conservation, only phonons with $k \simeq 0$ can be excited by the laser light. Diffuse x-ray scattering due to zero wave-vector phonons is located at the center of the Brillouin zone, which ordinarily corresponds to a Bragg reflection. Since very little effect is expected on Bragg reflections, we have chosen to explore *forbidden reflections* with zero structure factors which also correspond to $k = 0$. The reflection chosen was the (004), along the c axis. In absence of thermal vibrations, or for acoustic phonons, no intensity is present at (004). Only optical phonons, which cause disruption of the negative interference between equivalent atomic basal planes, can produce diffuse intensity for a reflection like (004).

Cu-$K\alpha$ radiation ($\lambda = 1.54$ Å), monochromatized by a curved quartz monochromator, was used throughout this experiment. The beam cross section was about 1×0.2 mm^2, converging on the sample with an angle of $\simeq 0.5°$. A standard fixed target tube (1.8-kW max power) was used with a conventional x-ray generator. Typical working conditions were 40 kV and 20 mA. The quartz crystal was a thin disk slab, 0.45 mm thick, 5 mm diameter, perpendicular to the c axis, stuck inside a cryostat on a copper block by means of a heat sink compound,[7] which is a good thermal conductor. The copper block was located in vacuum, at the bottom of the internal vessel of a Dewar filled with liquid nitrogen. The cryostat could also be used with liquid helium, but the hold time was too short, of the order of half an hour, due to the intense laser power (35 W average). Normally, the counting time was 12 h for each run. The x-ray windows were made out of Mylar, 0.002 in. thick, and the laser window was a slab of BaF_2, transparent to infrared radiation (see Fig. 1). The CO_2 laser (made by Coherent Radiation, model 41) was Q switched, at a frequency of 10 000 pulses/s, with a 200 ns pulse width, and an instantaneous power of more than 15 kW. In order to make sure that the x-ray and the laser beams were hitting the same spot on the crystal, a visible He-Ne laser was arranged in such a way that the two laser beams were exactly superimposed. The visible laser beam was then used for alignment purposes. The CO_2 laser beam was not focused, and its cross section was of the order of 20–25 mm^2, which greatly facilitated the alignment.

It was found experimentally that the light was vertically polarized, i.e., normal to the x-ray scattering plane. According to x-ray diffuse scattering theory,[8] the diffuse intensity is zero when the scattering vector is perpendicular to the direction of atomic vibrations. We thought that, even though this was the case in the first version of our experiment, the atomic vibrations stimulated by the laser light might have possessed a nonzero component along the scattering vector, due to the tensorial character of the stress-strain relationship for individual atoms in quartz.

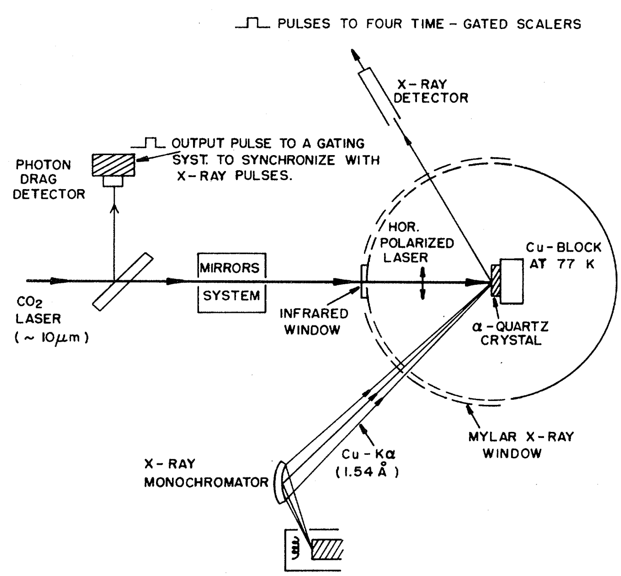

FIG. 1. Experimental setup. The polarization of the laser beam was found to be perpendicular to the plane of this figure. The "mirrors system" installed along the beam in the present configuration has the action of rotating the polarization by 90°.

The first experiment, performed as described in Fig. 1, but with the laser vertically polarized, gave a null result. It was found necessary to rotate the plane of polarization of the laser light by 90°, by means of three successive reflections from metal mirrors.[9] In order to obtain a nonzero component of the electric field of the laser light along the scattering vector, an asymmetric scattering geometry was adopted. Another thin quartz plate (0.5 mm thick) was prepared, with an angle of 15° between the c axis and the normal to the surface. In this way the $[00l]$ direction could be scanned with a fixed angle of 15° between the scattering vector and the laser beam, which means that only 7% of the atomic displacement was effective in producing diffuse scattering.

The laser light pulse was partially reflected into a photon drag detector,[10] which was used as a trigger for the detection system.

The counter was a scintillation detector[11] followed by a fast amplifier and pulse-height analyzer,[12] with a pulse pair resolution of 200 ns. The gating system was designed in such a way that, after a suitable delay following the pulse from the photon drag detector, four scalers were turned on in sequence for a time $\Delta t = 500$ ns each, with virtually no delay between two adjacent time slots. The pulses from the scintillation counter were also delayed, in such a way that the x-ray pulses emanating from the quartz crystal at the time when the laser was fired were counted by the second scaler. In this way the second channel corresponds to "laser on." We kept one empty channel (1) in order to check for possible errors in timing. A timing error amounting to more than one channel was out of the question.

In order to avoid systematic noise in channel 2, generated by the laser firing circuitry, we repeated all experiments in identical conditions, the only difference being that the laser beam was intercepted by an absorber before reaching the cryostat. Then the difference counting rates were considered, channel by channel. The experimental results are shown in Fig. 2. Some increase in diffuse scattering is clearly visible in the second channel.

A similar experiment was done for zone-boundary phonons ($\vec{k} = 0, 0, 4.5$) and the results are shown in Fig. 3. An increase in diffuse scattering is also visible here. Since the laser light is not able to generate large wave-vector phonons as a primary effect, we must assume that these nonequilibrium phonons are the result of anharmonic decay from the zone-center phonons. The effect is similar to that observed in GaAs,[1,2] and CaF_2.[3] The fact that large error bars are present in Figs. 2 and 3, a consequence of poor statistics, is due to the low duty factor of our time-resolved diffraction technique: 1:200.

It is clear that the available x-ray intensity is the primary limiting factor in this experiment. Plans are under way to continue this work using the high intensity of the National Synchrotron Light Source at Brookhaven.

The question may be asked whether or not the enhancement in diffuse scattering in Figs. 2 and 3 is due to thermal heating. We are not concerned, here, of an overall average temperature increase, which certainly takes place, but of a possible temperature fluctuation in phase with the laser light pulses. A rough estimate of the heating effect can be made by considering the diffusion of heat through a wall, into a semi-infinite medium. It is assumed that the free surface is suddenly subjected, at the instant $t = 0$, to a constant heat flow corresponding to the laser light pulse. From the theory

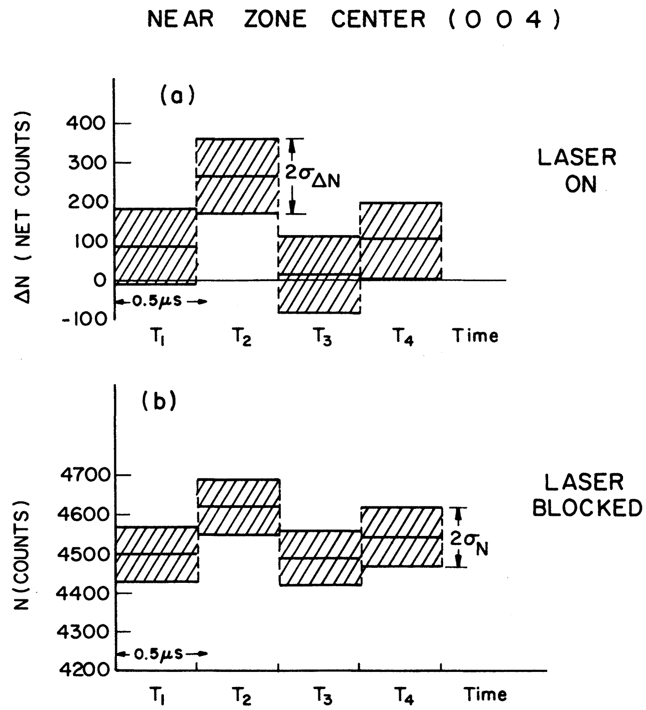

FIG. 2. Excess counting rates (laser on minus laser blocked) in four time-gated scalers. (a) The laser is turned on between $t = 0.5$ and 1 μs. (b) The laser beam is blocked. These are zone center phonons ($\vec{k} = 004$).

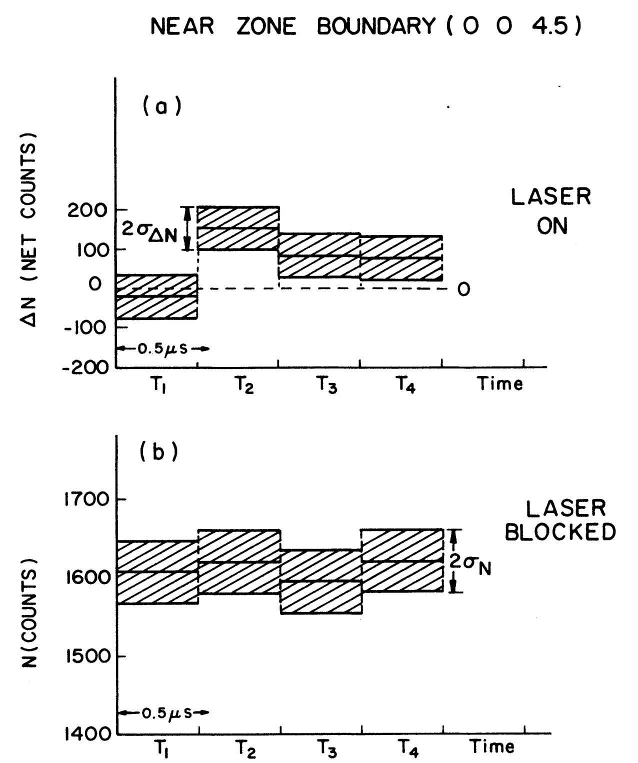

FIG. 3. Excess counting rates (laser on minus laser blocked) in four time-gated scalers. (a) The laser is turned on between $t = 0.5$ and 1 μs. (b) The laser beam is blocked. These are zone boundary phonons ($\vec{k} = 004.5$).

of heat diffusion in solids[13] it can be estimated that the temperature surge at the end of each light pulse, computed *at the surface* ($x = 0$), is of the order of 4 °C, and decreases to 0.4 °C at a depth of 5 μm inside the crystal. This estimate assumes no penetration of infrared photons, and neglects reflection from the surface of quartz (which is considerable). If penetration is taken into account [of the order of 15 μm (Ref. 4)], the estimated temperature surges are even smaller. It is clear that such a temperature increase cannot produce any appreciable increase in diffuse scattering.

The best proof that instantaneous heating is of no concern in this experiment is the fact that in our first attempt, with the x-ray scattering vector perpendicular to the electromagnetic field of the laser light, no effect was detected.

Similar experiments have been repeated using the transmission geometry (Laue case of diffraction), in which the (00*l*) scattering vector was parallel to the crystal surface. A systematic increase of diffuse scattering in the second scaler has always been observed.

We, therefore, conclude the direct electromagnetic stimulation of nonequilibrium transverse-optical phonons in quartz has been observed by x-ray scattering. The potentiality of this experimental method lies in the ability of the x-ray method to select wave vectors and polarization directions. A more complete characterization of this effect is planned to be done using synchrotron radiation x rays. The possibility of using a pulsed neutron source for inelastic scattering experiments will be considered.

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[12]Spectroscopy Amplifier Model 2020, followed by Model 2035A, Timing Single Channel Analyzer, both from Canberra Industries, Inc.

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