PHYSICAL REVIEW B VOLUME 39, NUMBER 2 15 JANUARY 1989-I

Saturation of a resonant phonon-band mode by far-infrared excitation

U. Werling and K. F. Renk
Institut für Angewandte Physik, Universität Regensburg, D-8400 Regensburg, West Germany

(Received 9 February 1988; revised manuscript received 12 September 1988)

We have observed saturation of a resonant phonon-band mode in an oxygen-doped silicon crystal. By use of a tunable pulsed high-power far-infrared laser, we excited the mode monochromatically and found that the absorption decreased strongly with increasing laser pulse energy. We show that the excitation resulted in a nonthermal state that decayed most likely by a process of spectral diffusion of phonons, caused by scattering at low-lying states.

It is well known that defects in crystals can induce resonant phonon-band modes.[1–3] For a resonant band mode with a resonance frequency within the phonon bands of the unperturbed crystal, the vibrational amplitude of a defect is much larger than the vibrational amplitude of the regular crystal atoms. In this paper we report the first observation of light-induced saturation of a resonant band mode. We have studied oxygen-doped silicon where the interstitial oxygen impurities give rise to a resonant band mode. We will also present an analysis of the absorption behavior of the resonant band mode by describing it as a saturable two-level system strongly coupled to a nonsaturable system of acoustic phonons, and we will discuss the decay of the coupled system after monochromatic excitation by absorption of far-infrared radiation.

Oxygen in silicon crystals occupies preferentially an interstitial site on the [111] axis between two silicon atoms; the corresponding Si—Si bond is replaced by covalent bonds with the oxygen atom. The oxygen atom is, however, slightly shifted away from the axis and can vibrate in a plane perpendicular to the [111] axis. This vibration can be described by a perturbed two-dimensional harmonic oscillator model with a potential energy that is rotationally symmetric with respect to the [111] axis (Fig. 1).[4] The corresponding energy levels are nonequidistant. The lowest vibrational transition (at an energy of 29.2 cm^{-1}), which is infrared active, lies in the acoustic phonon band of the silicon crystal. Interaction of this transition with the phonon system of the crystal by emission and reabsorption of resonant phonons, i.e., phonons that have the same frequency as the vibrational transition, gives rise to a resonant phonon-band mode.[5] Excitation of the mode leads to both an excitation of the $|1,\pm 1\rangle$ vibrational level of the oxygen vibration and to a population of phonon modes. The far-infrared absorption behavior is therefore determined by the occupation numbers of both subsystems.

Our silicon crystal, containing $1.8\times 10^{18}\ \mathrm{cm}^{-3}$ oxygen atoms had been annealed 2 h at a temperature of 600 °C and 2 h at 1090 °C to remove thermal donors. Other impurities in the crystal were boron ($<10^{14}\ \mathrm{cm}^{-3}$), phosphorus ($10^{14}\ \mathrm{cm}^{-3}$) and carbon ($<5\times 10^{15}\ \mathrm{cm}^{-3}$). The crystal was immersed in liquid helium at a temperature of 1.7 K. We used a pulsed high-power tunable CH_3F Raman laser[6] pumped by a high-pressure CO_2 laser that had strong emission at the oxygen resonance frequency. Far-infrared laser pulses (duration 70 ns, maximum energy 400 μJ, bandwidth 0.12 cm^{-1}) were focused on the crystal, with a maximum pulse intensity of about 100 $\mathrm{kW/cm}^2$ on a small spot exhibiting Gaussian profile ($\simeq 1.7$ mm diameter). Transmitted radiation was detected by a Golay detector. A small part of the radiation energy was focused to a reference Golay detector for monitoring the pulse energy of the incident laser beam. By replacing these detectors by Schottky diodes it was possible to observe synchronously the shapes of the incident and transmitted pulses.

We first measured the sample transmittance at low far-infrared pulse energies. The transmittance curve (Fig. 2) is mainly determined by interference of radiation reflected at the two parallel surfaces of the (5-mm-thick) crystal, but shows clearly the resonant band mode at a frequency of 29.2 cm^{-1}. Taking account of the interference and of the bandwidth of the laser radiation, we can describe the experimental transmittance spectrum by the solid curve of Fig. 2 and find that the oxygen resonance line has Lorentzian line shape with an absorption coefficient of 18 cm^{-1} in the line center, and a half width

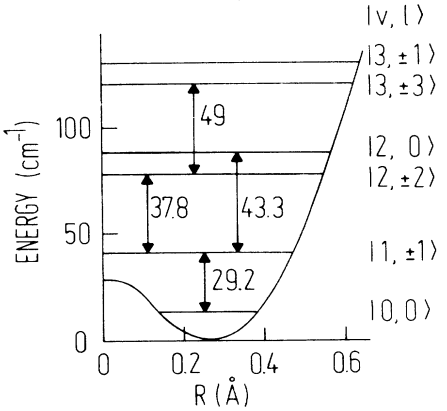

FIG. 1. Potential energy and vibrational energy levels of oxygen in silicon (Ref. 4); R is the distance of the oxygen atom from [111] axis and v and l are the quantum numbers of a two-dimensional harmonic oscillator.

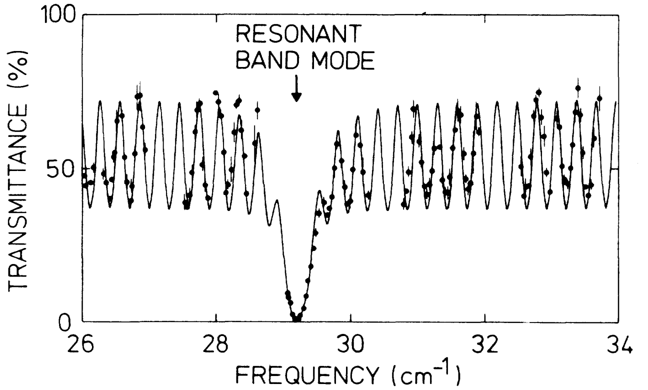

FIG. 2. Far-infrared transmittance of oxygen doped silicon; our far-infrared laser is tunable in the ranges of the points.

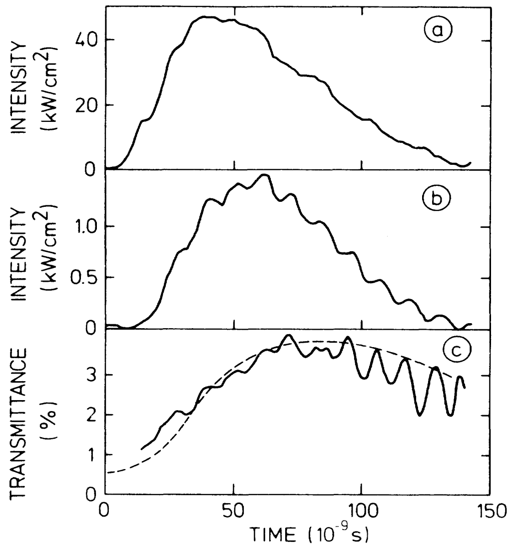

FIG. 4. Pulse shapes for the (a) incident and (b) transmitted laser pulses, and (c) transient transmittance; dashed curve, theoretical transmittance for the case of spectral phonon diffusion.

(full width at half maximum) of 0.13 cm^{-1}; our results are consistent with earlier far-infrared absorption measurements[4] and also with results of spectroscopic studies with phonons, performed by use of superconducting tunnel contacts.[7] The half width, which is also consistent with a theoretical estimate,[5] corresponds to a dephasing time (80 ps) due to energy exchange between the oxygen vibration and acoustic phonons.

We have measured the energy transmittance at line center for different laser pulse energies. We found (Fig. 3) that the transmittance increased strongly, from 0.2% at small pulse energy to 2% at large energy. Our result demonstrates clearly a saturation behavior of the absorption.

We have also investigated the temporal behavior of the absorption. Results are shown in Fig. 4 for a medium pulse energy (110 μJ). In comparison to the incident pulse [Fig. 4(a)], the transmitted pulse [Fig. 4(b)] was not only reduced in intensity, but had a different shape, indicating that during the first part of the pulse stronger absorption occurred. The corresponding transient transmittance is shown in Fig. 4(c). The transmittance increases strongly in the front of the pulse, shows a maximum, and decreases in the tail. In comparison to the incident pulse, the maximum of the transmittance is delayed. The results show that the excited-band mode state exists for a time longer than the laser pulse duration. However, the decrease in the tail indicates that a decay process sets in already during the laser pulse. We will suggest that this decay is mainly due to spectral diffusion of the resonant phonons caused by multiple inelastic scattering processes, with single frequency changes of the order of the spectral width of the oxygen resonance line; an originally monochromatic phonon distribution—as it results from the decay of the oxygen vibrations—broadens and the energy injected by far-infrared absorption is slowly removed from the coupled system of oxygen vibrations and resonant phonons.

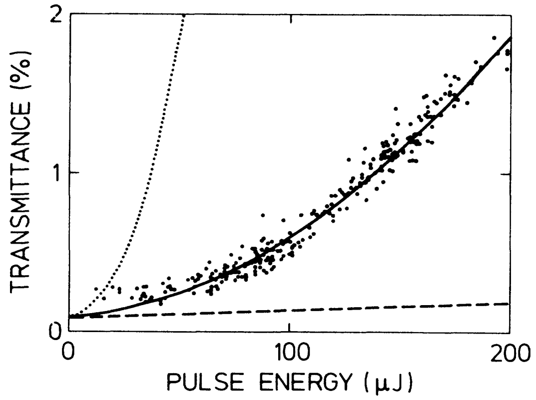

FIG. 3. Energy transmittance (points) of oxygen-doped silicon for pulsed radiation at 29.2 cm^{-1} and calculated curves for the cases of spectral phonon diffusion (solid line), of fast thermalization (dashed) and of nondecaying phonons (dotted).

For an analysis of our results we consider the resonant band mode as composed of two strongly coupled subsystems, namely the system of the oxygen vibrations, which can be regarded as saturable two-level systems (Fig. 1), and the nonsaturable system of the phonons of the silicon crystal. The coupling is performed by emission and reabsorption of resonant phonons by the oxygen vibrations. Using appropriate rate equations (see Appendix) we have first calculated the crystal transmittance assuming that the whole energy injected by far-infrared absorption remains stored in the coupled system during the laser-pulse duration, i.e., that the resonant phonons remain monochromatic; spatial escape of phonons from the excited volume during the laser pulse duration can be neglected because of spatial trapping of the phonons due to strong resonance scattering at the oxygen atoms. The calculated increase of transmittance (dotted curve in Fig. 3) is much larger than the observed increase. This indicates that a decay of the resonant band mode during the duration of the laser pulse occurred. For the other extreme case, namely for fast thermalization during the laser pulse duration, the calculation delivers almost no saturation (dashed line in Fig. 3). Thermal population of the oxygen vibrational levels due to heating of the crystal by the absorbed far-infrared radiation can therefore not be the reason for the observed strong nonlinear transmittance. However, we can consistently describe both the transient transmittance and the energy transmittance if we assume that spectral diffusion of the resonant phonons occurred. Spectral diffusion of phonons is characterized by a spectral diffusion constant $D_\nu = \nu_R^2/\tau_{\rm in}$, where ν_R is the mean frequency shift in a single scattering process and $\tau_{\rm in}^{-1}$ the inelastic scattering rate. With a value $D_\nu = 1.3\times10^{28}$ Hz^{2}s^{-1}, the results of our calculation shown in Fig. 4(c) (dashed line) and Fig. 3 (solid line) describe the experimental results reasonably well. Our analysis is consistent with the results of a time-of-flight experiment that shows typical characteristics of spectral phonon diffusion.[8,9] Since the inelastic scattering sets in already during the laser pulse we guess for the inelastic scattering rate a value $\tau_{\rm in}^{-1} \simeq 10^8$ s^{-1}, and find a mean frequency shift $\nu_R \simeq 10$ GHz for a single scattering process; this value is comparable with the width of the Lorentzian oxygen resonance line.

We have also taken into consideration other energy-loss mechanisms for the resonant band mode. For instance, we found that inelastic scattering processes with frequency changes of the phonons that are large compared with the linewidth of the oxygen resonance could not deliver a consistent description of both the energy transmittance and the transient transmittance. On the time scale of our experiment, anharmonic down-conversion[10] of phonons is too slow and should play no role. We have also considered phonon up-conversion, expected for large phonon occupation numbers. At the phonon occupation numbers (≤ 2) of our experiment phonon up-conversion is most likely not important, as we found by an estimate of conversion rates that follow from anharmonic parameters.[10]

In analogy to spectral diffusion of high-frequency phonons observed in Al_2O_3 containing vanadium and chromium ions[11] and in Al_2O_3 containing chromium ions,[12] where inelastic scattering is attributed to Raman scattering at low-lying electronic two-level systems, we suggest that in our oxygen-doped silicon crystal low-lying two-level systems, presumably of vibrational origin, are responsible for Raman scattering of high-frequency phonons. Evidence for low-lying energy levels, in undoped silicon crystals, is known from specific heat studies[13,14] and from a sound velocity study.[15] Our present investigation gives further evidence[11,12] that the dynamical behavior of high-frequency phonons can be markedly influenced by low-lying excitations. For a characterization of the nature of the corresponding defects and their interaction with phonons further studies are necessary.

In summary, we have found saturation of a resonant phonon-band mode in an oxygen-doped silicon crystal. For an analysis we take into account that the resonant band mode in silicon corresponds to saturable two-level systems coupled to a nonsaturable system of acoustic phonons. Our analysis gives evidence that the mode decays mainly by a process of spectral phonon diffusion due to interaction of high frequency phonons with low-lying excitations.

We have enjoyed very stimulating discussions with R. O. Pohl. We would like to thank W. Eisenmenger, K. Lassmann, and also P. Wagner, D. Huber, and J. Reffle (Wacker Chemitronic) for valuable discussions and for making available oxygen-doped silicon crystals.

APPENDIX

The equilibrium condition of the coupled system of oxygen vibrations, considered as two-level systems, and the phonons follows from the rate equation

$$\frac{dN_2(t)}{dt} = -\frac{N_2(t)}{T_1} + \int_0^\infty \frac{Z(\nu,t)}{\tau_{\rm res}(\nu)}\,d\nu \,, \tag{A1}$$

where N_2 is the density of excited oxygen vibrational states, T_1 the lifetime of these states against emission of a resonant phonon, $Z(\nu,t)$ the spectral phonon density, and $\tau_{\rm res}^{-1}(\nu)$ the resonance scattering rate for phonons of frequency ν. With[16]

$$\tau_{\rm res}^{-1}(\nu) = 4D^{-1}(\nu_0)\,g(\nu)(N-2N_2) \,, \tag{A2}$$

where N is the concentration of oxygen atoms, $D(\nu_0)$ the density of phonon states near the oxygen resonance frequency ν_0, and where $g(\nu) = \frac{1}{4}\Gamma^2[\frac{1}{4}\Gamma^2 + (\nu-\nu_0)^2]^{-1}$, with $\Gamma = (2\pi T_1)^{-1}$, is the Lorentzian line-shape function of the absorption line, we obtain the equilibrium condition

$$\frac{\pi}{2}D(\nu_0)\Gamma\frac{N_2}{N-2N_2} = \int_0^\infty Z(\nu)g(\nu)\,d\nu \,. \tag{A3}$$

Neglecting, first, the coupling between the two-level systems and the phonons, we can describe the propagation of the far-infrared radiation pulse inside the crystal by the rate equations

$$\frac{\partial N_2(t,z)}{\partial t} = [N-2N_2(t,z)]\int_0^\infty \sigma_{\rm FIR}(\nu)F(t,z,\nu)\,d\nu \,, \tag{A4a}$$

$$\frac{\partial F(t,z,\nu)}{\partial z} = -\sigma_{\rm FIR}(\nu)F(t,z,\nu)[N-2N_2(t,z)] \,, \tag{A4b}$$

where the z axis corresponds to the propagation direction of the far-infrared radiation, $F(t,z,\nu)$ is the far-infrared spectral photon flux, and $\sigma_{\rm FIR}(\nu)$ the far-infrared absorption cross section that follows from the transmission spectrum of Fig. 2. Since our experiment was performed at low temperature ($kT \ll h\nu$) we have the boundary condition $N_2(t=0,z) \simeq 0$ and $Z(t=0,z,\nu) \simeq 0$.

We have solved Eqs. (A4) numerically for our spectral photon flux density $F(t,0,\nu)$. In order to take into account the coupling of the two-level systems and the phonon system, we have divided the laser pulse (duration 70 ns) in single portions of 1 ns duration. Each of these pulse portions leads to an increase of the density N_2 of excited two-level systems according to Eq. (A4a). Energy loss by emission of resonant phonons can be calculated using Eq. (A3), and so a corrected value of the density N_2 can be found with which the procedure is repeated for the next 1-ns portion of the laser pulse. Using Eq. (A4b) the spectral photon flux density $F(t,d,\nu)$ behind a crystal of thickness d can be calculated stepwise. Taking into account the frequency distribution of the far-infrared radiation, we determined, from $\int F(t,d,\nu)d\nu$, the transient transmittance of the crystal; additional integration, in the time scale, delivered the energy transmittance for a laser pulse. In the calculation a triangular laser-pulse shape in the time scale and a Gaussian distribution over the beam cross section were assumed.

For description of spectral diffusion of the phonons we used the one-dimensional diffusion equation

$$\frac{\partial Z(\nu,t)}{\partial t}=D_\nu\frac{\partial^2 Z(\nu,t)}{\partial \nu^2}\ , \tag{A5}$$

where D_ν is the spectral diffusion constant. Spatial diffusion of the phonons during the laser pulse can be neglected because of the strong resonance scattering even in the wings of the Lorentzian oxygen resonance line. Since phonons are generated only in a small frequency interval around the resonance frequency ν_0, we obtain for phonons generated at time t_0 (within a 1-ns interval) the solution

$$Z(\nu,t)\sim D_\nu^{-1/2}(t-t_0)^{-1/2}\exp\left[-\frac{(\nu-\nu_0)^2}{4D_\nu(t-t_0)}\right]\ . \tag{A6}$$

Taking account of Eq. (A6), we have solved the rate Eqs. (A4) and obtained a good description [Fig. 4(c) dashed line and Fig. 3 solid line] of our experimental results.

---

[1] R. Brout and W. Visscher, Phys. Rev. Lett. **9**, 54 (1962).

[2] H. Bilz, D. Strauch and R. K. Wehner, in *Handbuch der Physik,* edited by L. Genzel (Springer-Verlag, Berlin, 1984), Vol. XXV/2d, p. 262.

[3] A. S. Barker, Jr. and A. J. Sievers, Rev. Mod. Phys. **47**, Suppl. No. 2, 1 (1975).

[4] D. R. Bosomworth, W. Hayes, A. R. L. Spray, and G. D. Watkins, Proc. R. Soc. London, Ser. A **317**, 133 (1970).

[5] D. K. Brice, Phys. Rev. **140**, A1211 (1965).

[6] U. Werling, K. F. Renk, and Wan Chong-Yi, Intern. J. Infrared Millimeter Waves **7**, 881 (1986).

[7] W. Eisenmenger, in *Nonequilibrium Superconductivity, Phonons and Kapitza Boundaries,* edited by K. E. Gray, NATO ASI Series, Vol. B65 (Plenum, New York, 1981), p. 73.

[8] U. Werling, Ph.D. thesis, Universität Regensburg, 1988.

[9] U. Werling and K. F. Renk, Jpn. J. Appl. Phys. Suppl. **26-3**, 671 (1987).

[10] A. Berke, A. P. Mayer, and R. K. Wehner, Solid State Comm. **54**, 395 (1985).

[11] U. Happek, T. Holstein, and K. F. Renk, Phys. Rev. Lett. **54**, 2091 (1985).

[12] N. Retzer, H. Lengfellner, and K. F. Renk (unpublished).

[13] H. J. Schink, H.v. Löhneysen, and B. Schröder, Appl. Phys. A **36**, 15 (1985).

[14] See also Ref. 11 of Ref. 15.

[15] R. N. Kleiman, G. Agnolet, and D. J. Bishop, Phys. Rev. Lett. **59**, 2079 (1987).

[16] K. F. Renk, in *Nonequilibrium Phonons in Nonmetallic Crystals,* edited by W. Eisenmenger and A. A. Kaplyanskii (North-Holland, Amsterdam, 1986), p. 317.