$\langle 233\rangle$, $\langle 2233\rangle$, and $\langle 223\rangle$ but, because[9] $b_\nu \approx (j+2)\times(1-x^2)(1-x^{1+2\delta})^{j+1}$ for $\nu = 2^j 3$ and $b_\nu \approx -x^{1-2\delta}\times(1-x^{1+2\delta})^{2(j+1)}$ for $\nu = 2^j 32^{j-i}3$, as $w^{q_\perp}\to 0$, only $\langle 223\rangle$ appears as a stable phase, between $\langle 23\rangle$ and $\langle 2\rangle$ with $\delta_3 - \delta_2 = O(w^{3q_\perp})$. More generally, by using these results in (9) at stages $n = j+1$ and $n = 2j+1$, respectively, an inductive argument can be constructed which yields the remaining conclusions.

We are indebted to the John Simon Guggenheim Memorial Foundation and to the Deutsche Forschungsgemeinschaft for the award of fellowships (to M.E.F. and W. S., respectively), during the tenure of which much of the work reported here was done. The hospitality of the Massachusetts Institute of Technology, Harvard University, and Boston University, and the support of the National Science Foundation, in part through the Materials Science Center at Cornell University, are gratefully acknowledged.

[1]See, e.g., *Solitons and Condensed Matter Physics*, edited by A. R. Bishop and T. Schneider (Springer-Verlag, Berlin, 1978); J. Villain, in Proceedings of the NATO Advanced Study Institute, Geilo, April, 1979 (to be published), and references therein.

[2]R. J. Elliott, Phys. Rev. 124, 346 (1961).

[3]P. Fischer *et al.*, J. Phys. C 11, 345 (1978); G. Meier *et al.*, J. Phys. C 11, 1173 (1978); J. Rossat-Mignod *et al.*, Phys. Rev. B 16, 440 (1977), and Physica (Utrecht) 86-88B, 129 (1977).

[4]J. von Boehm and P. Bak, Phys. Rev. Lett. 42, 122 (1979).

[5]J. Villain and M. Gordon, to be published.

[6]See J. E. Fischer and T. E. Thompson, Phys. Today, 31, No. 7, 36 (1978).

[7]S. A. Safran (to be published); compare also with Ref. 4.

[8]See S. Aubry, in *Solitons and Condensed Matter Physics*, edited by A. R. Bishop and T. Schneider (Springer-Verlag, Berlin, 1978), p. 264, who discusses the ground state of a classical one-dimensional model.

[9]M. E. Fisher and W. Selke, to be published.

[10a]P. Bak and J. von Boehm, in Proceedings of the Intermag Magnetism and Magnetic Materials Conference, New York, 17-20 July (to be published).

[10b]P. Bak and J. von Boehm, Phys. Rev. B 19, 1610 (1980).

[10c]See, also in *Solitons and Condensed Matter Physics*, edited by A. R. Bishop and T. Schneider (Springer-Verlag, Berlin, 1978).

[11]S. Redner and H. E. Stanley, Phys. Rev. B 16, 4901 (1977), and J. Phys. C 10, 4765 (1977).

[12a]W. Selke, Z. Phys. B 29, 133 (1978).

[12b]W. Selke and M. E. Fisher, Phys. Rev. B 20, 257 (1979).

[12c]W. Selke and M. E. Fisher, in Proceedings of the Intermag Magnetic Materials Conference, New York, 17-20 July, 1979 (to be published).

[13]See, e.g., S. I. Gass, *Linear Programming* (McGraw Hill, New York, 1964), or H. S. Wilf, *Mathematics for the Physical Sciences* (Wiley, New York, 1962).

Raman Scattering from Nonequilibrium LO Phonons with Picosecond Resolution

D. von der Linde, J. Kuhl, and H. Klingenberg
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Germany
(Received 31 December 1979)

A novel technique is described for time-resolved Raman scattering for studying the dynamics of nonequilibrium excitations on a picosecond time scale. The generation and the decay of nonthermal LO phonons in GaAs is measured, and $\tau' = 7 \pm 1$ ps is obtained for the relaxation time of the phonon population at 77 K.

PACS numbers: 63.20.Dj, 78.30.Gt

This paper describes a novel technique for time-resolved spontaneous Raman scattering. As a first application we investigate the generation and relaxation of nonequilibrium optical phonons in a solid. The relaxation of optical phonons occurs on a picosecond time scale and is still inadequately understood. The information on the phonon relaxation processes obtained from the analysis of the broadening of Raman and infrared spectra is rather indirect and incomplete. Direct measurements in the time domain, on the other hand, have provided a detailed picture of the dephasing of molecular vibrations[1] and of the decay of *coherent* optical phonons.[2-5] Here we present, for the first time, a measurement of the time revolution of nonequilibrium *incoherent* optical phonons. We observe the generation of optical phonons during the interaction of photoexcit-

ed hot electrons and holes with the lattice, and we obtain the relaxation time of a nonequilibrium population of LO lattice modes. Our method is suitable for studying the dynamics of other nonequilibrium excitations in a large variety of materials.

The experiment is based on a variant of the excite-and-probe scheme[6] in which two successive short light pulses with the same frequency and intensity but with orthogonal polarizations photoexcite the material. The strength of the excitations is probed by detecting the Raman light scattered off these excitations, i.e., we measure the anti-Stokes intensity which is proportional to the number of generated phonons. The scattered light produced by the first pulse (pump pulse) is eliminated by a suitably oriented analyzer in front of the detector such that only scattering due to the second pulse (probe pulse) is detected.[7]

The total signal of the probe pulse consists of two parts. First, there is light scattered off excitations left behind by the pump pulse. The variation of this contribution with the time delay Δt reveals the rise and decay of the excitations under study. Second, there is a signal caused by excitations generated by the probe pulse itself; this contribution is independent of Δt and thus leads to a constant background signal.

For photoexcitation and Raman scattering we use pulses from a synchronously mode-locked rhodamine 6G dye laser operating at $\lambda = 575$ nm ($\hbar\omega = 2.16$ eV). The laser generates a continuous pulse train at a rate of 80.6 MHz with an average power of 80 mW. The pulse duration was measured by the second-harmonic autocorrelation method[6] to be 2.5 ps.

The output of the laser is split to form two equally intense beams with a continuously variable time delay Δt. The two beams are then polarized perpendicular to each other and recombined on the surface of the sample. The backward-scattered light which carries the information about the nonequilibrium excitations is detected by a standard photon-counting Raman spectrometer.

In our experiment we study nonequilibrium LO phonons in GaAs which are produced as follows. The dye-laser pulses photoexcite electron-hole (e-h) pairs with an excess energy of 17 times the LO-phonon energy ($\hbar\omega_{LO} = 36.5$ meV). Free carriers in semiconductors of polar character lose their excess energy primarily by emitting LO phonons, because of the strong coupling with longitudinal lattice vibrations[8] (Fröhlich interaction). These phonons occupy a volume of the Brillouin zone which is determined by the conservation of energy and momentum for the carrier-phonon scattering. We estimate the upper and the lower limit of the range of phonon wave vectors (for interaction with conduction electrons) to be $q_{max} = 10^7$ cm^{-1} and $q_{min} = 3.2\times 10^5$ cm^{-1}, respectively. The details of the phonon distribution are not well known,[9-11] but the generation of long-wavelength phonons is strongly favored because the matrix element of the Fröhlich interaction varies as $1/q^2$. Raman scattering probes only a fraction of the excited modes near q_{min}: The wave vector of the phonons observed in backward anti-Stokes scattering ranges from 7.6 to 7.8×10^5 cm^{-1}. We estimate[12] that about two phonons per mode are generated in that range by excitation pulses producing 10^{17} e-h pairs per cubic centimeters.

Raman spectra of a GaAs crystal grown by molecular-beam epitaxy are measured at 77 K using picosecond dye-laser pulses. The crystal has a (100) surface, and the pump and the probe pulses are polarized along (010) and (001), respectively. The T_d point-group symmetry forbids TO scattering in this configuration, and LO scattering is polarized perpendicular to the incident light. An optical analyzer with (010) orientation blocks LO scattering due to the pump pulse.

Both Stokes (intensity S) and anti-Stokes (intensity A) LO lines are observed in the Raman spectrum. From the ratio we find the phonon occupation number, $N = (S/A - 1)^{-1} = 0.7$. The thermal equilibrium population corresponding to the crystal temperature of 77 K is only 3.8×10^{-3}. The following observations rule out heating of the sample by the light pulses as a possible explanation of the excess phonon population: (i) A thermal occupation number of $N = 0.7$ would imply a lattice temperature of about 480 K. In such a strongly heated crystal the LO-phonon frequency is expected[13] to be 289 cm^{-1}, much less than the experimentally observed value of (295 ± 1) cm^{-1} which is consistent with a lattice temperature of 77 K. (ii) The ratio S/A for LO and TO phonons is measured using a (111)-oriented GaAs sample in a configuration which permits both LO and TO Raman scattering. The ratio S/A for LO phonons is identical to that measured for the (100) crystal within the experimental accuracy. On the other hand, there is no detectable anti-Stokes scattering from TO phonons. We conclude that the observed anti-Stokes scattering is due to nonequilibrium LO phonons generated by photoexcitation.

Evidence of such nonequilibrium phonons has already been obtained earlier from Raman scattering with tightly focused cw-laser excitation.[9,14] However, the power density was typically 10^4 W/cm^2, and strong lattice heating occurred in these experiments.[9,14] The average power density in our experiment is less than 70 W/cm^2, and heating of the sample can be neglected.

The LO-phonon anti-Stokes Raman scattering is measured as a function of Δt for excitation conditions corresponding to 10^{17} e-h pairs per cubic centimeter. In Fig. 1 we plot the anti-Stokes count rate versus Δt. The signal for large negative Δt is due to scattering from phonons generated by the probe pulse as discussed earlier (background signal). At $\Delta t = -4$ ps the signal increases sharply and reaches a maximum at $\Delta t = 3$ ps. Subsequently, a slower decrease to the background level is measured as Δt is further increased.

The observed variation of the anti-Stokes signal with Δt is clear, direct evidence of the generation and relaxation of nonequilibrium phonons. The rise of the signal signifies the growth of the phonon population that is caused by the emission of LO phonons from the photoexcited hot electrons and holes.

The phonon emission is an extremely fast process. The theoretically expected energy-loss rates of electrons and holes in GaAs are a few times 10^{11} eV/s.[8,15] Such rapid energy relaxation has indeed been observed by Auston *et al.*,[16] who measured 4×10^{11} eV/s in GaAs. For our situation we calculate that 90% of the initial carrier excess energy is lost to LO phonons within 2 ps. A more detailed analysis based on taking the convolution of the probe pulse with the expected fast-phonon generation rate accounts very well for the observed rise time of the anti-Stokes signal of ~ 6 ps (10% to 90% of the maximum). With shorter light pulses providing higher time resolution details of the phonon generation process can be studied by our technique.

We now discuss the decrease of the anti-Stokes signal. The decay can be traced from $\Delta t = 5$ ps to about 30 ps. Phonon generation is negligible here because the carriers have already lost > 90% of their initial excess energy for $\Delta t > 5$ ps. Diffusion of phonons out of the probed crystal volume is also ruled out because optical phonons near the center of the Brillouin zone do not propagate. Thus we conclude that the decrease of the anti-Stokes signal signifies the relaxation of the LO-phonon population. Figure 2 depicts a semilog representation of a detailed investigation of the signal decay, which is seen to be well represented by an exponential, $\exp(-\Delta t/\tau')$. The relaxation time of the phonon population is measured to be $\tau' = 7 \pm 1$ ps at 77 K. The solid curve in Fig. 2 represents the calculated convolution of the pho-

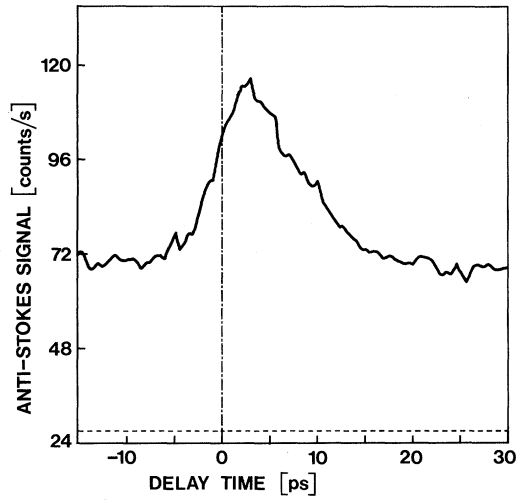

FIG. 1. Anti-Stokes Raman signal vs delay time Δt for the LO-phonon mode of GaAs at 77 K. The zero of the time scale is given by the maximum of the excitation pulse. The dashed horizontal line marks the background counting rate due to residual laser light and dark current of the detector.

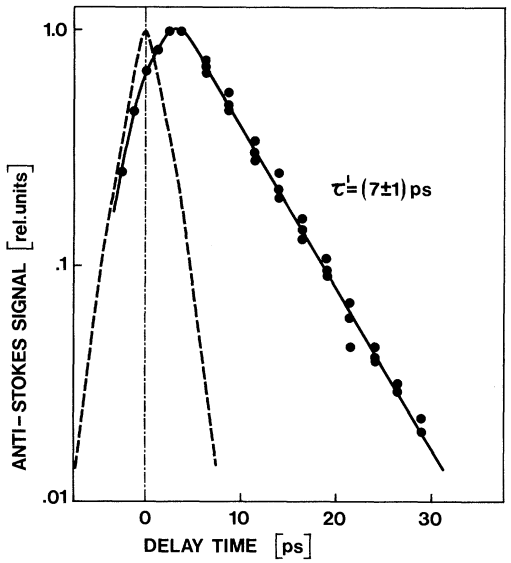

FIG. 2. Semilog representation of the anti-Stokes signal showing the decay of the LO-phonon population. The dashed curve is the measured autocorrelation function of the pulses. The solid curve is calculated.

non occupation $N(t)$ with the probe pulse. The dashed curve shows the autocorrelation of the pulses, indicating that the phonon relaxation process is indeed well resolved.

We point out that in principle there is a difference between the relaxation time τ' of the incoherent phonon population and the phonon lifetime proper, τ. The LO-phonon lifetime characterizes the decay of a single coherent lattice mode of frequency ω_{LO} and wave vector $\vec{q}$. Any scattering process destroying a phonon of that mode decreases the lifetime. The phonon lifetime can be determined by measuring the decay of such a mode using phase-matched coherent Raman scattering.[1] On the other hand, in our experiment we observe the total phonon population of a large number of LO modes near the center of the Brillouin zone. A redistribution of phonons over these modes by intrabranch scattering affects the phonon lifetime, but not the relaxation time of the population. The phonon lifetime τ and the population relaxation time τ' correspond to the dephasing time[1] and the lifetime,[17] respectively, of molecular vibrations in liquids and gases. For example, the ratio τ'/τ was measured to be ~ 80 for the CH vibration of ethanol.[17]

Our technique now permits us to measure τ' in a solid. In order to compare τ' with the phonon lifetime τ we performed a careful measurement of the LO-phonon linewidth. The measured value $\Delta\bar{\nu} = 0.85 \pm 0.1$ cm^{-1} (at 77 K) suggests $\tau = 6.3 \pm 0.7$ ps. Thus τ' and τ are the same within the experimental accuracy of the present measurements, indicating that intrabranch LO-phonon scattering is not important. Nevertheless, a more accurate direct measurement of the phonon lifetime with coherent Raman scattering might reveal the possible small difference between τ' and τ.

In summary, we have demonstrated a new light-scattering technique for directly measuring the time evolution of nonequilibrium excitations. The method uses a train of picosecond light pulses for excitation, and a photon-counting spectrometer for detection of the scattered light. Our measurements reveal for the first time the relaxation of the population of LO lattice modes. Other excitations such as TO phonons, plasmons, electrons, etc. can be readily investigated by our method. For instance, we have measured single-particle electronic Raman scattering from the photoexcited electrons and holes. Preliminary results indicate very rapid changes (beyond our present time resolution) of the velocity distribution of the electron-hole gas.

The authors gratefully acknowledge fruitful discussions with Professor H. J. Queisser. We are indebted to Dr. K. Ploog for supplying the GaAs crystals.

[1]D. von der Linde, A. Laubereau, and W. Kaiser, Phys. Rev. Lett. 26, 954 (1972).

[2]A. Laubereau, D. von der Linde, and W. Kaiser, Phys. Rev. Lett. 27, 802 (1971).

[3]R. R. Alfano and S. L. Shapiro, Phys. Rev. Lett. 26, 1247 (1971).

[4]A. Laubereau, D. von der Linde, and W. Kaiser, Opt. Commun. 7, 173 (1973).

[5]A. Laubereau, G. Wochner, and W. Kaiser, Opt. Commun. 14, 75 (1975).

[6]See, e.g., *Topics in Applied Physics*, edited by S. L. Shapiro (Springer-Verlag, Heidelberg, 1977), Vol. 18.

[7]Raman scattering must be polarized. A modification of the method for depolarized Raman scattering will be discussed elsewhere.

[8]E. M. Conwell, *High Field Transport in Semiconductors*, Suppl. 9 to *Solid State Physics*, edited by F. Seitz, D. Trunbull, and H. Ehrenreich (Academic, New York, 1967).

[9]J. Shah, R. C. C. Leite, and J. F. Scott, Solid State Commun. 8, 1089 (1970).

[10]Y. B. Levinson and B. N. Levinsky, Solid State Commun. 16, 713 (1975).

[11]A. R. Vasconcellos and R. Luzzi, Solid State Commun. 32, 1219 (1979).

[12]See Ref. 8. This calculation ignores energy relaxation via holes, and overestimated the phonon occupation number of the Raman active modes.

[13]R. K. Chang, J. M. Ralston, and D. E. Keating, in *Light Scattering of Solids*, edited by G. B. Wright (Springer-Verlag, New York, 1969), Paper E-3.

[14]J. C. V. Mattos and R. C. C. Leite, Solid State Commun. 12, 465 (1973).

[15]E. O. Göbel and O. Hildebrand, Phys. Status Solidi (b) 88, 645 (1978).

[16]D. M. Auston, S. McAfee, C. V. Shank, E. P. Ippen, and O. Teschke, Solid-State Electron. 21, 147 (1978).

[17]A. Laubereau, D. von der Linde, and W. Kaiser, Phys. Rev. Lett. 28, 1162 (1972).