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## Decay Time of Hot TO Phonons in Diamond

A. Laubereau, D. von der Linde, and W. Kaiser

*Physik-Department der Technischen Universität München, München, Germany*

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For a duration of several times  $10^{-12}$  sec, TO modes are excited to an occupation number exceeding the equilibrium value (at 300°K) by more than thirteen orders of magnitude. The relaxation times of these phonons are measured directly and found to agree with the known anharmonic decay at low power level. Phonon breakdown is not significant in our experiments.

The investigation of LO and TO phonons which are excited above thermal equilibrium has received increasing attention. Measurements have been reported for CdS,<sup>1</sup> GaAs,<sup>2</sup> and diamond.<sup>3</sup> Very recently the relaxation times of molecular systems have been measured directly. This method has been applied to the symmetric  $A_1$  vibration of liquid CCl<sub>4</sub>,<sup>4</sup> and to the internal vibration ( $A_1$ ) of CO<sub>3</sub><sup>2-</sup> in CaCO<sub>3</sub>.

In this Letter we wish to report on an investigation of the fundamental TO phonons of diamond. A small number of modes are excited to very high occupation numbers by use of the transient stimulated Raman effect. The decay of these modes is observed directly with the help of picosecond probe pulses.<sup>5b</sup> It was expected that the phonon decay would be altered significantly when a parametric process involving the TO and TA phonons becomes operative.<sup>6</sup> This breakdown mechanism of TO phonons in diamond was discussed recently in connection with the investigation of phonon-assisted fluorescence.<sup>3</sup>

Before discussing the observed relaxation times, it is interesting to calculate the optical-phonon density  $N_0$ , the phonon occupation number  $n_0$ , and the number of modes involved in our in-

vestigation.

We have made a detailed study of phonon generation via the transient stimulated Raman effect. The theory of transient stimulated Raman scattering has been discussed by others.<sup>7</sup> In Fig. 1 the phonon density  $N_0$  is presented as a function of the steady-state gain  $G_{SS} = gI_L z$  for different ratios  $t_p/\tau$ , where  $g$  is the gain factor of the medium,  $I_L$  is the peak pumping intensity, and  $z$  is the interaction length. It is readily seen from the figure that for larger relaxation times  $\tau$  (i.e., smaller values of  $t_p/\tau$ ), the phonon generation decreases markedly on account of the more transient nature of the excitation process. Figure 1 contains curves of constant conversion efficiencies of laser into Stokes light,  $K = I_S(\max)/I_L$ . Experimentally we worked at the following conditions: A measured energy-conversion efficiency of several per cent corresponds to an intensity conversion of  $K \approx 10\%$ ;  $t_p = 8.3$  psec and  $\tau = 3.4$  psec (at 77°K; see below) give  $t_p/\tau = 2.4$ . From these numbers we estimate that  $G_{SS} \approx 115$ , with the help of Fig. 1. Using the published value for diamond<sup>8</sup> of  $g = 9.2 \times 10^{-3}$  cm/MW (corrected for our wavelength of  $\lambda = 0.53$   $\mu$ m) and  $z = 0.7$  cm, we calculate  $I_L = 1.8 \times 10^{10}$  W/cm<sup>2</sup>. This number

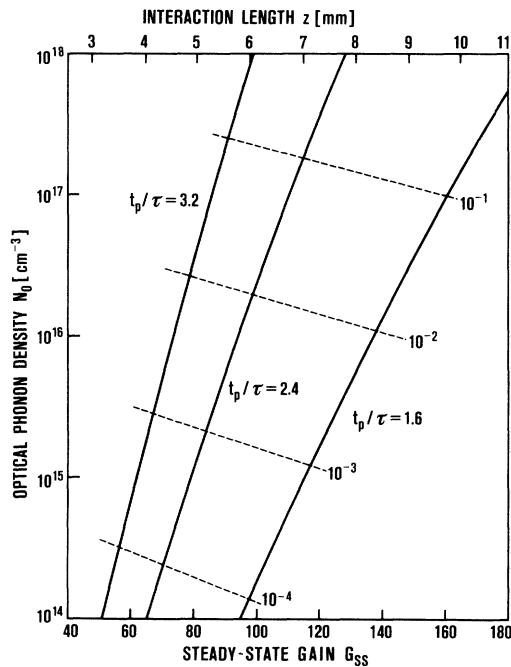


FIG. 1. Optical-phonon density  $N_0$  versus steady-state gain  $G_{SS} = gI_L z$  for three parameters  $t_p/\tau$  ( $g$ , steady-state gain factor;  $I_L$ , laser peak intensity;  $z$ , interaction length;  $t_p$ , pulse duration;  $\tau$ , relaxation time). Dashed lines: constant conversion efficiency  $K = I_S(\max)/I_L(\max)$  ( $I_S$ , Stokes intensity). Upper scale: interaction length  $z$  relevant to our experimental situation in diamond.

compares favorably with the peak laser power of  $(2 \text{ to } 3) \times 10^{10} \text{ W/cm}^2$  estimated from the experimental values of the energy of the single pulse, the pulse duration  $t_p$ , and the beam diameter.

Figure 1 demonstrates that in our experiments a maximum phonon density of  $N_0 = 2 \times 10^{17} \text{ cm}^{-3}$  is generated at the end of our crystal. The rapidly rising curves in Fig. 1 indicate that this high phonon density occurs in a small region of the crystal. In the following discussion we use an optical-phonon density of  $N_0 = 10^{17} \text{ cm}^{-3}$  for an interval of  $\Delta z = 4 \times 10^{-2} \text{ cm}$ . With our experimental beam diameter, we calculate a volume of high phonon density of  $V = 4 \times 10^{-6} \text{ cm}^3$ .

We now turn to the discussion of the mode density and the number of modes excited in our experiment. The density of optical modes is calculated from the equation  $N_m = k^2 \Delta k \Delta \Omega (2\pi)^{-3}$ . A value of  $N_m = 10^7 \text{ modes/cm}^3$  is estimated from the experimental data:  $k = 2 \times 10^4 \text{ cm}^{-1}$ ,  $\Delta k = 20 \text{ cm}^{-1}$ , and  $\Delta \Omega = 0.2 \text{ sr}$  (the last number is calculated from the measured divergence of the Stokes beam of  $2 \times 10^{-2} \text{ rad}$ ). Considering the small vol-

ume of high phonon density, the number of modes participating in the strong excitation process is approximately forty.

The phonon occupation number  $n_0$  is of special interest since large values of  $n_0$  indicate hot phonons. Using the numbers estimated above, we obtain  $n_0 = N_0/N_m = 10^{10}$ , i.e.,  $10^{10}$  quanta are generated per mode on account of the stimulated scattering process. For comparison we quote the thermal-equilibrium values  $n_0^T = [\exp(h\nu_p/kT) - 1]^{-1} \approx 10^{-3}$  and  $10^{-11}$  calculated for 300 and 77°K, respectively.

The numbers given above clearly show that the TO phonons of the diamond lattice are very strongly excited compared to the equilibrium value. The ratio of the occupation numbers is approximately equal to  $10^{13}$  at 300°K. It was thought of interest to study the decay time of these highly excited phonons and to compare the results with relaxation times obtained near thermal equilibrium. Direct measurements of the phonon lifetime are well suited for the investigation of these hot phonons. Common spontaneous Raman measurements, on the other hand, give information on the anharmonic decay process close to thermal equilibrium.

Our experimental system has been discussed in a previous Letter.<sup>4</sup> In brief, a single light pulse of  $t_p \approx 8 \text{ psec}$  duration and high peak power excites TO lattice modes at a frequency of  $\nu_p/c = 1332 \text{ cm}^{-1}$ . The decay of the phonon field is probed with a second light pulse of the same duration  $t_p$ . The anti-Stokes signals of the probe and of a reference pulse are measured simultaneously. The dispersion of diamond is well known and the phase-matching angles are readily calculated for our various light beams. The angles between the pump and probe beams are adjusted to  $10^{-1} \text{ rad}$ . Our specimen was a type Ia diamond, 7 mm in length, with front faces  $2 \times 3 \text{ mm}^2$ . Infrared measurements indicated a nitrogen concentration of approximately  $10^{20} \text{ cm}^{-3}$  in our crystal.<sup>9</sup>

We wish to stress the improved accuracy which is obtained with single picosecond light pulses and with a well-defined reference beam. Error bars are presented at two significant points for the room-temperature and the low-temperature measurements (see Fig. 2).

Our experimental data on the lifetime of hot TO phonons are presented in Fig. 2 for 295 and 77°K. The anti-Stokes signal  $S(t_p)$  of the probe pulse is plotted as a function of delay time  $t_d$  (time between pump pulse and probe pulse). Our experimental points extend over three orders of

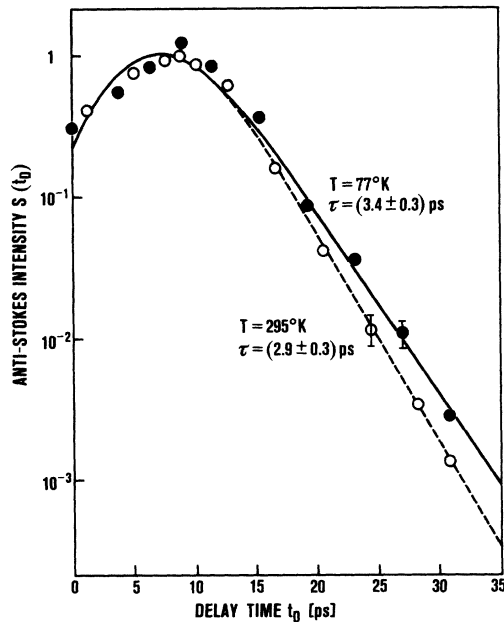


FIG. 2. Scattered anti-Stokes intensity versus delay time for two crystal temperatures, 77°K (solid line) and 295°K (dashed line).

magnitude; they represent average values obtained from ten different measurements. The anti-Stokes signal rises to a maximum at  $t_D \approx 8$  psec, which is characteristic for the phonon generation in the transient stimulated Raman effect. For longer delay times  $t_D$ , the phonons decay with their individual relaxation time  $\tau$ . From the exponential slopes in Fig. 2 we find values of  $\tau$  of  $(2.9 \pm 0.3) \times 10^{-12}$  sec and  $(3.4 \pm 0.3) \times 10^{-12}$  sec for 295 and 77°K, respectively.

Calculations of the anti-Stokes signals were made knowing the shape of the light pulses<sup>4,10</sup> and the  $\tau$  values (from the asymptotes). The calculated curves were adjusted to the (normalized) maximum of the anti-Stokes signal. It is interesting to see that the theoretical curves account very well for our experimental points at 295 and 77°K.

We now wish to compare our data on the relaxation times with the linewidth of spontaneous Raman scattering. At room temperature several investigators<sup>8,11,12</sup> give values of the Raman linewidth between 1.65 and 2.2  $\text{cm}^{-1}$  at 1332  $\text{cm}^{-1}$ ; at 78.8°K a linewidth of 1.48  $\text{cm}^{-1}$  was reported.<sup>12</sup> Our relaxation times correspond to a (Lorentzian) linewidth of  $1.83 \pm 0.2$  and  $1.56 \pm 0.15$   $\text{cm}^{-1}$  at 295 and 77°K, respectively. These numbers strongly suggest that our hot phonons decay with the same time constant as phonons excited at very low pow-

er levels in spontaneous Raman experiments.

To understand these results we calculate the vibrational amplitude of our highly excited phonons, and we discuss the effect of phonon breakdown on the relaxation time  $\tau$ . In crystals a large number of modes participate in the thermal vibration of the atoms. In diamond there are  $8.8 \times 10^{22}$  modes/ $\text{cm}^3$  in one phonon branch. The total rms amplitude of the C atom at 77°K is approximately 0.2 Å.<sup>13</sup> In our case, a small number of modes are excited to very large occupation numbers. One readily estimates that the vibrational amplitude of these hot phonons equals approximately  $10^{-4}$  Å, i.e., less than  $10^{-3}$  of the thermal amplitude. It is conceivable, therefore, that our hot phonons decay through the same anharmonic terms as the thermally excited TO phonons.

The parametric phonon breakdown (at 77°K) requires a more detailed discussion. In diamond, which has a center of inversion, the TO phonons decay into TA and LA phonons of approximately half the energy ( $h\nu_p/2$ ). Arguments similar to those of Ref. 6 lead to the following equation for the decay rate of TO phonons of occupation number  $n_0$ :

$$dn_0/dt = -(n_0/\tau)(1 + n_k + n_{-k}), \quad (1)$$

where  $n_k$  and  $n_{-k}$  are the nonequilibrium occupation numbers of the acoustic modes interacting with the TO phonons. In Eq. (1) the thermal-equilibrium values are  $n_k^T \approx n_{-k}^T \approx 10^{-5}$  at 77°K, and the reverse reactions have been neglected. Equation (1) simply states that the TO phonons decay with the relaxation time  $\tau$  as long as the occupation of the (terminal) acoustic modes may be neglected; the decay of the TO phonons will be altered when  $n_k$  and  $n_{-k} \gtrsim 1$ . The values of  $n_k$  and  $n_{-k}$  appropriate to our experimental situation are estimated from the density of states of the diamond lattice and the number of decaying TO phonons. Using the published density-of-states curve<sup>14</sup> we find  $N_A \approx 10^{20}$   $\text{cm}^{-3}$  acoustic modes at a frequency of  $\frac{1}{2}\nu_p$  and in a frequency interval of 1.5  $\text{cm}^{-1}$ . Considering the density of TO phonons of  $N_0 = 10^{17}$   $\text{cm}^{-3}$  which decay in  $2 \times 10^{17}$   $\text{cm}^{-3}$  acoustic phonons, we obtain an upper limit<sup>15</sup> of  $n_k, n_{-k} \approx 10^{-13}$ . With these small values for the occupation number of the acoustic phonons, our highly excited TO phonons are expected to decay with their characteristic relaxation time  $\tau$ . This prediction is in agreement with experimental observations.

It appears very unlikely that phonon breakdown

can be observed with picosecond light pulses in diamond or in any other crystal with a similar density of states in the acoustic branches. Considerably larger light intensities are required (and experimentally feasible); but saturation of the stimulated Raman scattering limits the phonon density  $N_0$ , and crystal damage restricts the practical light flux.

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## High-Temperature Spin-Fluctuation Resistivity in AlMn

E. Babić, R. Krsnik, B. Leontić, Z. Vučić, and I. Zorić

*Institute of Physics of the University of Zagreb, Zagreb, Yugoslavia*

and

C. Rizzuto

*Istituto di Scienze Fisiche and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Genova, Italy*

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The resistivity of AlMn alloys of concentrations up to 5% is found to decrease linearly in temperature above 50 K, while at lower temperatures it follows the same  $T^2$  behavior observed at lower concentrations. The linear behavior of  $\rho(T)$  rules out the possibility that AlMn is a Kondo system with  $T_K \approx 500$  K. Possible explanations in terms of localized spin fluctuations are suggested.

The AlMn alloy system can be defined as non-magnetic: It does not, in fact, show either a temperature-dependent magnetic susceptibility or the other characteristic electronic properties (e.g., the Kondo effect or a "giant" thermopower) shown by dilute magnetic alloys. It has, however, been shown that this system, together with AlCr, shows "weak" magnetic behavior in several low-temperature properties. It has been possible, in

particular, to observe a very weak resistivity minimum, followed at low temperatures by a quadratic temperature increase in the resistivity obeying a law of the type

$$\rho(T) = \rho(0)[1 - (T/\theta)^2], \quad (1)$$

where  $\rho(0)$  is the zero-temperature resistivity and  $\theta$  a characteristic temperature whose value was found to be  $530 \pm 30$  K.<sup>1</sup>