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# FREQUENCY-SELECTIVE TIME-RESOLVED PHONON SPECTROSCOPY USING FLUORESCENCE LINE NARROWING

M.J. VAN DORT, J.I. DIJKHUIS and H.W. DE WIJN
*Fysisch Laboratorium, Rijksuniversiteit Utrecht, P.O. Box, 80 000, 3508 TA Utrecht, The Netherlands*

We report on a new method, based on fluorescence line narrowing, for studying nonequilibrium acoustic phonons in a frequency-selective way. High-resolution phonon detection is achieved by exciting ruby directly into a homogeneous packet of the $\bar{E}(^2E)$ metastable state, and analyzing the enhanced $R_2$ luminescence following absorption of phonons in the transition from $\bar{E}(^2E)$ to $2\bar{A}(^2E)$. In the present experiment, a flat spectrum of phonons is injected with heat pulses of 100 ns duration. The phonon spectrum observed initially exhibits a dip, reflecting the absorption of resonant phonons. Following the heat pulse, the phonons escape with a rate increasing with the distance from resonance. The experiments suggest conversion of ballistic phonons as well as of bottlenecked phonons in the wings into resonant ones.

The aim of this paper is to demonstrate the potential of fluorescence line narrowing (FLN) in measuring nonequilibrium phonon occupations as a function of time and of spectral frequency. Spectral displacement of phonons by scattering from centers has been an important and longstanding problem in the field of phonon spectroscopy, yet the number of experiments addressing it is limited. Most of the work done in this field has been carried out on 29 $cm^{-1}$ phonons in interaction with the excited-state resonance $\bar{E}(^2E)$–$2\bar{A}(^2E)$ of $Cr^{3+}$ dilutely substituted in $Al_2O_3$ (ruby). Early evidence for diffusion in the frequency domain has been provided by a cw optical-pumping experiment [1], in which the nonequilibrium phonon packet resonant between $\bar{E}(^2E)$ and $2\bar{A}(^2E)$ at a distance 29 $cm^{-1}$ above was seen to widen with the metastable concentration $N^*$ of excited $Cr^{3+}$. The involvement of $Cr^{3+}$ pairs in spectral displacements, to the extent that the phonons suffer wipeout beyond resonance, has been inferred from the saturation with $N^*$ of the trapping time of bottlenecked phonons, as monitored via the decay of $2\bar{A}(^2E)$, at various concentrations of $Cr^{3+}$ [2,3]. Such communication among $Cr^{3+}$, but over frequency ranges as large as 0.6 $cm^{-1}$, has further been observed directly via the emission of hot luminescence originating from stronly coupled $Cr^{3+}$ pairs, the energy levels of which are well known [4], and by frequency-selective pulsed phonon generation in a wing of the $\bar{E}(^2E)$–$2\bar{A}(^2E)$ transition via infrared excitation of $V^{4+}$ dopants [5]. It has recently been established that the trapping time of 29 $cm^{-1}$ phonons depends on $N^*$ multiplied by the typical dimension of the pumped zone [3]. This has been found to be in quantitative accord with a model based on inelastic scattering produced by diagonal exchange of metastable $Cr^{3+}$ with nearby $Cr^{3+}$ in the $^4A_2$ ground state and subsequent ballistic escape in the event the associated spectral displacement carries the energy sufficiently far into the wings.

FLN adds to this in that it provides a direct means to observe the temporal development of the phonon occupation over a spectral range of a few times the linewidth, i.e., precisely that part of the spectrum which is relevant to the inelastic processes. The principle of FLN is in this case applied to a three-level scheme (fig. 1). A homogeneous packet of $Cr^{3+}$ in the metastable $\bar{E}(^2E)$ state is prepared by narrow-band cw laser excitation from the $^4A_2$ ground state. Thermal phonons are removed by cooling down to below 2 K. A nonequilibrium phonon injected from an outside source into the optically excited zone then is detected, with an efficiency given by the various transition rates involved, by the ensuing emission of an $R_2$ photon. The $R_2$ intensity is proportional to the quantity

$$N_2(\nu, t) = p(\nu, t) g(\nu) N^*, \tag{1}$$

in which $p(\nu, t)$ is the time-dependent occupation number of the phonon modes of frequency $\nu$, and $g(\nu)$ is the normalized shape of the $2\bar{A}(^2E)$–$\bar{E}(^2E)$ transition with respect to phonons. The way to extract $p(\nu, t)$ from the phonon-induced luminescence under FLN conditions

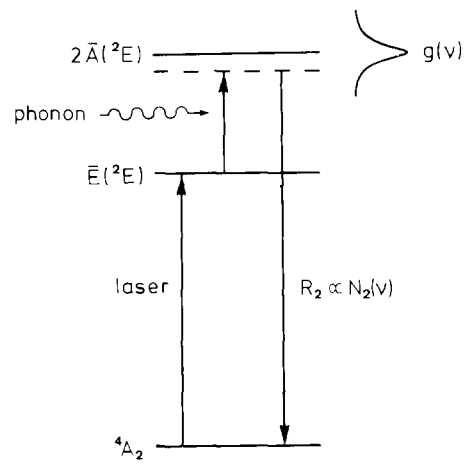


Fig. 1. Principle of frequency-selective phonon detection. The $\bar{E}(^2E)$ level is homogeneously populated. Part of the incoming phonons are converted into $R_2$ photons.

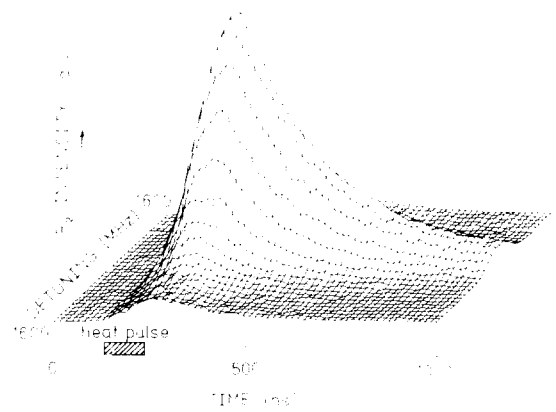


Fig. 2. Heat-pulse induced $R_2$ luminescence vs. time and frequency. Excited zone is a cylinder with diameter 30 μm, $N^* \approx 3 \times 10^{17}$ cm$^{-3}$. Only 1 in 4 points is shown.

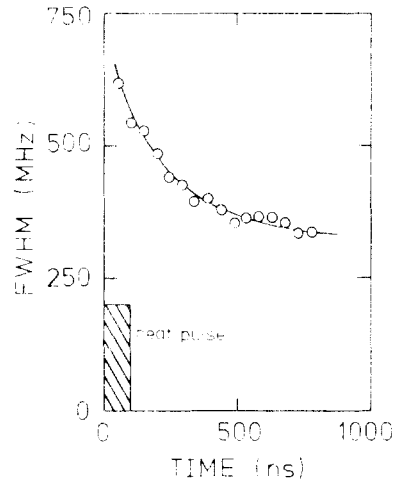


Fig. 3. Width of the heat-pulse induced $R_2$ luminescence vs. time. Time resolution is 50 ns. $N^* \approx 10^{17}$ cm$^{-3}$. For comparison, the homogeneous width of $2\bar{A}(^2E)$ is 440 MHz.

therefore is to divide the frequency distribution of the luminescence by $g(\nu)$. The latter quantity is known from infrared absorption spectroscopy [6], or may be measured by the present FLN scheme in the very specimen used by supplying a flat thermal phonon distribution produced by raising the temperature to about 6 K under otherwise the same conditions. We find that $g(\nu)$ is well described by a Lorentzian with full width at half maximum $\Delta\nu = 440$ MHz, implying $T_1 = 0.7$ ns. This result is in accord with both time-resolved [7] and far-infrared [6] experiments.

An example of the development of the $R_2$ intensity with time and spectral frequency is presented in fig. 2. Here, the phonons are injected into the specimen, a cube of Czochralsky-grown 500 ppm ruby of $4 \times 4 \times 4$ mm$^3$ in size, by use of a constantan heater of 50 nm thickness and $1 \times 1$ mm$^2$ area. The heater is driven at an electrical power of 15 W during 100 ns at 3 μs intervals. The $\bar{E}(^2E)$ population is maintained by pumping with a single-frequency cw ring dye laser operating at a power of 20 mW, and having a bandwidth less than 1 MHz. The zone of detection, typically a cylinder of 30 μm diameter and 200 μm length, located adjacent the heater, is selected by focusing the laser beam and further defined by the receiving optics. The $R_2$ light is analyzed with a Fabry–Perot interferometer to a resolution of better than 100 MHz. A double monochromator is inserted in the optical path to suppress the $R_1$ and pair luminescence. Time resolution is provided by standard photon-counting and time-to-amplitude conversion techniques. Typically 30 passes of 1-minute duration through the spectrum are accumulated to obtain data sets as in fig. 2.

For the scheme to work best, spontaneous one-phonon emission must be the predominant source of broadening of $2\bar{A}(^2E)$, energy transfer from one $\bar{E}(^2E)$ homogeneous packet to the next must be absent within the radiative lifetime $\tau_R$, and the homogeneous width of $\bar{E}(^2E)$ must be negligible with respect to the width of $2\bar{A}(^2E)$. In the case of ruby, the first two of these conditions are met [6,8]. The homogeneous width of $\bar{E}(^2E)$ in zero magnetic field is known from previous FLN work to amount to 65 MHz [9], substantially smaller than the width of $2\bar{A}(^2E)$, but comparable to the instrumental resolution. (The inhomogeneous width of $\bar{E}(^2E)$ is about 3 GHz in our specimen.) The finite homogeneous width of $\bar{E}(^2E)$ has been accounted for by convoluting a Lorentzian of 65 MHz width with the instrumental profile to obtain an effective instrumental profile. In the further analysis convolutions of the latter with $N_2(\nu, t)$ have been adjusted, at fixed time, to the data such as those in fig. 2. Here, it appeared that within errors $N_2(\nu, t)$ could be represented in analytical form by a Lorentzian to a power of order unity.

In fig. 3, the width of $N_2(\nu, t)$, as found by deconvoluting the $R_2$ luminescence, is presented as a function of the time elapsed since switching on the heater for $N^* \approx 10^{17}$ cm$^{-3}$, i.e., well in the regime of phonon bottlenecking. A noteworthy result is that $N_2(\nu, t)$ at longer times becomes narrower than the homogeneous linewidth. This demonstrates quite directly that the spectral distribution of phonons has not stayed uniform, but rather has become peaked around resonance. At short times, on the other hand, $N_2(\nu, t)$ is widened relative to $g(\nu)$, indicating a dip in the phonon spectrum. Indeed, this is borne out in more detail by use of eq. (1) in fig. 4, where the temporal development of the phonon spectrum is displayed as it is derived from the $N_2(\nu, t)$ adjusted to the data. Another way to view the result in fig. 4 is in the time domain at various distances from resonance. The trapping time, then, is seen to be larger for phonons at resonance than it is for phonons in the wings. This result is, of course, also contained in cross sections at fixed detuning through sets of data points as in fig. 2. Figure 5 provides two of such cross sections in the case of a bottlenecking roughly 3 times larger than in fig. 2.

A discussion of the physical processes governing the phonon trapping versus frequency may be based on rate-

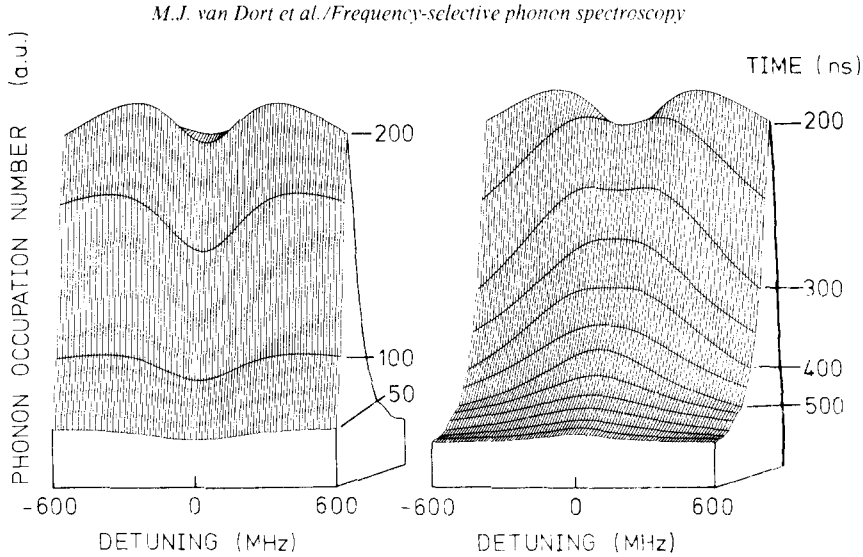


Fig. 4. Phonon spectrum vs. time for $N^* \approx 10^{17}$ cm$^{-3}$ as derived with eq. (1).

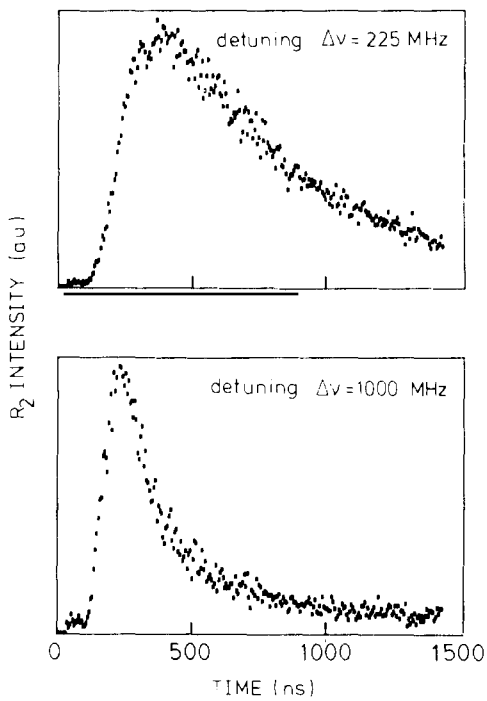


Fig. 5. $R_2$ intensity vs. time at fixed frequency. Duration of heat pulse is 100 ns. Diameter of the excited zone is $\approx 250$ μm. $N^* \approx 10^{17}$ cm$^{-3}$. In the vicinity of the resonance the $R_2$ intensity continues to rise after the heat pulse.

equation considerations [10]. We have, under bottleneck conditions,

$$[N^* g(\nu) + \rho] \frac{\mathrm{d}p(\nu, t)}{\mathrm{d}t} = -\rho \frac{p(\nu, t)}{\tau(\nu)} + Q(\nu, t), \qquad (2)$$

in which $\rho$ is the density of phonon states per unit of frequency, $\tau(\nu)$ is the phonon lifetime, and $Q(\nu, t)$ represents the feeding by the heat pulse. The response of $p(\nu, t)$ to the feeding is single-exponential with time constant $[\rho \ll N^* g(\nu)]$

$$T_{\mathrm{eff}} = N^* g(\nu) \tau(\nu) / \rho, \qquad (3)$$

which is in conformity with what is observed provided $\tau(\nu)$ is only weakly varying over the linewidth, in any case more weakly than for phonon lifetimes limited by spatial diffusion by $Cr^{3+}$. The physical processes underlying $Q(\nu, t)$ are quite involved. First, at the $N^*$ used, the phonon mean free path against scattering from isolated $Cr^{3+}$ ions, $\Lambda(\nu) = pt/T_1/N^* g(\nu)$, becomes as short as 1 μm at resonance. This implies that only phonons in the far-out wings can penetrate into the excited zone within the time scale of the experiment. These off-resonant phonons cannot be observed with the present FLN scheme (eq. 1). The fact that nevertheless a non-zero phonon population is observed already from the very beginning of the heat pulse, thus is direct evidence for inelastic processes converting off-resonant phonons into near-resonant ones, and that in a few steps only. Second, as is seen in fig. 5, near resonance $Q(\nu, t)$ continues after the heat pulse is switched off for several hundreds of ns, i.e., on a time scale much longer than the cooling time of the heater ($\approx 1$ ns), but much shorter than that expected for spatial diffusion ($\approx 10$ μs).

A model encompassing the phenomena observed is based on one-site Orbach processes of metastable $Cr^{3+}$ subject to an exchange field of a nearby $Cr^{3+}$ in $^4A_2$. The mechanism has previously been successful in accounting for 29 cm$^{-1}$ phonon relaxation in the case $\bar{E}(^2E)$ is populated over the full inhomogeneous width [3]. It involves the absorption from $\bar{E}(^2E)$ to $2\bar{A}(^2E)$ in a spin-nonflip transition and the subsequent return to $\bar{E}(^2E)$ in a spin-flip transition, resulting in a change of the phonon energy by an amount equal to the exchange parameter. The displacements may be sufficiently large for the phonons to become ballistic ("wipe out"). Conversely, however, in the present situation, where initially there is a paucity of phonons near resonance, the mechanism may convert the off-resonance phonons that have penetrated the excited

zone into near resonant ones ("wipe in"), and in this way give rises to a $Q(\nu, t)$ that is nearly flat over a few times the width of $g(\nu)$. With a frequency dependence of $T_{\text{eff}}$ as specified by eq. (3), this indeed results in the dip in the phonon occupation at short times. Once off-resonance phonons are converted into near-resonant ones, the latter may, in turn, undergo spectral redistribution, again by exchange-induced one-site Orbach processes, to include the remainder of the regime where phonons are trapped. This redistribution must be thought of as a dynamic process, and introduces a time constant in $Q(\nu, t)$, apparently elongating the feeding beyond the heat pulse.

In summary, the technique of FLN has been shown to allow the examination of the temporal development of the spectrum of nonequilibrium phonons interacting with a center. The spectrum has been found to modify substantially with time by inelastic scattering.

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