

Population dynamics of H^- local modes in $CaF_2:Lu^{3+}$ crystals studied using a free-electron laser

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 2137

(<http://iopscience.iop.org/0953-8984/13/10/308>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 11:34

Please note that [terms and conditions apply](#).

Population dynamics of H^- local modes in $\text{CaF}_2:\text{Lu}^{3+}$ crystals studied using a free-electron laser

Jon-Paul R Wells^{1,2,4}, Ian V Bradley^{1,2}, Glynn D Jones³ and Carl R Pidgeon¹

¹ Department of Physics, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK

² FELIX free electron laser facility, FOM—Institute for Plasmaphysics ‘Rijnhuizen’, PO Box 1207, 3430 BE Nieuwegein, The Netherlands

³ Department of Physics and Astronomy, University of Canterbury, PB 4800, Christchurch, New Zealand

E-mail: wells@rijnh.nl

Received 2 October 2000

Abstract

We report on pump–probe measurements of vibrational decay times for the H^- (X, Y) and Z local modes of $\text{CaF}_2:\text{Lu}^{3+}$ C_{4v} H^- centres using the Dutch free-electron laser. For excitation of the (X, Y) mode, a 10 K lifetime of 43 picoseconds is measured and is attributable to three-phonon anharmonic relaxation, which accounts well for the temperature dependence of the decay rate. The 10 K lifetime of the higher-energy Z mode results from a combination of one-phonon decay to the (X, Y) modes and three-phonon decay to the ground state. A simple rate equation model gives a good account of the observed transient.

1. Introduction

Over recent years the dynamics of vibrations in the condensed phase have begun to be explored using a variety of techniques such as pump–probe, transient grating and two-pulse (as well as three-pulse) photon-echo measurements [1–6]. It is the advent of the free-electron laser (FEL), and more recently mid-IR optical parametric amplifiers, which has made the majority of these studies possible. The particular advantage of the FEL in performing such measurements is the enormous flexibility as regards operational laser parameters available to the experimenter, a feature largely unmatched at this time by alternative sources such as solid-state-based parametric devices.

Localized modes of vibration have particular scientific significance largely due to the importance of spatially localized vibrations in the non-radiative decay of optically active materials such as Cr^{4+} - or Mn^{5+} -doped ionic crystals [7] as well as molecular impurities in glasses and liquids [8]. In this context, we use the expression localized mode to cover a broad

⁴ Author to whom any correspondence should be addressed. Address to: FELIX free electron laser facility, PO Box 1207, 3430 BE Nieuwegein, The Netherlands. Telephone: +31-30-6096894; fax: +31-30-6031204.

class of quasi-localized vibrational modes from gap modes to resonant impurity modes such as those recently observed for the trivalent rare earths in CaF₂-type crystals [9]. Localized modes are created upon the introduction of light impurities where the force constants between the impurity and host ions remain essentially unaltered when compared with the inter-host ion force constants.

Direct measurements of multiphonon decay in optically activated systems are typically difficult due to the many and complex decay pathways available to the impurity as well as the complexity involved in analysing such data. The H⁻ local modes are chosen as model systems where the primary decay path is non-radiative relaxation via multiphonon emission. They are also extremely convenient to study as they lie in the ten-micron region where there is a gap in atmospheric absorption and thus we may dispense with the necessity of purging the infrared beam path and our experiments may be performed on an open table top.

There are few studies in the literature of the dynamics of H⁻ local modes. The earliest measurements were performed using saturation techniques with pulses longer than the decay time of the H⁻ local modes supplied by the output of CO₂ lasers [10, 11]. More recently, researchers have measured the population decay time (at 10 K only) of the substitutional mode in CaF₂:H⁻ to be 45 ps and that of the CaF₂:La³⁺:H⁻ interstitial Z mode to be 6 ps [12]. These measurements were performed using the picosecond pulses of a free-electron laser. The present authors have used a four-wave-mixing technique in both the time and frequency domain to demonstrate ‘negative-time’ quantum beats arising from vibrational ladder climbing under femtosecond excitation provided by the Dutch free-electron laser FELIX [13]. Such measurements provided the first measurement of coherent properties of H⁻ local modes and present a novel approach to determining the overtone spectrum of vibrations. The present study is concerned with the determination of temperature-dependent population decay times and dynamics of interstitial H⁻ local modes in CaF₂:Lu³⁺:H⁻. In this case the (X, Y) and Z modes of H⁻ are separated by only 30 cm⁻¹ and the decay of the higher-energy Z mode can be understood using a simple rate equation model for the population dynamics of the system.

2. Experimental procedure

The calcium fluoride samples were grown, from crystal offcuts obtained from Optovac Incorporated (USA), by the Bridgman–Stockbarger technique using a 38 kW rf furnace. The appropriate amounts of LuF₃ were added to the start material which was placed into a graphite crucible and lowered at 4 mm h⁻¹ through the temperature gradient provided by the furnace induction coils. The Lu³⁺-doped CaF₂ samples were hydrogenated using the method of Hall and Schumacher [14]. A treatment of one to four hours at 850 °C in two thirds of an atmosphere of hydrogen gas was sufficient for CaF₂.

Infrared absorption spectra were measured with 0.25 cm⁻¹ resolution on a Bio-Rad FTS-40 Fourier transform infrared spectrometer. The crystal samples were mounted on a copper holder and cooled by thermal contact with the 10 K stage of a CTS LTS 0.1 closed-cycle helium cryostat.

The time domain measurements described in this article were performed at the Dutch free-electron laser in Nieuwegein (FELIX) which could be tuned to the fundamental resonance of the appropriate CaF₂:H⁻ local mode. FELIX operates with a train of 4 μs long ‘macropulses’ at a repetition rate of either 5 or 10 Hz. Each macropulse consists of a train of ‘micropulses’, of a width adjustable between 300 fs and 5 ps, with a pulse separation of 40 ns. In order to measure the population decay time (*T*₁), a three-beam pump, probe and reference technique has been used [15] to counter the fluctuations from macropulse to macropulse. From the input FELIX pulse, both probe and reference beams are split off by ZnSe beamsplitters with the

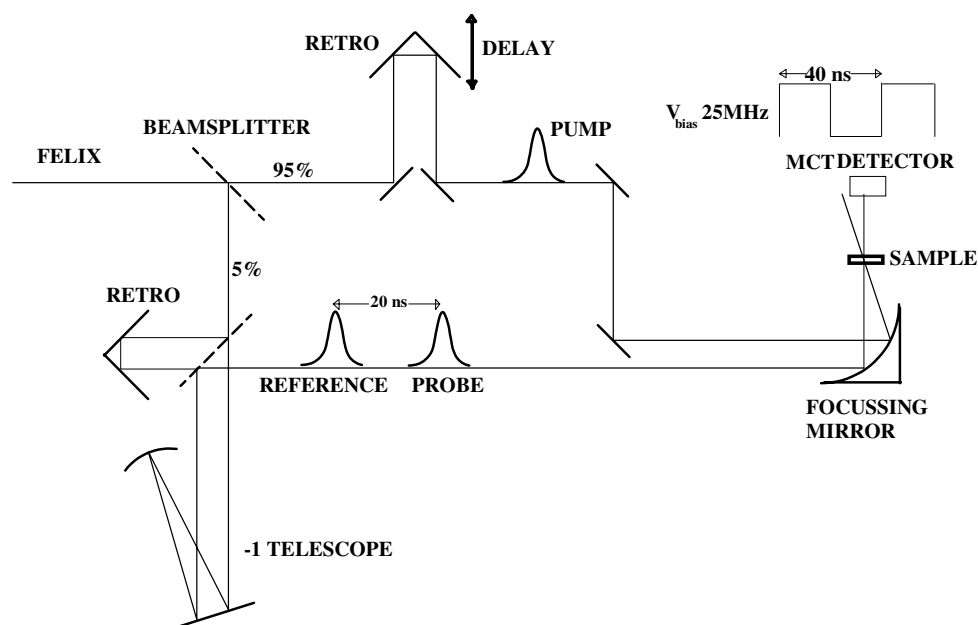


Figure 1. A schematic diagram of the pump-probe set up.

reference beam delayed by 20 ns and back-reflected to the beamsplitter with a -1 telescope onto the probe beam position. As a consequence, the probe and reference beams follow the same optical path, travel through the sample at the same position and are detected by the same liquid-nitrogen-cooled MCT detector. The detector bias is modulated at 25 MHz, synchronized to FELIX. This results in signals with opposite sign for the probe and reference beams. When the system is in balance, the integrating electronics give an apparent zero output signal. The three beams are focused onto the sample with an off-axis parabolic mirror of 12.5 cm focal length, as shown in figure 1. The samples were cooled with an Oxford Instruments ‘Microstat’ flow cryostat using an Oxford Instruments model ITC503 temperature controller to provide temperature variability.

3. Lutetium localized vibrational modes

The only hydrogenic centre formed in pure $CaF_2:H^-$ crystals consists of a single H^- ion having substitutionally replaced a F^- ion thus giving rise to a centre with tetrahedral (T_d) symmetry and a single fundamental vibrational resonance is observed [16]. For CaF_2 crystals containing trivalent rare-earth ions, H^- ions can serve as charge compensators. The single hydrogenic rare-earth centre produced has tetragonal C_{4v} symmetry with the trivalent rare-earth ion (RE^{3+}) charge compensated by an interstitial H^- ion located in the nearest-neighbour position along the [100] crystallographic direction, as shown in figure 2(a).

The vibrational spectrum of these C_{4v} symmetry modes consists of two transitions with a separation depending upon the RE^{3+} ion. In CaF_2 , the lower-frequency transition is associated with the doubly degenerate (X, Y) vibrations whilst the typically broader, higher-frequency transition is associated with the Z vibrational mode. For ions with an open-shell electronic configuration, small splittings ($<1\text{ cm}^{-1}$) of the (X, Y) modes can be attributed to the coupling between these local modes and the 4f electronic states through the electron-phonon interaction

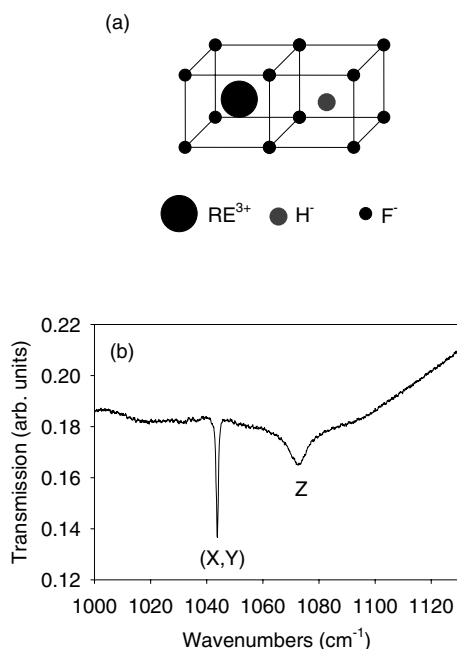


Figure 2. (a) A schematic diagram of the C_{4v} -symmetry $\text{CaF}_2:\text{RE}^{3+}:\text{H}^-$ centre. (b) The 10 K infrared absorption spectrum for $\text{CaF}_2:0.75\% \text{Lu}^{3+}:\text{H}^-$.

[17–19]. For the $\text{CaF}_2:0.75\% \text{Lu}^{3+}:\text{H}^-$ local modes under consideration in this work, the (X, Y) modes are not split (since Lu^{3+} has a filled $4f^{14}$ shell) and are separated from the Z mode by 30 cm^{-1} . The 10 K spectrum is shown in figure 2(b) with the (X, Y) mode at 1043.8 cm^{-1} and the Z mode at 1072.6 cm^{-1} . The measured 10 K linewidths are 1.0 and 9.3 cm^{-1} for the (X, Y) and Z modes respectively, a factor of approximately ten greater than the widths for $\text{CaF}_2:0.005\% \text{Lu}^{3+}:\text{H}^-$ crystals. This is a good indication that the line broadening is dominated by inhomogeneity due to strain fields set up in the crystal by the introduction of the Lu^{3+} dopant itself.

4. Vibrational lifetimes

4.1. (X, Y) modes

For FEL excitation of the $\text{CaF}_2:0.75\% \text{Lu}^{3+}:\text{H}^-$ (X, Y) local modes at 1043.8 cm^{-1} at 10 K, saturation of the local mode absorption is observed. Due to the comparatively narrow spectral widths of the local mode absorption line profile, the FEL spectral width was maintained at close to 4 cm^{-1} . Figure 3 shows the normalized probe transmission as a function of the time delay from a frequency-degenerate pump pulse. A small dip at around $t = 0$ is associated with the so-called coherent spike, a consequence of coupling between the pump and probe pulses. As this feature yields no information about the sample, we neglect it in the discussion to follow. The measured transient is a single exponential with a decay time of 43 picoseconds. This value is remarkably similar to that obtained for the substitutional (T_d -symmetry) H^- local mode of close to 45 picoseconds (as measured by the authors at FELIX [20] and other workers [12] utilizing the Stanford FEL), indicating that the decay of these vibrations perpendicular to the $\text{RE}^{3+}-\text{H}^-$ axis are not significantly shortened by the presence of the Lu^{3+} ion.

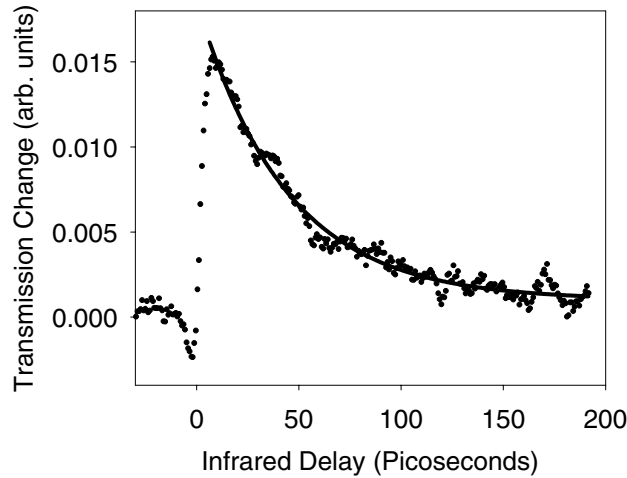


Figure 3. 10 K normalized probe transmission as a function of delay between the pump and probe pulses for resonant excitation of the (X, Y) modes at 1043.8 cm⁻¹. The solid line is a single-exponential fit to the data for the decay constant of 43 ps.

The temperature dependence of the local mode decay rate is plotted in figure 4. By 200 K, the decay rate of the (X, Y) mode is observed to increase by 40% from 23.3 GHz at 10 K to 32.3 GHz. As the band phonon cut-off frequency is 460 cm⁻¹ for the CaF₂ host lattice [21, 22], we attribute the residual 10 K decay rate to the spontaneous emission of three lattice band phonons via anharmonic terms in the vibrational potential. For three-phonon anharmonic decay, the temperature dependence of the H⁻ local mode decay rate $[T_1(T)]^{-1}$ can be expressed as

$$[T_1(T)]^{-1} = [T_1(0)]^{-1}[(1 + n_1)(1 + n_2)(1 + n_3) - n_1 n_2 n_3]$$

where $[T_1(0)]^{-1}$ is the zero-temperature decay rate which we approximate by the 10 K value. The n_i are the Bose–Einstein occupancy factors with $n_i = [\exp(\hbar\omega_i/kT) - 1]^{-1}$. Figure 4 shows the calculated decay rate as a function of temperature for three-phonon anharmonic decay. The closest qualitative approximation to the data is given for phonon frequencies of 394, 377 and 273 cm⁻¹ corresponding to (LO)X, (LO)L and (TO)L CaF₂ lattice phonons. We set $[T_1(0)]^{-1}$ to 23.3 GHz and the overall agreement is good. The implication is that LO phonons dominate the decay process with a mixture of low- and high-frequency band phonon modes being favoured. This observation is consistent with measurements for the H⁻ and D⁻ substitutional local modes in undoped CaF₂, SrF₂ and BaF₂ [20] crystals.

4.2. Z mode

The vibration of the H⁻ local mode along the H⁻–Lu³⁺ axis is at a higher frequency than those perpendicular to the high-symmetry axis (the (X, Y) mode vibrations) and appears as an intrinsically broader absorption line in FTIR measurements (see figure 2(b)). This makes it easier to saturate this mode as its absorption line profile is better matched to the minimum FELIX spectral width. Figure 5(a) shows the 10 K normalized probe transmission as a function of the delay between the pump and probe pulses for resonant excitation of the Z-mode vibration at 1072.6 cm⁻¹. The measured transient clearly exhibits fast and slow decay components. This multi-exponential behaviour is a consequence of the multiple decay pathways available to Z-mode vibrations which we schematically illustrate in figure 5(b).

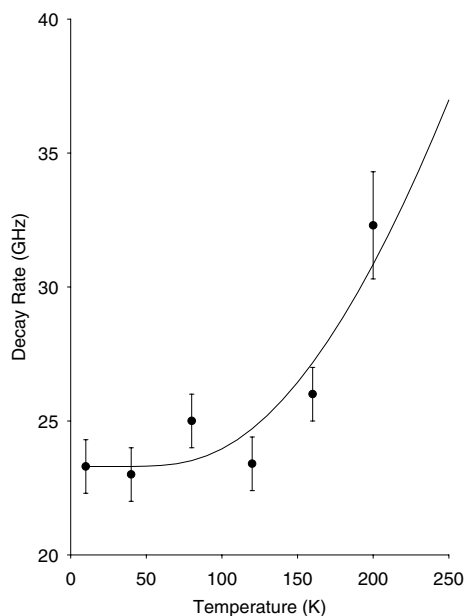


Figure 4. The rate of decay of the (X, Y) mode as a function of temperature. The solid line is a fit to three-phonon anharmonic decay into lattice modes at 394 (LO)X, 377 (LO)L and 273 cm^{-1} (TO)L band modes.

We may account for this pump–probe transient using a simple rate equation model as follows:

$$\begin{aligned} \frac{dn_{\text{GS}}(t)}{dt} &= +W_{\text{Z} \rightarrow \text{GS}}n_{\text{Z}}(t) + W_{\text{X,Y} \rightarrow \text{GS}}n_{\text{X,Y}}(t) \\ \frac{dn_{\text{X,Y}}(t)}{dt} &= +W_{\text{Z} \rightarrow \text{X,Y}}n_{\text{Z}}(t) - W_{\text{X,Y} \rightarrow \text{GS}}n_{\text{X,Y}}(t) \\ \frac{dn_{\text{Z}}(t)}{dt} &= -W_{\text{Z} \rightarrow \text{GS}}n_{\text{Z}}(t) + W_{\text{Z} \rightarrow \text{X,Y}}n_{\text{Z}}(t) \end{aligned}$$

where $n_{\text{Z}}(t)$, $n_{\text{X,Y}}(t)$ and $n_{\text{GS}}(t)$ are the Z, (X, Y) and ground-state populations, each as a function of time, and the $W_{\text{Z} \rightarrow \text{X,Y}}$, $W_{\text{Z} \rightarrow \text{GS}}$ and $W_{\text{X,Y} \rightarrow \text{GS}}$ are the appropriate decay rates (in GHz) for the various decay pathways. $W_{\text{Z} \rightarrow \text{X,Y}}$ represents a one-phonon decay process from the Z mode to the (X, Y) modes whilst the $W_{\text{Z} \rightarrow \text{GS}}$ and $W_{\text{X,Y} \rightarrow \text{GS}}$ are three-phonon anharmonic decay rates from the Z and (X, Y) modes to the ground state. After excitation by the pump pulse, no further pulse arrives during the decay time of the H^- local modes (except the probe which by definition only interrogates the response of the system to the pump). And, since we are only interested in the behaviour of the decay and not the absolute value of the absorption change $\Delta\alpha$, we can choose the initial conditions $n_{\text{Z}}(0) = 1$, $n_{\text{X,Y}}(0) = 0$ and $n_{\text{GS}}(0) = 0$. As a consequence of the fact that we are measuring a saturation of absorption, it is the ground-state recovery that we are interested in and thus the ground-state population, $n_{\text{GS}}(t)$. Using the model developed above, we obtain the solid line in figure 5(a) which shows the best fit to the data with optimized parameters $W_{\text{Z} \rightarrow \text{X,Y}} = 50.0$ GHz and $W_{\text{Z} \rightarrow \text{GS}} = 66.7$ GHz. The $W_{\text{X,Y} \rightarrow \text{GS}}$ rate was held fixed at 23.3 GHz, the value obtained from pump–probe measurements performed directly on the (X, Y) mode. These values correspond to lifetimes of $\tau_{\text{Z} \rightarrow \text{X,Y}} = 20$ ps, $\tau_{\text{Z} \rightarrow \text{GS}} = 15$ ps and $\tau_{\text{X,Y} \rightarrow \text{GS}} = 43$ ps. Figure 5(c) plots the calculated population dynamics of the vibrational

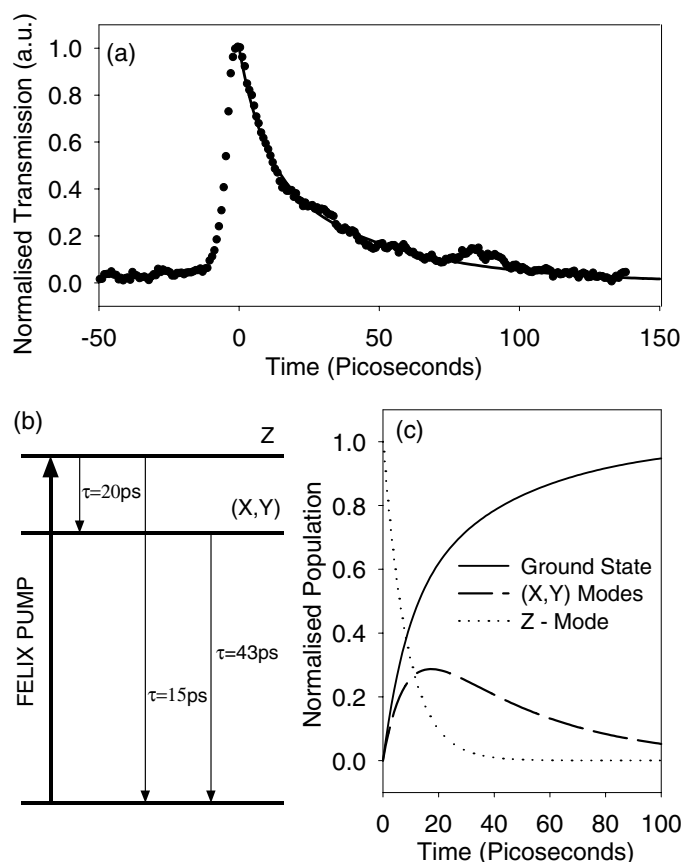


Figure 5. (a) 10 K probe transmission as a function of pulse delay exciting the Z mode at 1072.6 cm⁻¹. (b) A schematic energy level diagram for the C_{4v} H⁻ centre local modes showing the decay pathways. (c) The calculated population dynamics.

states of the tetrahedral symmetry oscillator. The long-time component of the transient is due to the (X, Y) lifetime whilst the faster effects are related to the Z-mode decay. The fact that the Z-mode decay is faster than that of the (X, Y) modes (the Z-mode lifetime is 8.6 picoseconds) is not insignificant as it provides an explanation for measurements on the SrF₂:RE³⁺ C_{4v} H⁻ centre local modes where the Z mode has a broader linewidth than the (X, Y) modes even when the Z mode lies at a lower energy than the (X, Y) modes.

5. Vibrational dephasing of the (X, Y) mode

The homogeneous dephasing time, T_2 , has contributions arising from the vibrational lifetime, T_1 , and the pure dephasing time which is due to quantum fluctuations of the vibrational transition energy about the average and causes the oscillators to lose phase with one another. We can express this as

$$\Gamma_{\text{hom}} = \frac{1}{\pi T_2} = \frac{1}{\pi T_2^*} + \frac{1}{2\pi T_1}.$$

Γ_{hom} is the homogeneous linewidth, and T_2^* is the pure dephasing time. Following the analyses of the substitutional H⁻ local mode linewidths for CaF₂ [16], we attribute these

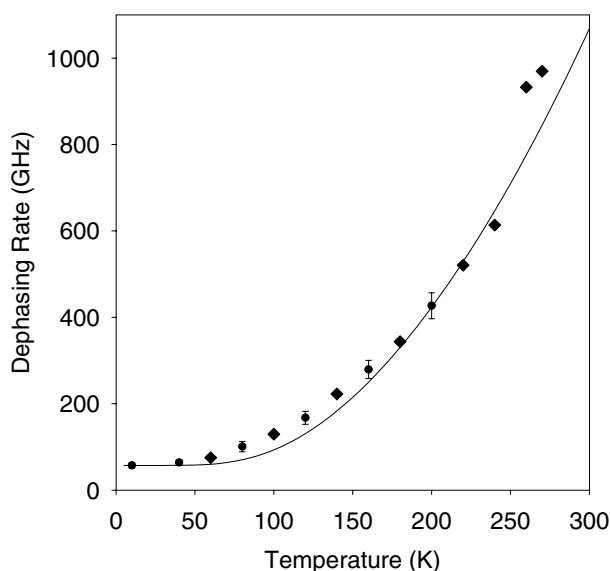


Figure 6. Pure dephasing rate of the (X, Y) modes as a function of temperature. The circles with error bars are purely experimental points, while the diamonds indicate data inferred from the calculated local mode lifetimes.

temperature-dependent processes to be elastic phonon scattering processes whereby lattice phonons are scattered off the defect without changing its vibrational state. Employing the Debye approximation for the host-lattice band phonon states we get

$$[T_2^*(T)]^{-1} = a + A \left(\frac{T}{T_D} \right)^7 \int_0^{T_D/T} \frac{x^6 e^x}{(e^x - 1)^2} dx$$

where A is the effective coupling constant, T_D is the Debye temperature for CaF_2 ($T_D = 519$ K [23]) and a is a temperature-independent term present to account for the fact that these modes are predominantly inhomogeneously broadened at low temperatures. Figure 6 shows the fit to the experimental data with the pure dephasing values determined from the pump–probe lifetimes and the measured linewidths from FTIR absorption shown as circles with error bars, and values determined from the calculated lifetimes (from the three-phonon anharmonic decay fit to the pump–probe data) and measured absorption linewidths indicated as diamonds. Good agreement is obtained for $A = 18.0$ THz with a set equal to 57.2 GHz. The A -value obtained is comparable to that for the substitutional H^- centre in CaF_2 (16 THz) [20].

6. Conclusions

The temperature-dependent lifetimes of the (X, Y) local modes of the C_{4v} H^- centre in $\text{CaF}_2:\text{Lu}^{3+}:\text{H}^-$ have been measured using a pump-and-probe technique and can be well accounted for by three-phonon anharmonic decay. The residual 10 K lifetime of 43 picoseconds is remarkably similar to that measured for the substitutional H^- centre in CaF_2 crystals, apparently indicating that the vibrations perpendicular to the $\text{Lu}^{3+}-\text{H}^-$ axis are not significantly altered by the presence of the rare-earth ion. From a combination of absorption linewidth measurements and the measured pump–probe lifetimes we can determine that the vibrational dephasing of the (X, Y) modes is well accounted for by elastic phonon scattering of lattice band modes.

The population decay of the Z mode is more complex and arises from a combination of one-phonon decay to the lower-energy (X, Y) modes and three-phonon decay to the ground state. A rate equation model for the population dynamics gives a good account of the observed 10 K transient. It is found that the decay of the Z mode to the ground state is intrinsically faster than that of the (X, Y) modes. This observation provides an explanation for measurements on the SrF₂:RE³⁺ C_{4v} H⁻-centre local modes where the Z mode has a broader linewidth than the (X, Y) modes even when the Z mode lies at a lower energy than the (X, Y) modes.

Acknowledgments

This work was supported by the Engineering and Physical Sciences Research Council (EPSRC) under research contract number GR/M/22374 and the Dutch FOM organization. We appreciate the skilful assistance of the FELIX staff, in particular Dr A F G van der Meer.

References

- [1] Rella C W, Kwok A, Rector K, Hill J R, Schwettman H A, Dlott D D and Fayer M D 1996 *Phys. Rev. Lett.* **77** 1648
- [2] Rector K D and Fayer M D 1998 *Nucl. Instrum. Methods Phys. Res. B* **144** 218
- [3] Rector K D and Fayer M D 1998 *Int. Rev. Phys. Chem.* **17** 261
- [4] Asplund M C, Lim M and Hochstrasser R M 2000 *Chem. Phys. Lett.* **323** 269
- [5] van der Voort M, Rella C W, van der Meer L F G, Akimov A V and Dijkhuis J I 2000 *Phys. Rev. Lett.* **84** 1236
- [6] Crepin C, Broquier M, Dubost H, Galaup J P, Le Gouet J L and Ortega J M 2000 *Phys. Rev. Lett.* **85** 964
- [7] Calistru D M, Demos S G and Alfano R R 1997 *Phys. Rev. Lett.* **78** 374
- [8] Engholm J R, Rella C W, Schwettman H A and Happek U 1996 *Phys. Rev. Lett.* **77** 1302
- [9] Jamison S P, Reeves R J, Pavlichuk P P and Jones G D 1999 *J. Lumin.* **83–84** 429
- [10] Lee L C and Faust W L 1971 *Phys. Rev. Lett.* **26** 648
- [11] Lang P T, Knott W J, Werling U, Renk K F, Campbell J A and Jones G D 1991 *Phys. Rev. B* **44** 6780
- [12] Davison C P, Campbell J A, Engholm J R, Schwettman H A and Happek U 1998 *J. Lumin.* **76+77** 628
- [13] Wells J-P R, Rella C W, Bradley I V, Galbraith I and Pidgeon C R 2000 *Phys. Rev. Lett.* **84** 4998
- [14] Hall J L and Schumacher R T 1962 *Phys. Rev.* **127** 1892
- [15] Findlay P C, Pidgeon C R, Kotitschke R, Hollingworth A, Murdin B N, Langerak C J G M, van der Meer A F G, Ciesla C M, Oswald J, Homer A, Springholz G and Bauer G 1998 *Phys. Rev. B* **58** 12 908
- [16] Elliott R J, Hayes W, Jones G D, Macdonald H F and Sennett C T 1965 *Proc. R. Soc. A* **289** 1
- [17] Jones G D, Peled S, Rosenwaks S and Yatsiv S 1969 *Phys. Rev.* **183** 353
- [18] Jacobs I T, Jones G D, Zdansky K and Satten R A 1971 *Phys. Rev. B* **3** 2888
- [19] Strickland N M and Jones G D 2000 *Phys. Rev. B* **61** 9399
- [20] Wells J-P R, Bradley I V, Jones G D and Pidgeon C R 2001 to be published
- [21] Elcombe M M and Pryor A W 1970 *J. Phys. C: Solid State Phys.* **3** 492
- [22] Ward R W and Whippey P W 1974 *Can. J. Phys.* **52** 1185
- [23] Hayes W 1974 *Crystals with the Fluorite Structure* (Oxford: Clarendon)