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Nonradiative energy transfer from the impurity ion into the host lattice for Cr^{4+}-doped forsterite laser crystal

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A theoretical model explaining the nonradiative energy transfer from a photoexcited impurity ion into the lattice in a laser crystal is presented. The energy-transfer mechanism consists of electronic energy transfer to local vibrations that then dissipate their energy to lattice (phonon) modes of the same energy creating a nonequilibrium phonon population. The model explains the experimental temporal profiles of nonequilibrium optical phonons probed by time-resolved Raman scattering in Cr-doped forsterite laser crystal. The electronic transition time and relaxation lifetimes for phonon and for local modes are ~3, 4, and 8 ps, respectively. [S0163-1829(97)06142-0]

INTRODUCTION

Understanding nonradiative processes occurring in impurity-doped crystals is of importance for the lasing properties of a material. Although the study of nonradiative relaxation was pioneered more than forty years ago (see paper by Huang and Rhys[1]) and has involved a significant amount of research (for references see the book by Englman[2]) many questions regarding the dynamics of nonradiative processes of photoexcited ions in host media have not yet received a satisfactory answer. Numerous theoretical models using various approaches for nonradiative relaxation mechanisms[3] have yielded varying results. Luminescence measurements (Sturge[4]) using a nanosecond time scale yield results which differ by several orders of magnitude from nonradiative decay rates derived from the activation energy law.[2] Only recently temporal profiles of lattice modes involved in nonradiative relaxation processes of ions in a laser crystal have been probed directly by Raman scattering with subpicosecond temporal resolution.[5]

In this paper, a theoretical model is applied to explain the dynamics of phonon modes measured in photoexcited $Cr:Mg_2SiO_4$. The electronic transition time and the phonon and local mode lifetimes are estimated from fitting the results of a theoretical model to the experimental data.

The present paper considers a laser crystal with deep impurity levels, where the proposed nonradiative energy-transfer mechanism from the photoexcited state of the impurity center into the lattice is quite different from the one reported in semiconductors.[6–9] The photoexcited zone-electron transfers energy directly to the lattice (phonon) modes. We consider for the first time coupling between local vibrations of an impurity center and phonon modes as the main path for energy redistribution. It will be demonstrated that when the energies of oscillation of local vibrations of the impurity center are close to the energies of optical phonons with zero quasimomentum, a nonequilibrium population of phonons is created.

The calculated dynamics of phonon occupation number excess

$$\overline{n(\varepsilon,t)}-n_0(\varepsilon) \tag{1}$$

relative to the equilibrium value

$$n_0(\varepsilon)=(e^{\varepsilon/kT}-1)^{-1}$$

is compared to the experimental results of Demos and Alfano.[5] In Eq. (1), $\overline{n(\varepsilon,t)}$ is the average occupation number of Raman-active phonons with energy ε at time moment t. Details of the derivation and solution of the rate equations are presented in the Appendixes.

MODEL FOR RELAXATION OF LOCAL AND PHONON MODES

The impurity centers will be considered as clusters made of an impurity ion and its nearest neighbors, possessing discrete electronic and vibrational states. The electronic levels of the center are located deep in the wide forbidden energy gap of the host crystal allowing one to neglect interactions between the electrons of the impurity and the rest of the crystal. Each mode of vibration of an impurity center (local mode) is characterized by its energy ε_c. Due to inhomogeneous interactions, this value differs slightly for different centers throughout the crystal, having the value $\varepsilon_c^{(i)}$ at the ith center. The set of values $\{\varepsilon_c^{(i)}\}$ form a band of local vibrations with its own density of states. Different sets of $\{\varepsilon_c^{(i)}\}$ will be considered independently. A harmonic interaction between local and phonon modes will be taken into account.

In such a model, the vibrational Hamiltonian of an impurity-doped crystal can be written as

$$H=\sum_i \varepsilon_c^{(i)}(B_i^\dagger B_i+1/2)+\sum_j \varepsilon_j(b_j^\dagger b_j+\tfrac{1}{2})+H_{\text{int}}. \quad (2)$$

In Eq. (2), $B_i^\dagger$, B_i are creation and annihilation operators of a local mode of energy $\varepsilon_c^{(i)}$, summation index i goes over all local modes of the same band. $b_j^\dagger$, b_j are creation and annihilation operators of the jth phonon mode of energy ε_j.

The H_{int} term is the sum of a harmonic (H_{h}) and an anharmonic (H_{anh}) term, as follows:

$$H_{\text{int}}=H_{\text{h}}+H_{\text{anh}},$$

$$H_{\text{h}}=\sum_{ij} \alpha_{ij}(B_i^\dagger+B_i)(b_j^\dagger+b_j),$$

$$H_{\text{anh}}=\frac{1}{6}\sum_{ljq} \eta_{ljq}(b_l^\dagger+b_l)(b_j^\dagger+b_j)(b_q^\dagger+b_q). \quad (3)$$

In Eqs. (3) α_{ij} is the constant of interaction of the ith local mode with the jth phonon mode and η_{ljq} is the constant of anharmonic interaction between the lth, jth, and qth phonon modes. The anharmonic term H_{anh} permits energy exchange between phonons of the host crystal. In the following derivation all harmonic interaction constants will be considered, for simplicity, independent of impurity mode number:

$$\alpha_{ij}=\alpha_j. \quad (4)$$

The equations for occupation numbers will be derived to the lowest possible order in H_{int}. To second order in the local mode-phonon coupling H_{h}, the transition rate from the N_ith local mode of energy $\varepsilon_c^{(i)}$ to a set of phonons with energies close to $\varepsilon_c^{(i)}$ is given by the Fermi golden rule as a sum over these lattice modes:

$$\frac{2\pi}{\hbar}\sum_j \alpha_j^2|\langle N_i,n_j|(b_j+b_j^\dagger)(B_i+B_i^\dagger)|N_i-1,n_j+1\rangle|^2$$
$$\times\delta(\varepsilon_c^{(i)}-\varepsilon_j)=\frac{2\pi}{\hbar}\sum_j \alpha_j^2\delta(\varepsilon_c^{(i)}-\varepsilon_j)N_i(n_j+1). \quad (5)$$

In Eq. (5), N_i is the occupation number for the ith local mode, n_j is the occupation number for the jth phonon mode. Similarly, the reverse transition rate from phonon states with energies close to $\varepsilon_c^{(i)}$ to local states is given by the expression

$$\frac{2\pi}{\hbar}\sum_j \alpha_j^2|\langle N_i,n_j|(b_j+b_j^\dagger)(B_i+B_i^\dagger)|N_i+1,n_j-1\rangle|^2$$
$$\times\delta(\varepsilon_c^{(i)}-\varepsilon_j)=\frac{2\pi}{\hbar}\sum_j \alpha_j^2\delta(\varepsilon_c^{(i)}-\varepsilon_j)(N_i+1)n_j. \quad (6)$$

If one neglects the anharmonic interaction (temporarily) and considers a purely harmonic crystal, the equation for the average occupation number of the ith local mode becomes

$$\frac{d\overline{N_i}(t)}{dt}=\frac{2\pi}{\hbar}\sum_j \alpha_j^2\delta(\varepsilon_c^{(i)}-\varepsilon_j)[-\overline{N_i}(t)+\overline{n_j}(t)], \quad (7)$$

$\overline{N_i}(t)$ is the average over time-dependent ensemble of the occupation number of the ith local mode, and $\overline{n_j}(t)$ is the corresponding average occupation number of the jth phonon mode.

In order to evaluate the sum in Eq. (7) for a continuous distribution of energies of phonon modes coupled to local modes the density of phonon states $g(\varepsilon)$ has to be introduced as was done, for example, by Louisell[10] where $g(\varepsilon)d\varepsilon$ equals the number of phonon states in the energy interval $d\varepsilon$. Introducing

$$\alpha(\varepsilon) \quad (8)$$

to characterize the coupling of the phonon mode of energy ε to local modes, one obtains

$$\sum_j \alpha_j^2\overline{n_j}(t)\delta(\varepsilon_c^{(i)}-\varepsilon_j)=\int d\varepsilon\,\delta(\varepsilon_c^{(i)}-\varepsilon)g(\varepsilon)\overline{n(\varepsilon,t)}\alpha^2(\varepsilon)$$
$$=g(\varepsilon_c^{(i)})\alpha^2(\varepsilon_c^{(i)})\overline{n(\varepsilon_c^{(i)},t)}. \quad (9)$$

Since the band of local vibrations is much narrower than the phonon band, one can consider the density of states of phonon modes as well as their occupation numbers to be constant within an interval of $\{\varepsilon_c^{(i)}\}$

$$g(\varepsilon_c^{(i)})=g(\varepsilon_c), \quad \overline{n(\varepsilon_c^{(i)},t)}=\overline{n(\varepsilon_c,t)}. \quad (10)$$

Assuming that the occupation number $\overline{N_i}(t)$ does not vary significantly among different local vibrations within the same band, i.e.,

$$\overline{N_i}(t)=\overline{N}(t), \quad (11)$$

one obtains an expression for the time derivative of $\overline{N}(t)$ from Eq. (7):

$$\frac{d\overline{N}(t)}{dt}=\gamma[-\overline{N}(t)+\overline{n(\varepsilon_c,t)}]. \quad (12)$$

The relaxation parameter γ in Eq. (12) is given by

$$\gamma=\frac{2\pi}{\hbar}g(\varepsilon_c)\alpha^2(\varepsilon_c). \quad (13)$$

In Eq. (12), phonon mode occupation number $\overline{n(\varepsilon_c,t)}$ depends on time. This time dependence makes Eq. (12) different from the well-known rate equation for the relaxation of an oscillator in contact with a reservoir[11,12] [see Eq. (15) below]. To obtain a simplified rate equation[11,12] from Eq. (12) the assumption that the lattice is always in thermal equilibrium can be made (temporarily):

$$\overline{n(\varepsilon_c,t)}=n_0(\varepsilon_c)=(e^{\varepsilon_c/kT}-1)^{-1}. \quad (14)$$

Equation (12) becomes

$$\frac{d\overline{N}(t)}{dt}=\gamma[-\overline{N}(t)+n_0(\varepsilon_c)]. \quad (15)$$

Then the occupation number $\overline{N}(t)$ behaves according to the equation of relaxation of a harmonic oscillator in contact with an equilibrium reservoir as discussed by Cheng and Lax[12] and Louisell and Walker.[13] The following treatment in which both local and phonon modes are out of equilibrium is similar to the more symmetric approach of Lax.[14]

Upon examining the validity of Eq. (15), we start by noting that the difference in transition rates between phonon modes and local modes for the jth phonon mode is

$$\frac{2\pi}{\hbar}\sum_i \alpha_j^2\,\delta(\varepsilon_c^{(i)}-\varepsilon_j)[-\overline{n_j}(t)+\overline{N_i}(t)], \tag{16}$$

which leads to the rate equation for occupation number of the jth phonon mode:

$$\frac{d\overline{n_j}(t)}{dt}=-\frac{2\pi}{\hbar}\,\alpha_j^2[\overline{n_j}(t)-\overline{N}(t)]G(\varepsilon_j). \tag{17}$$

In Eq. (17), $G(\varepsilon_j)$ is the density of local modes with the same energy as the phonon mode. One can rewrite Eq. (17) in continuous notation,

$$\frac{d\overline{n(\varepsilon,t)}}{dt}=\frac{2\pi}{\hbar}\,\alpha^2(\varepsilon)G(\varepsilon)[-\overline{n(\varepsilon,t)}+\overline{N}(t)]. \tag{18}$$

The density of phonon states $g(\varepsilon)$ is proportional to the number of atoms in the host crystal, while the density of local modes $G(\varepsilon)$ is proportional to the number of impurity atoms. If $g(\varepsilon)\gg G(\varepsilon)$ the relaxation of phonon modes due to their interaction with local vibrations is negligible. Then the relaxation of local modes does not change the occupation number of phonon modes, and Eq. (15) is correct. This case was considered in detail by Lax.[11] However, at the edges of the Brillouin zone the phonon density of states $g(\varepsilon)$ is small and becomes comparable with the local mode density of states $G(\varepsilon)$. This particular case, when the energies of local modes coincide with the energies of edge-zone phonon modes is considered in the present paper.

The rate equations for the occupation numbers for local vibrations and the phonon modes coupled to them, provided anharmonicity is not taken into account (yet), are

$$\frac{d\overline{N}(t)}{dt}=\gamma[-\overline{N}(t)+\overline{n(\varepsilon_c,t)}], \tag{19a}$$

$$\frac{d\overline{n(\varepsilon,t)}}{dt}=\mu(\varepsilon)[-\overline{n(\varepsilon,t)}+\overline{N}(t)], \tag{19b}$$

where the phonon relaxation parameter $\mu(\varepsilon)$ is

$$\mu(\varepsilon)=\frac{2\pi}{\hbar}\,\alpha^2(\varepsilon)G(\varepsilon). \tag{19c}$$

Since no information is available at this stage on the broadening of impurity levels in the crystal under consideration, it is reasonable to neglect the dispersion of $\mu(\varepsilon)$ within the band of local modes, setting

$$\mu(\varepsilon)\approx\mu. \tag{20}$$

Anharmonicity will add a term to Eq. (19b). Details of computation of this term are given in Appendix A. The final expression for the anharmonicity induced transition rate, when the ith phonon mode is not at equilibrium, is

$$-\frac{2\pi}{\hbar}\sum_{jk}\eta_{ijk}^2[\delta(\varepsilon_i-\varepsilon_j-\varepsilon_k)(1+n_{0j}+n_{0k})$$
$$+2\delta(\varepsilon_k-\varepsilon_i-\varepsilon_j)(n_{0j}-n_{0k})](\overline{n_i}(t)-n_{0i}). \tag{21}$$

Equations (19)–(21) yield equations for the occupation numbers for each local and phonon mode, respectively, (anharmonicity is taken into account)

$$\frac{d\overline{N}(t)}{dt}=\gamma[-\overline{N}(t)+\overline{n(\varepsilon_c,t)}],$$

$$\frac{d\overline{n(\varepsilon_c,t)}}{dt}=\mu[-\overline{n(\varepsilon_c,t)}+\overline{N}(t)]$$
$$+\zeta(\varepsilon_c)[-\overline{n(\varepsilon_c,t)}+n_0(\varepsilon_c)]. \tag{22}$$

In Eq. (22) the relaxation parameter due to anharmonicity $\zeta(\varepsilon)$ is obtained from Eq. (21) after converting the sum into an integral:

$$\zeta(\varepsilon)=\frac{2\pi}{\hbar}\int d\varepsilon'\{\eta^2(\varepsilon,\varepsilon',\varepsilon-\varepsilon')g(\varepsilon')g(\varepsilon-\varepsilon')$$
$$\times[1+n_0(\varepsilon')+n_0(\varepsilon-\varepsilon')]$$
$$+2\eta^2(\varepsilon,\varepsilon',\varepsilon'-\varepsilon)g(\varepsilon')$$
$$\times g(\varepsilon'-\varepsilon)[n_0(\varepsilon'-\varepsilon)-n_0(\varepsilon')]\}. \tag{23}$$

Equation (22) describes the energy-transfer process between phonons and local modes, without taking into account how the nonequilibrium population is produced. In this paper, we consider creation of nonequilibrium population of local modes due to nonradiative electronic transitions. The role of these transitions might be crucial in the energy exchange process. Weeks, Tully, and Kimerling[15] analyzed the situation when, due to an electronic transition, an energy of the order of electron volts was transferred to vibrations. An analogous situation with an electronic transition, accompanied by energy transfer to local vibrations, is discussed in the present work. The process is qualitatively presented in Fig. 1, with adiabatic potentials drawn (figuratively) for a single vibrational coordinate. Optical excitation brings the system into an excited state (step 1 on Fig. 1), which relaxes nonradiatively (step 2) via electronic transition, creating nonequilibrium population of local modes. We assume a rapid relaxation mechanism between local vibrations, some of which do not act as accepting modes (step 3). Due to this rapid relaxation we omit a backward energy flow from the modes into the photoexcited state. Since the excited state is created by a sharp pulse, its flow to the local modes can be characterized by the exponential time decay of the occupancy of the excited state. An exponential time decay acts as a source, $ke^{-\Gamma t}$, to the local vibrations. The system of equations describing the nonradiative relaxation of a phonon mode due to the relaxation of the photoexcited state then becomes

$$\frac{d\overline{N}(t)}{dt}=\gamma[-\overline{N}(t)+\overline{n(\varepsilon_c,t)}]+ke^{-\Gamma t},$$

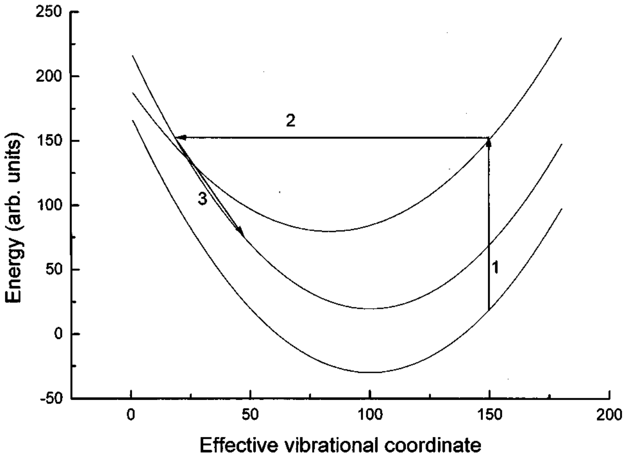

FIG. 1. Optical excitation and following nonradiative relaxation: (1) optical transition from the ground state to state producing bottleneck, (2) transition to a lower electronic state (in the present case, a spin triplet), (3) fast energy redistribution between local modes resulting in a loss of energy to the initial mode, with a redistribution (not shown) to other local modes.

$$\frac{d\overline{n(\varepsilon_c,t)}}{dt}=\mu[-\overline{n(\varepsilon_c,t)}+\overline{N(t)}]+\zeta(\varepsilon_c)[-\overline{n(\varepsilon_c,t)}+n_0(\varepsilon_c)]. \tag{24}$$

Equations (24) are solved for $\overline{N(t)}-N_0$, $\overline{n(t)}-n_0$, taking into account that equilibrium occupancies are equal,

$$N_0=n_0,$$

and by setting the initial conditions

$$N^{(0)}=n^{(0)}=n_0. \tag{25}$$

The general solution is presented in Appendix B. Here, to limit the number of parameters, the solution for $\overline{n}-n_0$ is specialized to the case $\mu=\gamma$,

$$\overline{n}-n_0=\frac{k\gamma}{R}\int_0^t d\tau\,\exp\left[-(t-\tau)\left(\gamma+\frac{\zeta}{2}\right)\right]\sinh[R(t-\tau)]\times\exp(-\Gamma\tau), \tag{26}$$

with R given by Eq. (B17):

$$R=\sqrt{\gamma^2+\zeta^2/4}. \tag{27}$$

The integration in Eq. (26) yields

$$\overline{n}-n_0=\frac{k\gamma}{R[(\Gamma-\gamma-\zeta/2)^2-R^2]}\{R\exp(-\Gamma t)+\exp[-(\gamma+\zeta/2)t][(\Gamma-\gamma-\zeta/2)\sinh(Rt)-R\cosh(Rt)]\}. \tag{28}$$

Eq. (28) will be used to fit the experimental data. A discussion of the fitting of theoretical results and the derivation of lifetimes Γ^{-1}, γ^{-1}, and ζ^{-1} follows.

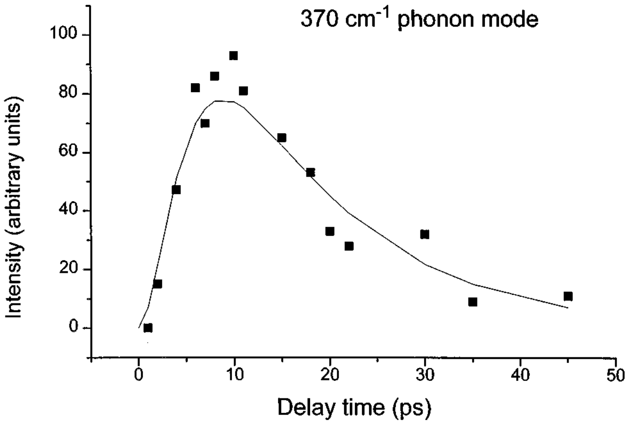

FIG. 2. Difference in Raman-scattering intensities between probe and pump pulses as a function of delay time for the 370 cm^{-1} phonon mode. The delay time is in picoseconds. Arbitrary units are used for the intensity. Experimental points are boxed (■). The solid line is the result of the theoretical computation of $\overline{n}-n_0$ [Eq. (28)] with lifetimes of 3 ps for decay of excited electronic state, 8 ps for relaxation of local vibrational excitation, and 4 ps for the decay of nonequilibrium population of optical phonons.

NONRADIATIVE RELAXATION PARAMETERS VALUES EXTRACTED FROM THE EXPERIMENTAL DATA

The above theoretical model will be fitted to experimental data[5] to extract the nonradiative relaxation fundamental parameters. Ultrafast pump-probe, time-resolved, Raman-scattering measurements were performed on a Cr:Mg_2SiO_4 laser crystal, having Cr^{4+} active centers,[16] using 500 fs, 590 nm linearly polarized pulses. The experimental setup uses an adjustable time delay line between the cross polarized pump and probe pulses.[5] Anti-Stokes Raman spectra were measured for different delay times between the pump and probe pulses. The differences in anti-Stokes Raman-scattering intensities for different delay times are presented in Ref. 5. It was shown[5] that only three Raman-active phonon modes demonstrate time-dependent behavior. Energies of these modes are equal to 335, 370, and 225 cm^{-1}. This conclusion was also confirmed by up-converted hot luminescence measurements.[17] Here for sake of brevity we present only time-dependent occupancy behavior for 370 cm^{-1} mode (Fig. 2).

The mechanism we propose to explain the temporal dependence of the phonon mode population is as follows. A 590 nm photon excites the Cr^{4+} impurity center in Cr:Mg_2SiO_4 from the ground state to a short-lived state interpreted by Demos, Takiguchi and Alfano[17] as a bottleneck. Adding the energy of the exciting photon of 16 960 cm^{-1} and the thermal energy of vibrations at room temperature of 210 cm^{-1}, one obtains that the photoexcited state of the impurity center is 17 170 cm^{-1} higher in energy than the ground $^3A_2$ state (for levels structure of Cr-doped forsterite, see paper[18] by Jia *et al.*). Results of Demos and co-workers[17] demonstrate that two luminescence peaks are close to this energy, at 17 213 cm^{-1} and 16 995 cm^{-1}. As stated in Ref. 17, the singlet spin state ^1E participates strongly in the creation of a bottleneck. Though the origin of the states related to these peaks is subject to discussion that is beyond scope of the present paper, it is clear that the photoexcited state has a vibrational energy of no more than 175 cm^{-1} (difference between 17 170 and 16 995 cm^{-1}), which is close to the thermal energy of 210 cm^{-1} corresponding to 300 K. In this case, the local vibrations obtain their excess energy not at once, but in the process of decay of the photoexcited state. The decay of the photoexcited state is mainly nonradiative. Emitted power from the bottleneck, as estimated from experiment, is of the order of 10^{-8} of the pump power, so the radiative relaxation channel can be neglected.

All electronic states of the Cr^{4+} impurity center with energies less than energy of the bottleneck are spin triplets.[18] The nonradiative transition rate between the spin singlet state, composing the bottleneck, and the spin triplet, is proportional to the spin-orbit interaction, which is of order of 100 cm^{-1} for the Cr^{4+} center,[18] about two or three times less than the energy of vibrations under consideration. The energy of the electron-phonon interaction for Cr^{4+} in forsterite is comparable to the energy of vibrations.[18] The closest spin triplet state with energy less than the energy of photoexcitation is at ~ 15500 cm^{-1} (see Ref. 18). So the energy interval between spin singlet and lower spin triplet approximately equals five energies of vibration.

The spin triplet states for Cr^{4+} form multilevel structures. Hot luminescence measurements[17] demonstrate that in this system relaxation occurs fast, practically without emission. In our simplified model the triplet states system is represented by one electronic state, with fast energy redistribution between local vibrations. This energy redistribution is the reason why backward energy flow into the photoexcited state is not taken into account.

Figure 1 is drawn on the assumption that electron-phonon interaction of the spin singlet state ${}^1E(e^2)$, which is produced by two e electrons, similarly to the ground state, ${}^3A_2(e^2)$, is weaker than for spin triplet T state, produced with participation of the t_2 electron.

As seen from Eq. (18), a nonnegligible change in occupation numbers of phonon modes takes place due to relaxation of local vibrations only if the densities of local vibrational states and of phonon modes are comparable. All three phonons that displayed time-dependent populations (225, 335, and 370 cm^{-1}) reported by Demos and co-workers[17] are Raman active and have quasimomentum close to zero.[19] Since no direct information on densities of states is available at this time, in order to reduce the number of fitting parameters the assumption that the density of states of local vibrations equals the density of zone-edge phonons is made. This yields equality of the relaxation parameters γ and μ used in the derivation of Eq. (28). Observable energy transfer from local vibrations to phonon modes takes place in $\mathrm{Cr{:}Mg_2SiO_4}$ due to the fact that the energies of local vibrations,[20] are close in value to the energy of zone-edge phonon modes.

In the case $k=0$ in Eq. (24), corresponding to the absence of energy transfer from the electronic state to local modes, the solution of Eq. (24) with initial conditions

$$\overline{N}=N^{(0)}\neq n_0, \quad n^{(0)}=n_0 \tag{29}$$

and $\gamma=\mu$ yields for the nonequilibrium population of phonon modes [see Eqs. (B11) and (B17)]

$$\overline{n}-n_0\propto\exp[-(\gamma+\zeta/2)t]\sinh(Rt). \tag{30}$$

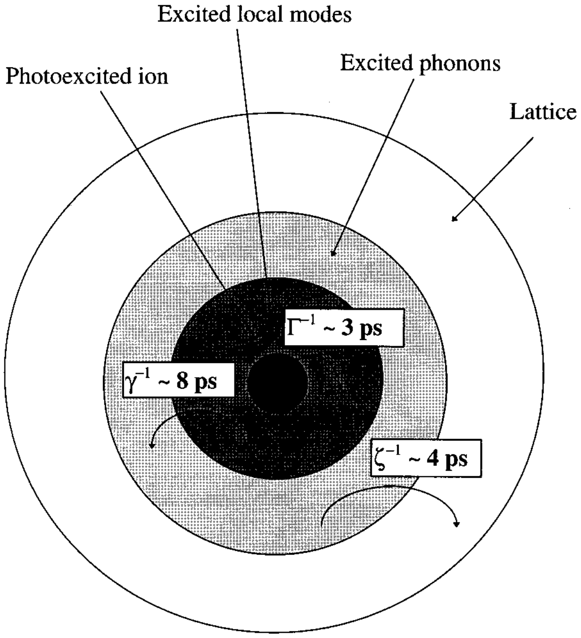

FIG. 3. Schematic diagram describing the proposed theoretical model and the fitted relaxation parameters.

The fitting to experiment in such a case is much worse than for three step energy transfer schematically presented on Fig. 1.

The right-hand side of Eq. (28) [obtained from Eq. (24) with $k\neq 0$ and initial conditions given by Eq. (25)] for long delay times the decay is proportional to

$$\overline{n}-n_0\propto\exp[-(\gamma-R+\zeta/2)t]. \tag{31}$$

Fitting of the experimental curve for long delay times requires

$$(\gamma-R+\zeta/2)^{-1}\approx 13 \text{ ps} \tag{32}$$

for modes of 335 and 370 cm^{-1} energy, and 14 ps for the 225 cm^{-1} energy mode. Keeping that in mind, one obtains the best fit with parameters

$$\gamma^{-1}\approx 8 \text{ ps}, \quad \text{and } \zeta^{-1}\approx 4 \text{ ps} \tag{33}$$

for the 370 cm^{-1} mode, and, correspondingly, 9 and 4 ps values for γ^{-1} and ζ^{-1} for 335 and 225 cm^{-1} modes. These values yield an approximate equation

$$\gamma\approx\zeta/2. \tag{34}$$

For all three modes the best fit yields an electronic transition time

$$\Gamma^{-1}\approx 3 \text{ ps}. \tag{35}$$

Results of fitting are presented in Fig. 2 for the 370 cm^{-1} mode. The curve shape is quite similar for two other modes.

DISCUSSION

A schematic diagram describing the theoretical model and the derived relaxation parameters is shown in Fig. 3. Following photoexcitation, an electronic relaxation with change in electronic state and creation of nonequilibrium population of local modes takes place. This process is characterized by the electronic transition time $\Gamma^{-1}\sim 3$ ps. The newly created nonequilibrium local mode population transfers energy to isoenergetic phonon modes located at the edges of the vibrational zones. The relaxation time of this process is $\gamma^{-1}\sim 8$ or 9 ps. Thermal equilibrium of the system is achieved due to anharmonicity described by the characteristic relaxation time $\zeta^{-1}\sim 4$ ps. The temporal behavior of the 225, 335, and 370 cm^{-1} phonon modes is described by approximately the same set of lifetime parameters γ, Γ, and ζ.

The value obtained for the electronic relaxation parameter Γ is surprisingly large:

$$\Gamma = 1/3 \ \ \mathrm{ps} \approx 3\times 10^{11} \ \ \mathrm{s}^{-1}. \tag{36}$$

This large value can be explained as follows. According to the paper of Henry and Lang,[20] the rate constant for nonradiative relaxation equals the probability of transition for one vibrational period, $2P_{\mathrm{LZ}}$, divided by the period T (P_{LZ} is the Landau-Zener transition probability during one crossing of electronic levels). Then Γ equals

$$\Gamma = 2P_{\mathrm{LZ}}/T. \tag{37}$$

For a vibration of $\sim 300\ \mathrm{cm}^{-1}$ energy this period equals approximately to 10^{-13} s so

$$\Gamma = 10^{13} \ \ \mathrm{s}^{-1}\cdot 2P_{\mathrm{LZ}}. \tag{38}$$

Equation (38) yields a small transition probability $P_{\mathrm{LZ}}\sim 10^{-2}$ for each crossing of the levels.

The present model of relaxation of local and phonon modes resembles a model used in the study of spin-lattice relaxation,[21] when cooling of multilevel system is due to interaction with phonons. Only certain lattice phonons effectively participate in the spin cooling. In our problem, the local modes are similar to spins in the spin-lattice relaxation problem. They are considered to be in thermal equilibrium with each other, but not with the lattice. Their relaxation changes equilibrium conditions for resonant phonons, as does cooling of spin system. The only qualitative difference from corresponding rate equations for spins discussed in Ref. 21 is presence of the electronic ''source'' in Eq. (24). In coming publications, we are going to perform an analysis of effective temperatures of vibrational subsystems in forsterite.

The model of nonradiative relaxation presented in this paper differs from the one discussed by Demos and Alfano[5] with respect to the first step of the relaxation. The rate equations used in Ref. 5 consider that the electronic energy of the impurity center is transferred directly into the lattice, while the contribution of local modes was not taken into account. Since the phenomenological rate equations were similar to the ones obtained in this paper, the results are comparable. In this paper, the total lifetime of the vibrational relaxation given by the sum of the lifetimes of local and phonon modes is 12 ps. In Ref. 5 almost the same number is obtained for the sum of the lifetimes of the intermediate electronic state and nonequilibrium phonon modes. The present paper provides different characteristic times: ~ 3 ps for the electronic transition, ~ 8 ps for the local mode lifetime at the impurity center, and ~ 4 ps for relaxation of the phonon modes.

CONCLUSION

In conclusion, we have shown that from the point of view of nonradiative relaxation there are two sets of vibrations in a Cr:$\mathrm{Mg_2SiO_4}$ crystal. One set (local modes) has a longer lifetime (~ 8 or 9 ps) while the other set (phonon modes) has shorter lifetimes (~ 4 ps). We have also shown for the first time that the occupation number of certain zone-edge phonon modes can be changed during the vibrational relaxation of the local mode.

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APPENDIX A. ANHARMONICITY INDUCED TERM IN RATE EQUATION

Let us compute change in occupancy of ith phonon mode due to anharmonic interaction, represented by H_{anh} in interaction Hamiltonian, Eq. (3). The Hamiltonian will be taken into account to the second order of perturbation theory. In H_{anh}, the term responsible for creation of ith phonon and annihilation of phonons k,j, equals

$$\eta_{ijk} b_i^{\dagger} b_j b_k. \tag{A1}$$

The rate of creation of the ith phonon due to annihilation of phonons j,k is

$$\frac{2\pi}{\hbar}\,|\eta_{ijk}|^2\,\delta(\varepsilon_i-\varepsilon_j-\varepsilon_k)\langle b_k^{\dagger} b_j^{\dagger} b_i b_i^{\dagger} b_j b_k\rangle$$

$$=\frac{2\pi}{\hbar}\,|\eta_{ijk}|^2\,\delta(\varepsilon_i-\varepsilon_j-\varepsilon_k)(\overline{n_i}+1)\overline{n_j n_k}. \tag{A2}$$

Total rate of creation of the ith phonon due to annihilation of a phonon pair equals

$$\frac{2\pi}{\hbar}\sum_{j,k}\,|\eta_{ijk}|^2\,\delta(\varepsilon_i-\varepsilon_j-\varepsilon_k)(\overline{n_i}+1)\overline{n_j n_k}. \tag{A3}$$

Corresponding rate of annihilation equals

$$\frac{2\pi}{\hbar}\sum_{j,k}\,|\eta_{ijk}|^2\,\delta(\varepsilon_i-\varepsilon_j-\varepsilon_k)\overline{n_i}(\overline{n_j}+1)(\overline{n_k}+1)/2. \tag{A4}$$

Combining Eqs. (A.3) and (A.4), one obtains rate of change of occupancy of ith phonon due to creation or annihilation of two other phonons:

$$\frac{2\pi}{\hbar}\sum_{j,k}\,|\eta_{ijk}|^2\,\delta(\varepsilon_i-\varepsilon_j-\varepsilon_k)\{(\overline{n_i}+1)\overline{n_j n_k} - \overline{n_i}(\overline{n_j}+1)(\overline{n_k}+1)\}/2. \tag{A5}$$

Equation (A5) can be simplified. Only ith phonon, interacting with the local vibrations, has nonequilibrium occupancy number. Replacing all $n_{j,k}$ in Eq. (A5) by equilibrium values and making use of the identity[22]

$$n_0(\varepsilon_1)(n_0(\varepsilon_2)+1)(n_0(\varepsilon_3)+1) \\ =(n_0(\varepsilon_1)+1)n_0(\varepsilon_2)n_0(\varepsilon_3)\exp\left(\frac{\varepsilon_2+\varepsilon_3-\varepsilon_1}{kT}\right) \tag{A6}$$

one obtains

$$\begin{aligned}(\overline{n_i}+1)\overline{n_j n_k}-\overline{n_i}(\overline{n_j}+1)(\overline{n_k}+1) &=(n_{0i}+1)n_{0j}n_{0k}+(\overline{n_i}-n_{0i})n_{0j}n_{0k}\\ &\quad -n_{0i}(n_{0j}+1)(n_{0k}+1)\\ &\quad -(\overline{n_i}-n_{0i})(n_{0j}+1)(n_{0k}+1)\\ &=-(\overline{n_i}-n_{0i})(1+n_{0j}+n_{0k}).\end{aligned} \tag{A7}$$

Combining Eq. (A5) and Eq. (A7), one obtains expression for change of occupancy of ith phonon due to creation or annihilation of a phonon pair

$$-\frac{2\pi}{\hbar}\sum_{j,k}|\eta_{ijk}|^2\delta(\varepsilon_i-\varepsilon_j-\varepsilon_k)(\overline{n_i}-n_{0i})(1+n_{0j}+n_{0k}). \tag{A8}$$

Other transitions, where ith phonon, together with the phonon of different energy, participates in annihilation or creation of another phonon, also change occupancy of the ith phonon state. Corresponding energy conservation is represented by δ function $\delta(\varepsilon_k-\varepsilon_i-\varepsilon_j)$. Operators responsible for these processes are proportional to $b_i^\dagger b_j^\dagger b_k, b_i b_j b_k^\dagger$, $b_i^\dagger b_j b_k^\dagger, b_i b_j^\dagger b_k$. Calculations are similar to those demonstrated by Eqs. (A2)–(A7), and yield the result

$$-\frac{2\pi}{\hbar}\sum_{j,k}|\eta_{ijk}|^2 2\,\delta(\varepsilon_i-\varepsilon_j-\varepsilon_k)(\overline{n_i}-n_{0i})(n_{0j}-n_{0k}). \tag{A9}$$

Combining Eq. (A8) and Eq. (A9), one obtains Eq. (21).

APPENDIX B. SOLUTION OF RATE EQS. (24)

First, the solution of Eq. (22) will be presented. Then, using this solution, the solution of the inhomogeneous Eq. (24) will be obtained.

Introducing the new variables

$$\Delta_c=\overline{N}(t)-n_0(\varepsilon_c);\quad \Delta_t=\overline{n(\varepsilon_c,t)}-n_0(\varepsilon_c). \tag{B1}$$

Equation (22) can be written as

$$\frac{d}{dt}\begin{pmatrix}\Delta_c\\ \Delta_l\end{pmatrix}=\begin{pmatrix}-\gamma & \gamma\\ \mu & -(\mu+\zeta)\end{pmatrix}\begin{pmatrix}\Delta_c\\ \Delta_l\end{pmatrix}. \tag{B2}$$

The solution of Eq. (B2) is [see, for example, Bellman[23]]

$$\begin{pmatrix}\Delta_c(t)\\ \Delta_l(t)\end{pmatrix}=\exp\left[t\begin{pmatrix}-\gamma & \gamma\\ \mu & -(\mu+\zeta)\end{pmatrix}\right]\begin{pmatrix}\Delta_c(0)\\ \Delta_l(0)\end{pmatrix}. \tag{B3}$$

One can express the matrix K,

$$K=\begin{pmatrix}\gamma & -\gamma\\ -\mu & (\mu+\zeta)\end{pmatrix} \tag{B4}$$

through the Pauli matrixes σ_x, σ_y, σ_z, and unit matrix σ_0:

$$K=\tfrac{1}{2}[\sigma_0(\gamma+\mu+\zeta)-(\gamma+\mu)\sigma_x+(\mu-\gamma)i\sigma_y \\ +(\gamma-\mu-\zeta)\sigma_z]. \tag{B5}$$

Then, the term $\exp(-Kt)$ can be written as

$$\exp(-Kt)=\exp[-t(\gamma+\mu+\zeta)/2]\exp\left(t\sum_j R_j\sigma_j\right), \tag{B6}$$

where $j=x,y,z$, and

$$R_x=(\gamma+\mu)/2;\quad R_y=i(\gamma-\mu)/2;\quad R_x=(\mu+\zeta-\gamma)/2.$$

Introducing R,

$$R=\sqrt{R_x^2+R_y^2+R_z^2}=\sqrt{\gamma\mu+(\zeta+\mu-\gamma)^2/4}, \tag{B7}$$

a unit vector $\mathbf{n}$ with components $n_j=R_j/R$ $(j=x,y,z)$, and vector $\boldsymbol{\sigma}$ with components $\sigma_x,\sigma_y,\sigma_z$, one can rewrite the second term in Eq. (B6) as

$$\exp\left(t\sum_j R_j\sigma_j\right)=\exp(tR\mathbf{n}\cdot\boldsymbol{\sigma})=\cosh(Rt)+\mathbf{n}\cdot\boldsymbol{\sigma}\sinh(Rt). \tag{B8}$$

Then Eq. (B3), which is the solution of Eq. (B2), yields

$$\begin{aligned}\Delta_c(t)&=\exp[-t(\gamma+\mu+\zeta)/2]\{[\cosh(Rt)\\ &\quad +n_z\sinh(Rt)]\Delta_c(0)+\sinh(Rt)(n_x-in_y)\Delta_l(0)\},\\ \Delta_l(t)&=\exp[-t(\gamma+\mu+\zeta)/2]\{[\cosh(Rt)\\ &\quad -n_z\sinh(Rt)]\Delta_l(0)+\sinh(Rt)(n_x+in_y)\Delta_c(0)\}.\end{aligned} \tag{B9}$$

For the relaxation taking place within the same electronic state the initial conditions are

$$\Delta_c(0)\neq 0;\quad \Delta_l(0)=0, \tag{B10}$$

and Eq. (B9) then simplifies:

$$\begin{aligned}\Delta_c(t)&=\exp[-t(\gamma+\mu+\zeta)/2]\\ &\quad\times[\cosh(Rt)+n_z\sinh(Rt)]\Delta_c(0),\\ \Delta_l(t)&=\exp[-t(\gamma+\mu+\zeta)/2]\sinh(Rt)(n_x+in_y)\Delta_c(0).\end{aligned} \tag{B11}$$

The inhomogeneous Eq. (24) can be written as

$$\frac{d}{dt}\begin{pmatrix}\Delta_c\\ \Delta_l\end{pmatrix}=\begin{pmatrix}-\gamma & \gamma\\ \mu & -(\mu+\zeta)\end{pmatrix}\begin{pmatrix}\Delta_c\\ \Delta_l\end{pmatrix}+\begin{pmatrix}k\exp(-\Gamma t)\\ 0\end{pmatrix}. \tag{B12}$$

Its solution is obtained with the help of the solution of the homogeneous Eq. (B2).[23] Eqs. (B3) and (B4) yield

$$\begin{pmatrix}\Delta_c(t)\\ \Delta_l(t)\end{pmatrix}=\exp(-tK)\begin{pmatrix}\Delta_c(0)\\ \Delta_l(0)\end{pmatrix}+\exp(-tK)\int_0^l d\,\tau\,\exp(K\tau) \\ \times\begin{pmatrix}k\exp(-\Gamma\tau)\\ 0\end{pmatrix}. \tag{B13}$$

Evaluation of Eq. (B13) with initial conditions

$$\Delta_c(0)=\Delta_l(0)=0 \tag{B14}$$

eliminates the first term on the right-hand side and yields

$$\begin{aligned}\Delta_c(t)&=k\int_0^t d\ \tau\ \exp[-(t-\tau)(\gamma+\mu+\zeta)/2]\{\cosh[R(t-\tau)]\\&\quad+n_z\sinh[R(t-\tau)]\}\exp(-\Gamma\tau),\\ \Delta_l(t)&=k\int_0^t d\ \tau\ \exp[-(t-\tau)(\gamma+\mu+\zeta)/2]\sinh[R(t-\tau)]\\&\quad\times(n_x+in_y)\exp(-\Gamma\tau).\end{aligned} \tag{B15}$$

The integration yields for the second of Eq. (B15)

$$\begin{aligned}\Delta_l(t)&=\frac{k(n_x+in_y)}{[\Gamma-(\gamma+\mu+\zeta)/2]^2-R^2}\{2R\ \exp(-\Gamma t)\\&\quad+\exp[-t(\gamma+\mu+\zeta)/2][\sinh(Rt)(\Gamma-(\gamma+\mu\\&\quad+\zeta)/2)-R\ \cosh(Rt)]\}.\end{aligned} \tag{B16}$$

In the special case $\gamma=\mu$, Eq. (B.16) remains valid with

$$n_x=\gamma/R;\quad n_y=0,\quad n_z=\zeta/(2R);\quad R=\sqrt{\gamma^2+\zeta^2/4}. \tag{B17}$$

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