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Phonon Lifetimes in Molecular Crystals with Isotopic Impurities

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The subject of phonon relaxation is the study of the processes which contribute to the finite lifetime of phonon states in a crystal. Phonons are collective crystal excitations, coupled together through anharmonic terms of the crystal Hamiltonian. These phonon-phonon interactions are responsible of the finite phonon lifetime. In molecular crystals phonon lifetimes typically range from few picoseconds to some hundred picoseconds at the liquid He temperature. For very isolated phonon levels, lifetimes can even reach higher values, up to several nanoseconds. As the temperature increases the lifetime decreases, since the number of decay channels increases with temperature.

The anharmonic phonon-phonon coupling terms of the crystal Hamiltonian give rise to two basically different relaxation processes. The first involves the simple loss of phase of the collective excitation due to scattering processes with thermal bath phonons. The second process is due to the decay of the phonon energy into the thermal bath, i.e. to a depopulation of the phonon state. In addition crystal defects and impurities, in particular isotopic impurities, give further contributions to the lifetime.

For molecular solids a convenient theoretical approach to the dynamics of anharmonic crystal vibrations is the perturbative expansion of the hamiltonian in terms of phonon normal coordinates. The perturbation expansion can be carried out in principle to any order in the Van Hove expansion parameter, although in practice the inclusion of fourth order terms is already a major task. In order to investigate the convergence of the perturbative expansion, we have compared the lattice dynamics calculations with a computer simulation of bandwidths and anharmonic shifts for some simple molecular systems. These calculations show that the bandwidths converge already at the fourth order of perturbation whereas shifts converge at much higher orders.

The interpretation of the experimental results has been thus made in terms of elementary relaxation processes involving third and fourth order phonon-phonon coupling mechanisms. If only third order processes are present, the inverse lifetime must show a linear variation with temperature in the classical regime. The occurrence of fourth order processes produces instead a T_2 dependence of the inverse lifetime.

Lifetime measurements can be made either in the time domain

by ps time-resolved CARS spectroscopy or in the frequency domain by high resolution Raman and IR spectroscopy. The two types of experiments are equivalent in principle, since the Fourier transform of the time domain relaxation curves gives the band profile in the frequency domain.

We have investigated in details the effect of isotopic impurities on the phonon lifetimes. Experimental data were collected for isotopically pure $^{35}\text{Cl}_2$ and $^{32}\text{S}_8$ as well as for the corresponding natural crystals.

In the case of chlorine we have measured the Raman spectrum of natural and 99% isotopically pure $^{35}\text{Cl}_2$ crystals, in the lattice and in the internal mode regions, using a high resolution Raman spectrometer. Measurements were made on a wide temperature range to obtain the temperature dependence of the linewidth for both the lattice and the internal vibrational modes. The data were analyzed in terms of anharmonic interactions and contributions from the isotopic disorder. The lattice phonons are little affected by the isotopic disorder, while the internal vibrons are extremely sensitive to the presence of isotopic impurities. In the latter case the linewidths of the A_g and B_{3g} internal vibrons are about one and two orders of magnitude, respectively, larger in the natural than in the isotopically pure sample. The Raman spectrum of natural chlorine in the internal region is correctly reproduced by an harmonic lattice dynamics calculation weighted over the statistical distribution of the isotopic species in the lattice.

We have also measured the bandwidths of several phonons and vibrons in single crystals of isotopically pure ^{32}S , grown in our laboratory. For most of the bands a linear variation of the inverse lifetime with temperature was observed in the classical regime. For some others, however, a strongly non-linear variation was instead obtained. We have also measured the bandwidth of the same phonons and vibrons in crystals of natural sulfur containing 4.22 % of ^{34}S isotopic impurities. The bandwidths are in most of the cases much larger when the impurities are present and in addition the difference with the isotopically pure crystal is temperature dependent.

Using the formalism of the retarded Green's functions we have developed a theory of the influence of isotopic impurities on phonon and vibron frequencies and linewidths. The theory takes into account both harmonic and anharmonic processes in the crystal and yields a proper self-energy, developed up to the second order, that includes impurity-activated contributions depending on the concentration of impurities and on the ratio of the masses of the isotopic species. Central to the theory is a technique of averaging the anharmonic phonon propagators over the ensemble of impurity configurations. The most important result is that the imaginary part of the proper self-energy includes two different contributions to the bandwidth, one which is temperature independent due to harmonic scattering processes and one which depends on T , due to anharmonic scattering processes. These theoretical predictions are correctly verified by experiments.

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