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Temperature dependence of the saturation of the H^- local-mode absorption in CaF_2 by use of a tunable carbon dioxide laser

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We have studied the temperature dependence of the saturation of the local-vibrational-mode absorption of H^- ions in CaF_2 crystals by use of a tunable, high-pressure carbon dioxide laser. We tuned the laser to the peak of the strongly temperature-dependent local-mode absorption line and found, in the temperature range 4 to 110 K, strongly temperature-dependent saturation behavior. An analysis of the results shows that the saturation behavior is determined by three-phonon decay of the local mode. From our results we derive an anharmonic lifetime of 17 ps at low temperature and we estimate, furthermore, an effective vibrational charge of about one electronic charge for the local mode.

I. INTRODUCTION

In 1971 Lee and Faust[1] demonstrated saturation of the H^- local-mode absorption in CaF_2. In this experiment, use was made of an accidental coincidence of an emission line of a TEA CO_2 laser with the local-mode infrared absorption line at a crystal temperature of 77 K. In this paper we report a study of the temperature dependence of the saturation behavior performed by use of a tunable CO_2 laser that allows tuning of the laser frequency to the peak of the temperature-dependent H^- local-mode absorption line and we present an analysis that gives the lifetime and the effective charge of the H^- local-mode; our values are noticeably different from the values estimated earlier.[1]

Experimental details are presented in Sec. II, while the results and their analysis are given in Sec. III.

II. EXPERIMENTAL DETAILS

For absorption saturation studies we used crystals with a transmission of typically 1% at the absorption maximum. Appropriate crystals should be uniformly and lightly hydrogenated because thin slices with high H^- ion concentration absorb so much energy during each laser pulse that the crystal temperature can increase, because of the relaxation of the excited H^- ions, by some tens of degrees even when immersed in superfluid helium. Both very lightly and uniformly hydrogenated crystals are therefore needed for minimizing thermal heating effects.

The usual method of hydrogenation[2] is to heat the crystals in contact with molten aluminum at 850 °C in a hydrogen atmosphere for periods ranging from 1 to 60 h. The amount of hydrogen introduced increases almost linearly with the duration of the hydrogenation treatment. However, it was found that, even for the shortest hydrogenation times (1 h) and the lowest hydrogenation temperatures (780 °C), most of the crystals produced were just too heavily and nonuniformly hydrogenated.

Another method tried with little success was to deuterate the crystals and rely on the traces (up to 2%) of hydrogen present in the deuterium gas to give a weak H^- localized mode line. It was expected that competition between the hydrogen and deuterium for available anion sites would give a significantly weaker H^- infrared absorption line. Nevertheless, the deuterated crystals frequently showed too much H^- localized mode absorption and this technique did not, in any case, yield optimally hydrogenated crystals having H^- lines of the narrowest linewidth.

The best crystal prepared for the saturation studies proved to be one treated with aluminum metal in a nominal vacuum. Traces of water vapor present in the system gave sufficient hydrogen, through reduction by the aluminum, to give a crystal having the narrowest attainable localized mode line of the appropriate intensity.

For the spectral measurements, the crystals were cooled either to 1.8 K by immersion in superfluid helium or down to temperatures of 10 K with a variable temperature cryostat.

Details of the high-pressure tunable carbon dioxide laser have already been published.[3] The essential aspect for the saturation studies reported here is that the laser delivers infrared pulses of energies of up to 250 mJ in several spectral ranges. The 965-cm^{-1} H^- local-mode line lies just within one of the tuning ranges of this laser. Pumping in the line center of the local-mode line is possible for crystal temperatures up to 110 K, while at higher temperatures the line shifts outside the laser tuning range. The temporal profile of a 200-mJ laser pulse is shown in Fig. 1. The pulse had a total duration of about 300 ns with most of the energy within 160 ns, a peak power up to 1.2 MW, and an almost trapezoidal shape (shown dashed in Fig. 1). The spectral bandwidth of the radiation was 0.16 cm^{-1}. The radiation was focused onto

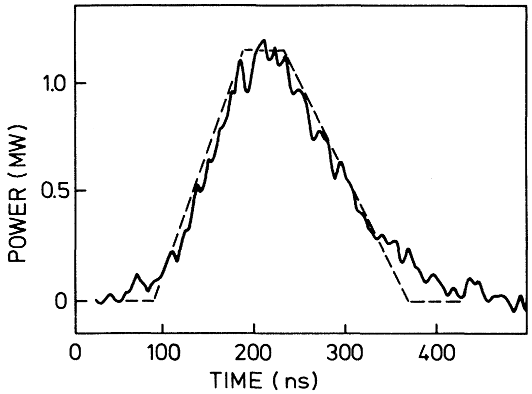

FIG. 1. Temporal profile of a typical pulse from the tunable carbon dioxide laser (solid line) and pulse shape adopted for the calculations (dashed line).

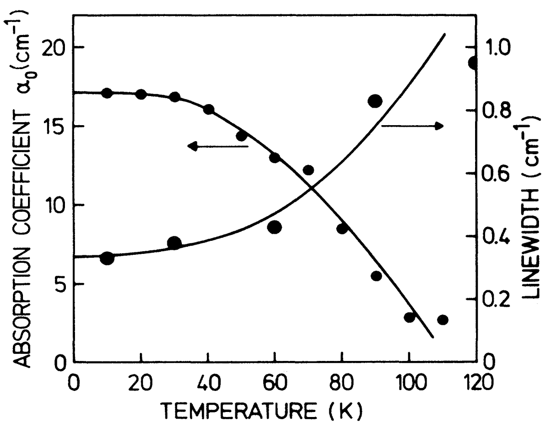

FIG. 3. Temperature dependence of the absorption coefficient at line maximum (●) and of the linewidth (●).

a small spot of about 670 μm diameter exhibiting a Gaussian profile. Both the input laser intensity and the transmitted laser intensity were monitored using pyroelectric detectors. Saturation of the absorption is indicated by an increase of the intensity of laser pulses transmitted by the crystal for pulses of high energy.

III. RESULTS AND ANALYSIS

A. Linear spectroscopy

Figure 2 shows the transmission of the optimally doped crystal, where the 965-cm^{-1} line has a width of 0.33 cm^{-1} at 10 K. The line contour is found to be close to Lorentzian, indicating a homogeneously broadened line even at 10 K. At higher temperatures, the local-mode line broadens (Fig. 3) by a phonon Raman-scattering process[4] yielding a quadratic increase of the linewidth with temperature, while the peak shifts to lower energies with a linear shift for temperatures above 60 K. The area under the absorption contour remains substantially constant over the measured temperature range.

Other crystals examined were deuterated ones having more H$^-$ than the optimally hydrogenated crystal. These gave closely similar absorption saturation results, despite having wider H$^-$ local-mode lines.

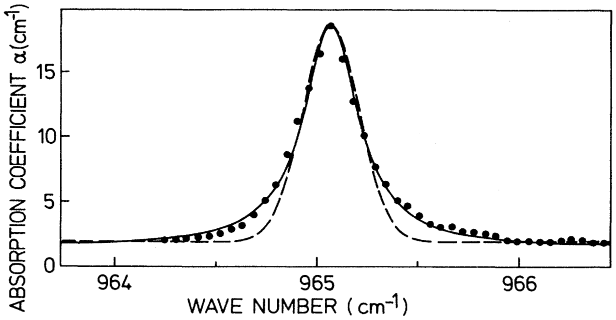

FIG. 2. Infrared absorption profile of the H$^-$ local-mode in CaF$_2$ in the weakly hydrogenated crystal. The solid and dashed lines are Lorentzian and Gaussian line profiles, respectively.

B. Saturation of the absorption

Saturation of the absorption of the local-mode line is demonstrated in Fig. 4, which gives the saturation curve for the optimum crystal at 10 K. The transmission of this 1.95-mm-thick crystal increases from 2.4% at low laser pulse energy to 60% at the highest available pulse energy of 50 mJ, i.e., nearly complete saturation of the absorption was realized.

As the crystal temperature is raised, the local-mode line broadens to give increased transmission at the line peak (Fig. 3) and increased laser pulse energies (Fig. 5) are needed to fully saturate the absorption.

The H$^-$ local-mode has a residual linewidth at the lowest temperatures, which is measured to be 0.33 cm^{-1}

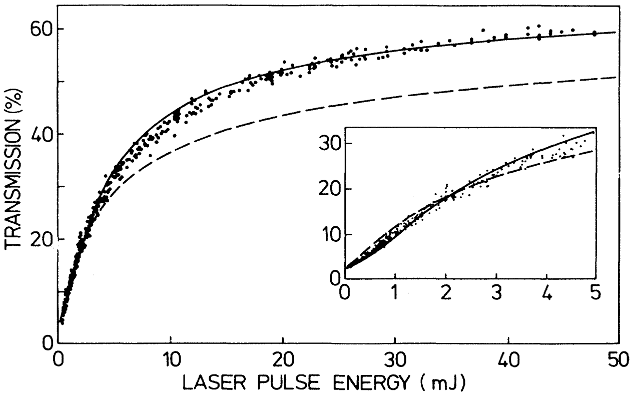

FIG. 4. Saturation of absorption. Experimental data (points); calculated saturation behavior for a homogeneous line with $I_S=0.39$ MW/cm^2 (solid line) and for an inhomogeneous line with $I_S=0.09$ MW/cm^2 (dashed line) are presented. The inset gives an expanded presentation of the initial part of the saturation curve.

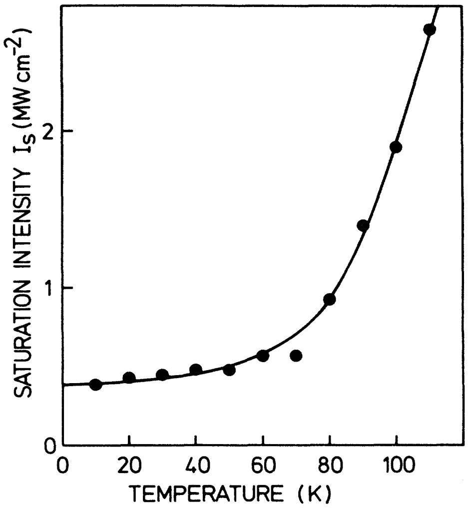

FIG. 5. Temperature dependence of the saturation intensity I_S at the line center.

for our optimally doped crystal (Fig. 6). Elliott *et al.*[4] consider various contributions to this linewidth, which include broadening arising from a random distribution of isotopes in the host crystal lattice, from internal strains in the crystal, and from possible interactions between vibrations of pairs of H^- ions. They conclude that all these contributions are negligible for H^- local-modes and consider the principal contribution to the residual linewidth to be the spontaneous decay of the H^- localized mode into three or more phonon band modes. Such processes lead to homogeneously broadened lines and, for these lines, the absorption coefficient α decreases from the initial value α_0 with increasing incident light intensity I according to the homogeneous line saturation relation[5,6]

$$\alpha=\alpha_0(1+I/I_S)^{-1} ,$$

where I_S is the saturation intensity, defined as the power per unit area required to reduce the absorption coefficient of the transition to one half of the unsaturated value.

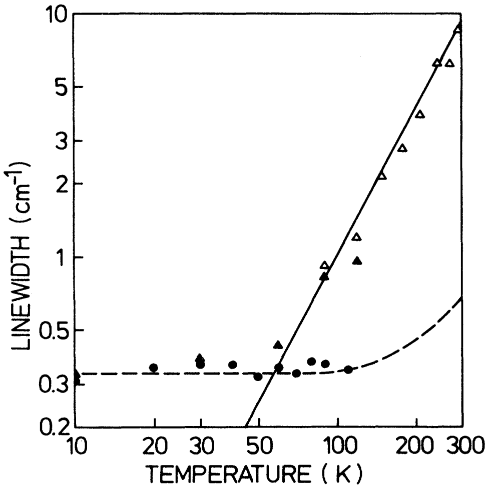

FIG. 6. Temperature dependence of the linewidth of the H^- local-mode in CaF_2. The triangles are the experimentally measured linewidths (▲ from laser scans, △ from infrared spectrometer scans). The linewidth is determined at low temperature by three-phonon anharmonic decay (dashed line) and at high temperature by phonon Raman scattering (solid line). The experimentally determined $1/2\pi c T_1$ values (dots) obtained from the saturation experiments follow the anharmonic decay process.

For an analysis of the experimental results using this homogeneous line saturation relation, it is necessary to consider the changes in both the spatial and temporal profile of the laser pulse as it passes through the crystal. The incident pulse is Gaussian (diameter 670 μm at FWHM) with the temporal profile depicted in Fig. 1. For the calculation of the net transmission of this pulse through the crystal, it is divided into circular spatial sections each of 10 μm width and into temporal sections each of 5 ns duration. The contribution to the net transmission of each of these spatial and temporal sections is computed for every 50-μm section of the 1.95-mm-thick crystal. The resulting overall calculated transmission of the crystal, for the best-fit I_S value of 0.39 MW/cm^2, is shown plotted through the experimental data points in Fig. 4. If a less sophisticated analysis is adopted, in which it is assumed that the laser pulse has constant intensity over a 670 μm diameter for a total time duration of 160 ns, a best-fit I_S value of 3 MW/cm^2 results, about eight times higher.

The saturation curves obtained for the higher-temperature runs were also fitted using the same homogeneous broadening relation, with the corresponding best-fit I_S values increasing with temperature, as shown in Fig. 5. For inhomogeneously broadened lines, the peak absorption coefficient α decreases from the initial value α_0 with increasing light intensity I according to the inhomogeneous saturation relation[5,6]

$$\alpha=\alpha_0(1+I/I_S)^{-1/2} ,$$

where I_S is now the saturation intensity for inhomogeneous broadening. The best-fit saturation curve using this inhomogeneous line saturation relation is also shown in the inset of Fig. 4 for an I_S value of 0.09 MW/cm^2 and does not satisfactorily reproduce the observed saturation behavior over the whole range of incident laser intensities. The inability to represent the observed saturation behavior adequately with the inhomogeneous saturation relation supports the conclusion that the 965-cm^{-1} line is homogeneously broadened even at 10 K.

In all these analyses, we assume implicitly that the H^- ions are uniformly distributed throughout the crystal thickness; an assumption that may only be justified for crystal thicknesses of 1 mm or less. The diffusion of H^- into the crystal gives an exponential decrease in the H^- ion concentration from the surface.[7] Crystals, whose faces have been ground down, show reduced H^- ion concentrations. While it is believed that our optimally hydrogenated crystal is essentially uniformly doped, the other higher concentration crystals measured may have nonuniform H^- doping, giving rise to I_S values different by up to 30% for crystals of the same peak absorption.

C. Population lifetime T_1

In the limit of high intensity, the population lifetime T_1 is given by[1,8]

$$T_1=\frac{N\hbar\omega}{2\alpha_0 I_S}\ ,$$

where N is the H^- ion concentration and $\hbar\omega$ the local-mode quantum energy. This is the relation used by Lee and Faust[1] to estimate T_1. It is independent of N in so far that N is proportional to α_0 and only the absorption cross section α_0/N is needed to calculate T_1. Lee and Faust adopted the value of 8.2×10^{-18} cm^2, as deduced from experimental measurements[9,10] of N for a given α_0.

Alternatively, N can be estimated from the absorption strength of the infrared local-mode line using a modified "Smakula formula" for local modes, where the mass of the vibrating ion replaces the electron mass.[11,12] For lines of Lorentzian shape, as appropriate to the lines studied here, the relation is

$$Nf=2.94\times10^{16}\frac{n}{(n^2+2)^2}\alpha_0\Delta\nu\ \mathrm{cm}^{-3}\ ,$$

where n is the refractive index of the crystal, α_0 is the absorption coefficient at the line maximum (in cm^{-1}), Δ_ν is the half-width (full width at half maximum, in cm^{-1}), and f is the oscillator strength. For $n=1.5$, as appropriate[13] for CaF_2 at 965 cm^{-1}, this relation simplifies to

$$Nf=2.4\times10^{15}\alpha_0\Delta\nu\ \mathrm{cm}^{-3}\ .$$

If we assume that the effective charge associated with each vibrating H^- ion is one electronic charge, f is unity. The value adopted by Lee and Faust[1] for α_0/N corresponds to f values of much less than unity, which they attribute to an effective charge for the H^- ion of 0.18e.

In the absence of any definitive confirmation of the Lee and Faust value for α_0/N, we take f to be unity in the modified Smakula formula given above, which yields an α_0/N value of 1.3×10^{-15} cm^2, and obtain a population lifetime T_1 of 17 ps at 10 K. This value is in very good agreement with the measured 10-K linewidth of 0.33 cm^{-1} (Fig. 6). The uncertainty in T_1 can be large because of the various assumptions made, but the primary conclusion is that the T_1 value is consistent with the measured limiting low-temperature linewidth. The effective vibrational charge of the H^- ion is closer to one electronic charge than hitherto concluded because the values derived here for the saturation intensity I_S are smaller than those given by Lee and Faust.

D. Analysis of the temperature dependence of the saturation

At higher temperatures, the various I_S values (as given in Fig. 5) are inversely proportional to the corresponding α_0 values and this yields population lifetimes T_1 almost independent of temperature (Fig. 6). This result can be qualitatively understood because T_1 itself is determined by an anharmonic process in which the local-mode decays into three or more lattice phonons,[4] a process which does not vary greatly with temperature. The temperature dependence of the decay rate $\tau^{-1}(T)$ of a three-phonon decay processes is given by

$$\tau^{-1}(T)=\tau^{-1}(0)[(1+n_1)(1+n_2)(1+n_3)-n_1n_2n_3]\ ,$$

where $\tau^{-1}(0)$ is the low-temperature relaxation rate, $n_i\sim\exp(-\hbar\omega/kT)$, and $\hbar\omega$ a typical phonon energy of about one-third of 965 cm^{-1}. Thus, $\tau^{-1}(T)$ changes little because $n_1\approx n_2\approx n_3$ vary only slightly for temperatures below 150 K. Figure 6 includes a plot of the expected temperature dependence of this decay process, which fits well our experimental results.

IV. CONCLUSIONS

In this paper we reported a study of the saturation of the 965-cm^{-1} H^- local-mode line in CaF_2. We studied the temperature dependence of saturation of this H^- local-mode absorption and presented an analysis giving, in comparison with a previous study, revised data on the lifetime of the H^- local-mode vibration and the effective charge of the H^- ion. Our results show that the saturation intensity I_S is strongly temperature dependent, according to the markedly temperature-dependent absorption line profile, while the lifetime T_1 of the local-mode is found to be nearly constant over the measured temperature range up to 110 K for this local-mode, as expected for a three-phonon decay process.

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