Measurement of the effect of uniaxial stress on the spectrum of CaF_2:Pr^{3+}:D^- using spectral hole burning

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Uniaxial stress coefficients have been measured for the $^3H_4(1) \leftrightarrow {}^1D_2(1)$ transition of several Pr^{3+} centers in CaF_2 doped with Pr^{3+} and D^- ions. For the $C_s(1)$ center at 6012.4 Å these measurements were made using persistent spectral hole burning. The holes showed a stress shift of 1.8 GHz/kg mm^{-2}. This shift is somewhat inhomogeneous, which limits the magnitude of stress that can usefully be applied.

I. INTRODUCTION

Spectral hole burning can provide a very sensitive probe of the effect of external perturbations on spectral lines. It has been used in measurements of the effects of electric and magnetic fields and hydrostatic stress on the electronic energy levels of solids.[1] Here we show its application to the measurement of static uniaxial-stress coefficients. The use of ac stress techniques to detect spectral holes has been demonstrated[2,3] and while these provide sensitive methods of detection they have not provided absolute stress coefficients for spectral line shifts or splittings.

The dependence of optical transition frequencies on stress can assist in determining models of defect centers through the symmetry information provided and it may also make possible the remote measurement of very small strains.[2] At a more fundamental level, stress bears directly on the magnitude of inhomogeneous broadening in solids since in almost all cases this arises from static internal crystal strains. In addition, the coupling between electronic states and acoustic phonons can, in some cases, be related to static stress coefficients.[4]

External stress can produce shifts of optical transition frequencies and associated line splittings if the orientational degeneracy of equivalent centers is removed.[5] This can be measured by persistent hole shifts, i.e., the shift of spectral holes whose lifetime is longer than the time required to apply the stress and make the measurements. The removal of electronic degeneracy may be observed in a similar way, or in addition by using transient hole burning if associated side holes or antiholes are observed. Because the spectral resolution afforded by hole burning is typically greater than 100 times that of conventional spectroscopy, small shifts and splittings can be measured, or conversely only small stresses need be applied. This is particularly advantageous with fragile materials or those which cleave easily.

For the same reason that $4f^n$-$4f^n$ transitions of rare-earth ions are narrow, i.e., the inner $4f$ electrons are shielded from the lattice, they show small spectral shifts under stress and few measurements of these shifts have been made.[6,7] In some cases stress coefficients have been determined by ac-modulation techniques[7] calibrated with reference to previously measured static values in CaF_2:Sm^{2+} and SrF_2:Sm^{2+}.[8]

In the present experiments we have studied the stress behavior of four centers in a CaF_2 crystal doped with Pr^{3+} and D^- ions. The substitution of divalent Ca^{2+} by trivalent Pr^{3+} requires charge compensation, leading to a number of spectroscopic centers characterized by different positions for the charge-compensating ion, the dominant center being the C_{4v}-symmetry F^- site. Additionally, the diffusion of deuterium into the crystal produces C_{4v} D^- centers where a D^- ion acts as the charge compensator in the [100] interstitial position. Other centers, labeled $C_s(n)$, of C_s point-group symmetry are derived from the C_{4v} D^- site by having one or more neighboring F^- ions replaced by D^-. Local-mode vibronic lines indicate that these additional D^- ions substitute for lattice F^- ions in the nearest-neighbor shell.[9] Several of the corresponding C_s centers in SrF_2:Pr^{3+}:D^- have been shown to exhibit persistent spectral hole burning,[10] which for rare-earth ions is otherwise only known in glass.[11]

II. EXPERIMENT

A crystal of CaF_2 doped with 0.05 mol% Pr^{3+} was diffused with deuterium as previously described.[12] The crystal was cleaved along parallel (111) planes and polished to the dimensions of $2.0 \times 3.9 \times 1.7$ mm^3. Pressure was applied to the 7.8-mm^2 face in a [111] direction. A simple uniaxial-stress apparatus was constructed consisting of a stainless-steel plunger inside a tube, surmounted by a platform to which weights could be added. The sample was sandwiched between cardboard and stainless-steel pads and a free metal sphere was used between the plunger and pad to ensure that stress was applied normal to the sample face. Absolute calibration of the applied stress is readily obtained in this configuration. The stress apparatus was placed in a liquid-helium-flow cryostat at ambient pressure and a temperature of 5 K. Since a vacuum seal did not have to be maintained

TABLE I. Uniaxial-stress coefficients for the $^3H_4(1)\leftrightarrow{}^1D_2(1)$ transitions of $CaF_2:Pr^{3+}:D^-$.

Center	Wavelength (Å)	Γ_{inh} (GHz)	[111] stress coefficient (GHz/kg mm^{-2})
C_{4v} F$^-$	5940.6	0.85	0.57[a]
C_{4v} D$^-$	5966.1	2.2	0.71[a]
$C_s(1)$	6012.4	5.5	2.0,[a] 1.8[b]
$C_s(2)$	6047.9	6.0	1.6[a]

[a]Measurement from the shift of the entire inhomogeneous line at 5 K.
[b]Measurement from spectral hole burning at 5 K.

around the plunger, friction at this point was eliminated. Spectral lines were measured in fluorescence excitation, the excitation source being a single mode cw dye laser of width < 10 MHz.

The tetragonal (C_{4v}) Pr^{3+} sites having F$^-$ or D$^-$ charge compensators along [100] directions have doubly-degenerate E ground states. The distortion of the site from C_{4v} to C_s symmetry associated with the additional D$^-$ ions in $C_s(n)$ centers is small, as shown by the small splitting of the E ground state. For the C_s centers in $CaF_2:Pr^{3+}:D^-$ this splitting varies from 0.5 to 20 cm^{-1} depending on the number and position of the D$^-$ ions. The spectroscopy of these centers is discussed in more detail elsewhere.[9] Here we have made measurements on the $^3H_4(1)\leftrightarrow{}^1D_2(1)$ transitions of C_{4v} F$^-$, C_{4v} D$^-$, $C_s(1)$, and $C_s(2)$ centers. The wavelengths of these transitions are given in Table I.

III. RESULTS

Two kinds of measurements were made. In the first, the shift of the entire inhomogeneous line was measured as a function of stress. Additionally, in the case of the $C_s(1)$ center the shift of the optical transition frequency was obtained from the stress-induced shift of a spectral hole.

The overall line shifts are shown in Fig. 1 for the four centers studied and the stress coefficients are given in Table I. The stress coefficients for the C_s sites containing additional D$^-$ ions are 2–3 times larger than that of the C_{4v} D$^-$ center from which they are derived. Apparently the presence of the D$^-$ ions increases the local compressibility around the Pr^{3+} ion.

The two C_{4v} centers do not show persistent hole burning. Since the ground states for these centers are doubly degenerate, there can be a stress splitting due to the removal of this degeneracy as well as the shift of the absorption line. This splitting can, in principle, be observed by measuring the change in the separation between the outer two of the six hyperfine components since they are very narrow (800 MHz). We used two narrow-band lasers: one to burn a hole by optical pumping of the superfine levels,[13] and the other to probe the transient hole. For stresses up to 1.5 kg mm^{-2}, the splitting of the E ground state was less than 200 MHz.

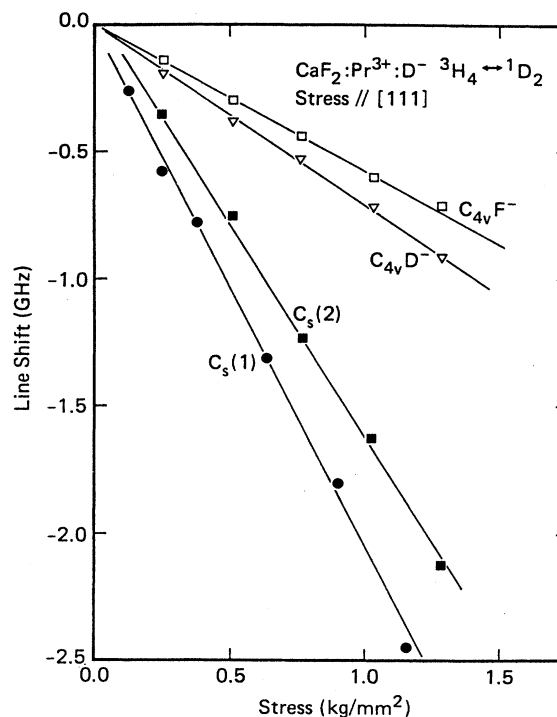The stress shift of the $C_s(1)$ center was also measured

FIG. 1. Stress-induced shifts of the total inhomogeneously broadened lines of four centers in $CaF_2:Pr^{3+}:D^-$ at 5 K.
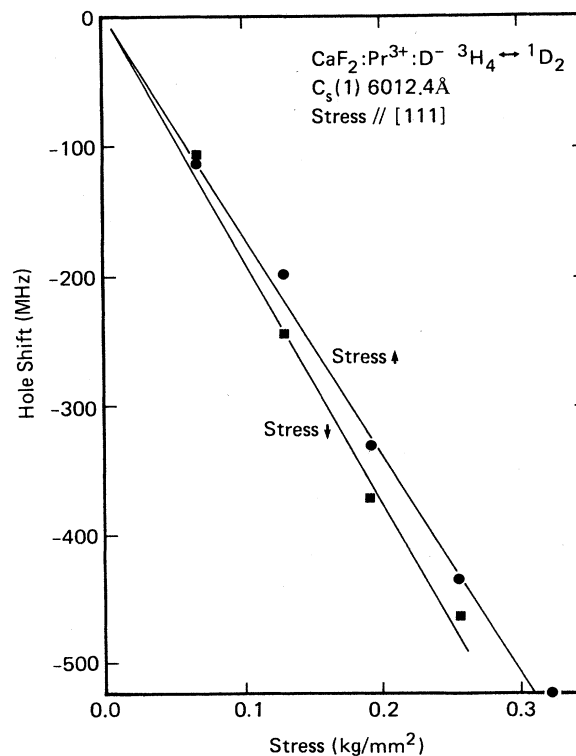

FIG. 2. Stress-induced shift of a persistent spectral hole in the 6012.4-Å line of the $C_s(1)$ center. There is a small hysteresis which probably comes from the stress apparatus.
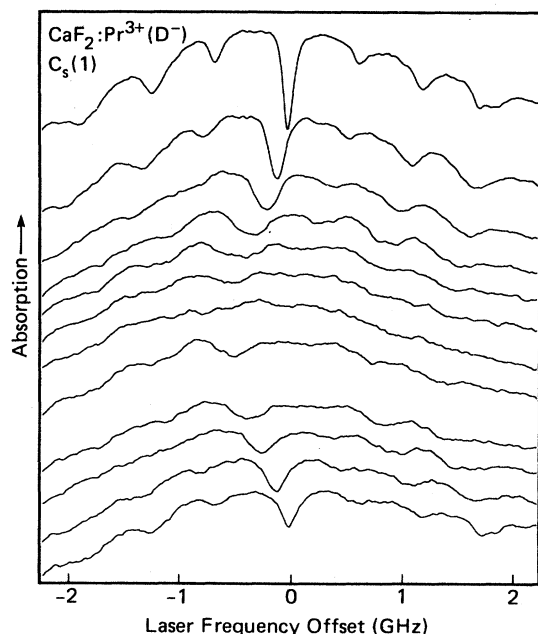
FIG. 3. Stress-induced shift of the hole in the 6012.4-Å line of the $C_s(1)$ center. The stress shift is seen to exhibit some inhomogeneity.

by spectral hole burning (Fig. 2). As the stress was applied, the hole also broadened and this ultimately limited the maximum useful stress in this experiment (Fig. 3). Upon removal of the stress the hole returned to its original position, though at a somewhat reduced intensity. This intensity reduction is due to bleaching of the entire spectral line during the reading phase of the hole-burning experiment in a similar manner to the broadband bleaching observed in these C_s centers.[9,10]

The stress effect on the spectral holes is inhomogeneous, as has been seen also for hydrostatic pressure shifts of spectral holes in dye-doped organic polymers.[14] The laser selects a set of ions which have different microscopic environments and hence the external stress can induce somewhat different shifts for these ions. The inhomo-

geneous width of the $C_s(1)$ center absorption is 5.5 GHz, and this increases by 700 MHz at 1 kg/mm^2. A comparable effect is seen for the holes in Fig. 3. Such inhomogeneous stress-induced broadening would make it possible to multiplex holes at different stresses in an analogous way to the Stark multiplexing in amorphous systems[15] or Zeeman multiplexing using an inhomogeneous Zeeman effect.[16]

For the $C_s(1)$ center the uniaxial-stress coefficient measured from spectral hole burning is about 10% less than that measured from the shift of the entire line, where the maximum stress was about 5 times that used to measure the hole shifts (Table I). We also note that the stress coefficients which we measure here for the $^3H_4 \leftrightarrow {}^1D_2$ transitions are similar in magnitude to those measured for the $^3H_4 \leftrightarrow {}^3P_0, {}^3P_1$ transitions by strain-modulation techniques.[7]

The inhomogeneous linewidths of the four centers studied are also given in Table I. Qualitatively, the narrow inhomogeneous lines are associated with smaller stress coefficients. Such a correlation can be expected, but we do not find a quantitative proportionality since measurements were made for stress in a single direction. The sensitivity of optical transitions to stress can also be used to calculate quantitatively the thermal broadening due to acoustic phonons, as shown for the case of ruby by Kushida and Kikuchi.[4]

IV. CONCLUSION

We have measured the small stress-induced optical frequency shifts for $4f^2$-$4f^2$ transitions of Pr^{3+} in several centers in CaF$_2$. In addition to measuring shifts of the entire inhomogeneous line, the shift of narrow spectral holes was observed. These holes showed an inhomogeneous stress shift which limits the amount of stress that can be usefully applied and may be a rather general effect in the measurement of stress-induced shifts using spectral hole burning. The stress coefficients for the rhombic C_s centers are more than twice that for the C_{4v} D$^-$ center from which they are derived. Evidently, the substitution of D$^-$ ions for F$^-$ ions in the lattice changes the local compressibility about the Pr^{3+} and increases the stress sensitivity of the optical transitions.

[1]For recent reviews, see, for example, R. M. Macfarlane and R. M. Shelby, in *Spectroscopy of Crystals Containing Rare Earth Ions,* edited by A. A. Kaplyanskii and R. M. Macfarlane (North-Holland, Amsterdam, 1987), R. M. Macfarlane and R. M. Shelby, in *Persistent Spectral Holeburning: Science and Applications,* edited by W. E. Moerner (Springer-Verlag, Berlin, 1987). D. Haarer, *ibid.* p. 79.

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