EFFECTS OF UNIAXIAL STRESS AND ELECTRIC FIELDS ON LOCALIZED VIBRATIONAL MODES

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A detailed discussion of the localized vibrational spectrum of H^- and D^- ions in the alkaline earth fluorides has been given recently.[1] It has been shown that the light ions dissolve in the crystals on fluorine sites[1,2] which have the point symmetry T_d. The localized-mode spectra have been fitted to the Hamiltonian

$$\mathcal{H} = \tfrac{1}{2}M\Omega^2r^2 + Bxyz + C_1(x^2y^2+y^2z^2+z^2x^2) + C_2(x^4+y^4+z^4), \qquad (1)$$

which includes terms to fourth order in the displacement of the light ion only; further terms in the Hamiltonian involving motion of the lattice ions are necessary to account for temperature-dependent widths and shifts of the lines.[1]

An energy-level diagram for the vibrations of H^- ions in CaF_2 is given in Fig. 1. Electric dipole transitions from the Γ_1 ground state are allowed only to Γ_5 excited states and the fundamental, one second harmonic, and two third harmonics have been observed in unperturbed crystals and are indicated by full lines in Fig. 1. The constants of the Hamiltonian (1) obtained from the measured frequencies of these lines at 20°K are

$$\Omega/c = 981.1\ \text{cm}^{-1}, \quad |B| = 7.87\times10^{12}\ \text{erg/cm}^3,$$
$$C_1 = -2.32\times10^{19}\ \text{erg/cm}^4,$$
$$C_2 = -1.01\times10^{19}\ \text{erg/cm}^4. \qquad (2)$$

Using these constans the positions of the other levels in Fig. 1 have been calculated.

We have investigated the effects of uniaxial compressional stress and high electric fields on the localized vibrational lines of H^- and D^- ions in CaF_2 in order to obtain more information about the interaction of the light impurities with the host lattice. These experiments are possible because of our narrow linewidths (~1 cm^{-1}) at low temperatures. The strain Hamiltonian for our cubic crystals under uniaxial stress P may be written

$$\mathcal{H} = P\{B_1(S_{11}+2S_{12})r^2 + B_3(S_{11}-S_{12})[(2n^2-l^2-m^2)\times(2z^2-x^2-y^2)+3(l^2-m^2)(x^2-y^2)] + B_5S_{44}(lmxy+mnyz+nlzx)\} \qquad (3)$$

for an arbitrary direction $[l,m,n]$ of P relative to the crystal axes; only terms linear in the displacement of the neighbors and quadratic in the displacement of the light ion are included. The strains associated with the parameters B_1, B_3, and B_5 transform like the irreducible representations Γ_1, Γ_3, and Γ_5 of the point group T_d and represent a uniform dilation (B_1), tetragonal and orthorhombic distortions (B_3), and a shear (B_5). The stiffness con-

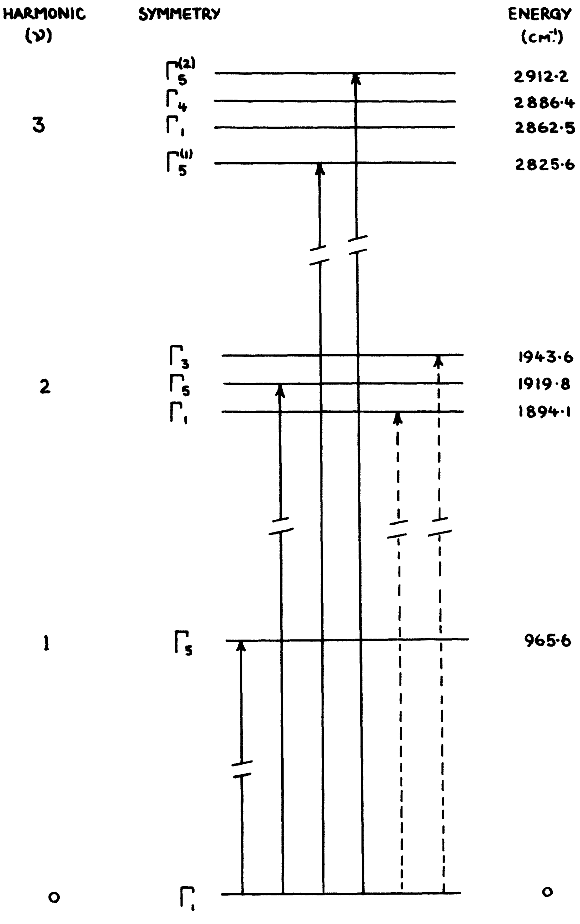

FIG. 1. Schematic representation of the lower vibrational energy levels of H^- in CaF_2 at 20°K. Observed transitions in unperturbed crystals are indicated by full vertical lines. The energies of the other levels have been calculated using the parameters (2) (see text). Additional transitions observed in crystals subjected to uniaxial compressional stress in the [111] direction at 77°K are indicated by broken vertical lines.

Table I. Energy levels and wave functions of the $\nu = 1$ levels of H^- ions in CaF_2 under uniaxial compressional stress P or an electric field E in the [111] direction. The polarization of light absorption from the ground state ($\nu = 0$) is included.

Perturbation	Wave functions	Polarization	Energy
P	$1/\sqrt{3}\,\lvert x+y+z\rangle$	$\vec{\epsilon}\parallel[111]$	$P[2(S_{11}+2S_{12})B_1+\frac{2}{3}S_{44}B_5]$
	$1/\sqrt{2}\,\lvert x-y\rangle$ $1/\sqrt{6}\,\lvert x+y-2z\rangle$	$\vec{\epsilon}\perp[111]$	$P[2(S_{11}+2S_{12})B_1-\frac{1}{3}S_{44}B_5]$
E	$1/\sqrt{3}\,\lvert x+y+z\rangle$	$\vec{\epsilon}\parallel[111]$	$\Lambda B_5'eE\hbar/(\sqrt{3}M^2\Omega^3)$
	$1/\sqrt{2}\,\lvert x-y\rangle$ $1/\sqrt{6}\,\lvert x+y-2z\rangle$	$\vec{\epsilon}\perp[111]$	$-\Lambda B_5'eE\hbar/(2\sqrt{3}M^2\Omega^3)$

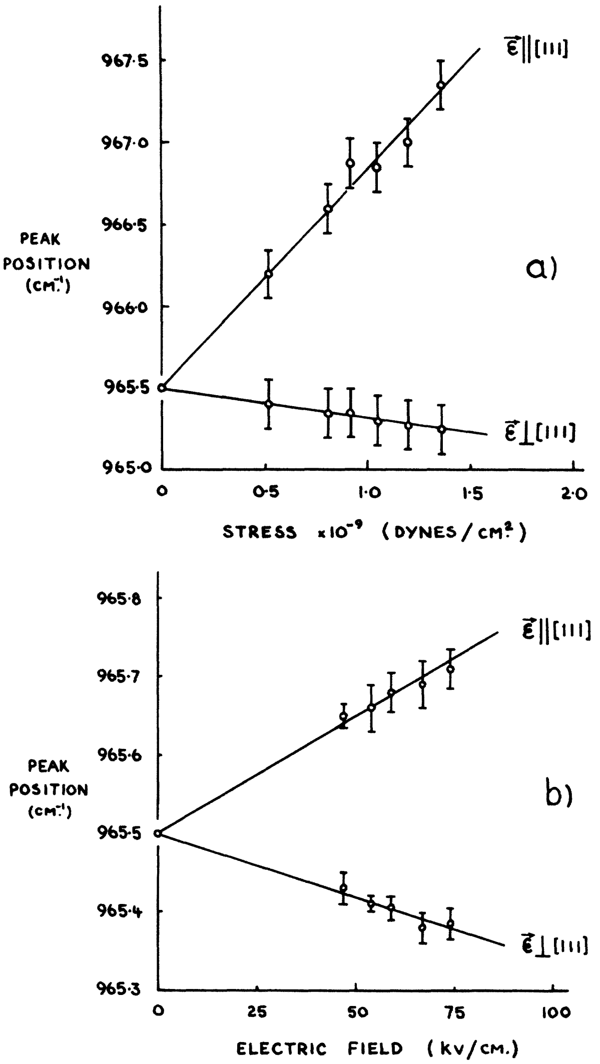

FIG. 2. Splitting of the fundamental vibrational line of H^- in CaF_2 at 20°K by (a) uniaxial compressional stress and (b) an electric field along the [111] direction. In both cases the high-energy line is observed with light with the electric vector $\vec{\epsilon}$ parallel to [111] and the low-energy line with $\vec{\epsilon}$ perpendicular to [111]. Continuous lines are drawn through the experimental points.

stants S_{ij} have been measured for CaF_2 over a wide range of temperatures,[3] and we shall make the approximation (see reference 1 for a discussion) in the analysis of our experimental results that these apply to the vibrations of the light impurities.

The Γ_5 levels (Fig. 1) have a threefold spatial degeneracy which may be raised by the application of stress. In a $\langle 110\rangle$ direction the degeneracy is completely raised and we observe three lines under stress. In both $\langle 100\rangle$ and $\langle 111\rangle$ directions each Γ_5 level splits into a doublet and a singlet and we observe two lines. We may, for example, describe the fundamental Γ_5 level ($\nu = 1$, Fig. 1) in terms of the degenerate states $\lvert x\rangle = \lvert 1, 0, 0\rangle$, $\lvert y\rangle = \lvert 0, 1, 0\rangle$, and $\lvert z\rangle = \lvert 0, 1, 0\rangle$ describing unit excitation of independent linear harmonic oscillators on the x, y, and z axes. Upon application of a stress P along the [111] direction, for example, this triplet splits into a singlet which is observed at higher energy with light with the electric vector $\vec{\epsilon}$ polarized parallel to [111], and a doublet at lower energy which is observed with $\vec{\epsilon}$ perpendicular to [111]; the wave functions and strain energies are given in Table I. The observed splittings obtained from the absorption of polarized infrared light at 20°K are given for this case in Fig. 2(a). A good fit to the observed splittings in the [100], [110], and [111] directions for the Γ_5 states of H^- in CaF_2 with $\nu = 1$ and 2 (see Fig. 1) has been obtained with

$$B_1 = (3.86 \pm 0.1)\times 10^{12}\ \mathrm{erg/cm^3},$$
$$B_3 = (0.41 \pm 0.1)\times 10^{12}\ \mathrm{erg/cm^3},$$
$$B_5 = (4.64 \pm 0.1)\times 10^{12}\ \mathrm{erg/cm^3}. \qquad (4)$$

There are two other levels for $\nu = 2$, Γ_1 (singly degenerate) and Γ_3 (doubly degenerate), in addition to Γ_5 (see Fig. 1). Transitions to these levels from the ground state are forbidden for electric dipole radiation and they are not observed in unperturbed crystals. However, the Γ_5 level may be admixed to Γ_1 and Γ_3 by application of a stress in any direction except ⟨100⟩, making transitions to these states observable. For example, under a stress of 2.4 $\times 10^9$ dyne/cm^2 along [111], we observe these transitions at 77°K at 1894.0 ± 2.0 cm^{-1} (Γ_1) and at 1943.5 ± 2.0 cm^{-1} (Γ_3) with intensities relative to the transition to the Γ_5 state of ~1/80 and ~1/180; our calculations predict relative intensities of 1/60 and 1/200. The observed positions of the Γ_1 and Γ_3 levels obtained in this way agree with the values obtained using the parameters (2) (see Fig. 1); frequency shifts between 77 and 20°K are less than our errors of measurement.

Application of an electric field to the crystal produces strain with Γ_5 symmetry, and we observe a Stark splitting of the localized vibrational levels which is linear in E because the light impurity ions are in lattice sites which lack inversion symmetry. For an arbitrary direction $[l, m, n]$ of the electric field relative to the crystal axes, the strain Hamiltonian may be written

$$\mathcal{H} = \Lambda C B_5' E e(lyz + mzx + nxy). \tag{5}$$

Here Λ is the local field (Lorentz) correction; the predicted variation of Λ with specimen shape is consistent with the experimental results using a value of 6.7 for the static dielectric constant.[4] C is a constant of dimensions (mass/time^2)$^{-1}$. If we assume that the lattice is not distorted by the field and only the light ion moves, $C = (M\Omega^2)^{-1}$ and $B_5' = B$ [see Eq. (1) for a definition of $M\Omega^2$ and B]; some distortion of the neighbors of the light ion is expected to occur, but we shall retain this value for C and define B_5' by (5). Experiments were carried out with E in the [100], [110], and [111] directions on the fundamental and second harmonic of H$^-$ in CaF$_2$. As an illustration, the effect on $\nu = 1$ for E along [111] is shown in Fig. 2(b). The eigenvalues are given in Table I together with the eigenfunctions which are the same as those for P along [111]. As in that case the high-energy line is polarized parallel to [111] and the low-energy line perpendicular to [111]. All the experiments are consistent with a value of

$$B_5' = (2.1 \pm 0.2) \times 10^{12} \text{ erg/cm}^3.$$

B_5' measures the anharmonicity of the light ion and should be related to the B's in (1) and (4) by a microscopic theory. An investigation of these results in the light of various models is being pursued.

Many of the measurements described above for H$^-$ ions have been repeated for D$^-$ ions and, in agreement with calculations, the experimental splittings obtained for D$^-$ are smaller than those for H$^-$ by a factor of about $\sqrt{2}$.

We shall give a more detailed account of the experimental techniques and experimental results at a later time.

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