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Localized Vibrations of Atomic Hydrogen in CaF_2†

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The infrared (ir) absorption spectrum of CaF_2 containing hydrogen has been measured over the range 590–2000 cm^{-1}. A strong, sharp line observed at 640 ± 0.5 cm^{-1} has been assigned to the localized mode of vibration associated with the interstitial neutral hydrogen atoms. The concentration of atomic hydrogen in the CaF_2 has been determined using both ir absorption and ESR absorption techniques. The measured concentration of 3×10^{19}/cm^3, together with the observed integrated absorption of the 640-cm^{-1} line of 73 cm^{-2}, indicates that the hydrogen-atom defect has an "apparent charge," as defined by Leigh and Szigeti, of 0.07 electrons. The observed localized-mode frequency has been compared with the result of an *ab initio* calculation of the interaction between the hydrogen defect and its eight fluoride neighbors. This calculation began with a Hartree-Fock-Roothaan self-consistent-field molecular-orbital calculation of the energy of an HF^- molecule. A localized-mode frequency of 560 cm^{-1} was obtained, in fair agreement with the observed frequency.

A STRONG peak has been observed in the infrared (ir) absorption spectrum of calcium fluoride containing hydrogen which appears to be caused by the localized mode of vibration associated with interstitial neutral hydrogen atoms. Evidence for this localized mode has been obtained previously by Feldman, Castle, and Murphy,[1] who used the much less direct method of measuring the spin-lattice relaxation time of the atomic hydrogen.[2] Our measurements have enabled us to determine accurately the frequency of vibration of this localized mode and to estimate the magnitude of the apparent charge on a hydrogen-atom impurity in CaF_2. Because of the simplicity of this system, we have been able to compare our localized-mode frequency with the result of an *ab initio* calculation of the interaction between the hydrogen defect and its eight fluoride neighbors. Similar calculations have been made by Wood, Öpik, and Gilbert[3] for a hydride-ion substitutional impurity in alkali-halide crystals.

Samples containing hydride (H^-) ions on fluoride sites[4] were prepared by heating, in a hydrogen atmosphere, CaF_2 single crystals[5] in contact with aluminum.[6] A hydride concentration of about 10^{20}/cm^3, about 10 times greater than previously reported, was attained by using a hydrogen pressure of about 50 atm.[7] After removing the Al by etching the crystal with NaOH, the sample was cleaved to the desired size. Hydride-ion defects were converted to hydrogen-atom defects by irradiating the sample at room temperature with x-rays.[8] The hydrogen-atom defects produced by this method are known to be situated on interstitial sites.[6,9]

Infrared absorption measurements were made over the range 590–2000 cm^{-1} with a Beckman IR-12 spectrometer. At 590 cm^{-1}, the thinnest sample that could be cleaved (0.1 mm) had essentially zero transmission because of strong absorption associated with the CaF_2 host crystal. Although measurements were made at several temperatures between 100°K and room temperature, only the 100°K measurements will be reported here.

Auxiliary ESR measurements of the atomic-hydrogen absorption were made at room temperature with a Varian X-band spectrometer. The external magnetic field was aligned parallel to the [111] direction of the CaF_2 crystal for these measurements. All ESR data were normalized to a diphenyl picryl hydrazyl (DPPH)[10] standard which was identical in area to the sample and was situated adjacent to it. This procedure minimized the dependence of the magnitude of the absorption on sample position. To avoid deterioration the standard was kept refrigerated in an argon atmosphere when not in use.

The prominent lines which were observed in the ir absorption spectrum of a sample previous to irradiation included (1) sharp lines at 965 and 1919 cm^{-1} which have

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† Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] D. W. Feldman, J. G. Castle, Jr., and J. Murphy, Phys. Rev. **138**, A1208 (1965).

[2] See A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273, and Vol. 19, p. 1, for an extensive review of point defects.

[3] R. F. Wood and U. Öpik, Phys. Rev. **162**, 736 (1967); R. F. Wood and R. L. Gilbert, *ibid.* **162**, 746 (1967).

[4] R. J. Elliott, W. Hayes, G. D. Jones, H. F. Macdonald, and C. T. Sennett, Proc. Roy. Soc. (London) **A289**, 1 (1965).

[5] Obtained from Harshaw Chemical Co., Cleveland, Ohio.

[6] J. L. Hall and R. T. Schumacher, Phys. Rev. **127**, 1892 (1962).

[7] R. E. Shamu and F. O. Bellinger, Bull. Am. Phys. Soc. **12**, 393 (1967).

[8] Always at 50 kV and 45 mA. A 1-mm Al filter was used to reduce the number of soft x rays.

[9] R. G. Bessent, W. Hayes, and J. W. Hodby, Proc. Roy. Soc. (London) **A297**, 376 (1967).

[10] The DPPH was obtained from Aldrich Chemical Co., Milwaukee, Wis.

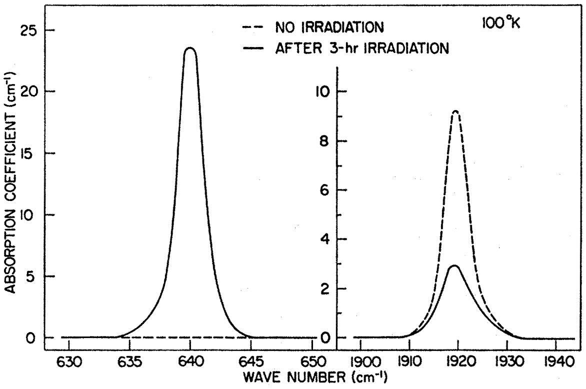

FIG. 1. Infrared absorption associated with the localized vibrations of atomic-hydrogen defects (left) and of hydride-ion defects (right) in a CaF_2 single crystal. A large, sloping background ($\alpha \approx 100$ cm^{-1}) due to absorption by the CaF_2 host crystal has been subtracted from the 640-cm^{-1} line. The linewidths are instrumental.

been attributed by Elliott *et al.*[4] to fundamental and second harmonic localized vibrations, respectively, of the hydride-ion impurity, and (2) a broader line at about 725 cm^{-1} which appears to be associated with a two-phonon combination band involving either the TO plus LO modes[11] or the LA plus LO modes[12] of the CaF_2 host crystal. After irradiation, a strong, sharp line appeared at 640±0.5 cm^{-1} (see Fig. 1). The position of this line is in agreement with the value of 591 ±42 cm^{-1} which Feldman *et al.*[1] have assigned to the localized mode associated with the hydrogen-atom defect in CaF_2 on the basis of their spin-relaxation measurements. Of these four lines, only the 725-cm^{-1} line was observed in the absorption spectrum of undoped CaF_2 crystals.

To test whether or not the 640-cm^{-1} line was indeed associated with the hydrogen-atom impurity, the magnitude of the integrated absorption coefficient of this line was studied for a 0.175-mm thick sample as a function of the concentration of atomic hydrogen. This concentration was varied by varying the x-ray irradiation time. The concentration was determined by measuring (1) the ESR absorption of the atomic hydrogen for a 0.5-mm thick sample taken from the same doped crystal as the ir sample and irradiated both concurrently and in the same geometry, and (2) the change in the magnitude of the integrated absorption coefficient of the 1919-cm^{-1} line. Similar ir and ESR studies of samples with thicknesses different from those stated above indicated that effects due to hardening of the x-rays in passing through the sample were not significant for these concentration measurements.

Figure 1 shows the ir absorption lines measured at 640 and 1919 cm^{-1} after no sample irradiation and after a 3-h sample irradiation. Of interest for the latter line is the change in the integrated absorption coefficient, i.e., the area between the two curves.

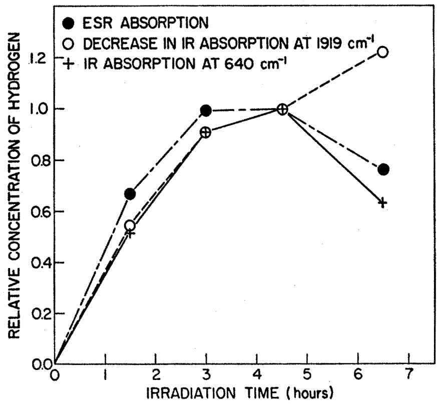

FIG. 2. Variation of atomic-hydrogen concentration with x-ray irradiation time for a CaF_2 single crystal containing hydride-ion defects.

Figure 2 shows the integrated absorption coefficient of the 640-cm^{-1} line and the change in the integrated absorption coefficient of the 1919-cm^{-1} line plotted as a function of irradiation time. Also shown is the magnitude of the ESR absorption of the atomic hydrogen versus irradiation time. For each curve the datum at irradiation time T was normalized to the datum at a T of $4\frac{1}{2}$ h. Since the change in the ir absorption at 1919 cm^{-1} is a measure of the change in hydride concentration, these ir data place only an upper limit on the atomic-hydrogen concentration. The ir absorption curve for the 640-cm^{-1} line agrees with the ESR absorption curve within experimental error, thus indicating that the integrated absorption coefficient for the ir line at 640 cm^{-1} is directly proportional to the concentration of atomic hydrogen in the sample. This agreement is strong evidence that the 640-cm^{-1} line is caused by the localized mode of vibration associated with the hydrogen-atom defect.

Additional evidence was obtained by destroying this defect. Measurements of the ESR absorption as a function of temperature indicated that this defect could be destroyed by maintaining the sample temperature at 130°C for about $\frac{1}{2}$ h. After the ir sample was treated in this manner, the line at 640 cm^{-1} was no longer present in the absorption spectrum.

The observed decrease in hydrogen concentration for an irradiation time greater than $4\frac{1}{2}$ h (see Fig. 2) is not understood. Possible explanations are (1) the atomic hydrogen diffuses out of the crystal, and/or (2) the unpaired electron associated with the atomic hydrogen becomes paired, e.g., with the electron of another hydrogen atom, thus forming H_2 in the crystal. Experiments by Atwater,[13] which indicated that heating a crystal even to 200°C does not drive out the hydrogen, suggest that the second explanation is correct.

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[11] W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, Phys. Rev. **127**, 1950 (1962).

[12] W. Zernik, Rev. Mod. Phys. **39**, 432 (1967).

[13] H. A. Atwater, J. Chem. Phys. **40**, 606 (1964).

The absolute concentration of atomic hydrogen was obtained for the data shown in Fig. 1 by two methods: (1) normalizing the ESR absorption of the 0.5-mm thick sample to that of a calibrated DPPH standard, and (2) measuring the change in the hydride concentration. Although, in principle, the latter method places only an upper limit on the atomic-hydrogen concentration, the data shown in Fig. 2 suggest that this method may provide accurate results for irradiation times up to about 3 h for our experiment. The initial hydride concentration was determined by relating the ir absorption at 1919 cm^{-1} both to the absorption of uv light by the hydride ions[14] and to the elastic scattering of neutrons by the protons associated with the hydride ions.[7]

The atomic-hydrogen concentrations obtained using method (1) and method (2)[15] were $3.1\times10^{19}/\mathrm{cm}^3$ and $2.9\times10^{19}/\mathrm{cm}^3$, respectively. These two results agree well within the estimated uncertainty for each measurement of about $\pm10\%$.

The observed integrated absorption of the 640-cm^{-1} peak was 73 cm^{-2}. This corresponds to an apparent charge[16] $|\mathrm{grad}_r M_x|=0.07$ electrons, where M_x is the crystal-dipole moment in a symmetry direction and the derivatives are with respect to the hydrogen atom position $\mathbf{r}$.

The calculation of the local mode frequency began with a Hartree-Fock-Roothaan self-consistent-field (SCF) molecular-orbital (MO) calculation of the energy of an HF^- molecule using the BISON computer program of Wahl and Bertoncini.[17] Exponents for the STO basis functions for F^- (5s functions and 4p functions) were taken from atomic calculations,[18] while the exponents for the two basis functions for H were determined by minimizing the total energy of the molecule. A least-squares fit to final energies E at six internuclear distances R gave a binding energy of $E+99.95950=-1.76025R^{-4}+3.47146\exp(-R/0.60898)$ hartree with an rms deviation of 2.0×10^{-6} hartree. The R^{-4} attractive term arises from the interaction between the charged F^- and the dipole moment induced on the H; the computed coefficient suggests a hydrogen atomic polarizability of 3.5 bohr^3. In the cubic solid this term will vanish by symmetry and the energy v of the H atom in a cage of eight F^- ions will be the sum of the short-range interactions V_i of the HF^- molecules, i.e.,

$$v=\sum_{i=1}^{8} V_i(\mathbf{R}_i-\mathbf{r}).$$

Then we have

$$\frac{\partial^2 v}{\partial r_x \partial r_y}=\delta_{xy}\frac{8}{3}\left[V''(R_0)+\frac{2V'(R_0)}{R_0}\right],$$

where the derivatives with respect to the molecular internuclear distance are evaluated at the equilibrium distance $R_0=4.46$ bohr. The local-mode frequency of the hydrogen atom of mass m is given by $\omega=(v_{xx}/m)^{1/2}=560\ \mathrm{cm}^{-1}$, in fair agreement with the observed frequency.

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[14] W. Hayes (private communication).

[15] The values obtained for the initial hydride ion concentration were $4.1\times10^{19}/\mathrm{cm}^3$ from uv absorption and $4.5\times10^{19}/\mathrm{cm}^3$ from neutron scattering. The average value was used to compute the atomic-hydrogen concentration quoted in the text.

[16] R. S. Leigh and B. Szigeti, Proc. Roy. Soc. (London) **A301**, 211 (1967).

[17] A. C. Wahl and P. J. Bertoncini, Argonne National Laboratory Report No. ANL 7271, 1967 (unpublished).

[18] P. Bagus and T. L. Gilbert (unpublished).