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Defect pairs of F centers and substitutional H^- ions (U centers) in alkali halides. Resonance Raman studies

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Defect pairs of F and U centers ["$F_H(H^-)$ centers"] were observed for the first time, created by laser-light induced aggregation of F centers in NaCl, KCl, and RbCl crystals doped with high concentrations of substitutional H^- defects (U centers). The formation of these pairs was indentified by the appearance of three sharp H^- local-mode lines in the Raman spectrum of F centers (due to the replacement of one of the 12 Cl^- neighbors by a small-mass H^- ion). Raman studies of these local mode lines observed in different scattering geometries (A_{1g}, E_g, T_{2g}) and in first and second order, reveal their symmetry and identify them as the three orthogonal linear vibrations of the H^- defect in a $\langle 110 \rangle$ pair configuration with the F center. A simple model, based on the Van der Waal interaction between the vibrating H^- dipole and the induced electronic dipole at the F center, explains well the observed local-model shifts. A speculative discussion is given on the absorption, emission, and photochemical properties of this pair formed from the two simplest prototypes of an electronic and local-model defect

I. INTRODUCTION

The F center (an electron bound to an anion vacancy) in alkali halides has served for a long time as the prototypical model system for an electronic point defect with strong coupling to the lattice. For its detailed understanding, it has been very important that this highly symmetric defect (with its isotropic optical response), can be associated to various other point defects, thus reducing its local symmetry and bringing about anisotropic optical properties. The possibility of forming, in a better than statistical way, these "*F aggregate centers*" from a pure F-center system is based on the following processes[1]: (a) Light irradiation into the F absorption band leads—at high enough temperatures—to the *ionization* of the F electron and its capture by another F-center, forming the two-electron F' center. (b) The empty anion vacancy, left behind, can migrate by *thermally activated diffusion* and can be *trapped* by other point defects. (c) As the F' center is not very stable at the considered temperatures, the second electron will be thermally re-emitted and return into the empty vacancy (trapped now at a point defect), thus creating the *F aggregate center*. These processes, initiated by light irradiation at temperatures between about 200 and 300 K, make it possible to produce in properly doped crystals F aggregate centers of various types, as illustrated in Fig. 1. The association of an F center with another F center yields the $\langle 110 \rangle$ oriented F_2 *center*,[2] the association with an alkali-ion impurity (like Li^+ or Na^+ in KCl) the $\langle 100 \rangle$ oriented F_A *center*,[3] and the association with a divalent-cation cation-vacancy pair the F_Z *center*.[4] These three types of F aggregate center have been identified and studied over a wide range of host and doping materials.

The fourth possibility, the association of an F center to an *anionic* impurity on a halide place ("F_H center") has been observed so far only in CsBr doped with Cl^- impurities, where (due to the bcc structure) a $\langle 100 \rangle$ aggregate center is formed.[5] The fact that in none of the alkali halides with NaCl structure the expected $\langle 110 \rangle$ oriented F_H-center configuration (Fig. 1) could be found may have one of two explanations. (i) Anionic impurities may not be efficient traps for the migrating anion vacancies. (ii) The perturbation from the [next-nearest-neighbor (nnn)] anionic impurity on the

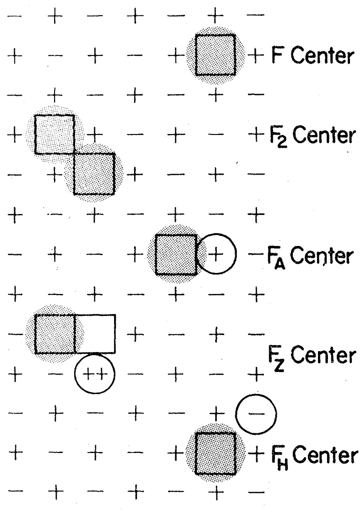

FIG. 1. Structural model of the F center in its isolated form, and in aggregation with four types of point defect [another F center (F_2), a monovalent cation defect (F_A), a divalent-cation-vacancy complex (F_Z), and a monovalent anion defect (F_H)].

electronic properties of the *F* band may be too weak to lead to a sizable splitting of the 2*p* excited state (like in the F_A case). Therefore, only a slightly shifted and broadened *F* absorption may result (as actually observed in mixed KCl-KBr crystals[6]).

An alternative approach to the detection of F_H centers, much more "specific" than the "integral" measurement of an absorption shape, would be a *Raman experiment*, in which the vibrations of the surrounding ions, coupling to the *F* electron, can be directly measured. This method is particularly promising if small-mass impurities, with high-frequency modes outside the frequency range of normal lattice phonons (and therefore easily detectable!) could be used. For F_A(li) centers in KCl, such *local modes* due to the Li^6 and Li^7 vibrations have been detected in the F_A resonance Raman spectrum.[7,8]

For anionic impurities, the defect with the smallest possible mass, a substitutional H^- defect (*U* center), should be the most attractive candidate. Its local mode, extensively studied both experimentally and theoretically, lies at very high frequencies (at 500 cm^{-1} for KCl), far outside the one-phonon spectrum.[9] While this local mode is not Raman active for the isolated *U* center, it should appear in the Raman response of an *F* center attached to the *U* center, and it should be split due to the reduced local symmetry. The experiments in this work verify these expectations, confirming for the first time the existence and ⟨110⟩ symmetry of the $F_H(\mathrm{H}^-)$ center, and determining the details of its local mode structure by Raman measurements.

II. EXPERIMENTAL TECHNIQUES AND APPARATUS

The crystals used were grown in the Utah Crystal Growth Laboratory from ultrapure material. The samples were first additively colored by a Van Doorn method[10] at temperatures close to their melting point, producing *F* centers of high concentration (several 10^{18} cm^{-3}). These *F* centers were converted into *U* centers by heating of the crystals under 20 atm of hydrogen gas, until full discoloration was achieved. Even higher *U*-center concentrations could be obtained by a simultaneous coloration and hydrogenation technique in which the crystal was heated in a mixture of alkali-metal vapor and hydrogen.[11]

Laser excitation for the optical conversion and Raman experiments was provided by Spectra Physics argon and krypton lasers. The optical system includes as the main part a 1400 Spex double grating monochromator, allowing an optimum resolution of about 1 cm^{-1}. A wave-number stepped digital photon-counting system was used for detecting the Raman signals.

III. EXPERIMENTAL RESULTS

The following procedure was used for the production of $F_H(\mathrm{H}^-)$ centers and their detection by Raman experiments: Crystals with high concentrations of *U* centers (10^{18}–10^{19} cm^{-3}) were x-irradiated at room temperature, such that a fraction of the *U* centers (several 10^{17} cm^{-3}) were converted into *F* centers. These crystals were then cooled to 10–20 K and their Raman spectrum was taken, using appropriate laser excitation in resonance with the *F* absorption band. The Raman response obtained consists of the characteristic one-phonon Raman spectrum of the *F* center (in the 0-300 cm^{-1} range), followed by a rather structureless tail extending to very high energies (several thousand cm^{-1}). The latter is reproducible under resonance excitation of the *F* centers,[8] though its origin (multiphonon Raman scattering and/or hot luminescence?) is not yet fully understood.

Besides this "normal" Raman response from *F* centers, the highly hydrogenated crystals exhibit very weak sharp Raman lines in the frequency range of the *U*-center local mode. The intensity of these lines increases drastically, if the crystals are *pulse annealed to higher temperatures under F band light* (above 120 K for KCl and RbCl and above 175 K for NaCl). Saturation of the intensity of these lines (under *F*-band laser light irradiation) is very quickly achieved at pulse annealing temperature of ~150 K for KCl and RbCl, and of 220 K for NaCl. Irradiation at higher temperatures does not produce further increases. Figure 2 shows for KCl, RbCl, and NaCl and two scattering geometries (⟨110⟩ ⟨110⟩ and ⟨1$\bar{1}$0⟩ ⟨110⟩) the Raman spectra obtained at this stage, consisting of the one-phonon spectrum, the high-energy tail, and sharp lines produced by laser irradiation above 150 K.

Figure 3 displays high-resolution spectra for the same substances in the 500-cm^{-1} range, measured (at the same time in the same samples) in three scattering geometries. A three-line spectrum appears in each of the crystals, with the strength of the three lines (indicated as ν_a, ν_b, and ν_c) depending drastically on the scattering geometry used. Comparison to the local mode frequency of the isolated *U* center (indicated by the dashed line at ν_0) shows that the observed Raman local mode lines are always shifted from ν_0 to *lower* energies.

Figure 4 displays similarly high-resolution Raman spectra in the second-harmonic region around 1000 cm^{-1} for the three materials. The most prominent response appears in the ⟨110⟩⟨110⟩ geometry and consists mainly of two lines, which

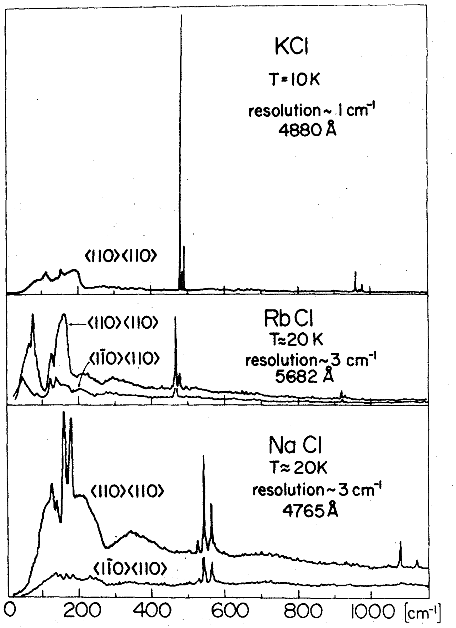

FIG. 2. Low-temperature Raman spectra of *F* centers in KCl, RbCl, and NaCl crystals with high H⁻ defect concentration, after laser illumination at temperature above ~150 K.

coincide closely with the ($2\nu_a$) and ($\nu_b+\nu_c$) frequency, obtained from the first harmonic spectrum.

Figure 5 shows, for the same three substances, the effect of various laser excitations on the Raman spectra. The following is observed for the *background* effects. (a) Excitation tuning *through the F absorption band* ($a\rightarrow b$ in all three cases) does not change the spectral structure of the *F* one-phonon spectrum, but changes the ratio of its strength to that of the high-energy tail. (b) Excitation tuning *from the F to the K band* (KCl and RbCl $b\rightarrow c$) changes very drastically the one-phonon spectrum of the *F*-center response. This behavior is characteristic and well confirmed for pure *F*-center systems,[8] and can be accounted for theoretically[12] by the diffuse nature of the excited state responsible for the *K* band.

The local mode spectrum appears at all excitation frequencies. Comparison of its strength to the strength of the *F* one-phonon spectrum shows very little variation with excitation tuning in KCl and RbCl. Only in NaCl a sizable increase of the local-mode strength going from (a) to (b), is observed.

The measured height of the local-mode lines depends critically on the spectrometer slit width at low temperatures, indicating that the linewidth lies below the resolution limit of the instrument. (In each of the measurements in Figs. 2–6 a constant slitwidth was used.) In order to obtain a better estimate on the true integrated strength of the local modes, some Raman measurements were done at higher temperatures, too. Figure 6 displays a result for KCl (at 144 K) and RbCl (at 81 K); the apparently considerable temperature broadening of the local-mode response washes out the three-line structure, but allows a better integration of the total local-mode Raman response.

The Raman spectra displayed in Figs. 2–6, did *not* change, when the crystals remained in the dark at room temperature (up to several days), or when irradiated with intense *F*-band light below 200 K for KCl and RbCl or below 250 K for NaCl. At higher temperatures, *F*-light irradiation leads to a back conversion of the *F* centers into *U* centers,

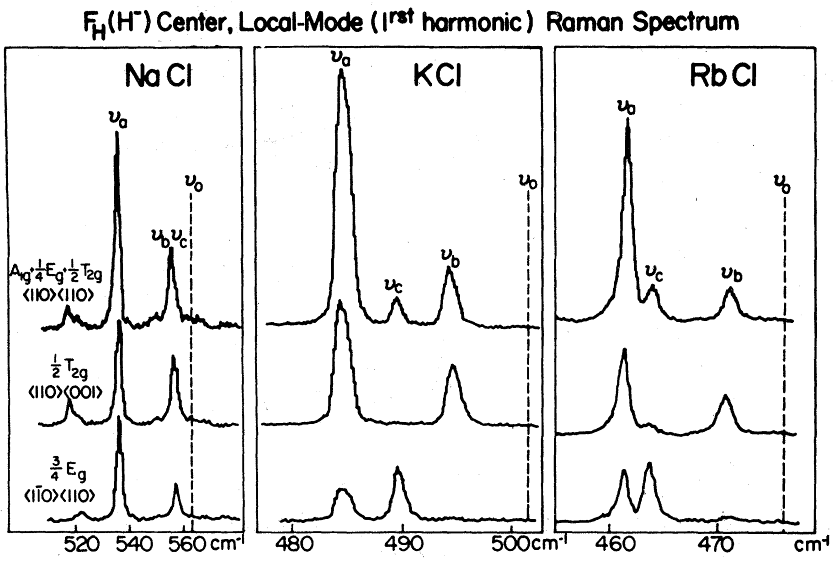

FIG. 3. High-resolution spectra of the first-harmonic $F_H(H^-)$ local-mode lines in NaCl, KCl, and RbCl, taken at 10 K in three different scattering geometries. (ν_0 indicates the ir local-mode position of the isolated H⁻ defect.)

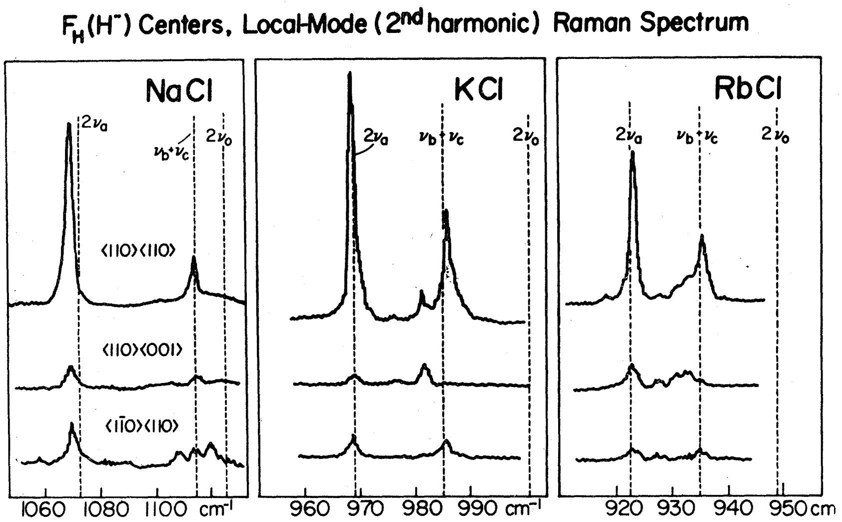

FIG. 4. Second-harmonic local-mode spectra in NaCl, KCl, and RbCl, taken at 10 K in three different scattering geometries.

which in Raman experiments is observed by the bleaching of the one-phonon spectrum. The local-mode spectrum is found to bleach in the same temperature range, with some indications that the one-phonon spectrum disappears somewhat faster compared to the local mode spectrum. Therefore, the centers responsible for the local modes are under light irradiation at least as stable as the normal *F* centers in these hydrogenated samples.

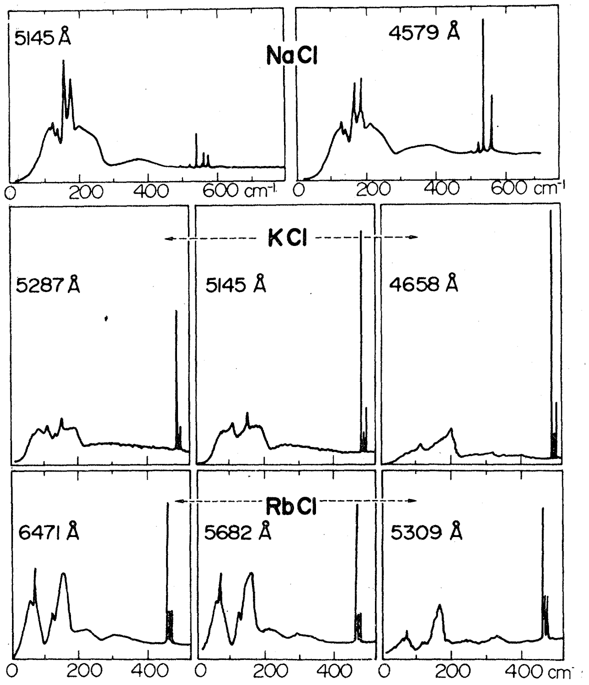

FIG. 5. Low-temperature Raman spectra of $F_H(H^-)$ centers in NaCl, KCl, and RbCl, obtained under various laser excitations.

IV. DISCUSSION

We interpret the fundamental local-mode structure which appears in the *F*-center Raman measurement after laser-light irradiation above 200 K as originating from *F centers associated with substitutional* H^- *defects* (*U* centers). These aggregates are formed (similar to F_2, F_A, and F_Z centers, see Sec. I) by optical *F*-center ionization, thermal activated motion of the anion vacancy, and association of the latter to *U* centers (which are by far the most prominent point defects in the crystal used). For the close configuration of this *U*-*F* association (a ⟨110⟩ pair), the threefold-degenerate local mode of the *U* center should split into three components ν_a, ν_b, and ν_c, as illustrated in Fig. 7.

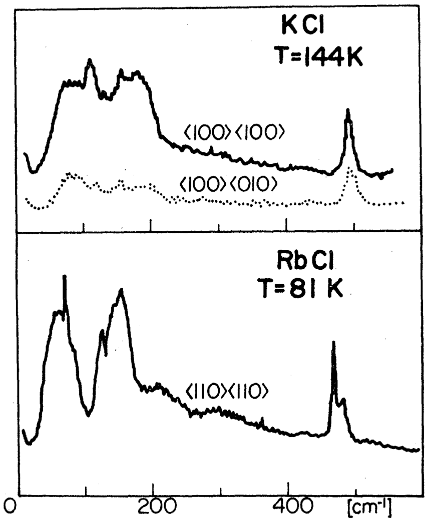

FIG. 6. Raman spectra of $F_H(H^-)$ centers in KCl and RbCl at higher temperatures.

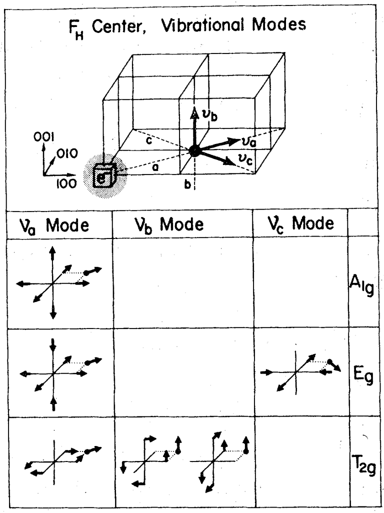

FIG. 7. Structural model of the $F_H(H^-)$ center with illustration of the three H^- local modes ν_a, ν_b, and ν_c and their projection into the nearest-neighbor motion of A_{1g}, T_{2g}, and E_g symmetry.

This three-line spectrum is indeed observed.

Looking from the side of the F center and its electron, the associated H^- defect replaces one of the 12 Cl^- neighbors in the (nnn) shell of surrounding ions. A Raman experiment of the F-center electron displays directly the spectra due to the vibrations (of A_{1g}, E_g, and T_{2g} symmetry) of surrounding ions. Due to the fairly large extent of the F-center wave function, the essential coupling of the F election to the lattice is spread over the two first shells of 6 nearest and 12 next-nearest neighbors. The replacement of only *one* of the 12 next-nearest neighbors by an H^- ion should therefore reduce the normal F-center Raman response only slightly and leave its spectral shape basically unchanged, while adding the three local-mode lines ν_a, ν_b, and ν_c from the H^- oscillator. This again is qualitatively observed.

How can we assign the three observed local modes to the three vibrations ν_a, ν_b, and ν_c of the H^- ion? In the lower part of Fig. 7 we illustrate (by arrows) the motion of the six nearest neighbors and of one of the next-nearest neighbors in vibrations of A_{1g}, E_g, and T_{2g} symmetry around the F center. Taking the next-nearest neighbor as the small mass H^- ion, we see directly from Fig. 7: (a) The H^- mode ν_a (parallel to the $\langle 110\rangle$ pair axis) should appear in the A_{1g}, E_g, and T_{2g} Raman spectrum of the F center. (b) The H^- mode ν_b ($[1\bar{1}0]$ perpendicular to the pair axis) should appear only in T_{2g} symmetry. (c) The H^- mode ν_c ([001] perpendicular to the pair axis) should appear only in E_g symmetry. In our experiments we used five geometries for the E vector of the exciting and scattered light:

(i) $\langle 100\rangle\langle 100\rangle$ yielding $A_{1g}+E_g$ spectra
(ii) $\langle 100\rangle\langle 010\rangle$ yielding $\frac{1}{2}T_{2g}$ spectra
(iii) $\langle 110\rangle\langle 110\rangle$ yielding $A_{1g}+\frac{1}{4}E_g+\frac{1}{2}T_{2g}$ spectra
(iv) $\langle 110\rangle\langle 1\bar{1}0\rangle$ yielding $\frac{3}{4}E_g$ spectra
(v) $\langle 110\rangle\langle 001\rangle$ yielding $\frac{1}{2}T_{2g}$ spectra

Comparison of the experimental results in these five scattering geometries to the predictions a, b, and c show clearly that the low-energy line, appearing in *all* scattering geometries is definitely due to the axial ν_a local mode. The line appearing in geometry (ii) and (v) should be the ν_b, and the line appearing in geometry (iv) should be the ν_c mode.

The consistent observation of these predicted selection rules for the three H^- modes in our experiments confirms the $\langle 110\rangle$ model of the U-F pair beyond any doubt, and produces a secure assignment of the observed lines to the ν_a, ν_b, and ν_c mode (as given in Fig. 3). While in KCl and RbCl all three modes are resolved, in NaCl the two perpendicular modes ν_b and ν_c apparently occur (within the instrumental resolution) at the same frequency.

After this experimental assignment of the observed lines to the local modes of the U-F pair, one can try to understand the sign and magnitude of the observed frequency shift $\nu_0-\nu_i (i=a,b,c)$. Such a shift can be formally accounted for by assuming that the energy of the unperturbed U center

$$U=\tfrac{1}{2}m\dot{x}^2+\tfrac{1}{2}m\omega_0 x^2 \tag{1}$$

is affected by slight changes in the force constant

$$U=\tfrac{1}{2}mx^2+\tfrac{1}{2}(m\omega_0^2+\Delta K_i)x^2 \quad (i=a,b,c) \tag{2}$$

due to the presence of the neighboring F center.

A somewhat similar situation was encountered in previous work[13] on pairs of H^- ions on $\langle 110\rangle$ neighboring places: there the observed local-mode shifts could be successfully explained by the electrostatic interaction energy between the two coupled vibrating dipoles. In the $\langle 110\rangle$ neighboring U-F pair one can try to argue in a similar way that the vibrating H^- dipole *induces* (in a dynamic way) at the F center an electronic dipole moment (due to mixing of the rather closely lying 1s and 2p states by the electric field from the vibrating H^- dipole). Assuming that the interaction energy between vibrating H^- and induced F-center dipole moment would be the main reason for the observed shifts in the H^- eigenfrequencies, the following would be predicted qualitatively. (a) This dipole-dipole interaction would always *lower* the total energy [contribute a negative ΔK_i in Eq. (2)], and therefore, shift the H⁻ eigenfrequencies from ν_0 to *smaller* frequencies, as observed. (b) The two dipoles when vibrating *along* their connecting pair axis (ν_a) should have twice the interaction energy compared to the situation when they vibrate *perpendicular* to this axis. This is roughly observed: the frequency shift for the axial vibration ($\nu_a - \nu_0$) is found always to be the larger one, having about the double value compared to the averaged frequency shift of the two perpendicular vibrations. (The splitting of ν_b and ν_c, observed in KCl and RbCl, would not be accounted for in this simple model.) This qualitative agreement encourages a more quantitative estimate of the interaction energy which would result from this Van der Waal interaction model. The electric field from the vibrating H⁻ electric dipole $\tilde{e}x$ ($\tilde{e}$ is the effective charge of the H⁻ defect)

$$E(r) = \tilde{e}x/2\pi\epsilon_0 r^3 \tag{3}$$

would induce (in vacuum) an electric dipole-moment at the F center of

$$p_F = \alpha_F E(r) . \tag{4}$$

The question of corrections due to the presence of the dielectric is a rather uncertain one for our case of very closely lying substitutional impurities. In the absence of a better estimate, we follow Mahan's treatment[14] (valid for large dipole distance), which introduces both an ϵ^{-1} screening factor for the field and a $\frac{1}{3}(\epsilon+2)$ Lorentz field-enhancement factor for the effective dipole moment. Using these correction factors, and the electronic polarizability α_F of the F center (at a frequency ω much lower than the F-center eigenfrequency ω_F)

$$\alpha_F = (e^2/m)(f/\omega_F^2) \tag{5}$$

we obtain for the total interaction energy of the vibrating and induced dipoles (in the axial configuration)

$$U = \frac{\tilde{e}^2}{4\pi^2\epsilon_0^2 r^6}\,\frac{e^2 f}{m_e\omega_F^2}\left(\frac{\epsilon+2}{3\epsilon}\right)^2 x^2 . \tag{6}$$

TABLE I. Calculated and observed splitting of the H⁻ local modes $\nu_i - \nu_0$ ($i = a, b, c$) in NaCl, KCl, and RbCl.

		NaCl	KCl	RbCl
$\nu_a - \nu_0$ (cm^{-1})	expt	−27.3	−16.9	−15.0
	calc	−23.2	−17.4	−16.8
$\nu_b - \nu_0$ (cm^{-1})	expt	−7.8	−7.0	−5.0
	calc	−11.6	−8.7	−8.4
$\nu_c - \nu_0$ (cm^{-1})	expt	−7.8	−11.9	−12.2
	calc	−11.6	−8.7	−8.4

As the polarizability of the F center is considerably larger than that of the Cl⁻ ion[15] ($\alpha_{\text{Cl}^-} \approx 3$ Å^3 compared to $\alpha_F \approx 20$ Å^3), the total energy of the system will be *lowered* by the substitution of an F center for a Cl⁻ ion. Therefore, ΔU produces a *softening* of the force constant for the H⁻ vibration, i.e., a negative force constant change [Eq. (2)] of

$$\Delta K_a = -2\Delta U/x^2 , \tag{7}$$

which will give rise to a negative shift of the local-mode frequency of

$$\frac{\omega_a - \omega_0}{\omega_0} = \frac{1}{2}\frac{\Delta K_a}{K_0} = \frac{-\tilde{e}^2}{m_{H^-}\omega_0^2}\left(\frac{fe^2}{m_e\omega_F^2} - \alpha_{\text{Cl}^-}\right) \times \frac{(\epsilon+2)^2}{4\pi^2\epsilon_0^2 \times 9\epsilon^2 r^6} \tag{8}$$

{and $[(\omega_{b,c} - \omega_0)/\omega_0]$ being one-half of this value}.

Using numerical values for the F-bound oscillator strength ($f = 0.8$) and the effective charge of the vibrating H⁻ defect[7] ($\tilde{e} = 0.8$), as well as the (high-frequency) dielectric constants ϵ, ω_F, and ω_0 for the materials, one obtains from Eq. (8) calculated frequency shifts which are summarized and compared to the observed values in Table I.

The amazingly close agreement of the experiment with this extremely simple model, shows that the Van der Waals interaction considered can indeed account in sign and magnitude for the observed frequency shifts. In spite of this essentially quantitative agreement, it is evident that the Van der Waals interaction will not be the *only* cause for changes in the H⁻ local-mode frequencies due to the presence of the F center. The exchange of the next-nearest neighbor Cl⁻ ion by an F center and the shifts of the surrounding ions produced by the F center will affect —particularly by a change in Born-Mayer interaction—the force constant of all three H⁻ vibrations. These effects must be responsible for the splitting of the transversal modes ν_b and ν_c, which is not explained in the Van der Waals model. It is interesting to note that this splitting $\nu_b - \nu_c$, which is found to be zero for NaCl, increases systematically with increasing cation-size Na⁺ → K⁺ → Rb⁺.

The fact that in second-order (Fig. 4), the Raman response appears mainly at ($\nu_a + \nu_a$) and at ($\nu_b + \nu_c$), cannot be accounted for in a simple qualitative way. This system may, however, supply for the theory a very attractive and simple model case for the understanding of (this specific and more general) second-order Raman effects: the fundamental Raman spectrum, from which the second-order effect should be obtainable by convolutions, consists in this case only of three local-mode lines of well-defined symmetry (and not, as usually, of complicated continuous phonon spectra).

Our observed local modes ν_a, ν_b, and ν_c should not only be Raman but ir active as well. In contrast to a Raman experiment (in which the unperturbed U-center local mode ν_0 does *not* appear, being symmetry forbidden), an ir experiment always shows the very strong local-mode ν_0 from the predominantly present isolated U center, thus making the observation of close-lying small satellite bands difficult. In our previous experiments,[13] in which H^- pairs were created by a process involving optical F-center aggregation into F_2 centers, some $F_H(H^-)$ centers must have been formed as a "by-product." The ir local-mode spectra showed indeed some lines on the low-energy side of ν_0 (e.g., at 488 and 496 cm^{-1} in KCl), not explained by H^- pairs, which very likely were due to $F_H(H^-)$ centers.

The combination of the most simple and best understood prototypes for an electronic (F) and local-mode (U) defect into a pair, should produce many interesting physical properties. The *electronic absorption properties* of the pair can be expected to be roughly the composite of the isolated F and U center properties, both perturbed somewhat by the presence of the other partner. Our Raman experiments show, in fact, that the excitation spectrum of the F electron in the pair follows basically the F band spectrum: the observed strength of the local-mode lines and of the normal F center Raman response vary pretty much in parallel under excitation tuning, i.e., both are affected similarly by the strong resonance enhancement, when tuning through the F band (Fig. 5).

It would be very interesting if Raman experiments could be extended towards uv excitation into the absorption range of the H^- electron: In this case only the axial ν_a mode should appear in the fundamental Raman spectrum. It goes without saying that all the local-mode properties displayed and discussed here should shift to lower frequencies by about $\sqrt{2}$ if D^- could substitute for H^-. The attractiveness of the $F_H(H^-)$ center for EPR or electron-nuclear-double-resonance measurements is evident.

Besides the ground-state and absorption properties, interesting behavior can be expected for the excited state, emission, and photochemical properties of the pair center. The electric field from the large amplitude vibrations of the H^- oscillator should introduce an extra strong mixing of the closely lying $2s$ and $2p$ states of the F center in its relaxed excited state configuration.[16] This should definitely affect lifetime and spectral properties of the F-electron emission. Due to the very closely lying $2s$ and $2p$ states (equal to the high electronic polarizability), the Van der Waals interaction and local-mode frequency shift should be considerably larger in the relaxed excited state compared to the ground state. These local modes of the excited $F_H(H^-)$ center could be detected by ir absorption measurements under strong pumping with F-band light.

U centers, when optically excited in their uv absorption, are known to be unstable and to produce photochemical conversion processes: At low temperatures, the H^- is ejected into an interstitial position leaving an empty vacancy behind[17]; at high temperatures, the ejected mobile hydrogen forms neutral interstitial H_2 molecules, while the electron occupies the anion vacancy forming F centers.[18] If the same processes hold under optical excitation of U centers associated with F centers, one could convert an $F_H(H^-)$ center system by uv irradiation at low or high temperatures directly in to F_2^+ or F_2 centers, respectively.

In view of this possibility, it is extremely interesting to find out what fraction of an F-center system can be optically converted by association to H^- defects into $F_H(H^-)$ centers. The measured ratio of the integrated local-mode spectrum $[\int I_{\text{loc}}(\omega)\,d\omega]$ to the integrated F-center one-phonon spectrum $[\int I_{\text{phon.}}(\omega)\,d\omega]$ is about 5%–10% (see Fig. 6). It is not, however, straightforward to draw conclusions from this on the actual concentration ratio of $F_H(H^-)$ centers to normal F centers. In the most simple treatment of this problem (assuming unchanged electronic wave functions and positions of the ions), we regard the H^- ion merely as a mass-defect with very high eigenfrequency, but unchanged electronic polarizability properties compared to the Cl^- ion it replaces. We assume further for a rough estimate, that about one-half of the F-center Raman response is due to the coupling of the electron to the second shell of 12 next-nearest neighbors (one of which is to be replaced by the H^- ion). With these assumptions, we obtain from the sum-rule for the integrated Raman response:

$$\frac{\int_0^\infty I_{\text{loc.}}(\omega)\times 2\omega\,d\omega}{\int_0^\infty I_{\text{phon.}}(\omega)\times 2\omega\,d\omega} \approx \frac{\omega_{\text{loc}}\int_0^\infty I_{\text{loc}}(\omega)\,d\omega}{\bar{\omega}\int_0^\infty I_{\text{phon}}(\omega)\,d\omega} = \frac{\frac{1}{12}1/M_{H^-}}{\frac{11}{12}1/M_{Cl^-}}\times\frac{1}{2} \tag{9}$$

or

$$\frac{\int I_{\text{loc}}(\omega)\,d\omega}{\int I_{\text{phon}}(\omega)\,d\omega} \approx \frac{\bar{\omega}}{\omega_{\text{loc}}}\,\frac{M_{Cl^-}}{22M_{H^-}} \approx \tfrac{1}{5}\times\tfrac{35}{22}\approx\tfrac{1}{3}$$

The observed integrated Raman ratio of 5%–10% would therefore indicate a 15%–30% concentration ratio of F_H to F centers. In view of the strongly simplified assumptions made, this can be regarded only as an order-of-magnitude estimate.

It seems not unlikely that with a thorough study of the optimum conditions for the optically induced

$F \rightarrow F_H(H^-)$ aggregation and by the use of crystals with the highest possible H^- doping, a better conversion could be achieved. A system with a high concentration ratio F_H:F has the potential to be, under uv or x irradiation, a source for the direct production of F_2 or F_2^+ centers. Such a possibility is of highest interest in view of the recently recognized and developed potential of some F aggregate centers (particularly the F_2^+ center) for tuneable ir-laser applications.[19] Experiments on the optimum conditions for the $F \rightarrow F_H(H^-)$ aggregation and on the absorption, emission, and photochemistry behavior of $F_H(H^-)$ center are under way and will be published in a second part of this work.[20]

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