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Absorption spectra of F-aggregate centers in KCl crystals

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We measured the absorption spectra of F-aggregate centers in KCl under high resolution at 2°K, using an apparatus which was very sensitive to small zero-phonon lines. The M, R, and N bands were carefully examined for zero-phonon lines hitherto undetected, but only one new line was found, in the M_4 band of the F_2 center. This line is unusually broad (22 cm^{-1}). The absence of a zero-phonon line in the M_1 band of the F_2 center represents a striking disagreement with the predictions of simple linear coupling theory. Four new zero-phonon lines were discovered which could be assigned to the perturbation of F_3 centers by impurities; for two of these lines the impurity was identified as sodium. A large number (64) of other zero-phonon lines were assigned to perturbation of F-aggregate centers by unknown impurities. The appearance of these lines is strongly dependent on very small amounts of impurity in the original KCl crystals; reasons for this strong dependence are discussed.

I. INTRODUCTION

The F center in alkali halide crystals, consisting of an electron trapped at a vacancy in the negative-ion sublattice, is one of the best-known defects in solids. The two simplest F-aggregate centers, F_2 and F_3, have also been extensively investigated.[1] The F_2 (or M) center is a pair of nearest-neighbor F centers with a $\langle 110\rangle$ axis, and the F_3 (or R) center is a triangular array of neighboring F centers with a triad axis parallel to one of the $\langle 111\rangle$ directions. The absorption bands due to electronic transitions within these aggregate centers are known as M and R bands, respectively, for historical reasons, and it is evident from the fact that most of these absorption bands are narrower than the F band that the coupling between electronic transitions and host lattice phonons is smaller for these "molecular type" centers than for the "atomic type" F center. Indeed, the R_2 absorption band arising from one of the electronic transitions of the F_3 center has a prominent zero-phonon line and a structured multiphonon sideband. Linear and quadratic electron-phonon coupling theory, as presented in Sec. II, has proved to be completely successful in fitting the intensity and thermal shift of this zero-phonon line, and the shape of the multiphonon sideband can also be fitted to reasonable phonon density-of-states distributions.[2] However this good agreement with theory turns out to be exceptional; other F-aggregate absorption bands do not have the zero-phonon line and structured sideband which would be expected on the basis of this theory. In particular, the F_2 center, which is considerably simpler in many respects than the F_3 center, has neither a zero-phonon line nor a structured sideband for its most intense absorption band, the M_1 band, even though the width of this band is almost the same as the R_2 band.

We recently constructed an apparatus which is capable of measuring very small and very narrow absorption bands. This apparatus was used to measure previously undetectable zero-phonon lines in the absorption spectrum of the S_2^- molecule-ion impurity in KI crystals,[3] and in the experiments reported here, it was used to examine the absorption spectra of KCl crystals containing F-aggregate centers, to see if a lack of sensitivity in previous experiments could account for the discrepancy between theory and experiment. This turned out not to be so; the discrepancy remains, but is now more closely defined. In the course of this investigation, because of the high sensitivity of the apparatus, we observed many new sharp zero-phonon lines, none of which are correlated with broad absorption bands of F-aggregate centers, and we also observed one rather broad new zero-phonon line which is associated with F_2 centers. A preliminary report on some aspects of this work has already appeared.[4]

II. THEORY

We wish to present here sufficient theory to put the experimental results in the proper context. The most recent and comprehensive account of the theory of defect spectra in insulating solids is in the paper of Mostoller, Ganguly, and Wood,[5] but we have chosen here to follow the simpler approach in the book by Flynn.[6] We will limit the theory to electronic transitions taking place in a defect in an insulating crystal, specifically potassium chloride, and will quote expressions for the optical absorption spectrum of such defects.

Using the Born-Oppenheimer approximation, the initial (i) and final (f) wave functions of the defect electron are

$$\chi_i(x,\xi)=\Phi_{i\mu}(x)\psi_i(x,\xi)\,,\qquad \chi_f(x,\xi)=\Phi_{f\mu'}(x)\psi_f(x,\xi)\,, \tag{1}$$

where the electron coordinate is ξ and the nuclear coordinates are x, Φ is a lattice vibrational wave function, and ψ is an electronic wave function appropriate to an electron moving in a lattice frozen at instantaneous nuclear positions x. Thus ψ depends parametrically on x. Subscripts μ and μ' refer to the lattice vibrational states corresponding to the initial and final electronic states, respectively. The transition probability for the change of state is thus proportional to

$$|\langle\psi_f(x,\xi)\,|\,\xi\,|\,\psi_i(x,\xi)\rangle|^2\,|\langle\Phi_{f\mu'}(x)\,|\,\Phi_{i\mu}(x)\rangle|^2\,, \tag{2}$$

and we now make the Condon approximation, that the dipole matrix element for the electron with the lattice held rigidly in configuration x (the first factor) is independent of x. Thus this factor is the same for transitions to every vibrational level, so that the fraction of transitions that take the electron to f and also take the lattice to μ' is

$$W_{\mu\mu'}=|\langle\Phi_{f\mu'}(x)\,|\,\Phi_{i\mu}(x)\rangle|^2\,. \tag{3}$$

We now assume that the lattice is harmonic, so that the lattice wave functions are products of $3N$ harmonic wave functions $\phi_n(q_\alpha)$ along the normal-mode axes in configuration space. Allowing for the fact that the normal modes of state f, $q_{\alpha'}$, may be different from the normal modes of state i, q_α, the lattice wave functions are

$$\Phi_{i\mu}=\prod_{\alpha=1}^{3N}\phi_n(q_\alpha)\,,\quad \Phi_{f\mu'}=\prod_{\alpha=1}^{3N}\phi_m(q_{\alpha'})\,, \tag{4}$$

where quantum numbers n denoting excitation levels of the oscillators α replace the quantum number μ denoting the lattice state in the previous notation; similarly the m replace μ'.

For the moment we assume that the electron couples to the lattice through a single configuration coordinate with linear coupling, such that initial- and final-mode frequencies remain the same (though the argument will be extended later to linear coupling with a large number of modes). In this case the transition probability for a process involving p phonons ($p=n-m$) is

$$W_p=\exp\left[\frac{p\hbar\omega}{2kT}-S\coth\left(\frac{\hbar\omega}{2kT}\right)\right]I_p\left[S\,\mathrm{csch}\left(\frac{\hbar\omega}{2kT}\right)\right]\,, \tag{5}$$

where ω is the lattice mode frequency, S is the coupling constant or Huang-Rhys factor (the number of phonons emitted in relaxation after a vertical absorption transition), and $I_p(x)$ is the Bessel function of the first kind with imaginary argument. At $T=0$ °K, the transition probability reduces to the simple formula

$$W_p=(S^p/p!)\,e^{-S}\,. \tag{6}$$

Now Eq. (5) is correct for each mode ω that causes broadening; the modes are independent so that the band shape for coupling to many modes is just the convolution of the widths contributed by each mode. We define S_α as the coupling constant of the electron to the αth mode, and

$$S=\sum_\alpha S_\alpha,\quad S_\alpha=\omega_\alpha\epsilon_\alpha^2/2\hbar \tag{7}$$

as the coupling strength, where ϵ_α is the displacement along q_α of the energy minimum of the final state relative to the initial state. Then the second moment of the absorption M_2 is given by

$$M_2(T)=\sum_\alpha M_{2\alpha}(T)=\sum_\alpha S_\alpha(\hbar\omega_\alpha)^2\coth\left(\frac{\hbar\omega_\alpha}{2kT}\right)\,. \tag{8}$$

If we have the situation where the coupling coefficient S is large, then the absorption spectrum is a structureless band, approximately Gaussian, whose peak corresponds to an energy $\hbar\omega_0$ where, at $T=0$ °K,

$$\hbar\omega_0=\Delta E_{if}+\sum_\alpha\tfrac{1}{2}\,\omega_\alpha^2\epsilon_\alpha^2=\Delta E_{if}+\sum_\alpha S_\alpha\hbar\omega_\alpha\,, \tag{9}$$

and since the half width H of a Gaussian is related to the second moment by $H=2.36M_2^{1/2}$, then

$$H(0)=2.36\left(\sum_\alpha S_\alpha\right)^{1/2}\hbar\omega_\alpha\,. \tag{10}$$

Equations (9) and (10) are useful approximate expressions for the energy shift and halfwidth of absorption transitions with large coupling to the lattice.

We are especially interested in the zero-phonon line probability. The probability that none of the modes change state in the transition is the product of probabilities that any mode undergoes no change in state, which is

$$W_0(T)=\prod_{\alpha=1}^{\nu}\exp\left[-S_\alpha\coth\left(\frac{\hbar\omega_\alpha}{2kT}\right)\right]I_0\left[S_\alpha\,\mathrm{csch}\left(\frac{\hbar\omega_\alpha}{2kT}\right)\right]\,, \tag{11}$$

where

$$I_0(x)=\sum_{n=0}^{\infty}\frac{(\frac{1}{4}x^2)^n}{(n!)^2}\,,$$

and at $T=0$ °K

$$W_0=\exp\left(-\sum_\alpha S_\alpha\right)=e^{-S}\,. \tag{12}$$

TABLE I. Potassium chloride single crystals used in this work.

Identification	Source	Purity	Coloration [a] batch
A	Harshaw [b]	Pure	1
B	Harshaw	Pure	1
C	Harshaw	Pure	2
D	Optovac [c]	Pure	1
E	Optovac	Pure	2
F	Vinor [d]	Pure	2
G	Oregon State University [e]	Pure (vacuum distilled)	2
H	Cornell University [f]	Pure (zone refined)	2
I	NRC [g]	Pure (grown in HCl)	2
J	NRC	Na^+ doped	3
K	NRC	OH^- doped	3
L	NRC	CO_3^{2-} doped	3
M	NRC	I^- doped	3
N	NRC	Ca^{2+} doped	3

[a] Batch 1 heated $4\frac{1}{2}$ h at 165-Torr potassium vapor pressure; batch 2 for $1\frac{3}{4}$ h at 165 Torr; batch 3 for $1\frac{1}{2}$ h at 180 Torr.

[b] Harshaw Chemical Co., Cleveland, Ohio.

[c] Optovac, Inc., North Brookfield, Mass.

[d] Vinor-Laboratories, Medford, Mass.

[e] Given by A. B. Scott.

[f] Given by D. F. Holcomb.

[g] Crystals grown in our laboratory.

There is a useful approximation for the relative strength of the zero-phonon line as a function of temperature, valid for low temperatures where $I_0(x) \rightarrow 1$, and assuming that the coupling parameters S_α vary inversely as the mode frequency so that $S_\alpha = \sigma/\omega_\alpha$. Employing the Debye approximation for the lattice modes, then

$$W_0(T) = \exp[-S(1 + 2\pi T^2/3\theta^2)] . \qquad (13)$$

III. EXPERIMENTAL TECHNIQUE

Specimens of KCl crystals containing F-aggregate centers were prepared by a two-stage process; first F centers were introduced into KCl single crystals, then these F centers were aggregated by irradiation with light absorbed in the F band. KCl crystals were obtained from several different sources as outlined in Table I, and F centers were introduced into these crystals by three methods; most frequently by additive coloration, less frequently, by x irradiation of crystals containg hydride ions, or by x irradiation of pure crystals. The additive coloration procedure was as follows: cleaved crystals approximately $4 \times 4 \times 10$ mm^3 in size were placed in a stainless-steel mesh crystal holder inside a nickel tube, which was then sealed into an evacuated Pyrex glass tube together with a freshly opened 1-g ampoule of pure potassium metal. Three batches of crystals were heated in a furnace at about 630 °C for approximately two hours, as detailed in Table I. After additive coloration the crystals were heated to 600 °C for 2 min and quickly quenched to room temperature in very dim light by placing the hot crystals on the polished surface of a large copper block. By this procedure crystals with predominantly isolated F centers were produced, with a concentration of about 10^{18} cm^{-3}.

Hydride ions were introduced by heating additively colored crystals in a Pyrex glass tube containing hydrogen at atmospheric pressure for 24 h at 605 °C. F centers were reformed in these crystals by irradiation with 50-kV x rays at room temperature.

The processes of coloration, and later of aggregation, were monitored by absorption spectrum measurements made at 77 °K with a simple cold-finger liquid-nitrogen cryostat in a Cary Model 17 spectrophotometer. A microscope illuminator with a narrow-band (10 nm) interference filter centered at 640 nm was used to irradiate the F centers in the long-wavelength tail of the F band (F-light irradiation).

For some experiments it was necessary to produce F_2 centers aligned preferentially along one of the ⟨110⟩ directions. It was found best to do this alignment at 77 °K to avoid producing higher aggregate centers, by irradiation with microscope illuminator light transmitted through a long-wavelength cutoff filter with a 650-nm cutoff and a Polaroid sheet. Even with this relatively intense illumination, an irradiation time of more than 5 h was necessary to produce the desired degree of alignment.

The processes of aggregation and alignment were found to vary tremendously in their speed between nominally pure KCl crystals obtained from different sources. We could not identify a particular impurity causing these large differences, but if we assume that the appearance of a large number of small zero-phonon lines after aggregation is a sign of an impure crystal, then in purer crystals F aggregation and F_2-center alignment are both slower.

Most of the high-resolution absorption spectra were measured on crystals held at 2 °K in a helium immersion cryostat. Some measurements were made at temperatures between 4 and 50 °K with a variable-temperature cryostat where flowing helium gas cooled the specimen, the temperature being measured with a germanium thermometer.

The high-resolution absorption apparatus is capable of measuring 10^{-4} transmittance change at a resolution of 0.05 nm.[3] The transmittance versus wavelength output of the apparatus was recorded digitally on magnetic tape, and in subsequent computer processing the wavelength calibration of the monochromator was taken into account to produce a final output of transmittance versus corrected wave number. Wavelength calibrations were done with a low-pressure mercury discharge lamp, and our over-all wave-number accuracy is approximately ± 2 cm^{-1}. Most of the absorption spectra presented here were traced from computer plots of the processed results.

IV. EXPERIMENTAL RESULTS

A. F_2 center

The F_2 center consists of two nearest-neighbor F centers; in the sodium chloride lattice the point group of such a defect is D_{2h}.[7] Electronically the F_2 center, which has two positive charges and two electrons, is analogous to the hydrogen molecule, so that the electronic states of the F_2 center can to first approximation be classified in the same way as those of the hydrogen molecule. However, since the D_{2h} symmetry of the F_2 center is lower than the $D_{\infty h}$ symmetry of the hydrogen molecule, all degenerate hydrogen molecule electronic states will be split into nondegenerate states in the F_2 center. In Fig. 1 is given a summary of the latest assignment, due to Engstrom,[8] of the lowest-energy singlet and triplet absorption bands of the F_2 center, labelled according to the hydrogen molecule $D_{\infty h}$ representations. This diagram will explain the references to absorption bands and electronic levels in the following description of our F_2-center experiments. Also listed in Fig. 1 are dipole moment orientations relative to a z axis parallel to the line joining the F centers, and the limiting low-temperature half widths determined by Hirai and Hashizume.[9]

The M_1 absorption is not only the most intense, but also the narrowest of the F_2-center absorptions, and is thus the first choice in a search for zero-phonon transitions. No complications due to level degeneracy can occur, conversions to other excited states are unlikely since this is the lowest-energy absorption transition, and the band is not overlapped by absorptions due to other F-center aggregates. We made many searches for the zero-phonon line, looking with the sensitive absorption apparatus in the region on the long-

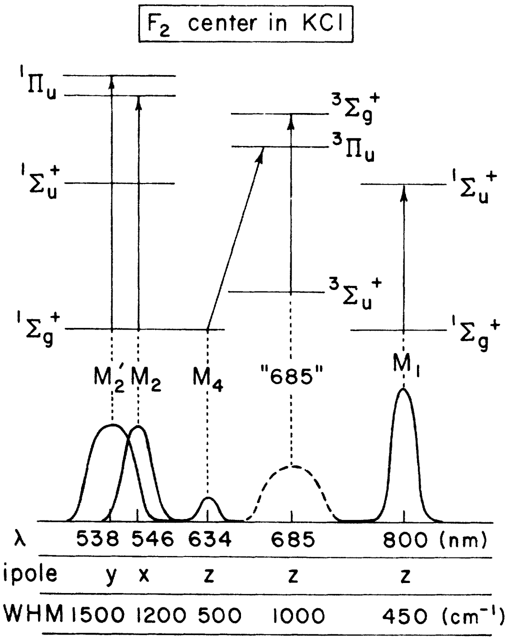

FIG. 1. Electronic energy levels of the F_2 center in KCl, according to the assignment of Engstrom (Ref. 8), labeled by representations of the point $D_{\infty h}$ (hydrogen-molecule approximation). The five lowest-energy singlet and triplet absorption bands are also sketched, the metastable triplet-triplet absorption band with a broken line. FWHM signifies full width at half maximum.

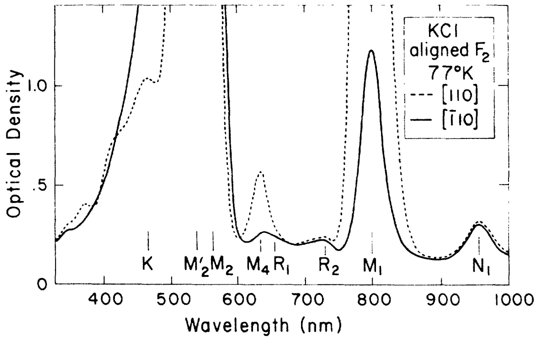

FIG. 2. Absorption spectrum of KCl crystal H, after the additive coloration, aggregation, heat-treatment, and F_2-center alignment process described in the text. The crystal was 0.080 cm thick.

wavelength side of the M_1 band; none were successful, so we will describe only one experi ment designed to locate the zero-phonon line with maximum sensitivity. For this experiment a crystal of the highest purity was used, with a highly anisotropic M_1 absorption and a minimum proportion of higher F-aggregate centers. The "purest" crystal was chosen by an empirical criterion; it was the crystal (Cornell) with the smallest number of zero-phonon lines after additive coloration and F-center aggregation. A freshly quenched, additively colored sample of Cornell KCl was irradiated with F light for 45 min at -5 °C to produce F_2 centers and some F_3 centers. The F_3 centers were thermally destroyed by heating the specimen to 100 °C for 15 min. To align the F_2 centers, light propagating parallel to [001] and polarized parallel to [110] was used to irradiate F_2 centers in their M_2 and M_2' absorption bands for $6\frac{1}{2}$ h at 77 °K; at the end of this irradiation most F_2 centers are aligned parallel to the [110] direction.[10] The absorption spectrum in Fig. 2 shows this clearly. Though most of the absorption is due to aligned F_2 centers, some isotropic bands remain, caused by F centers, F_3 centers (R_1, R_2), and higher aggregate centers (N_1). There is some doubt about the identity of the bands marked R_1, R_2 in Fig. 2; they may well be due to N-center transitions called R_3 by Tomiki[11] and called N_{R_1} and N_{R_2} by Hattori.[12]

It is possible to calculate the number of F_2 centers and their degree of alignment from the absorption spectrum in Fig. 2. The peak absorption of the M_1 band parallel to [110], which is well off scale, can be calculated by multiplying the peak absorption in the [110] M_4 band by the factor 44, the absorption ratio M_1/M_4 experimentally determined by Engstrom.[8] The result is an optical density of 14, and consequently, from the $[\bar{1}10]$ absorption in the M_1 band, there must be 14 times more F_2 centers aligned along [110] than along $[\bar{1}10]$. The F_2 concentration, denoted by $[F_2]$, can be calculated from the Smakula formula

$$f[F_2] = 0.87 \times 10^{17}[n/(n^2+2)^2]H\alpha ,$$

where $f = 0.38$ is the oscillator strength,[13] $n = 1.46$ is the refractive index of KCl at 800 nm, $H = 0.056$ eV is the full width at half maximum (FWHM) of the M_1 band,[9] and $\alpha = 403$ cm^{-1} is the absorption coefficient at the peak of the M_1 band. The result is that $[F_2] = 4.4 \times 10^{17}$ cm^{-3} aligned parallel to [110], and thus $[F_2] = 3.1 \times 10^{16}$ cm^{-3} parallel to $[\bar{1}10]$, from the alignment ratio.

The absorption spectrum of this crystal was measured at 2 °K under high resolution and a transmittance scale expanded by a factor 30. No zero-phonon line could be detected in either polarization in the wavelength range 850–990 nm, even though the sensitivity of the apparatus was such that a zero-phonon line causing a change in transmittance of 10^{-3} could have been detected with more than 99% certainty.

We also looked for the zero-phonon line of the M_1 band in many other crystals containing F_2 centers prepared in different ways, without success. We looked at the M_1 bands produced by F aggregation in additively colored crystals that were less pure than the Cornell crystal, as listed in Table I, and including the perturbed M_{1A} band in crystals containing sodium, at M_1 bands produced by random pairing of F centers in freshly quenched additively colored crystals, and at M_1 bands produced by x irradiation, of pure or hydride-doped crystals. Finally, to check whether the absence of a zero-phonon line was a property peculiar to KCl we measured the M_1 band in a KBr crystal which had been additively colored and irradiated in the F band. No zero-phonon line was found in KBr either.

There are four other absorption transitions in Fig. 1 which could be investigated for zero-phonon lines, but the intense M_2 and M_2' absorption bands are so effectively hidden by the very strong and broad F band centered at 536 nm that it is impossible to make measurements in the M_2' and M_2 bands with high photometric resolution. However it will be seen from Fig. 2 that the M_4 band is not appreciably overlapped by other absorption bands, and has the same pronounced dichroism as the M_1 band. When we examined the long-wavelength side of the M_4 band in this specimen at 2 °K under high resolution we obtained the result shown in Fig. 3, where an unmistakable, though rather

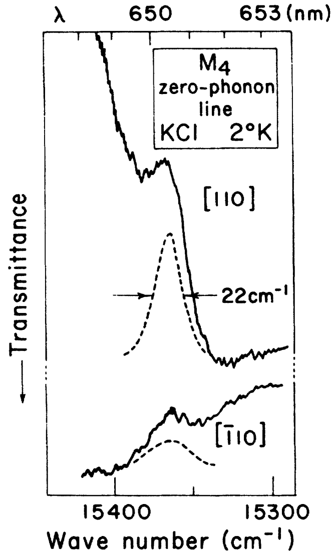

FIG. 3. Expanded scale absorption spectrum of the same specimen as in Fig. 2. Dashed lines were obtained by subtraction of an assumed smooth sloping background absorption from a smoothed transmittance trace.

broad, zero-phonon line can be seen, with the same dichroism as the M_4 band. Two possible reasons for this unexpected width are that the specimen might have been exceptionally strained, causing a larger inhomogeneous broadening, or that there is a high degree of quadratic electron-phonon coupling. To check these effects, we measured the intensity and halfwidth of the M_4 zero-phonon line as a function of temperature, and at the same time measured the intensity and halfwidth of the rather small R_2 zero-phonon line which could be seen in this specimen due to the presence of a small number of residual F_3 centers. The results are shown in Fig. 4. The behavior of the R_2 zero-phonon line can be explained by the theory given in Sec. II; the half width becomes temperature independent below 15 °K, probably because of inhomogeneous broadening caused by random strains in the specimen, and the half width rises smoothly with temperature above 15 °K, probably because of quadratic electron-phonon coupling effects.[2] The inhomogeneous linewidth that we measure is 6 cm^{-1}, slightly smaller than the 7 cm^{-1} originally reported by Fitchen *et al.*[14] Thus it is likely that our specimen is not unduly strained. The intensity as a function of temperature follows the logarithmic dependence against T^2 predicted by Eq. (13), and we find the same effective Debye temperature $\theta = 173$ °K as Fitchen *et al.*[14] The results for the M_4 zero-phonon line are not as accurate, because the line is so small, but even so, it is obvious from Fig. 4 that the large half width is independent of temperature, and it is also probable that the intensity of the line diminishes with temperature in accordance with equation (13). For the M_4 line we find $\theta = 192$ °K, assuming that $S = 7$.

We also looked for the zero-phonon line of the metastable 685-nm triplet-triplet absorption band of the F_2 center. Reference to Fig. 1 will show that this band can be made visible by irradiating F_2 centers in the M_4 absorption band. This populates the ${}^3\Sigma_u^+$ triplet ground state via the ${}^3\Pi_u$ excited state. The triplet ground state has a lifetime of 50–100 sec. against decay into the singlet ground state depending on the distance between F_2 centers and perturbing F centers.[15] We measured the 685-nm band in the steady-state condition produced by continuous irradiation with a 2-mW 633-nm He-Ne laser. The absorption spectrum at 2 °K is shown in Fig. 5. During a careful search under high magnification no zero-phonon line could be detected. The amount of perturbation of the F_2 centers was monitored by measuring the rate of fall of the 685 band after the laser was turned off. The measured lifetime was 88 sec, which implies that the F_2 centers are not perturbed by nearby F centers.[15]

B. F_3 center

The F_3 center is composed of three nearest-neighbor F centers arranged in an equilateral

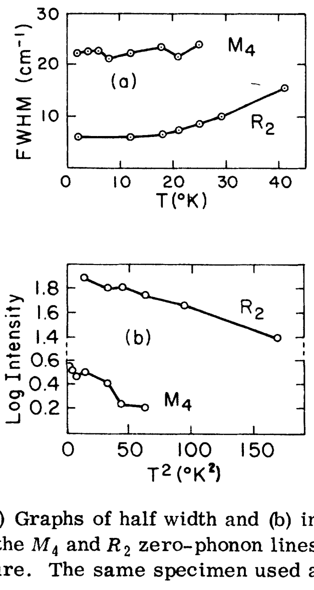

FIG. 4. (a) Graphs of half width and (b) integrated intensity of the M_4 and R_2 zero-phonon lines as functions of temperature. The same specimen used as in Figs. 2 and 3.

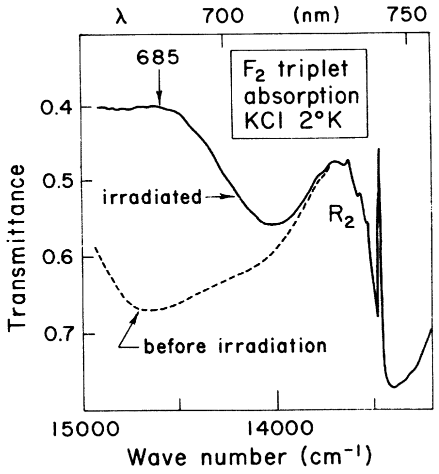

FIG. 5. Absorption spectrum of KCl crystal H measured at 2 °K during irradiation with a 2-mW He-Ne laser. Broken line shows absorption measured before irradiation.

triangle in a negative ion (111) plane as shown in Fig. 6. The absorption bands due to this center, called R bands for historical reasons,[1] were assigned to the energy levels shown in Fig. 6 by Silsbee[16] on the basis of stress-induced dichroism measurements. The most intense and well-known absorptions are the R_1 and R_2 bands, the R_2 band having a prominent zero-phonon line and a structured sideband which can be seen clearly in Fig. 5. Two other absorption bands lie towards longer wavelengths, the R_M band, which in KCl is heavily overlapped by the M_1 band, and the R_N band, the double-humped shape of which is thought to be due to the Jahn-Teller effect.[16]

We examined the regions round the R_1 band and the R_N band with the sensitive absorption apparatus to try to detect new zero-phonon lines. Of the other absorptions of the F_3 center, the R_2 zero-phonon line is already well known, and in the R_M band region the sensitivity of the apparatus is effectively very much reduced by the overlapping of the strong M_1 band. In all the crystals examined, including those where a large number of zero-phonon lines were detected, we were unable to detect a zero-phonon line related to the R_1 band, nor one related to the R_N band. To take a specific example, an Optovac D crystal was additively colored, quenched, and irradiated with F light at room temperature for 1 h, after which treatment the optical density, measured at 2 °K, in the peak of the R_2 zero-phonon line was 1.7. The only other zero-phonon lines detected in this crystal were two perturbed R_2 lines discussed later, and a line at 10 081 cm^{-1} with an intensity independent of the absorption in the R_N-band region, in agreement with the conclusions of Schneider and Kabler.[17]

We were also able to observe four new zero-phonon lines in some impure crystals that had been irradiated with F light to produce a large R_2 zero-phonon line, and we propose that these lines are due to a perturbation of the R_2 electronic transition of the F_3 center caused by a nearby impurity. In one case we were able to identify the impurity as the sodium ion by means of experiments such as those illustrated in Fig. 7. In this figure we have compared the absorption spectra of two crystals which had been heavily irradiated to produce F_2 and F_3 centers. The Optovac crystal contains sodium ion impurity, as deduced from the displacement of the M_1 band towards longer wavelengths,[18] shown in Fig. 7, and from the appearance of the sodium F_{A1} band[19] near the F band, outside the range of Fig. 7. By the same criteria, the Vinor crystal is free of sodium ion impurity, though it does contain impurities which cause two zero-phonon lines at 11 730 and 11 657 cm^{-1}. The two zero-phonon lines at 13 278 and 13 216 cm^{-1}, near the R_2 zero-phonon line, only occurred in Optovac crystals, and in crystal J which was doped with sodium. The broad absorption which can just be seen in Fig. 7 on the short-wavelength side of these zero-phonon

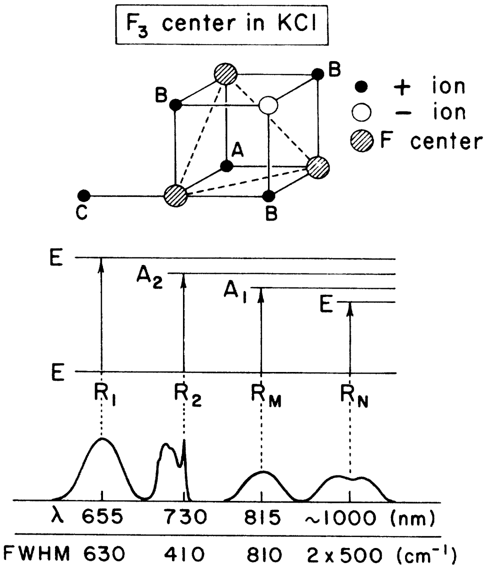

FIG. 6. Structure of the F_3 center with nearest-neighbor positive-ion sites of three different symmetries, its energy levels according to Silsbee (Ref. 16), and a sketch of the low-temperature absorption spectrum.

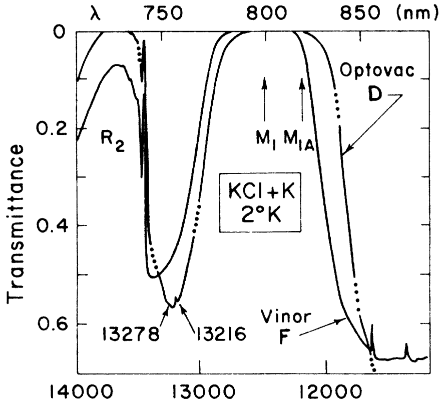

FIG. 7. Zero-phonon lines at 13 278 and 13 216 cm^{-1} due to perturbation of F_3 centers by sodium impurity. Note the shifted M_1 absorption band of the Optovac crystal indicating the presence of sodium. The Vinor crystal shown for comparison has lines at 11 730 and 11 657 cm^{-1} due to other impurities (see Table III).

lines could be multiphonon sideband of the zero-phonon lines, the "R_{2A} band" by analogy with the F_A and M_A bands.

An expanded scale absorption spectrum of the Optovac crystal is shown in Fig. 8. The breadth of the 13 278 line, and the fact that it is separated from 13 216 line by 62 cm^{-1}, suggest that the absorption peak at 13 278 cm^{-1} might be a peak in the phonon sideband of the 13 216 line. This is unlikely because its intensity relative to the 13 216 line varies from sample to sample; the following ratios were observed: 0.33 in *D*, 0.43 in *E*, 0.34 and 0.12 in two specimens of crystal *J*. We prefer the explanation that both are zero-phonon lines caused by two different perturbations of the F_3 center. If the sodium ions are nearest neighbors of the F_3 center, they can occupy 13 possible sites with three different symmetries. Referring to Fig. 6, there is one *A* site, the only site that preserves the threefold axis of the perturbed F_3 center, three *B* sites and nine *C* sites. It is probable that the sodium ion populations in these locations can vary according to the original sodium ion concentration and the irradiation treatment of the crystal, with a different perturbation of the R_2 electronic transition for different locations. We hope to resolve this question by studying the effect of uniaxial stress on these lines.

The two other zero-phonon lines that are probably also caused by a perturbation of the F_3 center can be seen in the spectrum of the Harshaw crystal shown in Fig. 8, but in this case the perturbing impurity is not known. These lines occurred in NRC *I* crystals, as well as in Harshaw crystals, they are narrower and more intense than the sodium-perturbed lines, and the higher-energy line is always more intense. However the energy separation of 63 cm^{-1} is almost identical with that of the sodium-perturbed lines. These results are summarized in Table II.

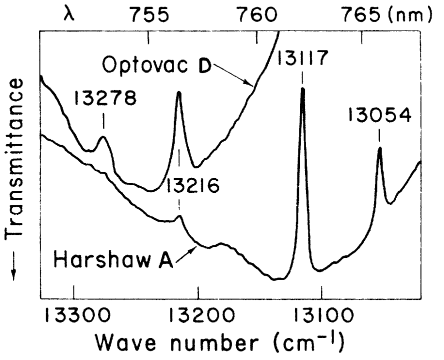

FIG. 8. Expanded scale absorption spectra of Optovac and Harshaw crystals which had been irradiated to produce a large R_2 absorption band. The lines at 13 117 and 13 054 cm^{-1} are assumed to be due to a perturbation of the F_3 center by an unknown impurity.

TABLE II. R_2 zero-phonon line and perturbed R_2 zero-phonon lines (measured at 2 °K).

Perturber	Zero-phonon lines Peak (cm^{-1})	FWHM (cm^{-1})
None	13 471	6.0
Sodium	13 278	...
	13 216	9.5
Unknown	13 117	6.0
	13 054	6.0

C. *N* centers

We use the convenient notation "*N* centers" to characterize centers which have broad absorption bands in the wavelength region 900–1100 nm. These centers are certainly due to aggregates of *F* centers not associated with impurities, because we observe *N*-band absorption in all the additively colored crystals listed in Table I, after suitable *F*-light irradiation. However the details of the band shapes, and the rates of growth of the bands, are very dependent on impurity concentration and on thermal treatment of the specimens.[17] There has been no reliable determination of the number of *F* centers which make up the aggregates, except for the R_N absorption of the F_3 center. In the *N*-band wavelength region of 900–1100 nm we were able to detect 38 zero-phonon lines, but

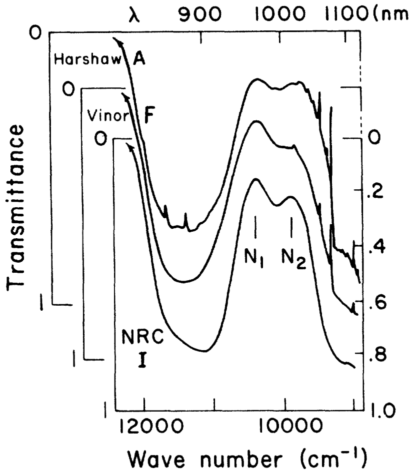

FIG. 9. Absorption spectra of three KCl crystals irradiated to produce *N*-band absorption measured at 2 °K. The spectra have been vertically offset for clarity. There is no correlation between the zero-phonon lines and the *N* bands.

a detailed comparison between the intensities of the lines and the intensity of the *N* bands indicated that there was no correlation between the lines and the bands. This is clearly seen in Fig. 9, where the absorption spectra of three different crystals with very similar *N* bands show very different zero-phonon lines. We therefore conclude that there are no zero-phonon lines associated with *N* centers.

D. Other zero-phonon lines

During this investigation we observed 64 zero-phonon lines which could not be assigned to any specific absorbing centers. Ten of these lines have been previously observed.[14,20,21] The occurrence of these lines depended very much on the original KCl single-crystal material, as well as the subsequent treatment, and in this section we will give an account of the experimental conditions under which these lines are formed, and will speculate on the centers responsible later, in the discussion section. The incidence of these lines, characterized by the wave number in cm^{-1} at the peak of the line, is summarized in Table III and IV, together with FWHM data for the stronger lines, and changes in the line intensity occurring after annealing specimens at 100 °C for 10 min.

Some tests were made to establish the experimental conditions necessary for the formation of these lines. The presence of *F* centers is a minimum requirement, since crystals without *F* centers that had been subjected to the same quenching technique showed no such lines. Furthermore, the *F* centers must be present in an aggregated form, because the lines could not be detected in freshly quenched additively colored crystals which had not been exposed to light. Finally, the aggregate must be composed of more than two *F* centers. This conclusion is based on the behavior of crystals doped with calcium or iodide, where the effect of *F*-light irradiation is predominantly to cause the formation of F_2 centers, with very little development of the *R* and *N* bands. In such irradiated crystals none of the zero-phonon lines under discussion could be detected.

The experiments on doped crystals detailed in Tables III and IV were designed to find out which impurities are responsible for the great differences in behavior between nominally pure crystals. However it proved to be impossible to find out the effect of the anion impurities O_2^-, NO_3^-, and HS^- on the zero-phonon line production, because KCl crystals doped with these impurities could not be additively colored. The additive coloration process produced *F* centers only in the outer 0.5 mm. thickness, and it was not possible to cleave out colored specimens of the minimum size required.

Four of the zero-phonon lines were strong enough that a reasonably well-defined multiphonon sideband could be measured. The results are shown in Fig. 10, where overlapping unrelated zero-phonon lines have been marked with asterisks to distinguish them from structure in the sideband. The sidebands are not unusual except for the sharp peak in the sideband of the 9280-cm^{-1} zero-phonon line, separated by 159 cm^{-1},

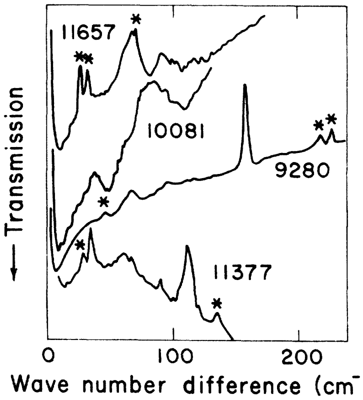

FIG. 10. Sidebands of the four largest zero-phonon lines in KCl crystals containing *F*-aggregate centers. Parent zero-phonon lines are superimposed on the left-hand edge. Peaks marked by asterisks are unrelated zero-phonon lines, and slowly varying backgrounds are due to nearby broad absorption bands.

TABLE III. Data on zero-phonon lines of unknown origin, appearing in more than one crystal. Measured at 2 °K on additively colored crystals.

Zero-phonon line		Occurence and maximum absorption coefficient (for strong lines) in cm^{-1}										Effect of
Peak (cm^{-1})	FWHM (cm^{-1})	Harshaw *A*,*B*,*C*	CO_3 doped *L*	Vinor *F*	OH doped *K*	Na doped *J*	Optovac *E*	NRC *I*	Oregon *G*	Cornell *H*	Optovac *D*	100 °C anneal
11 730		0.22		···								
11 689	3.7	···	0.49									
11 683	3.6	0.46							···			
11 657 [a]	4.0	2.7	···	···	···	···	···					–
11 632	6.0	···	0.49									
11 512		···				···	···					
11 494		···			2.1							
11 406		···			···							
11 377 [a]	4.6	2.5	···	···	···	···	···		···			–
11 357	7.7	0.47	···	···	···							–
11 304		···	···					···				
11 185	3.1	0.56	···	···			···					–
11 088	2.0	···	0.27									
11 074						···	···					
10 544	2.3	7.2		···								+
10 136	2.7	1.5		···								+
10 081 [a,b]	2.4	50		···		···	···	···	···	···	···	
10 060		···						0.29				–
10 011		···						0.35				
9791	3.0	···	1.6	···	···							
9778		0.14						···				–
9755		···	0.60	···	···							–
9706		0.30		···								+
9683 [a,b]	3.5	···	16	···	···	···	···	···				–
9640 [a]	3.5	···	1.2	···	···							–
9580 [a]	3.3	···	1.4	···	···		···	···				–
9521		···				···						
9508 [a]	2.5	···	···	···	···	12	···					–
9500	3.4	···	1.8	···	···							–
9428	1.6	···	2.6	···								–
9388		···	···									
9370 [b]		1.1		···			···	···				–
9327	3.2	···	0.43	···								–
9280 [a,b]	2.2	···	33	···	···	···	···					–
9265		···				1.1	···					
8958	1.5	···	5.7	···	···	···	···					–

[a] Observed by Fitchen *et al.* (Ref. 14).

[b] Observed by Pierce (Ref. 20).

TABLE IV. Additional weak zero-phonon lines, appearing only in the listed crystal (wave numbers in cm^{-1}).

Harshaw *A*,*B*,*C*		CO_3 doped *L*	OH doped *K*	Na doped *J*	NRC *I*	Oregon *G*
11319	10 790	9622	12 105	11 518	11 558	11 171
11 204	10 775	8807	11 996	11 420	11 296	
11 160	10 555		11 312	11 232		
11 094	10 254		9838			
11 079	9645					
11 066	9625					
10 967	9553					
10 912	9215					

previously identified[14] as a zero-phonon line. We identify this peak as sideband structure because in 16 different samples the absorption coefficient of this feature was always 2.6 ± 0.2 times smaller than the 9280-cm^{-1} line. In two sodium-doped samples the ratio changed to 1.6 and 1.1, but in both these specimens it was possible to destroy the 9280-cm^{-1} line by heating the crystal to 130 °C while the sharp feature at 9439 cm^{-1} remained. Thus the smaller ratio could be due to another uncorrelated zero-phonon line in the sodium-doped crystals. For these reasons we think that this sharp feature actually occurs in the phonon sideband of the 9280-cm^{-1} zero-phonon line.

Finally, we checked for correlations between these zero-phonon lines by making a pair-wise comparison of absorption coefficients. The only correlations found in this search were between sharp features in phonon sidebands and parent zero-phonon lines, as shown in Fig. 10.

V. DISCUSSION

A. Missing M_1 zero-phonon line

The M_1 absorption transition of the F_2 center should provide a very clear-cut comparison between experiment and theory, for the reasons detailed earlier. We will first use the experimental results of Hirai and Hashizume[9] to point out some inconsistencies which are evident even in the broad-band properties.

No zero-phonon line common to the emission and absorption bands has been observed, so that we do not know the energy ΔE_{if} in Eq. (9), but this equation can still be used to calculate the *difference* in energy ΔE between the peaks of the M_1 absorption and emission bands. For simplicity we assume that the sum $\sum_\alpha S_\alpha \hbar\omega_\alpha$ can be replaced by the product of an average coupling strength S and an average phonon energy $\hbar\omega$. Using subscripts abs and em for absorption and emission, respectively, from (9),

$$\Delta E = S_{abs}\hbar\omega_{abs} + S_{em}\hbar\omega_{em} . \tag{14}$$

The required quantities on the right-hand side of this equation can be calculated from the data on FWHM of the absorption and emission bands as a function of absolute temperature $H(T)$, using Eq. (8),

$$H(T) = 2.36\hbar\omega[S\coth(\hbar\omega/2kT)]^{1/2} , \tag{15}$$

and assuming that the bands are Gaussian in shape. From Hirai and Hashizume's results,[9] $S_{abs} = 4.1$, $S_{em} = 11.6$, $\hbar\omega_{abs} = 94$ cm^{-1}, and $\hbar\omega_{em} = 130$ cm^{-1}, and from (14) we calculate $\Delta E = 1890$ cm^{-1}. However this is very much smaller than the experimental value of 3200 cm^{-1}, so that there are inconsistencies even in the broad-band behavior.

Next we turn to calculations relative to the zero-phonon line and the M_1 absorption band. If the zero-phonon line has not been observed because the coupling constant is too large, then a lower limit for the coupling constant can be calculated from the sensitivity of the apparatus and an assumed width of the zero-phonon line, say 5 cm^{-1}, a typical value in the alkali halides. The apparatus is sensitive enough to detect with 99% certainty a zero-phonon line causing a change in optical density 6×10^{-4}, and such a line would have an integrated intensity of approximately 3×10^{-3} cm^{-1}. The crystal referred to in Fig. 2 had an optical density of 14 in the M_1 band in the [110] orientation, and the FWHM was 450 cm^{-1}, so the integrated absorption in the M_1 band is approximately 6.3×10^3 cm^{-1}. The ratio of these two quantities, according to Eq. (12), is equal to e^{-S}, and we can thus say that if the zero-phonon line has escaped detection because of coupling to the lattice, the coupling constant must be greater than 14.6. If the coupling constant really is so large, it is very hard to explain why the M_1 band is relatively narrow, without involving another physically unrealistic assumption that the coupling to the lattice phonons is almost entirely concentrated at the low-frequency end of the phonon spectrum.

There remains the possibility that the zero-phonon line of the M_1 band has escaped detection because it is very broad. This explanation could also account for the absence of structure in the M_1 band. If a zero-phonon line is broad as well as being weak, it is very difficult to detect unless some absolutely reliable method of determining the background absorption is available. However, if the coupling coefficient of the M_1 absorption really is about 4, then since the M_1 band used in the crucial experiment had an optical density of 14 the zero-phonon line should still be strong, even though broad. At a conservative estimate, the breadth of a zero-phonon line which is broad enough to escape detection is 100 cm^{-1}, a figure which is the same as the mean phonon frequency calculated from the change in halfwidth of the M_1 band as a function of temperature. It is very difficult to see what mechanism could cause a zero-phonon line to broaden to this extent. It cannot be a lifetime broadening; the radiative lifetime of the lowest excited state of the F_2 center is 28 nsec,[22] corresponding to a radiative linewidth of 2×10^{-4} cm^{-1}. If an accidental degeneracy with a broad triplet-state level had caused the broadening, then one would not expect an accidental degeneracy also to occur in potassium bromide, where we also failed to find an M_1 zero-phonon line. Quadratic coupling effects would be unlikely to be so large as to cause quadratic broadening at 2 °K. Finally, if the line has been broadened inhomogeneously by lattice strains, then the M_1 transition must have an exceptionally high strain coupling coefficient, or the KCl lattice must be highly strained. The latter conjecture is less likely because other zero-phonon lines observed in KCl crystals are not unusually wide. The argument for a large strain coupling coefficient is also given some support by the observation that the M_4 zero-phonon line is unusually broad, and temperature independent. This behavior could be explained by a large inhomogeneous broadening caused by a strong strain coupling to the M_4 transition of the F_2 center.

B. M_4 zero-phonon line

The M_4 zero-phonon line is not only broad but has a constant half width from 2 °K until the line disappears at about 30 °K. By the same arguments used in Sec. V A, we assume that this is due to inhomogeneous broadening caused by a large strain coupling with the lattice. The M_4 absorption behaves normally in all other respects. We made measurements at 2 °K of the integrated absorption in the zero-phonon line and the multiphonon sideband, and calculated the coupling constant to be $S=7$ from Eq. (12). An approximate calculation of the coupling constant can also be made from the broad-band measurements of Hirai and Hashizume,[9] using Eq. (10). However there is more than the usual uncertainty present in deciding on the mean phonon energy $\hbar\omega$, because the variation of the half width of the M_4 band can only be followed up to about 110 °K. At higher temperatures the F band strongly overlaps the M_4 band. For this reason Hirai and Hashizume consider their value of $\hbar\omega=67$ cm^{-1} to be too small, and suggest that the true value should be the same as for the M_1 band, $\hbar\omega=93$ cm^{-1}. The limiting half width $H(0)=492$ cm^{-1} of the M_4 band is accurate, however, and if the two values of $\hbar\omega$ are used to calculate the coupling constant, the results $S=10$ and $S=5$ are obtained. Our value $S=7$ is likely to be more accurate than either of the broad-band results, so that we can summarize the M_4 absorption as a transition with a relatively large coupling constant but with an unusually broad zero-phonon line.

C. Other absorptions of F_2 and F_3 centers

We failed to detect a zero-phonon line in the triplet-triplet absorption band of the F_2 center at 685 nm, but this is probably due to the fact that the zero-phonon line is too small to detect even with sensitive apparatus. The 685-nm band is quite wide,[23] with a FWHM of about 1000 cm^{-1}, and a coupling constant $S=22$, according to an approximate calculation using Eq. (10) and a mean phonon energy of 90 cm^{-1}. We could not detect a zero-phonon line with fractional intensity e^{-22} even if it was quite narrow.

No zero-phonon line could be detected in the R_1 band of the F_3 center, but in this case the actual electronic transition corresponding to this band is not certain, in the sense that it is not known whether the Jahn-Teller splitting is small, so that the broad-band R_1 splitting is undetectable, or whether it is so large that another split component of R_1 lies under the F band.[16] In any case, the simple Born-Oppenheimer theory presented here will not apply. The same argument will also apply to the R_N-band transitions of the F_3 center.

D. Other zero-phonon lines

A large number of zero-phonon lines of unknown origin were observed after additive coloration and F center aggregation. The extreme variability in the number of lines observed in different KCl crystals means that the formation of these lines must be extremely sensitive to the presence of impurities. Our assumption is that the zero-phonon lines are due to transitions within *F*-aggregate centers which are perturbed by a nearby impurity. Two questions need to be discussed to justify this assumption; why impurities are effective to a degree far greater than their fractional population, and why so many different zero-phonon lines are observed.

It is already well established that the *F*-aggregation processes which take place when additively colored crystals are irradiated with *F* light are very sensitive to impurities. The best-known occurrence of this effect is during the formation of F_A centers (*F* centers with neighboring alkali-metal impurity) in KCl crystals containing sodium. The process is so sensitive to sodium ions that almost complete conversion of *F* centers to F_A centers is observed when a nominally pure KCl crystal containing 3.5×10^{16} *F* centers per cm^3 is irradiated with *F* light at $-30\,^{\circ}$C.[24] At this temperature F_A centers are formed in preference to F_2 and higher aggregate centers, and it is clear that the effect of the irradiation is to cause the *F* centers to relocate themselves next to most of the available sodium ion impurities. At higher temperatures, around room temperature, *F*-light irradiation causes the formation of *F*-aggregate centers, and we found that this process is also very sensitive to impurities. *F*-aggregate centers formed very much more rapidly in Harshaw crystals than in other pure crystals.

The primary process which occurs on *F*-light irradiation is the decomposition of the *F* center into an anion vacancy and an electron, which is subsequently trapped by another *F* center to form an F^- center.[19] Since the anion vacancy is more mobile than any of the other defects present, the consequence of *F*-light irradiation is to make *F* centers mobile, because the anion vacancy after moving through the lattice will eventually be neutralized by an electron, thus forming an *F* center in a new position in the lattice. Even if there is only a slight tendency for anion vacancies to associate with impurities, the mobility caused by *F*-light irradiation ensures many opportunities for such association, and at the same time the lattice temperature does not rise, so that thermal dissociation does not take place. By such a mechanism the process of *F* aggregation could become extremely sensitive to the presence of impurities.

Finally, we propose an explanation for the large number of zero-phonon lines observed. Assume first that a particular impurity, which substitutionally replaces potassium ions in the KCl lattice, is present in very low concentration. By the arguments of the previous paragraph we infer that *F*-aggregate centers will preferentially form near to the impurity. Next, we notice from Table III that the zero-phonon lines are narrow (FWHM ~ 3 cm^{-1}) and from typical spectra in Fig. 10 that the coupling with the lattice is small. Thus, even though the integrated absorption due to a very small number of impurity-aggregate centers is also very small, we will be able to detect the absorption because it is concentrated into narrow zero-phonon lines and our apparatus can detect such lines very sensitively. We now assume that the number of *F* centers comprising the aggregate is greater than three, because the lower aggregate centers have already been accounted for. There are now a large number of different geometrical arrangments of the impurity and the aggregate. Consider the case of the F_4 center. There are two possible arrangements of F_4, one tetrahedral and one planar, and there are five different geometrical arrangements of a positive ion impurity around the F_4 center. These five different arrangements could cause five different perturbations and hence five zero-phonon lines of different frequency. This number can now be multiplied by the number of different impurities capable of associating with *F*-aggregate centers, and by the number of electronic transitions that can take place within the F_4 center in the wavelength range considered. Then if we allow the number of *F* centers in the aggregate center to increase to numbers greater than four, it is not difficult to conceive that the number of possible zero-phonon lines could increase to the number we actually observed.

VI. SUMMARY

In this investigation we have focussed attention on the lack of zero-phonon lines in the spectra of the simpler *F*-aggregate centers in KCl. The absence of the M_1 zero-phonon line in the F_2 center is particularly striking. One zero-phonon line was discovered in the absorption spectrum of F_2 centers, but it is unusually wide.

Though many zero-phonon lines may be detected in the absorption spectra of KCl crystals containing *F*-aggregate centers, we have shown that they are all due to the presence of impurities. (The line at 10 081 cm^{-1} is a possible exception.) The impurities are present in such small concentration that their identification is difficult.

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