where

$$\Delta=\tfrac{2}{5}\Omega\tau_N+(\Omega\tau_z)^{-1}.$$

In the limit $\Omega\tau_N\gg1$, $\tau_R\gg\tau_N$, the above approximation leads to

$$\tau(\mathbf{k},\Omega)=-i\Omega-\langle1|i\mathbf{k}\cdot\mathbf{c}|0\rangle$$
$$\times\langle0|\left[i(\mathbf{k}\cdot\mathbf{c}-\Omega)+\frac{1}{\tau_N}\right]^{-1}|0\rangle\langle0|i\mathbf{k}\cdot\mathbf{c}|1\rangle. \quad \text{(B12)}$$

Equations (B8), (B9), (B11), and (B12) are the expressions for $\tau(\mathbf{k},\Omega)$ which are used in the text. They can be conveniently summarized in a single approximate expression for $\tau(\mathbf{k},\Omega)$. This expression is

$$\tau(\mathbf{k},\Omega)^{-1}=-i\Omega+\tau_z+[s+\langle1|i\mathbf{k}\cdot\mathbf{c}|0\rangle]^2$$
$$\times\langle0|\left[i(\mathbf{k}\cdot\mathbf{c}-\Omega)+\frac{1}{\tau_N}+\frac{1}{\tau_R}\right]^{-1}|0\rangle, \quad \text{(B13)}$$

where $s=\langle0|\tau_N|0\rangle/\langle0|\tau_R|0\rangle$. It is this approximation to $\tau(\mathbf{k},\Omega)$ or equivalently $\kappa(\mathbf{k},\Omega)$ which leads to a correct expression for steady-state thermal conductivity, the existence of second sound, and the wide range of acoustic damping phenomena discussed in the text.

PHYSICAL REVIEW VOLUME 148, NUMBER 2 12 AUGUST 1966

F-Aggregate Centers in NaCl: Vibronic Structure and Symmetry Properties*

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(Received 31 March 1966)

Most color-center bands associated with *F*-aggregate centers in alkali halides show relatively strong 0-phonon lines and vibronic structure when observed at low temperature. The vibronic peak energies can in almost all cases be closely correlated on an empirical basis with zone-boundary critical-point energies of normal lattice phonon modes. However, without detailed knowledge of the defect geometries and electronic states involved, it is impossible to predict what the electron-phonon coupling should be. We present the observed vibronic spectrum for all the centers in NaCl which we have found to show fine structure, and discuss the apparent electron-phonon coupling seen. As a first step toward developing models for these centers, we also present results of stress splitting measurements on the 0-phonon lines in each case. The 0-phonon lines we have studied, their band assignments, and their observed symmetry as interpreted in terms of removal of orientational degeneracy, are as follows: 6329 Å, R_2, trigonal; 8375 Å, N_1, monoclinic I; 8681 Å, N_2, monoclinic I; 1.219 μ, ?, monoclinic I; 1.306 μ, M^+, monoclinic I; 1.404 μ, impurity, rhombic I; 1.549 μ, ?, rhombic I. In several cases the relative intensities of the line components can be analyzed to give the orientation of the dipole moment involved in the 0-phonon transition. Where it is possible to propose models by combining our stress measurements with the results of other experiments, we do so, with discussion as to the probable merit of each model.

I. INTRODUCTION

THE present state of knowledge of the group of color centers in the alkali halides known as the *F*-aggregate centers is quite meager. With the exception of the simplest of them, the *R* and *M* centers, this lack of knowledge extends even to almost complete uncertainty concerning the number and geometrical arrangement of the *F* centers which are assumed to coalesce to form them.[1] In addition, almost nothing is known about the details of their interaction with the surrounding lattice and each other. However, a particularly attractive approach to obtaining much of this information is available. This is due to the fact that many of the centers in this group are coupled to the lattice with an intermediate strength such that a relatively strong 0-phonon line and more or less detailed vibrational side-band structure is visible at low temperature. The presence of this fine structure makes a number of measurements feasible which are not possible with the usual broad band alone.

It has been observed in all cases where fine structure is present on the *F*-aggregate bands of the alkali halides that the numerical values of almost all of the vibrational peak energies, measured with respect to the 0-phonon line positions, correspond very closely to normal lattice phonon mode energies near Brillouin zone boundary critical points in high-symmetry directions.[2] This strongly suggests that the electron-phonon interaction at these centers is primarily with normal lattice modes rather than local modes, and that the coupling parameters are strongly peaked at the critical

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* This work was supported by the U. S. Atomic Energy Commission.

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[1] For a recent survey of this field see, e.g., W. Dale Compton and Herbert Rabin, *Solid State Physics* (Academic Press Inc., New York, 1964), Vol. 16, p. 121.

[2] C. B. Pierce, Phys. Rev. 135, A83 (1964).

points. If predictable, this sort of experimental information about normal-phonon-mode energies would be of great value in determining the properties of many optical materials. From naive symmetry arguments it would particularly appear that transitions of a given center in different materials of the same crystal structure, with presumably the same electronic states involved, would tend to couple only to certain phonon modes, and that these modes would be the same for all of the materials. However, experimentally it is observed that there are very wide variations in the number and type of phonon modes which couple to these centers.[2] This statement applies to any given defect in a variety of alkali halides, and to most of the centers which show vibronic structure in any given material. A group theoretical calculation has been made[3] to determine if there are selection rules applicable to phonon coupling at the R_2 center, assuming reasonable electronic states.[4] This attempt resulted in only limited success, in that, while a few selection rules were found, they did not apply to phonon modes at the critical points apparently observed experimentally. It would seem pointless to even attempt such a calculation for the more complex F-aggregate centers until there are at least relatively firm models established for the F-center geometry and electronic transitions involved.

The reasons pointed out above furnish the motivation for this study. We have undertaken to investigate the symmetry characteristics of a number of complex centers in NaCl by means of stress effects,[5] and to present models for these centers, where possible, based on these symmetry properties and other experiments. Also, we present the detailed vibronic spectra found to be associated with each of these bands and discuss briefly the apparent phonon coupling which is seen.

NaCl was chosen for this study for several reasons. We have observed several new bands in the infrared beyond the usual region of the N bands,[5,6] and wished to investigate them as thoroughly as possible. Two of these appear to be ionized states of previously observed F-aggregate centers,[6,7] and it was felt particularly that these assignments should be verified. The existence of centers in positive, neutral, and negatively charged states[8,9] immediately suggests that a concentrated study of these centers in all of the charge states should give much more information than the usual studies of the neutral state alone. Another reason for choosing NaCl is that the vibronic spectrum on the N_1 band is one of the most detailed seen and is one of the least ambiguous in interpretation in terms of normal lattice phonon modes.[2] It is hoped that a detailed study of the symmetry properties of this center will eventually help to shed some light on the validity of this interpretation. Finally, although each of the infrared bands we have observed appears to be associated with a different center, there are strong similarities in their vibronic spectra, and again it is hoped that a study of symmetry properties of the defects will help to eventually throw some light on the details of the electron-phonon coupling.

The symmetry properties of these centers are studied by means of applied uniaxial stress, which results in a splitting of the sharp 0-phonon lines into components in a manner determined by the defect symmetry. A given model of any defect center will fit into a regular crystal lattice in several different orientations. In the absence of external fields an electronic transition (0-phonon line) associated with this center will have the same energy for all orientations. In the presence of an applied stress field this "orientational" degeneracy is removed and transitions associated with defects in different orientations may have different energies. This problem of orientational degeneracy of anisotropic centers in cubic crystals under applied stress fields has been solved by application of group theory.[10] When this approach is applicable it is possible to uniquely determine the symmetry of any center by simply counting the number of components into which the 0-phonon line is split with application of stress in the [100], [111], and [110] crystallographic directions. This technique has recently begun to be exploited in the study of centers in a variety of materials.[4,11,12] Knowledge of defect symmetry, together with a minimal amount of other information allows, in principle, the determination of a unique model for any center which can be studied in this manner.

The additional use of polarized light in absorption measurements, with observation of differences in intensities of various components with different polarizations also allows in principle the determination of the direction and type of transition moments involved. Hence, information is obtained relating to the electronic states involved in the transition. All of our stress measurements have been made in this manner.

In addition to the simple orientational degeneracy, further degeneracies due to multiplicities in the electronic ground or excited states can be involved, and may be lifted by the application of stress. This situation has also been observed and discussed by several

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[3] L. Z. Kennedy, J. Chem. Phys. **44**, 1746 (1966).

[4] R. H. Silsbee, Phys. Rev. **138**, A180 (1965).

[5] C. B. Pierce, Bull. Am. Phys. Soc. **11**, 85 (1966). This was a preliminary account of some of the stress results presented here.

[6] C. B. Pierce, in *Proceedings of 1965 International Symposium on Color Centers in Alkali Halides* (University Illinois, of Urbana, Illinois, 1965), p. 114.

[7] I. Schneider and Herbert Rabin, Phys. Rev. Letters **13**, 690 (1964); Phys. Rev. **140**, A1983 (1965).

[8] M. Hirai, M. Ikezawa, and M. Ueta, J. Phys. Soc. Japan **17**, 1483 (1962).

[9] D. B. Fitchen, H. R. Fetterman, and C. B. Pierce, Solid State Commun. (to be published).

[10] A. A. Kaplyanskii, Opt. i Spektroskopiya **16**, 602 (1964) [English transl.: Opt. Spectry. **16**, 329 (1964)].

[11] G. Johannson, F. Lanzl, W. Von Der Osten, and W. Waidelich, Phys. Letters **15**, 110 (1965).

[12] A. E. Hughes and W. A. Runciman, Proc. Phys. Soc. **86**, 615 (1965).

authors.[4,12–14] In general it would seem that the relative magnitude of this effect should be much smaller than that for orientational degeneracy. Split ground states must be populated according to a Boltzmann factor ratio determined by the temperature and magnitude of the splitting. Where present, this result should be observable by means of stress and temperature dependence of relative intensities of transitions from the various ground states.[4,12] At the pumped helium temperatures of the present measurements, however, $kT\cong 2\times 10^{-4}$ eV, while our limiting resolution is approximately 10^{-3} eV in most cases. Thus, by the time any ground-state splitting is large enough to be resolved, only the lowest energy state should be significantly populated. Some relative intensity discrepancies which we observe, however, might be due to the fact that two such transitions of different polarizations are superimposed. On the other hand, transitions to a split excited state involve no such Boltzmann factor variation in intensity, and should appear simply as extra components. There are several cases to be discussed below where we see broadening apparently due to this excited state splitting.

In the section following we present a brief discussion of the experimental procedures, where pertinent. We have then chosen to present the experimental results and discussion pertaining to each center together, as the most coherent approach to presenting a rather large mass of varied data. This is followed by a brief summary of the results for all of the centers studied, with conclusions which we feel can be drawn from the complete study.

II. EXPERIMENTAL PROCEDURES

All of the optical absorption measurements presented here were made on a Cary Model 14 IR spectrophotometer, which allows monochromatic illumination of the sample during absorbance measurements from 0.22 μ to 3.0 μ. This has been the usual procedure, although some of the measurements entail the use of the "IR-2" source in the instrument. In this case the sample is illuminated with white light, which is analyzed by the monochromator after passing through the sample. A special four window, stainless steel, rotatable base Dewar with interchangeable cold fingers is used. For stress measurements particularly, the samples are immersed in helium pumped below the lambda point and observed directly through fused silica or sapphire "cold windows" in the cold finger. For most other measurements the samples are mounted in the Dewar vacuum in a hollow copper sample block such that copper surfaces in contact with liquid helium completely surround the sample except for the measuring light path. When it is necessary to illuminate the sample with an auxiliary light during measurement, another sample block is used, containing an aperture at 90° to the light path. The desired illuminating wavelength is selected by means of a dielectric monopass filter or a pair of high and low bandpass filters. With adequate shielding of the auxiliary source from the spectrophotometer detector, it is possible to make accurate absorbance measurements with the auxiliary light on.

All coloration in the samples discussed here was produced by two-MeV electron bombardment from a Van de Graaff accelerator, with subsequent optical bleach in a few cases. Samples used for stress measurements were cleaved and ground to the correct orientation, then polished and irradiated in air at room temperature. The were then mounted in the stress apparatus and immersed in the helium Dewar with cold windows. In most other cases a virgin sample was mounted in the copper block and all subsequent irradiations, absorbance measurements, temperature changes, bleaching procedures, etc., were made with the sample undisturbed within the Dewar vacuum. For electron irradiations in the Dewar, one of the outer windows is replaced with a thin aluminum "hat" which fits smoothly over a similar protuberance at the end of the Van de Graaff drift tube. This allows precise alignment of the sample with respect to the rectangularly scanned electron beam, but with separated vacuum systems for the accelerator and Dewar. The only disturbance of the beam is then by approximately 0.007 in. of aluminum foil, with effectively no air path.

Stress measurements are made with a concentric stainless steel tube arrangement. The sample is mounted on the end of the inner tube and is pushed against the bottom of the outer tube. The base is slotted so that absorption measurements can be made through either of two mutually perpendicular directions, and so that the sample can be illuminated from the side during absorbance measurements. The stress is continuously monitored by applying force to the inner tube through a mechanical force gauge with a dial readout. The force gauge fits into a holder mounted on the top of the outer tube, resulting in a completely self-contained unit. The stress apparatus fits into the Dewar through an O-ring seal at the top, and the gap between the tubes is sealed by two O-rings at room temperature near the top, thus allowing the helium reservoir to be easily pumped below the lambda point to eliminate bubbling.

Polarized light measurements are made with identical glan polarizers inserted at corresponding points in the sample and reference chambers to maintain identical light paths. With this arrangement, the base line can be adjusted to be flat to within 0.03 absorbance units over the entire spectral range of the instrument and to much better than this for the region of interest for a single measurement. Absorption measurements are made with light propagating perpendicular to the stress axis, and with light polarized so that the electric field vector is parallel or perpendicular to the stress direction. Under [110] stress, these crystals become biaxial and

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[13] A. A. Kaplyanskii, Opt. i Spektroskopiya **16**, 1031 (1964) [English transl.; Opt. Spectry. **16**, 557 (1964)].

[14] W. A. Runciman, Proc. Phys. Soc. **86**, 629 (1965).

TABLE I. Summary of data on F-aggregate-type centers in NaCl at liquid-helium temperature. Phonon assignments are made empirically by comparing experimental vibronic peak energies with theoretical zone-boundary critical-point phonon energies as listed in Table II.

	Broad band						
Band	Peak position (mμ)	Width eV	0-Phonon position (mμ)	Relative intensity 0-Phonon to broad band	Vibronic peak energies measured with respect to 0-phonon position (eV$\times10^2$)	Phonon assignment	Theoretical phonon energy (eV$\times10^2$)
R_1	543	0.16					
R_2	602	0.13	632.9	1.0×10^{-3}			
					1.5	TA[a] or TO[b] ⟨111⟩	1.55 or 1.63
					2.2	LA[c] ⟨111⟩ or TO ⟨100⟩	2.04 or 2.36
M	713	0.12					
N_1	825	0.04	837.5	$\sim3\times10^{-2}$			
					0.66	Pseudolocal mode	
					1.10	TA ⟨100⟩	1.07
					1.52	TA ⟨111⟩	1.55
					1.72	TO ⟨111⟩ or LA ⟨100⟩	1.63 or 1.77
					2.01	LA ⟨111⟩	2.04
					2.21	TO ⟨100⟩	2.36
					2.56	LO[d] ⟨100⟩	2.63
N_2	856	0.05	868.1	$0.5\text{–}1.5\times10^{-1}$			
	896–900	0.06	910.8				
			944.3				
			966.0				
	1160	0.08	1219	$\sim2\times10^{-2}$			
					1.21	TA ⟨111⟩	1.55
					1.56	TO ⟨111⟩	1.63
					1.88	LA ⟨100⟩ or ⟨111⟩	1.77 or 2.04
					3.09	2$\times$TA ⟨111⟩	3.10
					4.31	3$\times$TA ⟨111⟩	4.65
					5.69	4$\times$TA ⟨111⟩	6.2
Impurity	1282	0.09	1404	$\sim2\times10^{-3}$			
					1.31	TA ⟨111⟩	1.55
					1.49	TO ⟨111⟩	1.63
					1.94	LA ⟨111⟩	2.04
					2.69	2$\times$TA ⟨111⟩	3.1
					4.11	3$\times$TA ⟨111⟩	4.65
					5.50	4$\times$TA ⟨111⟩	6.2
					6.87	5$\times$TA ⟨111⟩	7.75
					8.05	6$\times$TA ⟨111⟩	9.3
M^+	1215	0.08	1306	$0.5\text{–}1\times10^{-2}$			
					0.76	Pseudolocal mode	
					1.39	TA ⟨111⟩	1.55
					1.50	TO ⟨111⟩	1.63
					1.73	LA ⟨100⟩	1.77
					2.9	2$\times$TA ⟨111⟩	3.1
					4.2	3$\times$TA ⟨111⟩	4.65
					5.6	4$\times$TA ⟨111⟩	6.2
R^+(?)	1468	0.07	1549	$\sim3\times10^{-2}$			
					1.3	TA ⟨111⟩	1.55
					1.55	TO ⟨111⟩	1.63
					3.2	2$\times$TO ⟨111⟩	3.26

[a] Transverse acoustic. [b] Transverse optic. [c] Longitudinal acoustic. [d] Longitudinal optic.

measurements are made with light incident on both (001) and ($1\bar{1}0$) faces.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In the presentation and discussion of results for each of the centers mentioned below we show figures of the observed vibronic structure, and also results of stress splitting of the 0-phonon lines. Energy of each vibronic peak, measured with respect to its 0-phonon line position, is shown on the corresponding figure. These measured values for all of the peaks observed on all the bands in NaCl which show fine structure are gathered together in Table I. The empirical phonon assignments given are made, as was discussed more fully in Ref. 2, by comparison with theoretically calculated phonon energies[15] at the Brillouin zone boundary in high-symmetry directions. These theoretical values are listed in Table II. The appropriate ones are also listed for each

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[15] A. M. Karo and J. R. Hardy, Phys. Rev. **141**, 696 (1966). This is a more detailed calculation than those used in Ref. 2, but none of the conclusions drawn there needs to be significantly changed.

case in Table I for comparison with the experimental results. Along with the above information in Table I, we list experimental values for the half-widths of all the *F*-aggregate–type centers we have consistently seen in NaCl, as most of these numbers do not seem to be in the literature. Finally, we list approximate values for the ratios of integrated 0-phonon line intensities to their associated broad band intensities. Uncertainties are due primarily to difficulty in determining a good base line for each band on the absorption curves. These ratios enable one to obtain estimates for the number of vibrational quanta, S, excited at the broad band peak from the expression[16] $e^{-S}=I_0/I_b$, where I_0/I_b is the intensity ratio given in the Table. S values obtained range from 2 to 7, and are in reasonable agreement with the bandwidths.

Experimentally, the splitting of all the 0-phonon lines measured is found to be linear with stress. In this approximation the energy shift δ_i of a given component under stress is proportional to the elastic deformation and related to the stress tensor $\{\sigma_{ik}\}$ by a set of constant coefficients A_{ik} which may be considered as a symmetric "piezospectroscopic" tensor $\{A_{ik}\}$, following the notation of Kaplyanskii.[10] Specifying the coefficients A_{ik} then specifies the magnitude of the splitting of each component as a function of stress. These coefficients, defined according to Table III in Ref. 10, are given in all cases where it has been possible to obtain reasonably consistent values. In all cases, the number of observed components is consistent with that expected for simple orientational degeneracy of the possible symmetry types given in Ref. 10. There are several cases where some components are obviously broadened, probably due to partial removal of electronic degeneracies in excited-state levels but perhaps in some cases due to deformation of the samples with resultant inhomogeneous strain. Also, most of the relative intensity measurements can be reasonably interpreted in terms of simple electronic dipole transition moments, where the absorption intensity $I=(\mathbf{E}\cdot\mathbf{D})^2$, where $\mathbf{E}$ is the electric field and $\mathbf{D}$ the dipole transition moment. Where this interpretation is inferred, the expected intensities are indicated on the figures showing stress results. There are some discrepancies in intensities where we assume the transition is of this type, perhaps because of superposition of transitions of different polarizations involving almost degenerate electronic states. In one case we have not been able to interpret the observed intensities in terms of any simple type of transition. All of the experimental results for stress measurements of the centers studied are summarized in Table III.

TABLE II. Theoretical zone-boundary critical-point energies of normal lattice phonon modes (transverse acoustic, longitudinal acoustic, transverse optical, and longitudinal optical) propagating in ⟨100⟩ and ⟨111⟩ directions. Values are obtained from dispersion curves given in Ref. 15.

	TA	LA	TO	LO
⟨100⟩	1.07	1.77	2.36	2.63
⟨111⟩	1.55	2.04	1.63	3.00

A. *R* Bands

Details of the vibronic structure visible on the R_2 band are shown in Fig. 1. Two reasonably prominent shoulders are present on the low-energy side of the broad band, at 0.015 eV and 0.022 eV from the 0-phonon line. These values are in fairly good agreement with theoretical zone-boundary phonon energies, as listed in Table I. The R_2 0-phonon line has a true width at half-maximum of approximately 4.5 Å (1.4×10^{-3} eV) as measured at helium temperature. Splitting of the 0-phonon line with the application of uniaxial stress is

TABLE III. Summary of experimental results of stress measurements on *F*-aggregate centers in NaCl. Proposed models are based on stress measurements plus other available experimental evidence. Probable validity of each model is discussed in text.

Band and 0-phonon position	Number of components stress direction			Symmetry	Direction of dipole transition moment	Model
	[100]	[111]	[110]			
R_2 6329 Å	1	2	2	Trigonal	⟨112⟩ and ⟨110⟩ in ⟨111⟩ plane of defect	3 *F* centers
N_1 8375 Å	2	3	4	Monoclinic I	⟨112⟩	2 *F* centers in ⟨112⟩ directions
N_2 8681 Å	2	3	4	same	⟨110⟩ Symmetry axis	4 *F* centers Pick N_1 Model
1.219 μ	2	3	4	same	⟨110⟩	?
M^+ 1.306 μ	2	3	4	same	⟨112⟩	2 *F* centers in ⟨110⟩ directions. One ionized with distorted surroundings
Impurity 1.404 μ	2	2	3	Rhombic I	?	Perhaps halogen impurity with 2 *F*-center neighbors in ⟨110⟩ directions
1.549 μ	2	2	3	same	⟨110⟩ Symmetry axis	R^+ from growth behavior but not consistent with symmetry.

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[16] D. B. Fitchen, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965), p. 383.

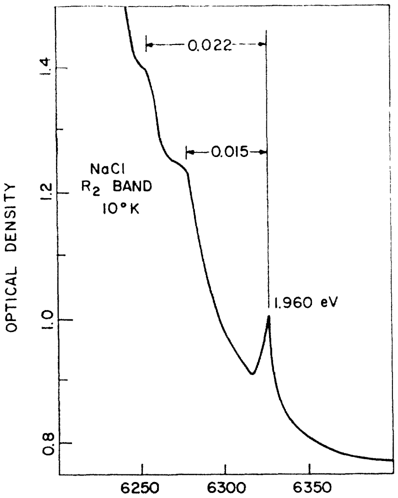

FIG. 1. R_2 band in NaCl near liquid-helium temperature showing 0-phonon line and vibronic structure.

shown in Fig. 2. The unstressed position of the line is indicated by the heavy vertical line at 6329 Å. The solid curves indicate results obtained with the electric vector of the light polarized parallel to the stress axis, and the dashed curves with it perpendicular to the stress axis. Under [110] stress measurements are made with light incident on both the (001) and (1$\bar{1}$0) faces, as indicated. All the intensities are normalized so that the 0-phonon intensity at zero stress is unity. The results clearly indicate splitting into one, two, and two components under the listed stress directions, as expected for a defect of trigonal symmetry. This result gives further confirmation[4,12,17] to the F_3 model for this center as originally proposed by Van Doorn and Haven[18] and Pick.[19] This model consists of three F centers at nearest-neighbor positions in an equilateral triangle in {111} planes.

Silsbee[4] has discussed the properties of the electronic states to be expected for a continuum model of the F_3 center. The 0-phonon transition should be from a doubly degenerate ground state of E-type symmetry to an excited state of A_2 symmetry which would have dipole moment transitions along ⟨110⟩ and ⟨112⟩ directions in the {111} planes of the defect. In general it should be possible to distinguish the two states by observation of a stress- and temperature-dependent dichroism. At 2°K, we obtain best agreement with the observed intensities by assuming that ground states involving both types of transition moments remain approximately equally populated. That is, the splitting due to removal of orientational degeneracy is much greater than that due to removal of electronic ground-state degeneracy. The preferred ⟨112⟩ and ⟨110⟩ transition moment directions for each defect orientation seem to be those which are most strongly compressed by the application of stress, and not a single set of mutually perpendicular transition moments. This point perhaps requires some elaboration. For each orientation of the undistorted R center, with perfect trigonal symmetry, there are three equivalent sets of mutually perpendicular ⟨112⟩ and ⟨110⟩ directions in the {111} planes of the defect. With applied stress, electronic states resulting in transition moments along these directions are no longer all equivalent. There are at least two alternative processes which might then take place. (1) A single set (or two equivalent sets) of ground states involved in mutually perpendicular transition moments might first be preferred so that all electrons for a given R center orientation would be shifted into this pair of ground states. Increasing stress would then gradually split these states, with the eventual result that all electrons would be in the single lowest energy state, and only one transition moment would be observed. This seems to be the case in KCl.[4] Another interpretation seems to fit our results in NaCl somewhat better. (2) This is to assume that Jahn-Teller distortion initially selects out a particular set of states for each R center in a random fashion. Applied stress should then,

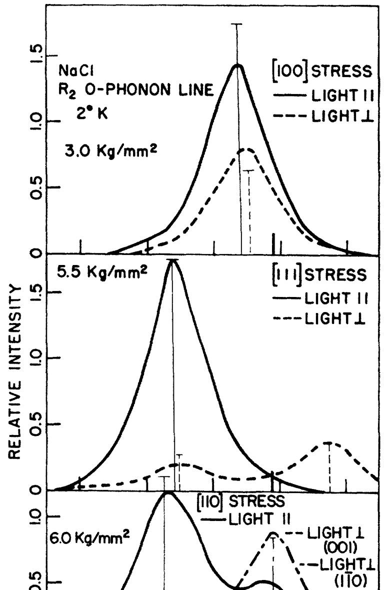

FIG. 2. Stress splitting results in R_2 0-phonon line under [100] [111], and [110] stress directions. Trigonal symmetry is indicated. Intensities are normalized to unity at zero stress. Solid curves give results with light polarized parallel to stress axis, and dashed curves with light polarized perpendicular. Under [110] stress the crystals become biaxial and measurements are made with light incident normal to (001) and (1$\bar{1}$0) faces, as indicated. The unstressed position is given by the heavy vertical line. The thin vertical lines give positions of each component calculated from best values of stress splitting coefficients and also expected intensities assuming equally strong ⟨110⟩ and ⟨112⟩ electric dipole transition moments.

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[17] F. Lanzl and W. Von Der Osten, Phys. Letters **15**, 208 (1965).

[18] C. Z. Van Doorn and Y. Haven, Phillips Res. Rept. **11**, 479 (1956).

[19] H. Pick, Z. Physik **159**, 69 (1960).

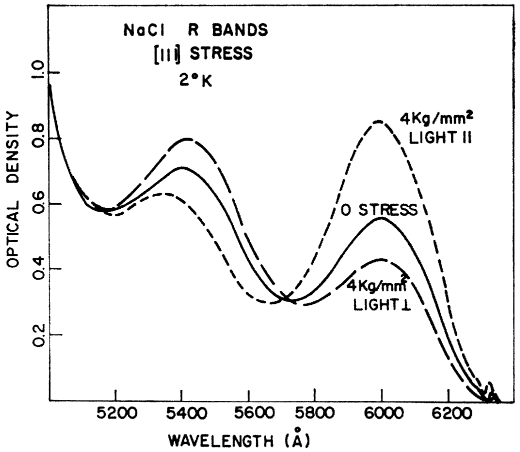

FIG. 3. Effects of stress on intensity of R_1 and R_2 broad bands in NaCl.

in general, cause a splitting off of these sets of states from each other, as well as a splitting within each set. Barring a tunneling process between different sets of states, the electrons would remain in the lowest state within a given set. In some centers this would be the state resulting in a $\langle 112\rangle$ transition; in others the $\langle 110\rangle$ transition would result, and both types of transitions would be observed.

Calculated intensities, based on the assumption that each component consists of an equal mixture of transitions with $\langle 110\rangle$ and $\langle 112\rangle$ polarizations, are indicated on Fig. 2 by thin vertical lines. Positions of these thin lines are calculated from the relations given in Ref. 10, using the stress coefficients listed below, to show the expected splitting of each component. Lines showing expected intensities for the different light polarizations are slightly displaced for clarity. Our best values for the stress coefficients are: $A_1 = 1.9 \pm 0.2$, and $A_2 = -1.8 \pm 0.2$, in $\text{cm}^{-1}\,\text{kg}^{-1}\,\text{mm}^2$.

Applied stress also has a significant effect on the broad R_1 and R_2 bands as is shown in Fig. 3 for the case of [111] stress. This is in agreement with similar results in KCl.[4] For all stress directions measured, the R_2 broad-band intensity increases or decreases in approximate proportion to the 0-phonon line intensity, while the R_1 band intensity changes in the opposite sense and by a smaller fraction. These are the only bands among all those we have studied in NaCl which show any significant effect of stress on broad-band intensity.

B. *N* Bands

There are at least three prominent bands, and probably more, in the spectral region just beyond the M band in relatively heavily colored NaCl. An example of the absorption in this region is shown in Fig. 4. The closest peak to the M band, with maximum at about 8250 Å, is the only one to show detailed vibronic structure. Its spectral location and symmetry characteristics as presented here indicate that it probably corresponds to the band called N_1 in other alkali halides, and will be so-called here. The second band, peaking at about 8550 Å, is never well resolved, but it does show a relatively strong 0-phonon line at 8681 Å with essentially no vibronic structure. We call this the N_2 band, because of its location and symmetry properties. The third band, peaking at about 8960 Å, and other bands perhaps present do not show any fine structure, although we have occasionally seen small 0-phonon lines at approximately 9108, 9443, and 9660 Å. The N_1 band is almost always the most prominent of the bands in this region, but the others are found to vary in order of intensity.

1. N_1 Band

The vibronic structure associated with this center is among the most detailed and varied we have seen in any of the alkali halides. The results shown in Fig. 4 were previously reported,[2] but we present them again here for completeness of this paper. There are seven different vibronic peaks resolvable.[20] The first of these appears to be a pseudolocalized mode arising out of the TA $\langle 110\rangle$ mode density of states, while each of the others agree to considerably better than 10% with a theoretical normal-lattice phonon critical-point energy at the zone boundary in a high-symmetry direction. These correlations are listed in Table I.

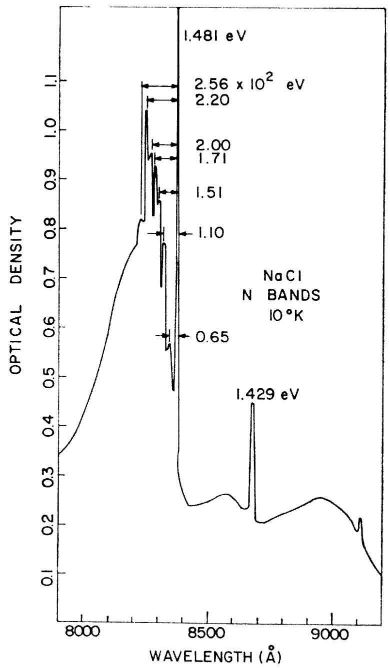

FIG. 4. N band region in NaCl near-liquid-helium temperature showing N_1 and N_2 0-phonon lines and very detailed vibronic structure on N_1 band.

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[20] A. E. Hughes, Proc. Phys. Soc. **87**, 535 (1966). This detailed study of the N_1-center symmetry and vibronic structure appeared as the present manuscript was in the final stages of preparation. With increased resolution the vibronic spectrum is found to be even more detailed than indicated here. The symmetry results are in substantial agreement with those presented here.

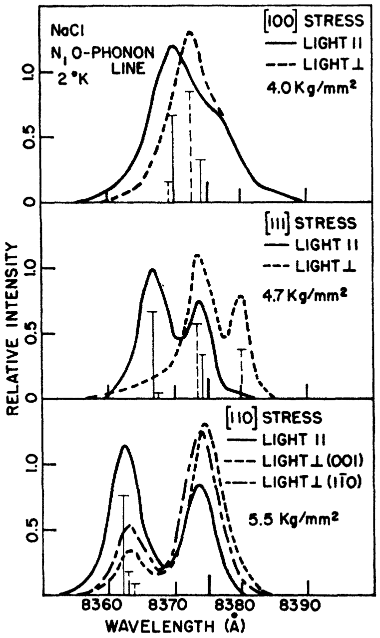

FIG. 5. Stress splitting results on N_1 0-phonon line, as in Fig. 2. Results indicate monoclinic I symmetry. Calculated intensities are for electric dipole transition in $\langle 112\rangle$ direction perpendicular to $\langle 110\rangle$ symmetry axis, and in (111) plane of defect. Intensities are not indicated for unresolved components under [110] stress.

Observed splitting of the N_1 0-phonon line by application of uniaxial stress is shown in Fig. 5. Unfortunately, the N bands in NaCl are in a spectral region where the resolution and signal-to-noise ratio of the spectrophotometer are at their worst. As a result, it is quite difficult in some cases to obtain completely well defined resolution of the lines into their components. Measured linewidth of the N_1 line under optimum conditions in this instrument is about 5 Å. This, however, is with an effective slit width of about 2.5 Å, so the true linewidth is considerably smaller.

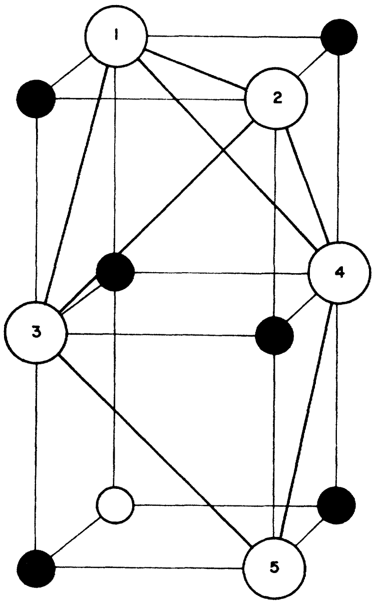

FIG. 6. Segment of rocksalt-crystal structure. Small solid circles are alkali ions, and large open circles are possible F-center sites.

Resolution into the proper number of components for an allowed orientational degeneracy is particularly difficult for [110] stress. However, the very clear splitting into three components under [111] stress is sufficient to give unambiguous indication of monoclinic I type symmetry, assuming only orientational degeneracy. This implies two components under [100] stress and four under [110] stress. Due to the incomplete resolution into components we have not been able to obtain reliable values for the stress coefficients. The measured relative intensities appear to be most nearly consistent with an assumed electric dipole transition moment in $\langle 112\rangle$ directions, although the absolute values are mostly somewhat larger than the expected intensities for this transition moment indicated on the figure.

There are two equally reasonable F-aggregate models for this symmetry and transition moment. The first is the Pick N_1 model,[19] consisting of four F centers arranged in a parallelogram in $\{111\}$ planes, with the transition moment directed along the $\langle 112\rangle$ diagonal. With reference to Fig. 6, this model would consist of the four F centers numbered 1, 3, 5, and 4, with the transition moment along the line connecting 1 and 5. The second possibility is a model of two F centers such as those numbered 1 and 5 in Fig. 6, with the transition moment along the line connecting the two components. The second model seems to be strongly favored by the results of growth kinetics measurements in KCl,[21] which indicate that the N_1 band in that material is associated with two F centers. In order to resolve this question it will probably be necessary to do both the stress and growth kinetics measurements on the same material.

The effect of stress on the N_1 broad band is not nearly so dramatic as on the R bands. The only apparent result we see is a slight smearing out of the vibronic structure, probably due to the splitting of the pure electronic transition to which the vibronic transitions are coupled.

2. N_2 Band

The band associated with the 0-phonon line shown in Fig. 4 at 8681 Å is never well resolved from the other broad bands in the same region of the spectrum, and never shows significant vibronic structure. Limitations as to resolution of the line under stress apply more strongly to this line than to the N_1 line, as it is generally somewhat less intense. The best data we have been able to obtain are shown in Fig. 7. We find the same number of components as with the N_1 line, that is two, three, and four under the three stress directions. In fact, even though the apparent widths are somewhat broader due to even poorer resolution, the components are more clearly separated than in the case of the N_1 line. Although the symmetry type must be the same, monoclinic I, the relative intensities of the components are quite different. In this case the intensities are reasonably

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[21] S. Schnatterly and W. Dale Compton, Phys. Rev. 135, A227 (1964).

close to that expected for dipole transitions along the ⟨110⟩ symmetry axes of the defects. Calculated intensities based on this assumption are shown on the figure, and agreement is probably within our experimental error. Calculated values for the peizospectroscopic tensor components are: $A_1=-0.7$, $A_2=1.6$, $A_3=2.9$, $A_4=-0.7$, with estimated errors of approximately ± 0.2.

The same *F*-aggregate models discussed above for the N_1 center are appropriate here. However, the transition moments are in the ⟨110⟩ symmetry axis directions, that is, along the line connecting *F* centers numbered 3 and 4 in Fig. 6. On the basis of these symmetry arguments alone, a model of three *F* centers in the shape of an obtuse triangle, such as *F* centers numbered 1, 3, and 5, is equally appropriate. The Pick N_1 model seems to be preferred on the basis of the growth kinetics measurements in KCl,[21] but again, both measurements will have to be made on the same material in order to completely resolve the question.

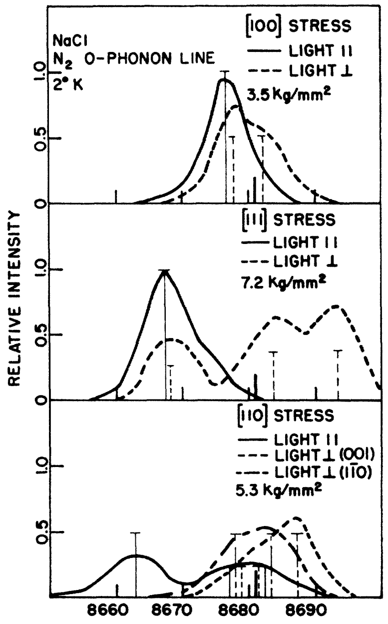

FIG. 7. Stress splitting results on N_2 0-phonon line. Monoclinic I symmetry is indicated, as for the N_1 line, but intensities are more nearly consistent with a dipole transition moment parallel to ⟨110⟩ symmetry axis. Calculated intensities are based on this assumption.

C. 1.16-μ Band

In quite heavily colored samples another band which appears to be associated with an intrinsic defect is found to grow in the infrared beyond the *N* bands. This band is visible immediately upon cooling from room temperature in the dark, and hence must be stable at room temperature. It is shown in Fig. 8. The vibronic structure is fairly detailed, with coupling to three modes being apparent. All of the infrared bands yet to be discussed appear to couple to at least the first two of these modes, but with varying relative strengths. The measured energies of the first phonon peak vary from 0.0121 eV in this case to 0.0139 eV for the M^+ band to be discussed below. These values are about midway between theoretical phonon energies for the transverse acoustic (TA) ⟨100⟩ and ⟨111⟩ modes of 0.0107 eV and 0.0155 eV. Measured values for the second peak range from 0.0149 to 0.0156 eV. These are very near to the TA ⟨111⟩ mode energy, but are also quite close to the transverse optic (TO) ⟨111⟩ mode energy of 0.0163 eV. It is our feeling that in each case the two observed peaks correspond to coupling to TA and TO ⟨111⟩ modes. This view is based primarily on the fact that the theoretical density of states functions show very strong and sharp peaks at these two points, while there is only a relatively weak shoulder in the density of states at the TA ⟨100⟩ critical point.[15]

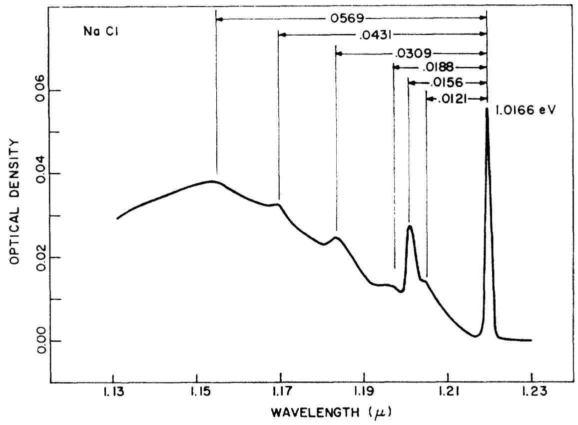

FIG. 8. 1.16-μ band showing 0-phonon line and vibronic structure.

Unfortunately, this band is so small relative to the usual *F*, *R*, *M*, and *N* bands that it is impossible at this

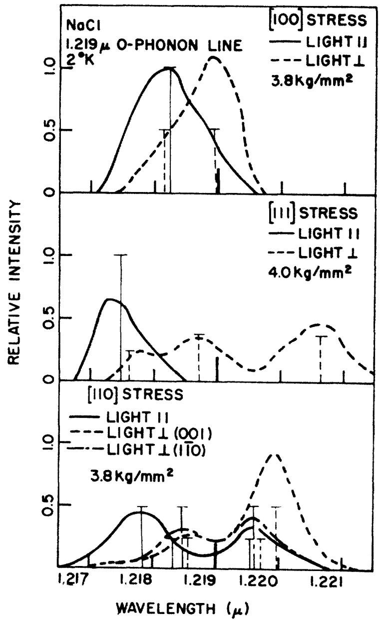

FIG. 9. Stress splitting results on 0-phonon line of 1.16-μ band. Results are indicative of monoclinic I symmetry with dipole transition moment parallel to ⟨110⟩ symmetry axis.

time to make any statement from its growth behavior as to its relationship to the more often seen F-aggregate centers. We have successfully observed stress splitting of its 0-phonon line at 1.220 μ, however, with the results shown in Fig. 9. The splittings are clearly consistent with monoclinic I type symmetry, and the relative intensities of the components are reasonably close to that expected for an electric dipole transition parallel to the [110] symmetry axis, as for the N_2 line. With no further information available there is very little justification for speculation as to the nature of the responsible center. However, it might be pointed out that the symmetry properties are consistent with the model of three F centers in an obtuse triangular arrangement such as the ones numbered 1, 3, and 5 in Fig. 6.

D. Impurity Center

All of the absorption bands which we have discussed up to this point appear to be associated with intrinsic defects in the pure but damaged host crystal. We have seen one center in the near infrared region of NaCl which seems to be an F-aggregate center associated with an impurity. This is shown in Fig. 10. This center is found to grow with extensive room-temperature irradiation in crystals from at least two sources (Harshaw and Semi-Elements). However, for similar samples subjected to the same treatment the concentration is almost an order of magnitude larger in the Semi-Elements material. For example, 10 to 20 min at 1 or 2 μA/cm^2 is generally sufficient for easy observation in the Semi-Elements material. All other bands grow approximately the same way in all nominally pure crystals we have used. This is the basis for the claim that this is an impurity associated center, together with the fact that the concentration saturates with very large irradiation dose. We have had a semiquantitative spectral analysis done on samples from both sources, with no indication from relative metallic impurity concentrations that the responsible element is in this category. Halogen or negative radical impurities are probably the most likely candidates.

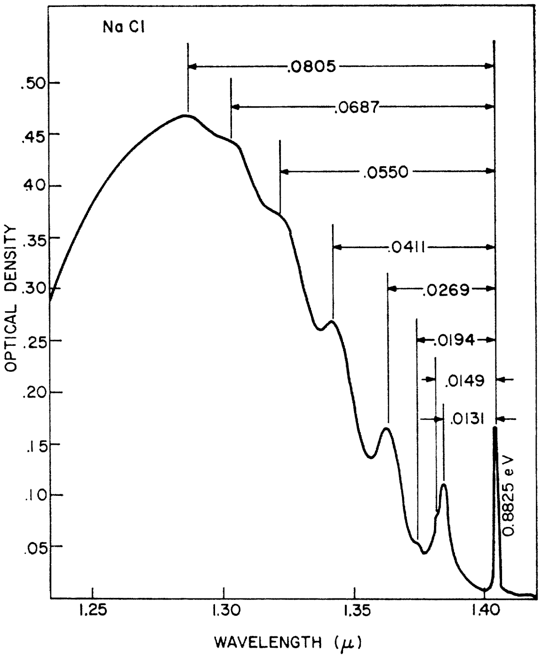

FIG. 10. Impurity-associated center showing 0-phonon line and vibronic structure.

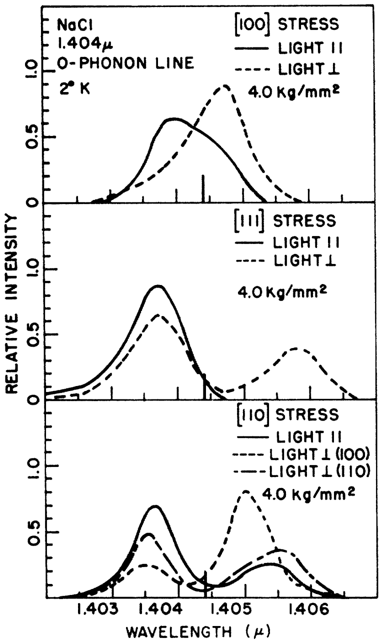

FIG. 11. Stress splitting results on 0-phonon line of impurity-associated center.

Phonon coupling appears to be to essentially the same modes as on the band discussed just above. However, the relative strengths of the TA ⟨111⟩ and TO ⟨111⟩ mode couplings are reversed. This is reflected further in the shorter interval between successive large peaks associated with multiple excitation.

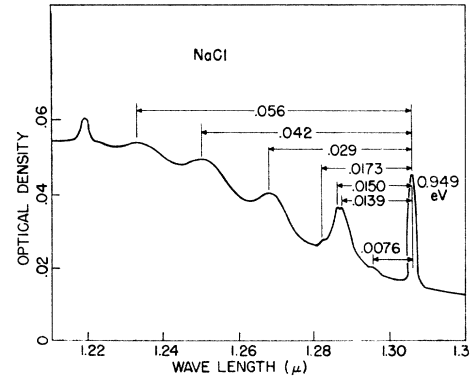

FIG. 12. M^+ band showing 0-phonon line and vibronic structure. Data taken while sample illuminated with white light from "IR 2" source. Peak at 1.22 μ is 0-phonon line of band shown in Fig. 8.

Results of stress splittings are shown in Fig. 11. The splitting into two, two, and three components seems to be unambiguous and is indicative of a defect with rhombic I symmetry. This is the symmetry expected for the *M* center, and would be consistent, for example, with a defect consisting of a halogen impurity and two neighboring *F* centers along ⟨110⟩ directions. However, measured intensities do not seem to be consistent with any reasonable assumption relating to the type of transition moment involved.

E. Ionized Centers

In addition to the centers we have already discussed, and which are stable at room temperature, we have observed two centers in heavily colored NaCl which appear to be associated with positively ionized *F*-aggregate centers. These are produced by illumination at low temperature with white light or monochromatic light of certain wavelengths. Their general behavior is similar, and we will discuss them together here. The band shapes and vibronic structure are shown in Figs. 12 and 13. The electron-lattice coupling is quite similar in both of these cases, and also quite similar to that of the two bands just previously discussed. In the band shown in Fig. 12 the TA and TO ⟨111⟩ modes are coupled with almost the same strength, and the spacing of peaks associated with multiple excitation is midway between that shown in Figs. 8 and 10. In addition, there is a weak pseudolocalized mode. The results for the second center in this category, shown in Fig. 13, indicate coupling to only the TA and TO ⟨111⟩ modes.

The band peaking at 1.2 μ with its 0-phonon line at 1.306 μ is produced most efficiently with illumination in the *M* region of 6500 to 7500 Å, while the band peaking at 1.47 μ is generally produced with comparable efficiency by illumination anywhere in the range from 4000 to 7000 Å. Growth rates and maximum intensity obtained depend upon light intensity as well as wavelength, with several minutes generally being required to approach an asymptotic value. When the exciting light is turned off, up to 50% of the band intensity is sometimes seen to decay within one second, although the usual fraction is much less. Part of the remaining intensity decays over a period of minutes, and a considerable fraction is generally stable over at least a period of hours. A typical growth and decay curve under various conditions for the 1.306-μ line is shown in Fig. 14. While the bands are produced in sufficient concentration for precise measurement, they are still so much smaller than the *R*, *M*, or *N* bands from which they must form that we have not been able to correlate growth of one with decay of others. On the basis of the growth characteristics described above, the most likely assignments for these bands would seem to be M^+ and R^+ for the 1.2-μ and 1.47-μ bands, respectively.

Results for apparently similar bands in several other alkali halides have been recently published.[7] In that case bands identified as M^+ and R^+ were observed in KCl and KBr. These were produced by x raying fairly heavily colored samples at helium temperature, in order to produce hole centers, followed by optical bleach in the spectral region of these hole centers. This results in a reduction of intensity in both the hole centers and *F*-aggregate centers, and the growth of new bands. The growth rate of two of the new bands is found to be directly proportional to the decay of the *M* and *R* bands and they are presumably due to positively ionized centers of these two types, the extra electron being removed by recombination with the holes optically excited away from the hole centers. These new bands could be enhanced by illumination in the *R* and *M* regions at liquid-helium temperature. In some cases they were also found to be present immediately following low temperature x irradiation, due to direct ionization of the neutral centers by the x rays. Also, the reverse process is initiated by *F* light illumination, presumably resulting from *F* electron capture.

We have reproduced most of these results in KCl, substituting 2-MeV electron irradiation for the x irradiation at helium temperature. We were unsuccessful, however, in attempts to produce the ionized centers

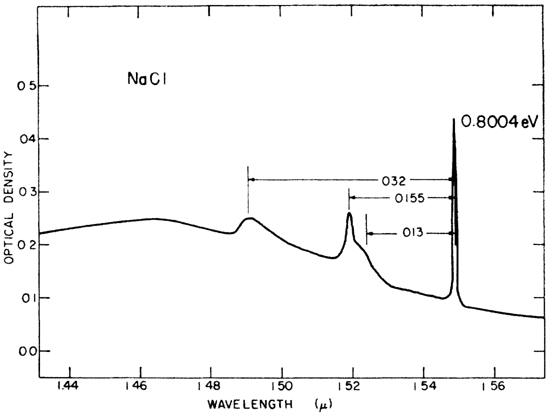

FIG. 13. Ionized center band at 1.47 μ showing 0-phonon line and vibronic structure.

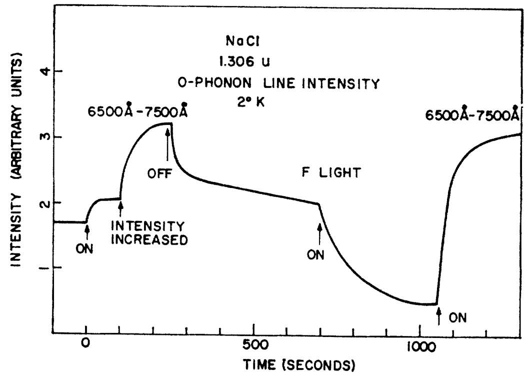

FIG. 14. Typical growth and decay characteristic of 0-phonon line at 1.306 μ associated with ionized center shown in Fig. 12.

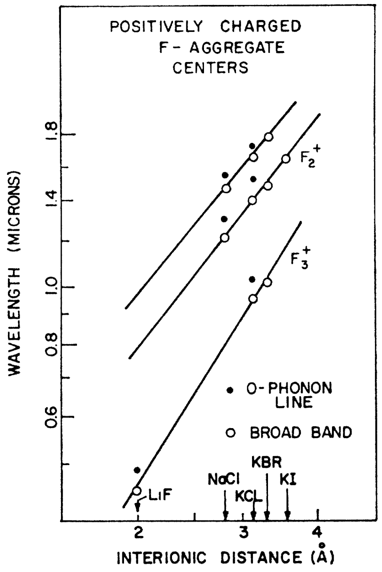

FIG. 15. Mollwo-Ivey plot for centers identified as positively ionized F-aggregate centers. NaCl data are from the present work; KCl, KBr, and KI data are from Ref. 7; and LiF data are from Ref. 22.

in KCl by optical bleach alone without the low-temperature irradiation. In NaCl we find the 1.47-μ band produced directly upon low-temperature irradiation, but were unsuccessful in attempts to produce the ionized centers by bleach in the hole-center region. As in KCl, both of the bands are decreased in intensity by F bleach at helium temperature.

Broad band and 0-phonon line positions for our ionized centers in NaCl, for the bands seen by Schneider and Rabin[7] in KCl, KBr, and KI, and also for some very recent results of Farge *et al.*,[22,23] in LiF are shown in Fig. 15 in the form of a Mollwo-Ivey plot. This plot strongly confirms the assignment of our 1.2-μ band as M^+. Our 1.47-μ band falls right on a line with the centers in KCl and KBr which Schneider and Rabin tentatively identify as N_1^+. Their identification seems to be primarily based on the observation that these new centers were seen only in crystals containing fairly large concentrations of N_1 centers. The excellent straight lines defined by all these centers strongly indicate that all of the bands on a given line are associated with a single center. However, the growth behavior of our 1.47-μ band in NaCl strongly indicates that it is *not* associated with N centers. We have never been able to produce it by exciting with light in the N band region, and have almost always been successful in producing it with light anywhere in the region from the long-wavelength side of the F band, through the R-band region, to the short-wavelength side of the M band. Also, on one occasion we produced the 1.47-μ band in fairly high concentration by low-temperature irradiation in a sample containing very few N centers.

We have not seen any bands growing in the region between the M and N_1 bands in NaCl appropriate to the position predicted for the F_3^+ band by the lower line in Fig. 15. However, this should probably not be construed as convincing evidence that this band cannot be produced in NaCl. Most of our samples are already very heavily colored in this region. Particularly, they have always contained very large M bands.

In an attempt to obtain more information about these centers we performed stress measurements on their 0-phonon lines. Results for the 1.306-μ line are given in Fig. 16. The splitting observed can only be interpreted in terms of monoclinic I type symmetry, as has been found for the N bands and the 1.220-μ line. The relative intensities are quite close to that expected for a dipole transition in ⟨112⟩ directions, and these calculated values are indicated on the figure. While this is certainly not the result expected for the rhombic I symmetry of the M center, it is easy to qualitatively understand how the positively ionized M center might be distorted into monoclinic I symmetry. It is only necessary to assume that the remaining electron is predominantly localized in one of the halogen vacancies. There would then be a mutual repulsion of all the alkali ions surrounding the ionized vacancy, removing two of the symmetry elements of the M center, and leaving only the single twofold axis along the ⟨110⟩ directions connecting the two components of the defect. To explain the observed results for the intensities of the 1.306-μ line components, it seems necessary to assume that the transition moments are in the ⟨112⟩ directions perpendicular to the ⟨110⟩ defect axes.

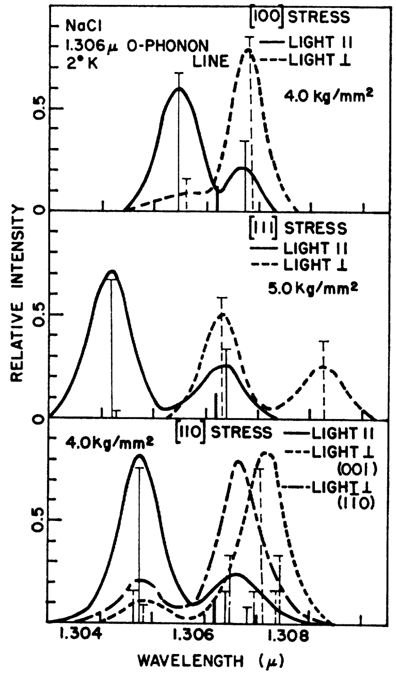

FIG. 16. Stress splitting results on M^+ 0-phonon line at 1.306 μ. Symmetry is monoclinic I and intensities are nearly consistent with assumed transition moment in ⟨112⟩ direction perpendicular to ⟨110⟩ symmetry axis.

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[22] Y. Farge, G. Toulouse, and M. Lambert, J. Phys. (Paris) (to be published).

[23] *Note added in proof.* Y. Farge, G. Toulouse, and M. Lambert, Compt. Rend. **262B**, 1012 (1966). These authors have also observed the F_2^+ center in LiF, peaking at 6450 Å, with 0-phonon line at 7633Å.

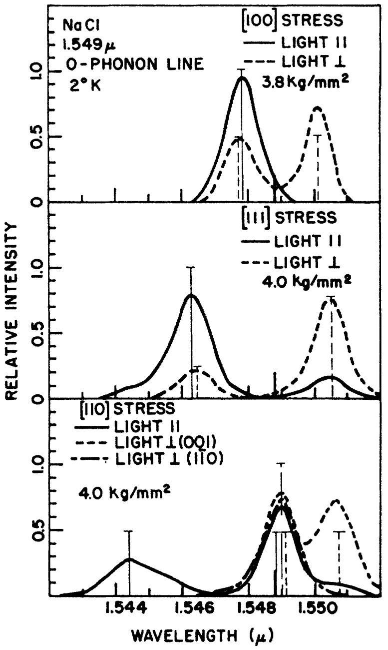

FIG. 17. Stress splitting results of 1.549-μ 0-phonon line. Symmetry is clearly rhombic I. Intensities are essentially consistent with electric dipole transition parallel to ⟨110⟩ symmetry axis. See text for discussion of broadening of widely split components.

Results for the stress splitting of the 1.549-μ line are shown in Fig. 17. The splitting is quite well defined into two, two, and three components, which is that expected for a rhombic I center. A reasonable theoretical fit to the observed splitting is obtained with our best values for the stress coefficients as follows: $A_1 = -1.3 \pm 0.2$, $A_2 = 1.3 \pm 0.2$, and $A_3 = 3.5 \pm 0.2$. At larger stresses each of the widely split components is broadened, with the appearance of further interior structure. We have found the shape of these individual components to vary somewhat from sample to sample, but it is generally reasonable to resolve them into four components. If this is a real effect, it can only be due to removal of electronic degeneracy, and if it were associated with ground-state splitting would imply the existence of a three electron system with spin 3/2. If this were the case, this band might be associated with a metastable quartet state of the *R* center. However, we have observed no consistent variation of relative intensities with the magnitude of splitting, so it appears that this structure must be due to splitting of the excited state involved or possibly is simply a spurious effect due to inhomogeneous strain in the samples. In any case, it is difficult to see how any excited, or ionized state of the *R* center or present models of the *N* centers could exhibit rhombic I type symmetry.

Further evidence against this being a metastable state is found in the fact that the lifetime is quite long while the limiting intensity we have been able to produce is still extremely small compared to that of the *R* bands. If this were a metastable state with the observed lifetime, the intensity should continue to increase during the excitation process, at least until the ground and excited states were equally populated. On the other hand, the concentration of an ionized center would reach an equilibrium value dependent on the intensity of the exciting light, and on the mobility and lifetime of the free electrons produced by the light. The sudden decrease in intensity observed when the light is turned off is consistent with rapid recombination of some of the ionized centers with free electrons, with the concentration of persisting ionized centers being determined by the number of electrons trapped elsewhere in the crystal. On balance, then, it appears that this is an ionized center, although at present we see no way to reconcile the observed symmetry with the growth behavior, or with the assignment of apparently similar centers in KCl and KBr as N_1^+.

Finally, it should be pointed out that we have seen no evidence for the existence of negatively charged *F*-aggregate centers in NaCl, although *R'* and/or *M'* centers have now been tentatively identified in five other alkali halides.[9]

IV. SUMMARY AND CONCLUSIONS

We have presented experimental results showing the detailed shapes of the vibronic side bands associated with a number of color-center absorption bands in NaCl at helium temperature. The observed vibronic peak energies can be very closely correlated in almost all cases with zone-boundary critical point energies of normal lattice phonons in high-symmetry directions. The only two vibronic peaks observed in NaCl (on the N_1 and M^+ bands) which cannot be accounted for in this manner are much lower in energy than any theoretical critical point phonon energies and appear to be due to pseudolocalized modes arising out of the normal density of states of transverse acoustic modes. All of these results are summarized in Table I. Even though this empirical correlation of almost thirty observed vibronic peaks appears to be almost unique, there is no real theoretical justification for making these assignments. Also, while the agreement is quite good with theoretical critical point energies, there seems to be essentially no consistent agreement with theoretically predicted density-of-states functions. On a statistical basis, coupling to TO ⟨111⟩ and TA ⟨111⟩ modes seems to be preferred. Most of the models proposed consist of various aggregations of *F* centers in {111} planes. Perhaps it is reasonable, then, to conclude that coupling tends to be with transverse phonon modes propagating in ⟨111⟩ directions perpendicular to the defect planes, so that the defect surroundings oscillate predominantly in this plane. However, it must also be pointed out that, in total, there are just as many cases where the apparent coupling is to longitudinal modes or phonons propagating in ⟨100⟩ directions. Finally, the observed phonon coupling at four near infrared centers (all those beyond the *N* bands) is quite similar, with apparent strong coupling to TO and TA ⟨111⟩ modes in all four cases, and weaker coupling to longitudinal acoustic modes in at least three cases. This is in spite of the fact that, from their over-all behavior, these bands appear to be associated with at least three different types of centers.

It is obvious that no final conclusions can be drawn about the electron-phonon coupling at these centers until firm models for these centers and their electronic states are established. As a first step in this direction, we have presented results of measurements of the stress-induced splitting of 0-phonon lines of all the centers in NaCl that we have been able to find which show fine structure at helium temperature. All of these measurements can be reasonably interpreted in terms of the removal of orientational degeneracy, with the result that the symmetry type of each of the centers studied can be unambiguously given. These results are summarized in Table III.

In several cases the relative intensities of line components under stress, as viewed with light polarized in different directions, allows relatively firm conclusions to be drawn as to nature and orientation of the transition moment associated with a given center. These results are also given in Table III.

Stress splittings for the R_2 0-phonon line further verify the well established conclusion that the R center consists of three F centers in an equilateral triangle. Measured relative intensities of the components are in good agreement with the assumption that the transition is from a doubly degenerate ground state to a singlet excited state, with electric dipole transition moments in $\langle 112\rangle$ and $\langle 110\rangle$ directions in the $\{111\}$ planes of the center. Splitting of the degenerate electronic state with stress is almost negligible compared to that due to orientational degeneracy.

The N_1, N_2, and 1.220 μ 0-phonon line stress splittings must be interpreted as being indicative of monoclinic I type symmetry. Relative intensities of the N_1 line components are indicative of an electric dipole transition moment in $\langle 112\rangle$ directions perpendicular to the $\langle 110\rangle$ symmetry axes. The N_2 and 1.220-μ line intensities are more nearly consistent with electric dipole transition moments parallel to the $\langle 110\rangle$ symmetry axes of the defects. In none of these cases is the agreement with calculated intensities perfect, but it is probably within our experimental error. Considering these stress results together with growth kinetics studies[21] of the N_1 and N_2 bands in KCl, probable models for these two centers are apparent. The N_1 center should consist of two F centers along $\langle 112\rangle$ directions, with the transition moment along the line connecting them. The N_2 center would appear to consist of four F centers in $\{111\}$ planes, produced by adding one more F center to an R center in the same plane, and with the transition moment along the $\langle 110\rangle$ symmetry axes across the short diagonal of the resulting parallelograms. In order to firmly establish these models, however, it will be necessary to perform both growth kinetic and stress measurements on the same material. The 1.220-μ line may possibly be associated with a center consisting of three F centers in an obtuse triangular array in $\{111\}$ planes. This model is consistent with the observed symmetry properties and the fact that it does appear to be an intrinsic defect, but is otherwise completely speculative.

The band with its 0-phonon line at 1.40 μ must be associated with some sort of impurity–F-aggregate complex. Spectral analyses of materials in which this band is produced with an order of magnitude difference in intensity with identical treatment give no indication from relative metallic impurity concentrations that the pertinent impurity is in this category. Halogen impurities or radical inclusions remain a possibility. The symmetry is clearly rhombic I. We have no real basis for proposing any model, but one simple possibility consistent with this symmetry is that of a halogen impurity with two F-center neighbors along $\langle 110\rangle$ directions.

The centers with 0-phonon lines at 1.306 μ and 1.549 μ are in yet a different category, being produced only in heavily colored samples when illuminated or irradiated at near helium temperature. The 1.306-μ line and associated band are produced most efficiently by illumination in the region of the M band, and we feel the predominance of the evidence indicates this is the positively ionized M center (M^+). The stress splitting results indicate monoclinic I symmetry, while the M center has rhombic I symmetry. The rhombic I symmetry is reduced to monoclinic I upon ionization, however, if it is assumed that the remaining electron remains somewhat localized at one of the F-center components. The 1.549-μ line and associated band are produced most efficiently by illumination in the region of the R bands, and for this reason would perhaps appear to be associated with the positively ionized R center. However, the symmetry seems clearly to be rhombic I, and the correct assignment of this band must remain uncertain until further work can be done.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the technical assistance of D. D. TerHaar and A. W. Lynch in performing many of the measurements at various stages of this experiment.