F Centers in Additively Colored KCl:NaCl Crystals

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Two centers have been investigated which, like the F_A center, are produced by optical conversion from F centers in sodium-doped KCl crystals. They each have one absorption band on the long-wavelength side of the F band, and they each contain one F center. One of these, the F_B center, absorbs at around 636 nm and luminesces at 1240 nm, while the other, the F_C center, absorbs at approximately 620 nm and luminesces at around 1310 nm. Like the F and F_A centers, the F_B and F_C centers are each able to trap a second electron, forming a qualitatively similar primed center, and they each have a single ionized form which lacks visible and near-infrared transitions. The dependences of the F_B and F_C center on sodium concentration further indicate that the F_B center contains two Na^+ ions and the F_C center three. From the details of their anisotropic behavior, it is likely that the F center lies between the two ions in the F_B center and lies in the same (100) plane with the three ions in the F_C center.

I. INTRODUCTION

THE optical excitation of F centers near room temperature (RT) in pure KCl results in their conversion to F-aggregate centers (M, R, and N centers).[1] In sodium-doped crystals, this excitation produces additional centers such as the F_A center, which is an F center with a nearest-neighbor Na^+ ion,[2-5] the M_A center, which is an M center next to an Na^+ ion,[6,7] and the F_B center (or B center),[8] which in a very recent investigation has been attributed to an F center located between two nearest-neighbor Na^+ ions, all along one $\langle 100 \rangle$ direction.[9] This paper contains a more complete account of the F_B center and presents evidence for yet another center, referred to as the F_C, consisting of an F center with probably three neighboring Na^+ ions.

II. EXPERIMENTAL PROCEDURES

All crystals used in these experiments were grown in an argon atmosphere using the Kyropoulus technique from material supplied by E. Merck (Suprapur grade). Analyses for NaCl content were made through flame-emission spectroscopy. Crystals were additively colored in a conventional closed bomb containing the potassium metal to produce F-center concentrations typically ranging from about 0.8 to 5×10^{17} cm^{-3}. Just prior to use, each sample was cleaved to an appropriate size, wrapped in aluminum foil, reheated to about 500°C for several minutes, and rapidly quenched to RT. Crystals were mounted in total darkness on the cold finger of an optical stainless-steel Dewar which was specially designed for use in a Cary 14MR spectrometer, with which all absorption measurements were made. Dichroic spectra were obtained with light that was polarized using type-HN polaroid sheets mounted in the light path of the spectrometer.

Luminescence studies involved excitation with light from either a xenon or tungsten source which was focused on the sample after passing through a grating monochrometer and chopper. The emission, viewed at right angles to the excitation, passed through a second grating monochrometer to a PbS detector, the signal being fed from the detector to a synchronous amplifier and recorder. Spin resonance measurements were made with a Varian E-3 EPR spectrometer, g values being determined separately under resonance conditions by accurately measuring both the field using proton resonance techniques and the microwave frequency using a transfer oscillator and counter.
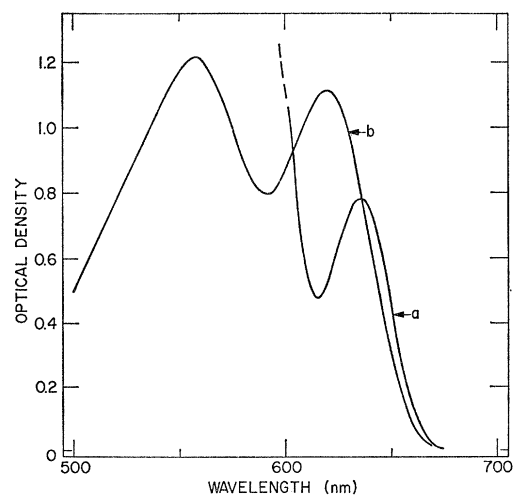

FIG. 1. Absorption spectra measured at LHeT of two crystals differing primarily in Na^+ concentration. Each crystal was exposed to F light (539 nm) at RT for about 2 min. Curve a refers to a sample containing 0.6 mole % NaCl (2.5 mm thick, $\alpha_{A1}/\alpha_{B1} \approx 3.1$); curve b, to a sample containing 3.1 mole % NaCl (1.5 mm thick).

[1] For an excellent review of F-aggregate centers and the aggregation process, see W. D. Compton and H. Rabin, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16.

[2] I. Masakazu and E. Sugioka, Phys. Rev. **110**, 1070 (1958).

[3] K. Kojima, N. Nishimaki, and T. Kojima, J. Phys. Soc. Japan **16**, 2033 (1961).

[4] F. Lüty, Z. Physik **165**, 17 (1961).

[5] R. L. Mieher, Phys. Rev. Letters **8**, 362 (1962).

[6] I. Schneider, Phys. Rev. Letters **16**, 743 (1966); Solid State Commun. **4**, 569 (1966).

[7] S. Wang, Phys. Status Solidi **23**, 401 (1967).

[8] This refers specifically to the center described by Lüty in Ref. 4.

[9] I. Schneider, Phys. Rev. Letters **20**, 790 (1968).

III. EXPERIMENTAL RESULTS

The defects that are produced from F centers in sodium-doped KCl depend largely on sodium concentration $[Na^+]$. The absorption spectrum of a moderately-doped sample (curve a, Fig. 1) has a distinct absorption band at 636 nm which has been attributed to the F_B center.[4,9] The spectrum for a more heavily doped sample (curve b, Fig. 1) contains a previously unreported band near 620 nm which will be attributed to the F_C center. This center may also be responsible for absorption peaking near 560 nm in the F-spectral region.

F_B and F_C centers can be produced like F_A centers by exciting F centers optically above about $-50°C$. At RT, all three form at the expense of F centers, reach maximum concentrations, and then decrease with prolonged F-light exposure.[10] This later decrease is often accompanied by the appearance of aggregate centers. At relatively low conversion temperatures like $-35°C$, all three monotonically approach saturation values with prolonged exposure without any accompanying aggregate-center formation. In addition, one finds at $-35°C$ that comparatively fewer F_B and F_C centers form than at RT and that all three centers are optically stable, so that F centers are not regenerated.[11]

F_A centers can be practically the only conversion product at $-35°C$ in crystals containing about 0.05 mole% NaCl. As one would expect, the maximum achievable F_A-center concentrations become greater for crystals with increasing $[Na^+]$.[2-4] The increase with $[Na^+]$, however, is evidently faster for F_B centers and fastest for F_C centers. F_B centers first appear in crystals with about 0.08 mole% NaCl, the ratio $[F_B]/[F_A]$ increasing linearly with $[Na^+]$ to at least 1 mole%.[9] F_C centers, on the other hand, are first observed in crystals with roughly 1 mole% NaCl and are a significant conversion product in crystals with over 2 mole%.

The degeneracy of the F-center $2p$ state is partially removed in the F_A center by the presence of the neighboring Na^+ ion. This causes the $1s$-$2p$ transition to split into two bands for the F_A center (see curve 1a, b of Fig. 2). One lies at 585 nm (the F_{A_1} band) on the long-wavelength side of the F band and has an associated dipole moment oriented along the $\langle 100 \rangle$ vacancy-impurity axis, while the other lies at 530 nm (the F_{A_2} band) and has a moment in the plane perpendicular to this axis.[3,4] $\langle 100 \rangle$ dichroism is induced in both bands at liquid-nitrogen temperature (LNT) by exposing the crystal to F_{A_1} light polarized along a $\langle 100 \rangle$ direction (see

[10] F light refers to light in the range from roughly 500 to about 580 nm, the so-called F spectral region.

[11] Absorption changes which occur at $-35°C$ were found to be due entirely to simple reorientations for F_A centers and to an apparent bleaching for F_B and F_C centers. Based on the F_B and F_C models proposed in the discussion, this apparent bleaching can also be thought of as a type of reorientation.
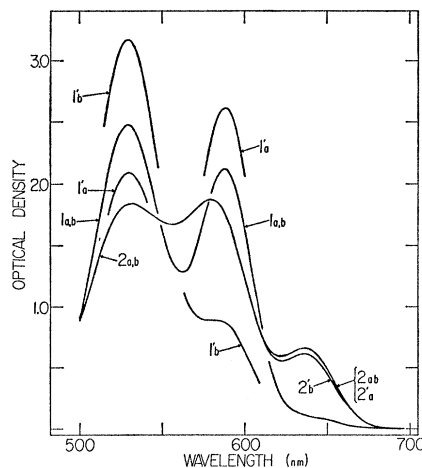

FIG. 2. Absorption spectra measured at LNT for a sample with 0.6 mole % NaCl (1.8 mm thick). After exposure to unpolarized F light (499 nm) for 10 min at $-35°C$, measured with unpolarized or $\langle 100 \rangle$ polarized light (curve 1a, b); after exposure to [010] 612-nm light for 15 min at LNT, measured with [001] (curve 1'a) and [010] (curve 1'b) light; after exposure to unpolarized F light (499 nm) at RT measured with unpolarized or $\langle 100 \rangle$ polarized light (curve 2a, b); after exposure to [010] 660 nm light for 1 min at LNT, measured with [001] (curve 2'a) and [010] (curve 2'b) light. All excitation and measuring light was incident normal to the (100) crystal surface.

curves 1'a and 1'b of Fig. 2). The dichroism in this case arises as a result of F_A-center reorientations.[3]

The crystal of Fig. 2 was subsequently warmed to RT, thereby destroying the dichroism, and exposed to F light to produce F_B centers. Besides the 636 nm or F_{B_1} band, shown in curve 2a, b of Fig. 2, the F_B center also has an absorption near the F band.[4] Subsequent exposure of the crystal at LNT to F_{B_1} light polarized along a $\langle 100 \rangle$ direction resulted in $\langle 100 \rangle$ dichroism both in the F_{B_1} band (see curves 2'a and 2'b of Fig. 2) and in the F-spectral region (not shown).[12] Since the F_{B_1} ab-
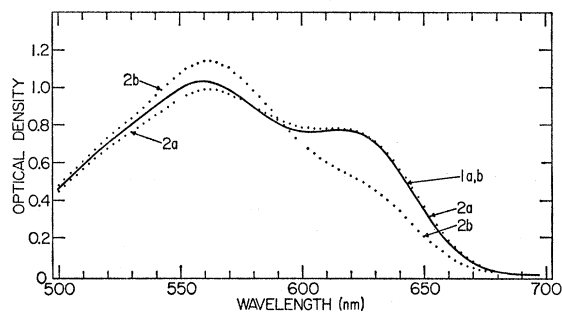

FIG. 3. Absorption spectra measured at LNT for a sample with about 3.1 mole % NaCl (1.7 mm thick). After exposure to unpolarized F light (499 nm) for 3 min at RT, measured with unpolarized or $\langle 100 \rangle$ polarized light (curve 1a, b); after exposure to [010] 660 nm light for 20 sec at LNT, measured with [001] (curve 2a) and [010] (curve 2b) light. The excitation and measuring light was incident normal to the (100) crystal surface.

[12] The unexpectedly small $\langle 100 \rangle$ dichroism appearing in the F spectral region (not shown in Figure), could be due to the partial cancellation of dichroism due to bleaching of F_B centers and formation of new defects (see discussion).
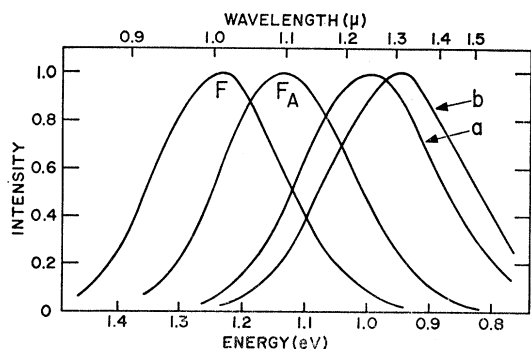
FIG. 4. Normalized emission spectra measured at LHeT of the F, F_A, F_B (curve a), and F_C (curve b) centers, the latter two obtained, respectively, for the corresponding crystals of Fig. 1. The emission was produced with excitation in the longest-wavelength absorption of each center. (The emission monochrometer had fixed slits set for a 12.8-nm-band pass.)

sorption has changed only when measured with light polarized along the same direction as the excitation the dichroism would appear to result from the bleaching (not reorientation) of F_B centers. Furthermore, the transition moment of the F_{B_1} band lies along a single $\langle 100 \rangle$ direction. In addition, one finds that "bleached" F_B centers can be regenerated at LNT with F light and that $\langle 100 \rangle$ dichroism can be induced in the F_{B_1} band also with polarized F light. On the other hand, one cannot induce $\langle 110 \rangle$ dichroism anywhere in the F_B-absorption spectrum. This behavior is consistent with a center of $\langle 100 \rangle$ symmetry.[4,13]

A more heavily doped sample containing a substantial number of F_C centers was exposed at LNT to 660 nm light polarized along a $\langle 100 \rangle$ direction. As shown in Fig. 3, $\langle 100 \rangle$ dichroism was induced mostly in the 620 nm- and the F-spectral regions. As was the case for the F_B center, this type of experiment leads one to conclude that the dichroism is caused by bleaching and that the transition moment of the long-wavelength F_C absorption (F_{C_1} band) lies along a single $\langle 100 \rangle$ direction. The F_C center is more easily bleached than the F_B, can be regenerated at LNT with F light and is also found to have $\langle 100 \rangle$ symmetry.

The F and the F_A center each luminesce in the near infrared at 1.01 and 1.10 μm, respectively.[14,15] Figure 4 shows the similarity between their emission bands and that due to the F_B center at 1.24 μm (curve a) and to the F_C center at 1.31 μm (curve b). Each emission was produced with excitation in the longest-wavelength absorption of the respective center. In addition, the excitation spectrum for the F_B emission has one band peaking near 636 nm, as well as a contribution from the F region, although the peak position in the F-spectral region was difficult to determine because

of comparatively large F_A-center absorptions. The excitation spectrum for the F_C-center emission has peaks at 620 nm and 560 nm, each approximately coinciding with the absorptions shown in curve b of Fig. 1 and the dichroic peaks in Fig. 3.

The F and F_A centers each form "primed" centers by capturing a second electron, usually upon exposure of the crystal to F light.[16,17] Each primed center gives rise to a broad absorption band lying principally on the long-wavelength side of the F-spectral region (see Fig. 5), and each is easily bleached optically even at liquid-helium temperature (LHeT). F_B' and F_C' centers are also produced with F light, and are as easily bleached. As shown in Fig. 5, they each absorb at slightly shorter wavelengths than the F_A' center, which in turn absorbs at shorter wavelengths than the F' center. Curve a refers to a crystal with both F_A' and F_B' centers, curve b to a crystal with mostly F_C centers.

Defects with unpaired electrons should be paramagnetic, as has been found to be the case for F and F_A centers.[5,18] The EPR spectrum of a crystal containing mostly F_C centers (the optical absorption similar to curve b of Fig. 1) is an inhomogeneously broadened line approximately 90 G wide centered at about $g = 1.995$. This is compared in Fig. 6 with the F_A-center signal, which is 75 G wide at $g = 1.995$ and the F-center signal, which is 45 G wide at $g = 1.996$. The sensitivity was adjusted to give traces with approximately equal magnitudes. A signal reliably attributable to the F_B center was not obtained because these centers were generally produced along with comparatively predominant F_A-center concentrations.

Excess electron centers often can be ionized at LHeT by exposing the crystal to x rays and then to 335-nm light. The x raying introduces defects such as negative-ion vacancies (α centers) and self-trapped holes (V_K centers) that can trap electrons in processes induced subsequently through optical excitation.[19,20] F_B and F_C centers ionize easily and can be regenerated afterwards with F light, presumably through the capture of F-center electrons. The ionized F_B and F_C centers, like the α and α_A centers,[21,22] have no apparent optical transitions between 300 and 2100 nm.

IV. DISCUSSION

The absorption of light by F centers often leads to their ionization and subsequent conversion to α-F' pairs.

[13] See the discussion on symmetry in Ref. 1.

[14] Th. P. J. Botden, C. Z. van Doorn, and Y. Haven, Philips Res. Rept. **9**, 469 (1954).

[15] F. Lüty and H. Pick, J. Phys. Soc. Japan Suppl. II **18**, 240 (1963).

[16] H. Pick, Ann. Phys. **31**, 365 (1938); **37**, 421 (1940).

[17] K. Kojima and N. Nishimaki, J. Phys. Soc. Japan **16**, 121 (1961).

[18] G. Feher, Phys. Rev. **105**, 1122 (1957).

[19] I. Schneider and H. Rabin, Phys. Rev. Letters **13**, 690 (1964).

[20] M. A. Aegerter and F. Lüty Bull. Am. Phys. Soc. **13**, 393 (1968).

[21] C. Delbecq, P. Pringsheim, and P. Yuster, J. Chem. Phys. **19**, 574 (1951); **20**, 746 (1952).

[22] F. Lüty and W. Zizelmann, Solid State Commun. **2**, 179 (1964); V. Topa, L. Matei, and T. Serban, Phys. Status Solidi **9**, 55 (1965).

α centers[23] are mobile above $-50°C$, migrating through the lattice until they either recapture thermally ionized F' electrons or are themselves trapped. The latter process could convert F centers to a variety of defects depending on the specific traps that are present in the crystal. Temperature is important for the conversion since it influences both the α-center migration distances and the stability of the conversion products.

In relatively pure crystals, the migration of α centers leads to the formation of F aggregates. That is, α centers are trapped first by F centers leading to the formation of M centers and then by M centers leading to the formation of R centers.[24,25] The conversion to F_A centers in sodium-doped crystals presumably occurs because the average initial separation between α centers and isolated Na^+ ions is smaller than the average initial separation between F centers. At temperatures like $-35°C$, F_A centers are optically stable and could therefore be the only important conversion product. Near RT, however, the F light which produces F_A centers can also bleach them. α centers, which are regenerated in this way, might then migrate further forming F-aggregate centers. In the discussion that follows, the same migration process and stability considerations are assumed important for the formation of F_B and F_C centers, where α centers now are trapped at sites associated with these defects. By determining the nature of these traps, one can hope to arrive at the most reasonable models for the centers.

The possibility that the F_B and F_C centers contain three F centers each can immediately be ruled out because this would require that M or M_A centers be present at the time they form. Likewise, two-F-center configurations present difficulties,[26] one of which being that the formation properties of the F_B and F_C centers differ considerably from those of the M and M_A centers. All four should form in a similar way since they all involve comparable α-center migration distances. These considerations, therefore, lead one to conclude that the F_B and F_C centers each contain just one F center.

Under this assumption, certain properties of the F_B and F_C centers ought to be similar to those of the F and F_A centers. Except for the F center, which is isotropic and has one band corresponding to its $1s$-$2p$-like transition, each other center has $\langle 100 \rangle$ symmetry with at least one absorption near the F peak and one on the long-wavelength side of the F band. Aggregate centers also absorb in the F-spectral region, but by contrast they also have a prominent absorption (or absorptions) at substantially lower energies. F, F_A, F_B, and F_C centers all have a single emission band in the infrared region

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[23] There is evidence that the α center is the mobile defect in the aggregation process and will be assumed to be throughout this discussion. See E. Link and F. Lüty, Color Center Symposium, Urbana, Illinois, 1965 (unpublished).

[24] C. J. Delbecq, Z. Physik **171**, 560 (1963).

[25] Y. Farge, M. Lambert, and R. Smoluchowski, Solid State Commun. **4**, 333 (1966).
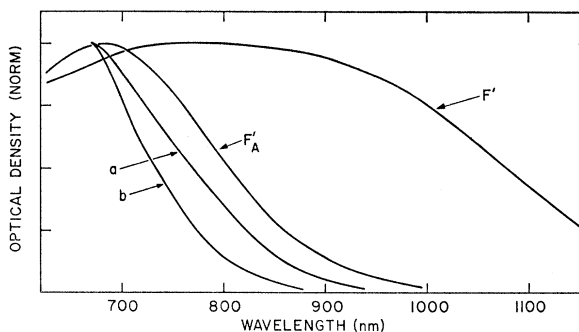
[26] See the discussion in Ref. 9.

FIG. 5. Absorption spectra measured at LHeT of the F' and F_A' centers normalized at their respective maxima and of an overlap of F_A' and F_B' centers (curve a) and F_C' centers (curve b) normalized to their values at 670 nm, the latter two measured for the corresponding crystals of Fig. 1. Primed centers were all produced at $-150°C$ with F light (539 nm).

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differing only slightly in peak position (see Fig. 4). Each can trap a second electron forming qualitatively similar primed centers (see Fig. 5) and each can be singly ionized forming centers for which there are no observable visible near-infrared electronic transitions. This is again in contrast with ionized F-aggregate centers, which do absorb in this range.[19] Finally, the paramagnetism of the F and F_A centers has clearly been established.[5,18] The F_B center has been reported to be paramagnetic in prior work[27] and the F_C center is possibly so from the present study (see Fig. 6). For neither, however, has a detailed correlation been made between their optical and EPR absorptions.

F_A centers form through the trapping of α centers at isolated Na^+ ions. The concentration of these ions is roughly proportional to the total sodium content of the crystal, $[Na^+]$.[28] The trapping sites for F_B- and the F_C-center formation probably contain some unique complex of n Na^+ ions whose maximum concentration might be assumed proportional to $[Na^+]^n$. The exponent n was determined for the F_B center using the
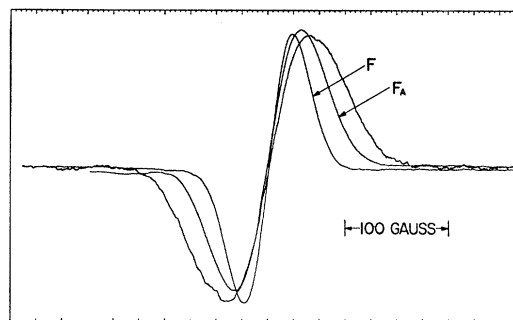

FIG. 6. The EPR spectra measured at RT for three crystals, respectively, containing F centers alone, F_A centers alone, and mostly F_C centers (optical absorption similar to curve b, Fig. 1).

[27] H. Ohkura and K. Murase, J. Phys. Soc. Japan Suppl. II **18**, 255 (1963).

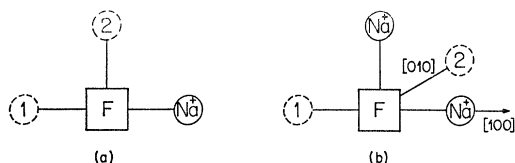[28] H. Härtel and F. Lüty, Z. Physik **177**, 369 (1964).

FIG. 7. Possible models for the F_B center (a) and the F_C center (b), assuming each consists, respectively, of an F center with two and an F center with three Na^+ ions. The alternatives are represented as an Na^+ ion either in position 1 or 2, all other components being fixed.

simple statistical relationship

$$[F_B]/[F_A] = [Na^+]^{n-1} \qquad (1)$$

using data obtained for crystals containing from 0.08 to 1 mole% NaCl. The F_A and F_B centers were produced by optical conversion from F centers at $-35°C$. The results clearly indicated that the F_B center contains two Na^+ ions (see Fig. 2 of Ref. 9).

F_C centers first appear in more heavily doped samples and have an even stronger dependence on $[Na^+]$. For this reason, the value of n for the F_C center is most likely three. Unfortunately, n is more difficult to determine accurately for the F_C center because in crystals with very large $[Na^+]$, one would no longer expect a proportionality between the concentration of n-ion complexes and $[Na^+]^n$ and also $[F_C]$ and $[F_A]$ values would be considerably less reliable because of the likely existence of unknown centers whose absorptions might overlap the F_{C_1} and F_{A_1} bands.

Figure 7 shows all possible configurations for an F center and two Na^+ ions and for an F center and three Na^+ ions, assuming the ions are nearest neighbors to the F center. Based on the foregoing discussion, these would refer to the alternatives for the F_B center [Fig. 7(a)] and for the F_C center [Fig. 7(b)]. The only two alternatives for each center are represented schematically as an Na^+ ion either occupying position one or position two, all other components being fixed. The splitting caused by the presence of a single Na^+ ion in the F_A center results in two bands, one of which lies on the low-energy side of the F band and has a dipole moment along the unique $\langle 100 \rangle$ vacancy-impurity axis.

Since a p function interacting with one Na^+ ion reduces the $1s$-$2p$ transition energy, one would expect an even greater reduction for two such symmetrically located ions. Position one is, therefore, clearly favored for both the F_B and F_C centers since it alone leads to a configuration for which a unique $\langle 100 \rangle$ axis, the direction for a nondegenerate p-like wave function, contains two Na^+ ions. An Na^+ ion in position two for the F_C-center configuration would result in three equivalent $\langle 100 \rangle$ axes where all three transitions would be degenerate. Thus, if this were the configuration, one would not even expect to observe optical anisotropy.

The reorientation of an F_A center at low temperatures involves the movement of the F center to an alternative neighboring location. For this process, only the direction of the dipole moments change. Any movement of an F center relative to the fixed Na^+ ions of the F_B and F_C centers, however, must produce substantially different centers which would be expected to absorb at distinctly different wavelengths. This would account for their apparent bleaching at low temperatures when excited optically. Furthermore, since F_B and F_C centers are regenerated with F light, their modified forms probably absorb also in the F spectral region.

The configurations chosen for the F_B and F_C centers do not preclude the existence of centers whose structures are illustrated as position 2 of Fig. 7. These might be comparatively less stable than the F_B and F_C centers or if they were to form, might have absorptions which lie in the already complicated F-F_A spectral regions, making them very difficult to detect. Fortunately, since all such centers would contain an unpaired electron, they might conceivably be detected and identified through the future use of double resonance techniques (ENDOR).

ACKNOWLEDGMENTS