

F_B CENTER IN ADDITIVELY COLORED KCl

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One of the most widely investigated impurity centers in alkali-halide crystals is the F_A center, an F center with a foreign alkali ion at a nearest-neighbor site.¹⁻⁵ What is not generally realized is that its formation in sodium-doped KCl is often accompanied by the appearance of yet another defect, the B center,⁶ of which comparatively little is known. The purpose of this note is to report evidence which indicates that the B center is an F center with two neighboring Na^+ ions, the most probable configuration being one in which the F center lies between the two ions. In view of these results, this center will be tentatively redesignated as the F_B center.

Figure 1 shows the changes in optical absorption which occur when a sodium-doped crystal initially containing F centers is exposed to F light near room temperature. The F centers rapidly bleach while F_A and F_B centers appear. These absorb at 585 and 636 nm, respectively, and each has an additional transition near the F peak.³ F_B centers are produced more slowly here than F_A centers, although each forms considerably faster than M or M_A centers⁷ (absorption bands at 800 and 820 nm). Furthermore, F_B centers are produced at an approximately constant initial rate.

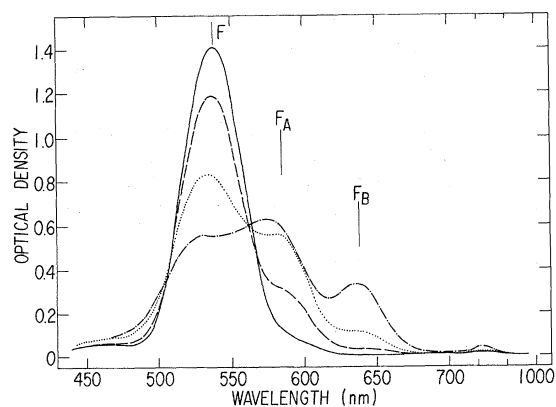


FIG. 1. Absorption spectra of a sodium-doped additively colored KCl crystal measured at 77°K, initially (solid curve) and after a total of 4 sec (dashed curve), 24 sec (dotted curve), and 4 min (dot-dashed curve) of exposure to F light (539 nm) at room temperature (2.1 mm thick, 0.9 mole% NaCl).

Unlike the M or M_A centers, F_B centers also form at temperatures as low as -35°C , though not in as large a concentration as at room temperature. Figure 2 shows that the maximum number of F_B centers produced at -35°C increases relative to the number of F_A centers in samples with increasing Na^+ concentration. In these measurements, samples were exposed to F light to convert as many F centers as possible to either F_A or F_B centers, both of which are optically stable at this temperature.⁸

The F_B center may reasonably be expected to contain some integral number of F centers. Any number greater than one, however, leads to certain difficulties. Since F_B centers are produced in crystals that contain mostly F and F_A centers, the only aggregate centers that can form are those which involve the union of two F centers or the union of an F center with an F_A center. Two F centers undoubtedly combine as the usual M center, i.e., two nearest-neighbor F centers along a $\langle 110 \rangle$ axis. The F and F_A centers might conceivably combine in two distinct configurations. One is an M center next to an Na^+ ion, i.e., an M_A center; the other, two F centers on opposite sides of an Na^+ ion.⁹ The M and M_A centers have been identified^{7,10} and have similar properties that

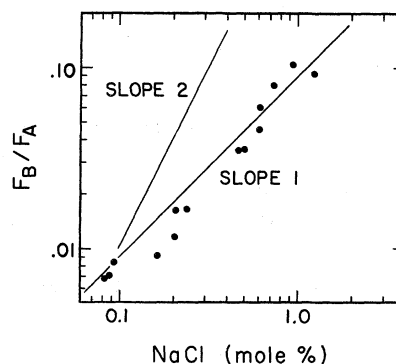


FIG. 2. The ratio of concentrations, F_B/F_A , versus the NaCl content in mole%. These centers were produced at -35°C in crystals initially containing F centers by exposure to F light (499 nm). F_B/F_A was determined from absorption spectra measured at liquid-helium temperatures assuming equal oscillator strengths for their long-wavelength absorptions. The Na^+ concentration was subsequently determined through flame emission on the samples which were actually used.

are distinct from those of the F_B center. As indicated above, they form later in the aggregation process (Fig. 1) and cannot form at temperatures as low as can the F_B center. The third configuration can be ruled out as a possible model because its formation properties would most probably be similar to those of the M and M_A centers. Furthermore, assuming this were the correct model, the reorientation of M_A centers ought to produce some F_B centers and vice versa. Conversions of this type were not observed here, nor have they been reported in former studies involving the M_A center.⁷

The F_A center forms when an F center is trapped at an isolated Na^+ ion. Let us assume that the F_B center involves a unique complex of n Na^+ ions so that whenever an F center is trapped at this complex, an F_B center is produced. The relative number of F_A and F_B centers which form in the optical conversion from F centers (Fig. 2) should depend on the concentration of isolated ions relative to that of complexes. For total sodium concentrations of less than about 1 mole%, we may further assume that the concentration of isolated ions and of complexes is proportional, respectively, to $[\text{Na}^+]$ and $[\text{Na}^+]^n$. Then at equilibrium

$$[F_B]/[F_A] = K[\text{Na}^+]^{n-1}, \quad (1)$$

where K is a constant. The approximately unit slope¹¹ for the data of Fig. 2 then evidently implies that the F_B center contains two Na^+ ions.

A further indication of the correct F_B model may be obtained simply by comparing the properties of the F_A - and F_B -center long-wavelength absorptions. The F_A absorption at 585 nm is 0.18 eV below the F peak, has a transition moment along the $\langle 100 \rangle$ vacancy-impurity axis, and becomes dichroic at low temperatures as a result of F_A -center reorientations in which the vacancy assumes different positions relative to a neighboring, fixed, Na^+ ion.^{2,3} The F_B absorption at 636 nm is 0.35 eV below the F peak and has now been found to have a transition moment along a single $\langle 100 \rangle$ lattice direction¹²; but unlike the F_A center, it becomes dichroic at low temperatures as a result of an apparent bleaching of F_B centers rather than reorientation.¹³

The two most reasonable configurations for the F_B center are shown in Fig. 3. They are (1) an F center lying between two Na^+ ions,

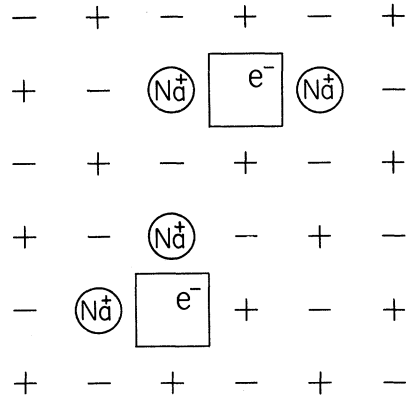


FIG. 3. Two possible configurations of the F_B center in KCl.

and (2) an F center next to two nearest-neighbor Na^+ ions. A center with either configuration could be expected to bleach at low temperatures because the movement of the vacancy from the locations shown would in effect substantially modify the centers. An important distinction between the two, however, is that the nondegenerate $\langle 100 \rangle$ axis, along which the transition moment of the 636-nm band must lie, includes two Na^+ ions for configuration (1) and none for configuration (2). This clearly favors (1) because the presence of the Na^+ ions would be expected to result in a lower transition energy, as in the case for the F_A center. Furthermore, because two ions are now interacting equally with one F -like p orbital, the F_B absorption would lie at a lower energy than the F_A . These arguments certainly do not rule out the possible existence of a center with configuration (2); it is felt that a center of this type would be difficult to detect because its absorption would probably overlap those of the F_A center.

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¹I. Masakazu and E. Sugioka, Phys. Rev. **110**, 1070 (1958).

²K. Kojima, N. Nishimaki, and T. Kojima, J. Phys. Soc. Japan **16**, 2033 (1961).

³F. Lüty, Z. Physik **165**, 17 (1961).

⁴H. Härtel and F. Lüty, Z. Physik **177**, 369 (1964).

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

⁶This refers specifically to the center discovered by Lüty (see Ref. 3). The original B band reported by Petroff [S. Petroff, Z. Physik **127**, 443 (1950)] later

turned out to be another transition of the F_A center. Nor should the center be confused with those responsible for the B band in silver- and in thallium-doped KCl.

⁷I. Schneider, Phys. Rev. Letters **16**, 743 (1966), and Solid State Commun. **4**, 569 (1966).

⁸This stability does not include the interconversions that occur between these centers and their primed center (F' , F_A' , etc.) forms. This was a relatively minor complication since the primed centers are easily eliminated by subsequently exposing the crystal to infrared light and thereby restoring the uncharged forms.

⁹This configuration has been suggested by Lüty (see

Ref. 3) as a possible model of the B center primarily because it has the required $\langle 100 \rangle$ symmetry.

¹⁰For a discussion of the evidence for the M -center model, see W. D. Compton and H. Rabin, Solid State Phys. **16**, 121 (1964).

¹¹The least-squares value of the slope was 1.08.

¹²Lüty has established the $\langle 100 \rangle$ symmetry of the center (see Ref. 3) without specifically identifying the transition moment directions of its absorptions.

¹³The bleached centers can subsequently be regenerated by exciting with light in a spectral range closer to the F peak.

MAGNETIC POLARIZABILITY OF CLOSED SHELLS

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The polarizability of closed atomic shells near field inhomogeneities is discussed in connection with several problems of physical interest. We find that magnetically "neutral" $S=0$ atoms or closed shells are attracted and polarized by magnetic field gradients. The effect is demonstrated through sample calculations for noninteracting as well as for interacting electrons.

The helium atom having total spin $S=0$ and angular momentum $L=0$ is generally presumed not to respond to externally applied magnetic fields, the ground state being an eigenstate of the interaction Hamiltonian belonging to eigenvalue precisely zero. The purpose of this note is to point out that closed shells of arbitrary atoms and molecules, as well as noble gases, have their energy lowered in a spatially inhomogeneous magnetic field as a consequence of electronic spin paramagnetism. Inhomogeneous exchange splitting provides a qualitatively similar but markedly stronger mechanism that should be a source of attraction of noble gases to the surface of ferromagnetic metals. A different application of the mechanism under consideration is to the Knight shift in superconductors.¹ The Meissner effect is a mechanism causing inhomogeneity in the magnetic field, in the superconducting state only, and the consequent polarization of closed shells can result

in polarizing nuclei via hyperfine coupling. This mechanism is lacking in the normal state, in which case the closed shells are magnetically inert, as described in the opening remarks.

The magnitude of the effect we describe should be orders of magnitude smaller than the spin paramagnetism of paramagnetic atoms, and it should be independent of temperature instead of obeying a Curie law. In these respects it is similar to Van Vleck's temperature-independent orbital paramagnetism which, it has been estimated,² might be responsible for a third of the Knight shift in Sn. Inhomogeneous exchange splitting may be many orders of magnitude larger than Van Vleck's mechanism.

The actual calculation of the response of closed shells to inhomogeneous fields is straightforward. The field is decomposed into Fourier components $h(q)$ and the perturbation, for a two-electron system, is separated into singlet and triplet components, as follows:

$$H' = \sum_q h(q) [S_{1z} e^{iq \cdot r_1} + S_{2z} e^{iq \cdot r_2}] = \sum_q h(q) \left[\frac{1}{2} (S_{1z} + S_{2z}) (e^{iq \cdot r_1} + e^{iq \cdot r_2}) + \frac{1}{2} (S_{1z} - S_{2z}) (e^{iq \cdot r_1} - e^{iq \cdot r_2}) \right]. \quad (1)$$

The first part has eigenvalue zero in the singlet state. The second part has nonvanishing matrix elements connecting the singlet to the $M=0$ component of each triplet excited state. As an example, we have calculated the matrix element H' between the singlet configuration $(1s)^2$ and the $M=0$ com-