Question of the Paramagnetism of the M Center in Sodium Fluoride*†

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A strong optical absorption band is observed in NaF at 507 mμ, and identified as the M band by Ivey's law and by experiments on formation kinetics and polarization of luminescence by other workers. Not only is a substantial change in the relative intensities of the F and M bands possible in this substance, but also the M band can be made strong compared to the F without the appearance of other bands. The existence of magnetic centers in NaF is studied by means of electron spin resonance. The correlation of resonance intensity with optical studies demonstrates that no paramagnetism arises from the M centers. The optical F band is positively correlated with a resonance line. Resonance lines belonging to an unidentified center are reported, as are lines belonging to paramagnetic impurities.

I. INTRODUCTION

COLOR centers in alkali halides have been investigated for many years. This activity has amply demonstrated the general complexity of the subject. One important result is the confirmation of the de Boer model[1] of the F center; an electron trapped at the site of a negative-ion vacancy.

However, a model for the M center, i.e., the environment of the trapped electron(s), associated with this optical absorption band has become a subject of controversy. On the basis of optical bleaching measurements one knows that the M center has a symmetry axis along the [110] crystal axis. Seitz[2] has summarized the bulk of these experiments and assigned a plausible tentative model. Further work[3-11] has shown this model to be incorrect. It now appears likely[5] that the M center consists of two F centers joined in a [110] direction. This center is not expected to be paramagnetic since the spins of the electrons would probably pair off into a nonmagnetic singlet state. Studies of the paramagnetism of the M center should therefore help distinguish the correct model.

In most of the alkali halides the M band is always weak compared to the F band, and when the M band is produced in substantial concentration, numerous other bands are always present. In NaF, on the other hand, the M-center concentration, determined by optical measurements, can be made large compared to the concentration of all other centers, including the F center. Since the F center is magnetic, its magnetism may obscure that of the M center. NaF is therefore well suited to a study of the M-center paramagnetism.

In this paper, we report the results of electron spin resonance (ESR) studies of NaF. We conclude that the M center is not paramagnetic, in agreement with the model that it is a pair of F centers.

II. SAMPLE PREPARATION AND OPTICAL MEASUREMENTS

Sodium fluoride single crystals were obtained from Harshaw and Semi-Elements. They were exposed to 50 kVp x rays at 20 mA at room temperature for from 2 to 70 h until the F-center concentration was large (10^{17}–10^{18} F centers/cm³). Two optical bands were found; one at 342 mμ and the other at 507 mμ (room temperature). These bands were identified by the use of the Mollwo relation,[12] refined by Ivey,[13] as the F and M bands, respectively. The F band is 0.51 eV wide and the M band is 0.16 eV wide at room temperature.

Anisotropic bleaching experiments were attempted in order to more positively identify the 507-mμ band. In these experiments, the 507-mμ band was bleached at room temperature with polarized light as in the experiments of Ueta and others.[14] Anisotropy did appear in this band but the results are not simple and cannot demonstrate the characteristic [110] symmetry of the M center. However, Compton[15] has studied the polarized luminescence and has proved that this band has [110] symmetry. Furthermore, Rabin[16] has studied

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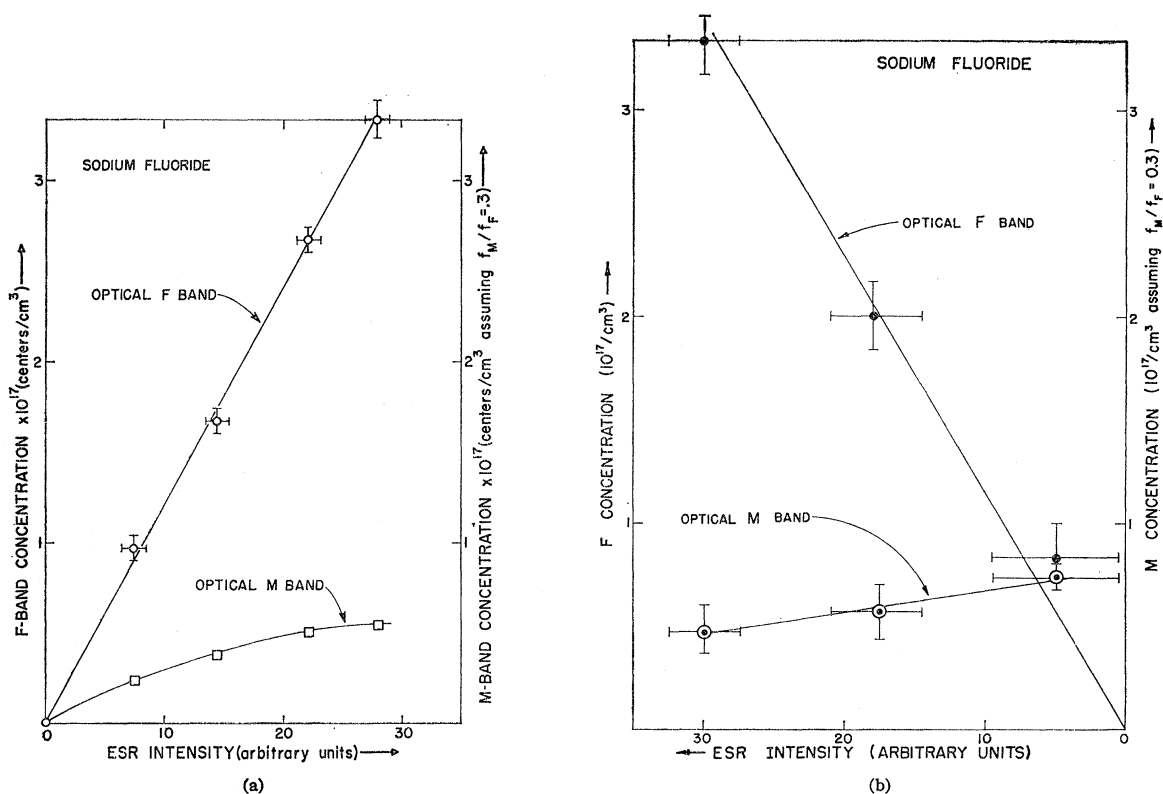[16] H. Rabin (private communication).

FIG. 1. F- and M-center optical intensity vs amplitude of the ESR line seen (a) during irradiation, (b) as the F band is bleached.

the formation of this band and has shown that its concentration goes with the square of the F-center concentration as with other M centers.

During the irradiation the F- and M-center concentrations, determined by optical measurements, were compared with the ESR line produced [see Fig. 1(a)]. The x-irradiated crystals were then bleached with light

in the F band. By this means, the M-center concentration is greatly increased (see Fig. 2). The ESR was again monitored [see Fig. 1(b)].

In Fig. 1, we see (a) that the F-band concentration is proportional to the ESR intensity, (b) that the F-band concentration and ESR intensity both rise and fall together, (c) that the M band does *not* form pro-
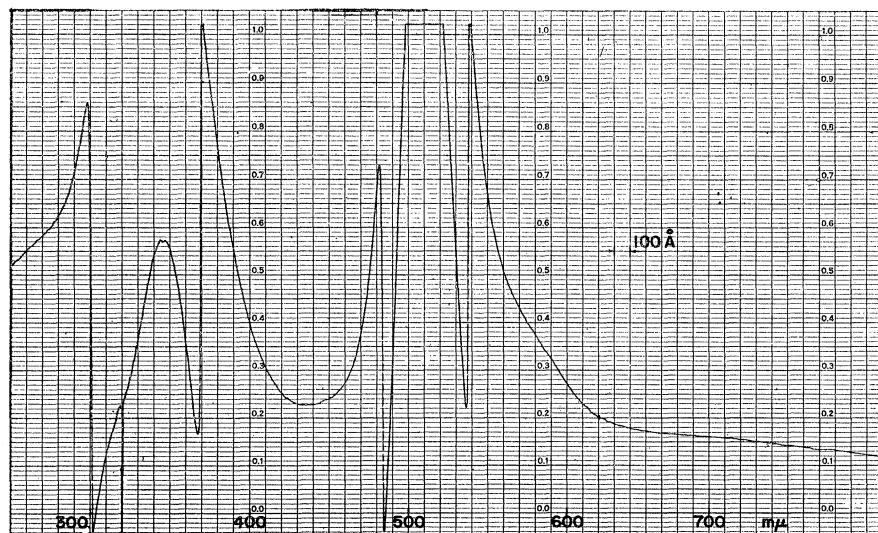

FIG. 2. Typical optical absorption curve for sodium fluoride showing the large M band at 507 mμ and the F band at 342 mμ. The spectrophotometer switches scale automatically at optical densities greater than one so that the range of the instrument is zero to two without modification.

portional to the ESR intensity, and (d) that the M concentration actually rises while the F band and the ESR line bleach.

Measurements made after extensive bleaching (Fig. 3), when the F concentration has been reduced to less than $10^{15}/cm^3$, show that the ESR line associated with the F center has dropped in intensity by about a factor of 300.

If we assume that initially all F centers are converted into M centers, we find that the ratio of the oscillator strengths, $f_M/f_F=0.62$, where we have also assumed that two F centers go to make one M center. However, this estimate is not completely reliable[9] because the F centers also go to form other centers. In Fig. 1, we have assumed $f_M/f_F=0.3$. With this assumption, we are able to produce an M-center concentration greater than $10^{17}/cm^3$.

A resonance line associated with the M center with the same linewidth and g value could possibly be hidden by the F-center resonance. However, assuming $f_M/f_F=0.3$, we can achieve a concentration ratio of M to F centers of at least 300 (Fig. 3) and we can say that more than 90% of the observed resonance line (Fig. 1) is associated with the F center. Therefore, the upper limit for the ratio of the magnetization of an M center to that of an F center is 3×10^{-4}.

III. ESR MEASUREMENTS

Paramagnetic resonance experiments were performed on the prepared samples at room temperature and at 1.3°K. The X-band resonance spectrometer has been described in detail elsewhere.[17] It consists of a well-stabilized V58 klystron transmitter with a superheterodyne, balanced mixer receiver. The local oscillator is phase locked to the transmitter. Fast- and slow-passage
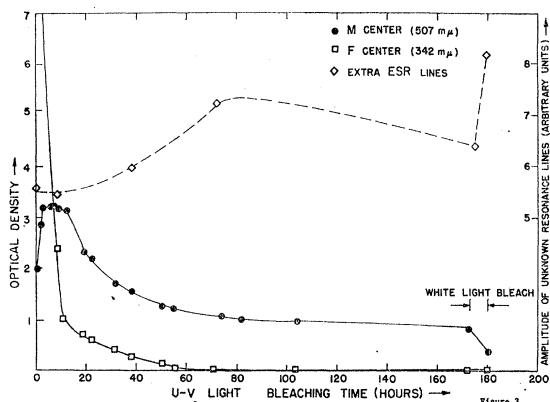
FIG. 3. F- and M-center optical intensity (left ordinate) and intensity of extra ESR lines (right ordinate) as a function of bleaching time.

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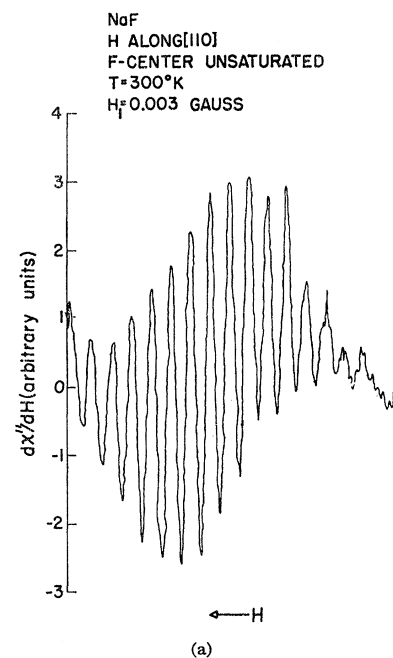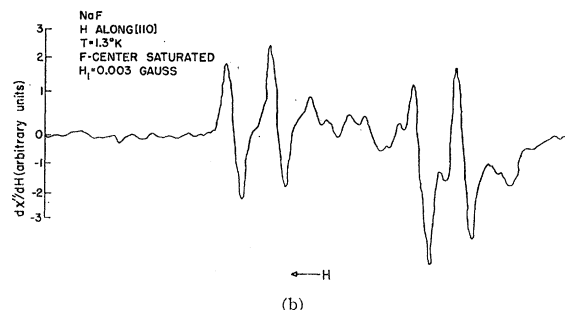
FIG. 4. ESR absorption derivatives for (a) unsaturated, and (b) saturated F centers.

work was done. In fast passage at 1.3°K, one can see approximately 10^{12} centers.

In fast passage, at 1.3°K, aside from paramagnetic impurities, only F centers were seen in sweeps over the region 0 to 10^4 G. In the slow-passage experiments the temperature of the sample and the microwave power incident on the sample were varied so that the F-center signal was saturated under various conditions. Resonance lines were seen to lie under the F center. These lines do not correlate in intensity with the F or M centers (Fig. 3). The ESR intensity measurements are all taken relative to a small piece of DPPH placed in the microwave cavity. This ensures that any possible changes in gain or sensitivity of the spectrometer are not reflected in the measurements. Figure 4 shows the ESR absorption derivative signal for saturated and unsaturated F centers. Figure 5 shows the angular variation of the extra lines as the magnetic field is rotated about a [100] crystal axis. The interpretation of this angular variation has not been found.

Resonance lines of centers present in low concentration (1 part in 10^8) were found at $g=2.2938$ and $g=4.346$. These g values are very similar to those of
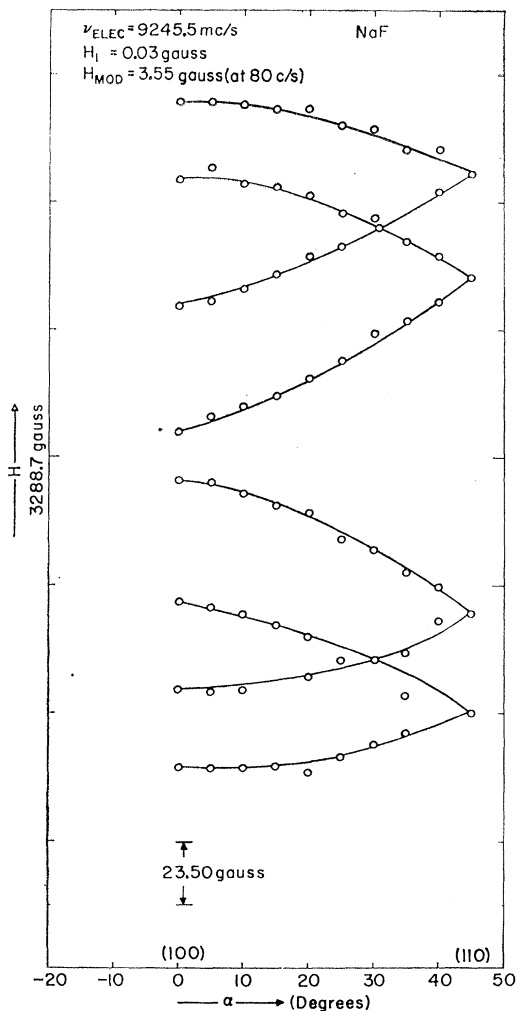
ν_{ELEC} = 9245.5 mc/s   NaF
H_1 = 0.03 gauss
H_{MOD} = 3.55 gauss (at 80 c/s)

$\overset{\uparrow}{H}$ 3288.7 gauss

$\top$
23.50 gauss
$\bot$

(100)   (110)
-20   -10   0   10   20   30   40   50
——— a ——→ (Degrees)

FIG. 5. Angular variation of the unidentified ESR
lines in sodium fluoride.

paramagnetic ions in cubic fields.[18] The g=4.346 reso-
nance in NaF has been reported by Bleaney and

Hayes.[19] They ascribe it to Fe^+. They also mention an
intense pink coloration (characteristic of the presence
of M centers) and a lack of correlating resonance lines.

From its g value and structure we identify the other
resonance lines as Ni^{2+} occupying a sodium-ion posi-
tion. Resolved structure from the surrounding fluorines
can be seen. The fluorine hyperfine components are
displaced in magnetic field from the center of the line by

$$\Delta H = \sum_k I_{zk}[a_k + b_k(3 \cos^2\theta_k - 1)], \qquad (1)$$

where the sum is over the fluorine neighbors and a_k
measures the contact interaction between the electron
and the various neighbors, and b_k the dipole-dipole
interaction. θ_k is the angle between the external mag-
netic field and a line from the center of the impurity
site to the kth neighbor. We find $a_k = 27.8 \pm 0.5$ G,
$b_k = 11.6 \pm 0.5$ G for the six equivalent nearest-neighbor
fluorines.

IV. CONCLUSIONS

The absence of resonance lines which correlate with
the M-center concentration together with the large
concentration of M centers forces one to conclude that
the M center is, at most, very weakly paramagnetic.
This conclusion is in agreement with all the other ex-
perimental work done.[20] The maximum magnetism rela-
tive to the F center is 3 parts in 10^4.

ACKNOWLEDGMENTS

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