

EVIDENCE FOR THE DOUBLE  $F$  MODEL OF THE  $M$  CENTER

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Recent results of van Doorn<sup>1</sup> on the thermal equilibrium of  $F$  and  $M$  centers in KCl show that the concentration of  $M$  centers varies quadratically with the concentration of  $F$  centers. This result supports the proposal of van Doorn and Haven<sup>2</sup> and Pick<sup>3</sup> that the model of the  $M$  center is a pair of associated  $F$  centers ( $F_2$  model) rather than a vacancy pair plus a single  $F$  center as suggested earlier by Seitz<sup>4</sup> and modified by Knox.<sup>5</sup> This Letter presents new results on the relative concentration of  $F$  and  $M$  centers induced by irradiation, and the implication of these results on the  $M$ -center model.

Thin plates of KBr and KCl, approximately 0.09-0.20 mm thick, have been irradiated at liquid helium and liquid nitrogen temperatures with x rays from a 50-kv dc generator for periods up to sixty hours. Sensitive optical absorption measurements show that a weak  $M$  band appears with the generation of  $F$  centers in KBr, KBr doped with Ca, KCl, and KCl doped with Sr. The data for KBr (Fig. 1) show that the concentration of  $M$  centers produced by these low-temperature irradiations is a quadratic function of the  $F$ -center concentration. A

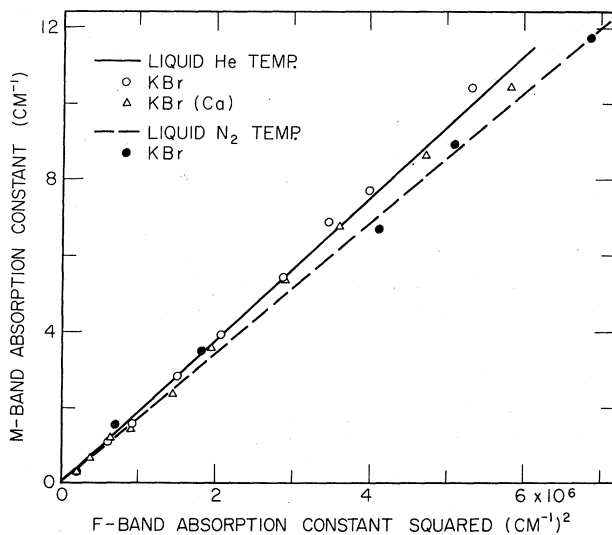


FIG. 1. Absorption constant of the  $M$  band vs absorption constant of the  $F$  band squared for x-rayed KBr at liquid helium and nitrogen temperatures. The optical measurements were taken at the irradiation temperature.

similar result was found in the KCl specimens. As is shown below, this is evidence that an  $M$  center is composed of two  $F$  centers. The fact that the divalent impurities and accompanying positive-ion vacancies did not alter the relative concentrations of  $F$  and  $M$  centers (see Fig. 1) is additional evidence that the positive-ion vacancy is not essential to  $M$ -center production.

The x-ray production of  $M$  centers is predictable from the probability of forming two  $F$  centers as neighbors. If it is assumed all  $F$  centers are produced with equal likelihood, the probability that two  $F$  centers will be formed as neighbors is proportional to  $(n_F/N)^2$ , where  $n_F$  is the concentration of  $F$  centers and  $N$  is the concentration of negative-ion sites in the normal lattice. Thus the concentration of  $M$  centers is given by

$$n_M = Kn_F^2/N, \quad (1)$$

where  $K$  is a constant. Figure 1 shows this predicted quadratic dependence. Using the Gaussian form of Smakula's formula<sup>6</sup> for both  $F$  and  $M$  centers, it follows that

$$\left(\frac{\alpha_M}{\alpha_F^2}\right)\left(\frac{W_M}{W_F^2}\right)\left(\frac{f_F^2}{f_M}\right) = 0.87 \times 10^{17} \left(\frac{K}{N}\right)\left(\frac{C_F^2}{C_M}\right), \quad (2)$$

where  $C = \mu/(\mu^2 + 2)^2$ ,  $\mu$  being the index of refraction,  $\alpha$  = absorption constant in  $\text{cm}^{-1}$ ,  $W$  = the absorption half-width in eV, and  $f$  = the oscillator strength. The indices  $F$  and  $M$  refer to the  $F$  and  $M$  centers, respectively. Table I gives a tabulation of the half-widths and values of  $\alpha_M/\alpha_F^2$  obtained from a least-squares fit of the data of Fig. 1. Assuming that negligible diffusion of  $F$  centers occurs at liquid helium and nitrogen temperatures,  $M$  centers can only be formed during x raying when two  $F$  centers are formed as nearest neighbors. In this case  $K=12$ , corresponding to the number of nearest negative-ion sites surrounding an  $F$  center. Average values of  $f_F$  are taken from the literature.<sup>7,8</sup> The values of  $f_M$  so calculated (0.12 to 0.20, Table I) appear quite reasonable in view of the simplicity of the calculation.<sup>9</sup>

In light of the low-temperature results, two examples of  $M$ -center formation at higher temperatures can be considered. First, the  $M$ -center concentration in KBr and KCl crystals x-rayed at

Table I. Data for calculating  $f_M$  for KBr and KCl assuming  $K=12$ .

	$\alpha_M/\alpha_F^2$ (cm)	$W_M/W_F$ (ev/ev)	$f_F/f_M^a$	$f_M$
KBr (He temp.)	$1.87 \times 10^{-6}$	0.052/0.158	3.2	0.15
KBr (N <sub>2</sub> temp.)	$1.71 \times 10^{-6}$	0.063/0.190	4.0	0.12
KCl (He temp.)	$1.95 \times 10^{-6}$	0.056/0.169	2.7	0.20
KCl (N <sub>2</sub> temp.)	$1.96 \times 10^{-6}$	0.066/0.194	2.9	0.18

<sup>a</sup>Average values of  $f_F$  are taken from the literature for a Gaussian  $F$  band:  $\langle f_F \rangle_{av}$  (KBr) = 0.48,<sup>7</sup> and  $\langle f_F \rangle_{av}$  (KCl) = 0.53.<sup>8</sup>

liquid helium or nitrogen temperatures increased by a factor of about fifty upon warming to room temperature.<sup>10</sup> This suggests that  $F$  centers some distance apart aggregate to form  $M$  centers during warmup. Second,  $F$ - and  $M$ -center equilibrium after room-temperature x raying may be studied. The published data of Mador *et al.*<sup>11</sup> for NaCl and LiF are particularly appropriate for this purpose since optical absorption measurements were made transversely to the x-ray direction, insuring uniform coloration along the optical path. A treatment of their data to test the quadratic relation between  $\alpha_M$  and  $\alpha_F$  is shown in Fig. 2. It is again seen that  $\alpha_M$  is a linear function of  $\alpha_F^2$ . Equation

(2) can now be used to compute a value of  $K$  for NaCl and LiF at room temperature, assuming a value of the oscillator strengths.<sup>12</sup>  $K$  may now be interpreted as follows. If two  $F$  centers are contained in a spherical volume of  $K$  negative-ion sites, they associate to form an  $M$  center. If  $a$  is the lattice constant, i.e., the distance between like ions along a  $\langle 100 \rangle$  direction, then a "sphere of interaction" for  $F$  centers of radius  $r$  is given approximately by the relation  $(4\pi/3)r^3 \approx Ka^3/4$ . It follows that  $r/a \approx 0.39(K)^{1/3}$ , which is the maximum number of lattice constants over which  $F$  centers join to form  $M$  centers. Using values of  $K$  calculated from Eq. (2) from the least-squares slopes of Fig. 2,  $r/a$  can thus be determined. Values of  $K$  and  $r/a$  are as follows:

	$K$	$r/a$
NaCl	7000	7.4
LiF	4400	6.4

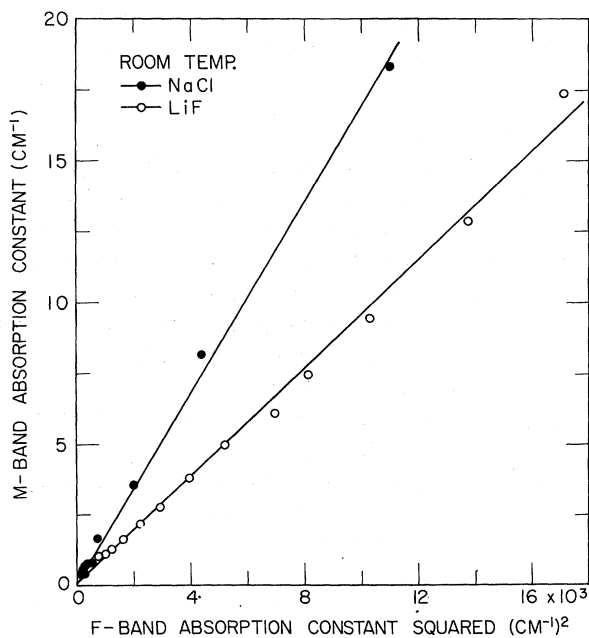


FIG. 2. Absorption constant of the  $M$  band vs absorption constant of the  $F$  band squared for NaCl and LiF x-rayed and measured at room temperature, taken from Mador *et al.*<sup>11</sup>

This result implies that the interaction of two  $F$  centers is sufficiently great at room temperature that two  $F$  centers separated by six or seven lattice constants join to form  $M$  centers. The nature of the mechanism which promotes such an association is not understood. Alternatively this might be taken as evidence for a nonrandom distribution of  $F$  centers.

A value of  $K$  for KCl can also be determined for van Doorn's high-temperature data<sup>1</sup> ( $\sim 1000^\circ\text{K}$ ). This value is roughly a factor of ten lower than the room-temperature values, suggesting an equilibrium between the formation and the breakup of  $M$  centers at the high temperature.

A substantial amount of evidence now appears to support the  $F_2$  model of the  $M$  center. It has been demonstrated that  $F$  and  $M$  centers are quadratically related in cases of both thermal quench-

ing and x raying over a wide temperature and concentration range in a variety of alkali halides. Furthermore, this model is in accord with the requirement of inversion symmetry,<sup>13</sup> the absence of dielectric loss<sup>14</sup> and magnetic susceptibility,<sup>15</sup> and the inconclusiveness of electron spin resonance<sup>16</sup> of the *M* center.

In light of the above discussion the suggestion of Pick<sup>3</sup> that the *R* and *N* centers are higher aggregates of *F* centers has been examined. Treating unpublished data<sup>17</sup> for NaCl that had been uniformly irradiated with gamma rays at room temperature, it was found that the *R*<sub>2</sub>-center absorption varied approximately as the 1.5 power of the *M*-center absorption. This supports the contention that the *R* center is an aggregate of an *M* and *F* center, or simply three *F* centers as suggested by Pick. A more extensive study is indicated.

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<sup>1</sup>C. Z. van Doorn, Phys. Rev. Letters 4, 236 (1960).

<sup>2</sup>C. Z. van Doorn and Y. Haven, Philips Research Repts. 11, 479 (1956), and C. Z. van Doorn, Philips Research Repts. 12, 309 (1957).

<sup>3</sup>H. Pick, Z. Physik 159, 69 (1960).

<sup>4</sup>F. Seitz, Revs. Modern Phys. 18, 384 (1946).

<sup>5</sup>R. S. Knox, Phys. Rev. Letters 2, 87 (1959).

<sup>6</sup>D. L. Dexter, Phys. Rev. 101, 48 (1956), Eq. (27).

<sup>7</sup>See, for example, C. J. Rauch and C. V. Heer, Phys.

Rev. 105, 914 (1957), and F. Lüty, Z. Physik 160, 1 (1960).

<sup>8</sup>In addition to reference 7 see F. G. Kleinschrod, Ann. Physik 27, 97 (1936), and R. H. Silsbee, Phys. Rev. 103, 1675 (1956). Also a treatment by Seitz<sup>4</sup> of data from H. Pick, Ann. Physik 31, 365 (1938).

<sup>9</sup>Although there appears to be good agreement with Okura's value of  $f_F/f_M$  of 2.4 determined from *F*-center bleaching of KCl, a linear rather than quadratic relation between *F* and *M* centers was assumed; see H. Okura, J. Phys. Soc. Japan 12, 1313 (1957). In the case of two *F* centers per *M* center Okura's value is reduced to 1.2, a factor of about two to three lower than those given in Table I. It is quite possible that the bleaching technique ignores the formation of other centers, like the *A* center; see, for example, M. Hirai, J. Phys. Soc. Japan 14, 1400 (1959).

<sup>10</sup>It should be pointed out that this technique provides a method of obtaining comparatively large *M*-center concentrations.

<sup>11</sup>I. L. Mador, R. F. Wallis, M. C. Williams, and R. C. Herman, Phys. Rev. 96, 617 (1954), Figs. 7 and 9.

<sup>12</sup>The value of  $f_F^2/f_M$  is taken to be 1.61 using the average of the data for KBr and KCl from Table I.

<sup>13</sup>A. W. Overhauser and H. Rüdhardt, Phys. Rev. 112, 722 (1958).

<sup>14</sup>G. Jacobs, J. Chem. Phys. 27, 217 (1957).

<sup>15</sup>E. Sonder, Bull. Am. Phys. Soc. 6, 114 (1961).

<sup>16</sup>W. C. Holton, H. Blum, and C. P. Slichter, Phys. Rev. Letters 5, 197 (1960).

<sup>17</sup>Obtained in connection with an earlier study, W. D. Compton, Phys. Rev. 107, 1271 (1957).

## SIZE-DEPENDENT RELAXATION TIMES AT LIQUID HELIUM TEMPERATURES\*

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Recovery times have been observed in one of the copper Tutton salts which depend upon the size of the crystal(s) employed.<sup>1</sup> The salt in question is fully concentrated  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The paramagnetic ion is  $\text{Cu}^{+2}$  ( $S = \frac{1}{2}$ ) and the two ions per unit cell give rise to two lines.<sup>2</sup> However, at high concentrations the two lines coalesce to form one broad line whose full width at half maximum varies from 170 to 450 oersteds depending upon the angle between the crystal axis and the magnetic field.

The relaxation times were measured with an X-band pulse-decay superheterodyne spectrometer, the output of which was the dynamic recovery curve of the spin system.<sup>3</sup> The relaxation times were determined from the exponential

tails of the decays, in the region where the spin temperature  $\approx$  lattice temperature.

The crystals reported on were prepared in two different ways. In the first instance a fine powder of crystallites was allowed to grow slowly over a period of 24 hours. The second method involved the preparation of a supersaturated solution by heating. The solution was stirred continually as it cooled to room temperature with the result that a fine powder of tiny crystals was deposited in the bottom of the beaker. In both cases the crystals were then dried by exposure to air and carefully sorted according to size using a series of sieves. The hole sizes in the ten sieves ranged from 37 to 1000 microns. Only naturally grown single crystals were used