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X-Ray Generation of M Centers in Alkali Halides

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Recent studies of the *M* center point to the F_2 model as the appropriate model of this center. A discussion is given of a number of points relating to *M*-center formation at room and low temperatures as well as of the *M*-center oscillator strength based on low temperature x-ray irradiation.

Investigation of the reaction kinetics of *M*-center formation in alkali halide crystals by additive coloration[1)] and by ionizing radiation[2)] support the van Doorn-Haven or F_2 model of the *M* center. This paper is concerned with the nonequilibrium formation of *M* centers which occurs as a result of x-raying, and explores the details of production and migration of *F* centers in contributing to *M* center formation.

A technique for greatly enhancing the ratio of concentrations n_M/n_F of crystals x-rayed at low temperature is to warm the crystals in the dark following the x-ray exposure. It is seen in Fig. 1 that the onset of *M*-center formation occurs at about 207°K, presumably marking the initiation of migration of *F* centers. It is not clear, however, that the *F*-center aggregation occurs directly by a thermally activated process. The possibility exists that the process is activated by the thermoluminescent glow of the warmed crystal. The existence of such luminescence has been observed in x-rayed KCl[3),4)], and moreover, there is a component of this glow which reaches a maximum intensity in the vicinity of 200°K and occurs in the spectral region of the *F* band[4)]. Furthermore, there is a marked similarity of the temperature dependence of the optical $F \rightarrow M$ conversion in additively colored crystals[5)] to that shown in Fig. 1.

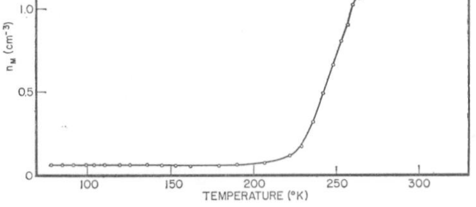

Fig. 1. The *M*-center concentration of a KCl crystal as a function of temperature following x-ray exposure at liquid nitrogen temperature. The rate of warming is approximately one degree per minute.

A mechanism has been proposed[5)] for the optical conversion of $F \rightarrow M$ centers via a mutual coulomb interaction of short lived F' centers and negative-ion vacancies created from the *F* centers,

$$F+F \rightarrow F'+\square \rightarrow F+F \cdots\cdots\cdots \rightarrow M\,. \quad (1)$$

The negative-ion vacancy diffuses toward the F' center preferentially due to a mutual coulomb attraction before the F' center decays to re-form two *F* centers. A succession of steps of this sort under *F*-band light results in the association of two *F* centers to form an *M* center. According to this mechanism, the onset of *M*-center formation at 207°K in Fig. 1 indicates the initiation of vacancy migration under the action of luminescence within the crystal. There are, however, several alternatives which do not require that internal luminescence play a significant role. First, sufficient energy may be liberated within a crystal by nonradiative processes to induce the metastable formation of F' centers and negative ion vacancies. In this case the process indicated in Eq. (1) proceeds without the requirement of optical activation. Second, the possibility exists that free charge released in warming[3),6)] plays a significant role in *M*-center formation. In the latter case vacancy clusters might be disrupted upon the trapping of free charge, and *M* centers may result as products of this disruption.

The concensus of experimental results seems to indicate that if the migration of *F* centers is the dominant process for *M*-

center formation above 207°K, such migration almost certainly does not occur below this temperature. First, optical $F \rightarrow M$ conversion of additively colored crystals is vanishingly small at 207°K and lower. Second, in the case of x-rayed crystals, the ratio, n_M/n_F is the same if the x-raying is performed at either liquid nitrogen or liquid helium temperatures[2], and moreover, warming to 207°K after x-raying at liquid nitrogen temperature also produces no discernible change in the *M*-center concentration (Fig. 1). The complete absence of temperature dependence of *M*-center formation under x-rays at low temperature argues against a mechanism involving the diffusion of a defect at these temperatures.

In the absence of the migration of *F* centers at low temperature it has been argued on the basis of a quadratic relation between the *F*- and *M*-center concentrations that the mechanism of *M*-center formation by x-rays is dependent on the creation of *F* centers at neighboring negative-ion sites. The "apparent" oscillator strength* of the *M* center in KCl computed on this basis is 0.38 using the gaussian form of Smakula's equation[2]. This value is in reasonable agreement with values computed from optical $F \rightarrow M$ conversion[7,8] with appropriate modification for a two *F*-center model of the *M*, center, Table I.

Table I. *M*-center oscillator strength in KCl (for a gaussian band shape); optical conversion is based on a correction to the height of the *F* band (a) of one-half the magnitude of the height of the *M* band, and (b) equal to the height of the *M* band, due to excited states of the *M* center underlying the *F* band.

Reference	f_M	Method
H. Okura[7]	0.27(a), 0.20(b)	Optical $F \rightarrow M$ conversion
T. Tomiki[8]	0.35(a), 0.23(b)	Optical $F \rightarrow M$ conversion
Faraday, Rabin, and Compton[2]	0.38	Low temperature x-raying

Because of an extremely large ratio of *F* to *M* centers at low temperature, the oscillator strength determined from low temperature x-raying has the advantage of being free of corrections due to overlapping *M*-center excited states. Also the accompanying suppression of other *F*-aggregate centers in the case of low temperature x-raying eliminates another possible source of error that is present in optical $F \rightarrow M$ conversion at room temperature. The question arises, however, as to the validity of the oscillator strength based on low temperature x-raying in the event of some small number of jumps of the *F* center (or negative-ion vacancy) as an aftermath to the act of creation of this center (or vacancy). The oscillator strengh of 0.38 determined from low temperature x-raying assumes that *M* centers result only from *F* centers created as neighbors. Since there are 12 neighboring negative-ion sites surrounding a given *F* center, the number 12 appears as an essential numerical factor in the determination of the oscillator strength. (The oscillator strength is actually inversely proportional to this factor[2].) In the event there is a net contribution to the formation of *M* centers due to jumping of the *F* center during low temperature x-raying, an appropriate correction to the above oscillator strength must be made. This correction would take into account an effectively larger number of sites surrounding a given *F* center that contribute to *M* center formation. We have argued above that the evidence strongly suggests that defect migration does not occur below about 207°K. The possibility nevertheless exists that *F* centers are induced to make either a single or some small number of atomic jumps in dissipating excess local energy expended in the act which creates the *F* center at low temperature. Under certain circumstances such jumping significantly affects the value of the oscillator

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* The "apparent" oscillator strength refers to that number substituted into Smakula's equation for the oscillator strength which gives the correct concentration of centers. In the case of the *M* center which has (110) symmetry, the true oscillator strength is a factor of 3 larger than the apparent oscillator strength since on the average only one-third of the *M* centers are seen in measurements with unpolarized light. The true oscillator strength for the transition to the lowest excited level of the *M* center is accordingly in the neighborhood of unity. For a two electron center and a total oscillator strength of 2, one unit of oscillator strength remains for distribution among the other excited transitions of the *M* center (see F. Okamoto: Phys. Rev. **124** (1961) 1090 for a discussion of these excited states).

strength.

If all F centers which are within one atomic jump of forming an M center partake in M center formation, an additional 42 negative-ion sites are brought into play. The oscillator strength in this case would require a correction of more than a factor of four, $0.38\times 12/(12+42)=0.08$. This correction or others based on more than a single jump appear prohibitively large in view of the agreement of data of Table I. The fact remains, however, in the instance of a single atomic jump, all 42 sites are not equivalent. A total of 6 of these sites are located a distance $2c$ from a given F center (c is the separation of unlike ions in the lattice), 24 are located a distance $\sqrt{6}\,c$, and 12 are located a distance of $2\sqrt{2}\,c$. Thus the *minimum* number of equivalent single jumps resulting in M-center formation introduces an uncertainty in the M-band oscillator strength of 50%, $0.38\times 12/(12+6)=0.25$.

The possibility for single atomic jumps of an F center or jumps of the negative-ion vacancy from which the F center is eventually formed, cannot be ruled out completely in the low temperature formation of M centers by x-rays, but the influence of such jumping on the magnitude of the oscillator strength does not occur if the jumping is done in a completely random way. In order to be random the jump of a newly created F center must be completely oblivious to an existing nearby (or neighboring) F center. This assumption is reasonable if the excess local energy at a newly created F center is larger than the energy to be gained by the F center in aggregating with a nearby F center. In this case an F center has the same probability of jumping to a negative-ion site that is adjacent to an existing F center as jumping to a site that does not have an F center adjacent to it. It also means that an F center created next to an existing F center may destroy a possible M center by jumping away. It can be shown quite simply that in such randomized jumping, the M-center oscillator strength determined from low temperature measurements is not at all affected. Regardless of single random jumps or multiple random jumps the geometrical factor remains 12, as if no jumping occurred.

Let us consider in detail only the simplest case, that of a single random jump. We consider an F center to be located at the origin (0,0,0). The second F center may be initially fall at 12 equivalent (1,1,0) positions, 6 equivalent (2,0,0) positions, 24 equivalent (2,1,1) positions, or 12 equivalent (2,2,0) positions in the negative-ion sublattice. The second F center has a total of 12 negative-ion sites available to it for the single atomic jump. If the second F center is created at one of the (1,1,0) positions, 5 of its possible 12 jumps will result in M-center formation. (Four will remain adjacent to the (0,0,0) F center and the fifth will interchange places with it.) Thus the probability of a (1,1,0) F center contributing to the creation of an M center is 5/12. Since there are a total of 12 such sites, 5 of these sites on the average contribute to M-center formation ($12\times 5/12$). These results are summarized in Table II together with the results for the remaining sites. As shown in this table the total effective number of negative-ion sites surrounding a given F center is again 12 even in the instance of one atomic jump. This can also be shown to be the case for more than a single jump if the process is a random one. The basis for this fact is that for every jumping sequence that brings two F centers together to form an M center, there is a completely equivalent but oppositely directed sequence of jumping that destroys an M center if the process is fully randomized. This situation is then such that the oscillator strength of 0.38 determined from the quadratic relation between F and M centers at low temperature, requires no adjustment

Table II. Total effective number of sites contributing to M center formation in the case of a single random jump of the F center at low temperature.

Site Location	No. of Sites	Probability of Site Contributing to M center Formation	No. of Sites Contributing to M center Formation
(1,1,0)	12	5/12	5
(2,0,0)	6	4/12	2
(2,1,1)	24	2/12	4
(2,2,0)	12	1/12	1
		Total	12

for a completely randomized jumping process. If, however, the forces between closely spaced *F* centers are sufficiently great to induce a directed single jump, the oscillator strength may require a correction of at least 50% as pointed out above.

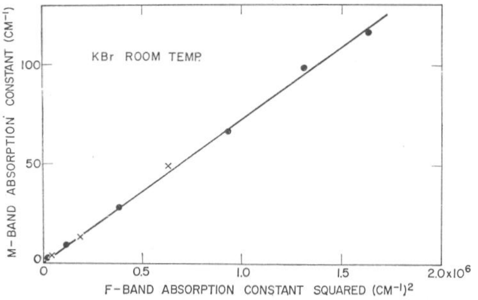

Fig. 2. Absorption constant of the *M* band *vs* absorption constant of the *F* band squared for KBr x-rayed at room temperature in the dark. Data for two samples are plotted.

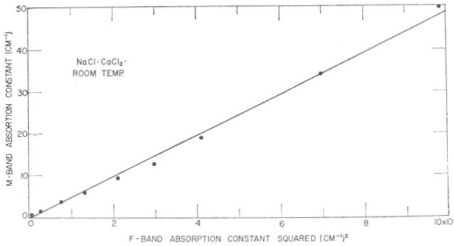

Fig. 3. Absorption constant of the *M* band *vs* absorption constant of the *F* band squared for NaCl doped with $CaCl_2$ (0.5 mole percent added to the melt). x-raying was performed in the dark at room temperature.

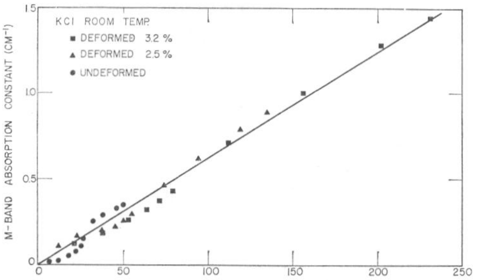

Fig. 4. Absorption constant of the *M* band *vs* absorption constant of the *F* band squared for undeformed and deformed KCl x-rayed at room temperature in the dark. Data taken from W. E. Bron, see Table III.

Table III. *K′* at room temperature for crystals x-rayed in the dark (in units of $10^{-21}cm^3$)

Crystal	*K′*	Reference
KBr:KH	negligible	H. W. Etzel: Private communication
KBr	7.9	Present author: Fig. 2.
LiF	36	I. L. Mador *et al.*: Phys. Rev. **96** (1954) 617.
NaCl:$CaCl_2$	45	Present author: Fig. 3.
NaCl	110	M. F. Merriam: Private communication
	160	I. L. Mador *et al.*: Same as above
KCl (def. & undeformed)	610	W. E. Bron: Phys. Rev. **119** (1960) 1853, Fig. 4 in this text.

A quadratic relation between *F* and *M* centers ($n_M = K'n_F^2$, $K' =$const.), similar to that observed at low temperature is observed for alkali halides x-rayed at room temperature. The constant of proportionality at room temperature reflects the much enhanced ratio of *M* centers to *F* centers due presumably to the ability of the *F* center to migrate. Table III gives a composite of values of *K′*. The data for KBr is taken from Fig. 2, the data for calcium doped NaCl is taken from Fig. 3, and the data for KCl is taken from the work of Bron and replotted in Fig. 4 to show the quadratic relationship between *F* and *M* centers. A similar relationship for LiF and NaCl has been previously reported in treating the data of Mador *et al.*[2] It is apparent that there are significant variations in the relative *M* to *F* ratio for various alkali halides. As this ratio becomes appreciable, proper account of the contribution of *M* center excited states under the *F* band is required[9]. There is also appreciable variation for samples of the same alkali halide. For example, the presence of a divalent impurity like calcium has the effect of suppressing the concentration ratio, while hydride addition seems to inhibit *M* center formation (see Table III). On the other hand the degree of deformation (and presumably the dislocation content) does not affect the quadratic proportionality (Fig. 4), although both the *F* and *M* center concentrations individually are markedly affected. The increase in the *M* center content in x-raying at room temperature can in a general way be attributed to either an enhanced migration of *F* centers requiring a long range interaction, or conversely, a short range interaction acting between highly concentrated F centers, but the details of the process cannot be understood with any degree of clarity in the absence of a deeper insight into the many structure-sensitive properties of F center formation at the same temperature.

The author would like to acknowledge many helpful discussions with Dr. James H. Schulman.

References

1 C. Z. van Doorn: Phys. Rev. Letters **4** (1960) 236.

2 B. J. Faraday, H. Rabin, and W. D. Compton: Phys. Rev. Letters **7** (1961) 57, 433.

3 D. Dutton and R. Maurer: Phys. Rev. **90** (1953) 126; G. Bonissoni *et al.*: *Proc. Internat. Conf. on Color Centers and Crystal Lum., Torino, Italy (1960)* Fig. 8.

4 A. Halperin and N. Kristianpoller: J. Optical Soc. Am. **48** (1958) 996.

5 F. Lüty: Z. Physik **165** (1961) 17.

6 A. A. Braner *et al.*: *Proc. Internat. Conf. on Color Centers & Crystal Lum., Torino, Italy (1969)* p. 46.

7 H. Okura: J. Phys. Soc. Japan **12** (1957) 1313.

8 T. Tomiki: J. Phys. Soc. Japan **15** (1960) 488.

9 W. A. Sibley and E. Sonder have shown that an appropriate correction must be made in the case of gamma irradiated KCl after sufficiently long irradiation (private communication).

DISCUSSION

Crawford, J. H.: Sonder and Sibley have studied slopes of the M center concentration *vs* the square of the F center concentration at room temperature for a wide variety of KCl crystals. The slope of divalent cation doped crystal is much lower than that of commercial crystals (Harshaw, Isomet and Optovac). Therefore, it was thought that the slope of the $[M]$ *vs* $[F]^2$ curve might be indicative of divalent cation content. However recent studies of high purity zone refined crystals reveal that these also exhibit a low slope. Hence the factors responsible for slope of the $[M]$ *vs* $[F]^2$ curves at room temperature are quite obscure.

Rabin, H.: I concur in the obscurity of the role of structure sensitive properties in the slope of the $[M]$ *vs* $[F]^2$ curve. I am ever surprised that there is at all a linear proportionality between $[M]$ and $[F]^2$ in the room temperature range in a variety of alkali halides covering a wide range of structure sensitivity.

Pick, H.: Don't you think that the luminescence, which occurs under x-irradiation has some importance for the M production?

Rabin, H.: Until evidence is submitted to the contrary, we must consider this as a definite possibility. As matters stand there are experimental reports of x-ray induced photoluminescent emission overlapping the spectral region of the F band, and aside from questions relating to the quantity of this emission, which will have to be evaluated, there does not appear to be any fundamental objection to an internally generated photon inducing optical $F \rightarrow M$ conversion.

Smoluchowski, R.: Formation of a vacancy near an F center may or may not lead to an M center depending upon whether the probability of electron capture by the vacancy is larger or smaller than the probability that the electric field of the vacancy will eliminate the electron from the $2p$-state of the F center, if it is excited. This will affect the F to M ratio differently in different alkali halides.

Rabin, H.: I would expect that the electron will be shared by the pair of negative ion vacancies rather than being ejected, much as one would expect for the center described by Seitz for the R_1 band. It is true that in the event the electron is ejected, the probability of M center formation is greatly reduced owing to the anticipated instability of a pair or adjacent negative ion vacancies, and accordingly the M to F ratio would be affected. I would think that it would be more likely for the F center electron to be ejected in the act which created the negative ion vacancy as a neighbor, rather than the ejection taking place subsequently by the specific action of the electric field of the created vacancy.

Nowick, A. S.: For optical bleaching above 200°K both optical excitation and thermal activation (with activation energy that we have shown to be equal 0.4 ev) are required. Would it not be worth considering, then, that the F center migrates with this low activation energy only when it is in the excited state?

Rabin, H.: If optical $F \rightarrow M$ conversion is governed by a comparatively low activation energy as indicated in your results the number of possibilities for the mechanism is considerably reduced and the process you suggest appears to be in prime contention. In my estimation the ultimate determination of the mechanism or mechanisms which lead to the aggregation of F centers will be decided by cleverly conceived experiments.

Perio, P.: Would you please state what absorption band you associate with M centers in LiF? If it is, as I presume, the 4500 Å band, I feel somewhat unhappy since there is some evidence that this band is complex and may be sometimes resolved into two peaks.

Rabin, H.: Conventionally one assumes the M band to fall in the vicinity of 4500 Å and I likewise have made the same assumption. If there is any ambiguity in the M band in LiF, one will have to take a fresh look at the quadratic relationship between F and M centers in LiF as reported by Faraday, Rabin and Compton (and extracted from the earlier work of Mador, Wallis, Williams and Herman).

Clark, C. D.: What evidence have you that the 2500 Å band in LiF is that associated with the F center?

We have studied the properties of the 2500 Å band in LiF at 293 and 120°K. We find that its properties are not similar to those of the F bands in other alkali halides. Particularly, when we optically bleach the 2500 Å band with 2537 Å radiation, a band at 4500 Å is barely detected.

Rabin, H.: Although LiF has been known to show peculiarities not exhibited in other alkali halides, it has been my distinct impression that 2500 Å band in LiF is indeed a reasonable good F band. To be specific it is the principal optical band which appears upon irradiation, it shifts with temperature like other F centers, its half-width shows the anticipated temperature dependence, it follows a Mollwo relation with other F bands, and its magnetic resonance spectrum is accounted for as reported at this Conference by Professor Slichter.* Your observation of inefficient optical $F \rightarrow M$ conversion may be related to the specific kinetics of F center aggregation in the LiF crystals employed, and I think this observation in itself does not necessarily reflect on the 2500 Å band as an F band.

* *Proc. Int. Conf. Cryst. Latt. Def.* (*1962*): J. Phys. Soc. Japan **18** Suppl. II (1963) 254.

Klick, C. C.: I believe that Van Doorn in a recent thesis has also seen evidence by bleaching for structure in the M band in materials other than LiF.

Slichter, C. P.: In the ENDOR experiments, Holton and Blum have plotted the wave-function of the F center out to 7 lattice shells. The structure is that of a normal F center. This center was produced by x-raying at room temperature. Precise measurements have not been made to correlate the optical and resonance intensities (as Blum has done for NaF), but rough measurements correlate the intensity of the ESR and optical band usually called the F band.