

Production and Destruction of F and M Centers by X Rays in Alkali Halides at Low Temperatures

R. F. WALLIS AND B. J. FARADAY

U. S. Naval Research Laboratory, Washington, D. C.

(Received 16 August 1963; revised manuscript received 18 November 1963)

An approximate theoretical analysis is given of the production and destruction of F and M centers by x rays in alkali halides at low temperatures. Kinetic equations describing the time rates of change of F - and M -center concentrations are formulated. Conditions on the kinetic coefficients are established for the validity of the square-law relation between F - and M -center concentrations when the concentration of F centers is not a linear function of x-ray irradiation time. Two mechanisms which lead to a saturation of F -center production are analyzed in some detail. A comparison of theoretical and experimental results leads to information concerning the processes involved in the production and destruction of color centers by x rays.

I. INTRODUCTION

IN a recent paper,¹ Faraday, Rabin, and Compton have shown that the concentrations of F and M centers bear a simple relationship to one another during their production by x rays in a number of alkali halide crystals. These authors observe that the M -center concentration is proportional to the square of the F -center concentration and cite this experimental fact as evidence in favor of the F_2 model of the M center; i.e., two F centers occupying adjacent anion sites.

Another interesting fact is that the square-law relation between F - and M -center concentrations remains valid even through the F -center growth curve has deviated significantly from a straight line and in some cases has approached saturation. If the F centers and M centers are sufficiently mobile, the square-law relation might be a manifestation of a quasiequilibrium between F and M centers. Experimental evidence cited by Sonder and Sibley² supports the view that such a quasiequilibrium exists during x irradiation at room temperature. At temperatures near liquid-nitrogen temperature and below, however, the F and M centers appear to be immobile and quasiequilibrium is unlikely. It is the purpose of the present paper to show under what circumstances the square-law relation between F - and M -center concentrations may be expected to hold at low temperatures. Some implications regarding the processes occurring are discussed.

II. THEORETICAL DEVELOPMENT

A simple kinetic equation can be written for the time rate of change of the F -center concentration which includes the possibility of saturation. Such an equation is

$$dn_F/dt = A - Bn_F, \quad (1)$$

where n_F is the F -center concentration at time t , A is the gross rate of production of F centers, and B is a kinetic coefficient for a process leading to saturation of F -center production. For the moment no assumptions

will be made concerning the nature of the processes involved in Eq. (1).

The solution to Eq. (1) for the initial condition $n_F=0$ for $t=0$ may be written as

$$n_F = (A/B)(1 - e^{-Bt}). \quad (2)$$

As t becomes very large, n_F approaches its saturation value A/B .

The square-law relation between F - and M -center concentrations can be written in the form

$$n_M = \frac{1}{2}pn_F^2, \quad (3)$$

where n_M is the M -center concentration and p is a constant. Differentiating Eq. (3) with respect to t , we get

$$dn_M/dt = pn_F(dn_F/dt). \quad (4)$$

Substituting Eq. (1) into Eq. (4) and utilizing Eq. (3) leads to the result

$$dn_M/dt = Apn_F - 2Bn_M. \quad (5)$$

The first term on the right-hand side of Eq. (5) corresponds to the production of M centers from F centers, while the second term corresponds to a process leading to M -center saturation. A very interesting feature of this saturation term is that its kinetic coefficient $2B$ is exactly twice the kinetic coefficient for the F -center saturation term in Eq. (1). This restriction is imposed by the square-law relation and might not be expected *a priori*. It must be a natural consequence of any mechanism proposed for the processes involved in Eqs. (1) and (5).

The solution to Eq. (5) subject to the initial conditions $n_F=n_M=0$ can be written as

$$n_M = \frac{1}{2}p(A/B)^2(1 - e^{-Bt})^2. \quad (6)$$

Equation (6) is, of course, consistent with the square law specified by Eq. (3).

In analyzing experimental data it is convenient to have equations expressed in terms of the absorption coefficients α_F and α_M , rather than in terms of the concentrations n_F and n_M . Let us restrict our attention to KCl at liquid-nitrogen temperature. Utilizing Smakula's

¹ B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters **7**, 57 (1961).

² E. Sonder and W. A. Sibley, Phys. Rev. **129**, 1578 (1963).

formula and data given by Faraday, Rabin, and Compton, one finds that

$$n_F/\alpha_F \approx n_M/\alpha_M \approx 2 \times 10^{15} \text{ cm}^{-2} = q. \quad (7)$$

We ignore the possibility that the M center may have some oscillator strength under the F band. Under the condition $n_F \gg n_M$, and to the order of precision required in this paper, such a simplification is justified. If Eqs. (1)-(6) are transformed to replace n_F and n_M by α_F and α_M , respectively, then the kinetic coefficients must be transformed as follows:

$$A \rightarrow A' = A/q, \quad (8a)$$

$$B \rightarrow B, \quad (8b)$$

$$p \rightarrow p' = pq. \quad (8c)$$

The results after transforming Eqs. (2) and (6) will be needed subsequently and are given explicitly:

$$\alpha_F = (A'/B)(1 - e^{-Bt}), \quad (9)$$

$$\alpha_M = \frac{1}{2}p'(A'/B)^2(1 - e^{-Bt})^2. \quad (10)$$

III. COMPARISON WITH EXPERIMENT

In Fig. 1 experimental absorption coefficients of F and M centers in KCl are plotted as functions of x -irradiation time at liquid-nitrogen temperature. The experimental procedure used was that of Faraday, Rabin, and Compton.¹ Also shown in Fig. 1 are theoretical curves based on Eqs. (9) and (10). Although no exhaustive effort was made to find the optimum fit to the data, one sees that a reasonably good fit has been obtained. The values of the various parameters used in Fig. 1 are

$$A' = 166 \text{ cm}^{-1} \text{ h}^{-1},$$

$$B = 0.065 \text{ h}^{-1},$$

$$p' = 3.8 \times 10^{-6} \text{ cm}.$$

Utilizing Eqs. (7) and (8) we obtain

$$A = 3.32 \times 10^{17} \text{ cm}^{-3} \text{ h}^{-1},$$

$$p = 1.9 \times 10^{-21} \text{ cm}^3.$$

Fairly good fits may also be obtained for KBr data at liquid-nitrogen temperature leading to values for the various constants which do not differ substantially from those for KCl. Somewhat poorer fits result when one considers KCl and KBr data at liquid-helium temperature. At the latter temperature the absorption coefficients of F and M centers after very short irradiation times are too large to be consistent with Eqs. (9) and (10). Additional processes not considered in deriving Eqs. (9) and (10) appear to be required to explain the liquid-helium data.

IV. COMMENTS ON MECHANISM

The results obtained in the previous sections may be utilized to shed some light on the mechanism of the

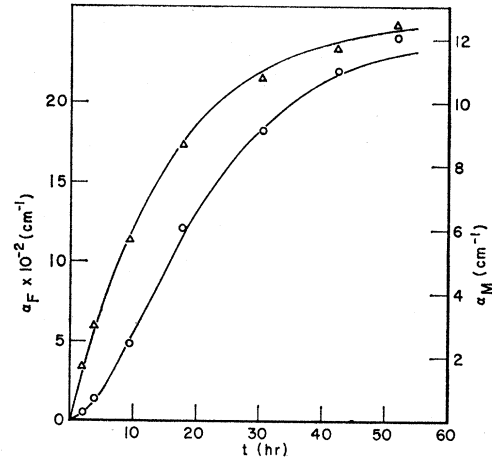


FIG. 1. Absorption coefficients for F and M centers in KCl plotted as functions of x -irradiation time at liquid-nitrogen temperature. The solid curves are theoretical fits to the experimental data for F centers (Δ) and M centers (\circ).

production and destruction of F and M centers by x irradiation at liquid-nitrogen temperature. We analyze one mechanism and show that it does not fit the experimental data no matter how the parameters are chosen. We analyze a second mechanism and show that it gives a good fit to the data for values of the parameters which are physically reasonable. Let us assume that x rays create F centers at random on anion sites and that the F centers are not mobile. When two F centers are created on adjacent anion sites, an M center is formed. At first, let us assume that F centers cannot be destroyed except by transformation to M centers and that M centers cannot be destroyed except by transformation to higher centers such as R centers. Under these assumptions the kinetic equations can be written in the forms

$$\frac{dn_F}{dt} = \gamma(N - n_T)[1 - (n_T/N)]^{K_F} - \gamma K_F n_F, \quad (11)$$

$$\frac{dn_M}{dt} = \gamma K_F n_F [1 - (n_T/N)]^{K_{F'}} - \gamma K_M n_M, \quad (12)$$

where

$$n_T = n_F + 2n_M + 3n_R \dots \quad (13)$$

is the total concentration of occupied sites, N is the total concentration of anion sites, γ is the probability per unit time that a given anion site is converted to a vacancy plus trapped electron, and K_F and K_M are the coordination numbers for F and M centers. The quantity $K_{F'}$ is the number of anion nearest neighbors to a given anion site but excluding one of the nearest-neighbor sites and those sites which are simultaneously nearest neighbors of the latter site and the given site. The factor involving $K_{F'}$ in Eq. (12) accounts for the fact that no M center is formed if a center is created at an anion site which is a nearest neighbor of each of two F centers. For KCl, we have $K_F = 12$, $K_M = 18$, and $K_{F'} = 7$.

Equations (11) and (12) are difficult to solve as they stand. Approximate equations can be obtained by

assuming that $n_R \ll n_M \ll n_F$ and that the concentrations of higher centers are negligible. Then a power series expansion leads to the following equations which are correct to a consistent order of approximation;

$$dn_F/dt = \gamma \{ N - (2K_F + 1)n_F - [(K_F + 1)n_M] \}, \quad (14)$$

$$dn_M/dt = \gamma \{ K_F n_F - (2K_F' + K_M)n_M - [K_F'(2K_F - K_F' + 1)n_F n_M / N] \}. \quad (15)$$

In order for the square law given by Eq. (3) to be consistent with Eqs. (11) and (12) it is necessary that

$$p = K_F / N, \quad (16a)$$

$$2K_F' + K_M = 2(2K_F + 1), \quad (16b)$$

$$K_F'(2K_F - K_F' + 1) = K_F(K_F + 1). \quad (16c)$$

Utilizing the appropriate values for KCl we see immediately that neither Eq. (16b) nor Eq. (16c) is valid. We further note that the coefficients of the terms linear in n_F in Eqs. (14) and (15) have magnitudes $\gamma(2K_F + 1)$ and γK_F , respectively, which differ by approximately a factor of two. On the other hand, the corresponding magnitudes in Eqs. (1) and (5), namely B and A_p , have been found by comparison with experimental data in Sec. III to differ by two orders of magnitude. Physically, saturation of F -center production in the mechanism under consideration occurs only when n_T is an appreciable fraction of N , whereas experimentally saturation occurs much sooner. It is therefore clear that the mechanism considered above requires significant modification.

Before considering a new mechanism, however, we shall assess the validity of Eqs. (14) and (15) by comparing their solutions with the results of a Monte Carlo generation of F and M centers on a two-dimensional lattice.

The solutions to Eqs. (14) and (15) may be written in the form

$$n_F = n_F^{(0)} + \Delta n_F, \quad (17a)$$

$$n_M = n_M^{(0)} + \Delta n_M, \quad (17b)$$

where $n_F^{(0)}$ and $n_M^{(0)}$ are solutions obtained by omitting the square bracketed terms on the right-hand sides of Eqs. (14) and (15). Expressions for $n_F^{(0)}$ and $n_M^{(0)}$ are

$$n_F^{(0)} = (A_1/B_1)(1 - e^{-B_1 t}), \quad (18)$$

$$n_M^{(0)} = \frac{A_1 A_2}{B_1 B_2 (B_2 - B_1)} \times \{ (B_2 - B_1) - B_2 e^{-B_1 t} + B_1 e^{-B_2 t} \}, \quad (19)$$

where

$$A_1 = \gamma N, \quad (20a)$$

$$A_2 = \gamma K_F, \quad (20b)$$

$$B_1 = \gamma(2K_F + 1), \quad (20c)$$

$$B_2 = \gamma(2K_F' + K_M). \quad (20d)$$

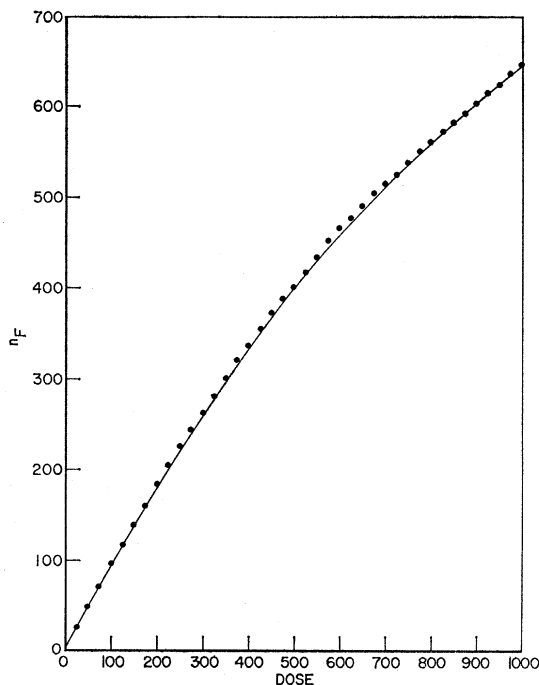


FIG. 2. Number of F centers as a function of dose for a two-dimensional model. The circles are the results of the Monte Carlo determination. The solid curve is the theoretical result.

Substitution of Eqs. (18) and (19) into the square bracketed terms in Eqs. (14) and (15) and integration of the resulting equations leads to consistent approximate results for Δn_F and Δn_M , which may be written as

$$\Delta n_F = -D_1 \{ [(B_2 - B_1)/B_1](1 - e^{-B_1 t}) - B_2 t e^{-B_1 t} + [B_1/(B_1 - B_2)](e^{-B_2 t} - e^{-B_1 t}) \}, \quad (21)$$

$$\Delta n_M = -D_2 \{ [(B_2 - B_1)/B_2](1 - e^{-B_2 t}) - [B_2/(B_2 - B_1)](e^{-B_1 t} - e^{-B_2 t}) + B_1 t e^{-B_2 t} + [B_2/(B_2 - 2B_1)](e^{-2B_1 t} - e^{-B_2 t}) - e^{-B_1 t} + e^{-(B_2 + B_1)t} \}, \quad (22)$$

where

$$D_1 = \frac{\gamma(K_F + 1)A_1 A_2}{B_1 B_2 (B_2 - B_1)}, \quad (23a)$$

$$D_2 = \frac{\gamma K_F'(2K_F - K_F' + 1)A_1^2 A_2}{N B_1^2 B_2 (B_2 - B_1)}. \quad (23b)$$

The Monte Carlo generation of F and M centers was accomplished by placing points one at a time on the sites of a simple square lattice containing 10^4 sites. For the simple square lattice, $K_F = 4$, $K_M = 6$, and $K_F' = 3$. The coordinates of the points were taken from a book of random numbers.³ A point occupying a site whose nearest-neighbor sites were empty was labeled an F center, while two points occupying nearest-neighbor

³ The Rand Corporation, *A Book of Random Digits* (The Free Press, Glencoe, Illinois, 1955).

sites, but with the nearest neighbors to these sites empty, constituted an M center. If a point fell on a site already occupied, it was assumed that the original center remained unchanged. The numbers of F and M centers present were tabulated after each point was put down. Five separate runs were made with a total dose of 10^8 points. The results were averaged over the five runs at intervals of 25 points.

The results for the averages over the five runs are plotted as functions of dose for F centers in Fig. 2 and for M centers in Fig. 3. The theoretical curve specified by Eqs. (17a), (18), and (21) is given in Fig. 2 and the theoretical curve specified by Eqs. (17b), (19), and (22) is given in Fig. 3. Also shown in Fig. 3 is the maximum range of M -center numbers at various doses. The maximum range of F -center numbers is relatively small at the doses indicated in Fig. 2 and is not shown. It may be seen that the agreement between theory and "experiment" is rather good for both F and M centers. A discrepancy of a few percent might be expected since edge effects have been omitted in the theory.

The dashed curve in Fig. 3 gives the smoothed variation of the number of M centers to be expected from the "experimental" F -center numbers given in Fig. 2 if the square-law Eq. (3) were valid. One sees that not only is there a substantial discrepancy between the square-law predicted and the averaged "experimental" value, but also the square-law prediction falls outside the maximum range of M -center numbers at the higher doses.

Returning now to the question of mechanism, from the experimental fact that $A\dot{p} \ll B$ in Eqs. (1) and (5), one may conclude that additional processes leading to saturation of F -center production are required. Let us therefore assume that F centers may be destroyed by x rays not only through conversion to M centers but also through conversion to other entities which will not be further specified. If one of the centers thus destroyed is part of an M center, the M center is thereby destroyed leaving an F center. In view of the experimental relation $A\dot{p} \ll B$, we shall henceforth neglect the saturation of F - and M -center production by transformation to M and R centers, respectively. Also, since $n_M \ll n_F$ under the experimental conditions of interest, we shall neglect the regeneration of F centers arising from the destruction of M centers. Utilizing these assumptions, we may write the kinetic equations in the form

$$dn_F/dt = \gamma N - \beta n_F, \quad (24)$$

$$dn_M/dt = \gamma K_F n_F - 2\beta' n_M, \quad (25)$$

where β is the probability per unit time that a vacancy-electron complex constituting an F center is destroyed and β' is the probability that one of the vacancy-electron complexes in an M center is destroyed. Comparison with Eqs. (1) and (5) indicates that Eqs. (24) and (25) are consistent with the square-law relation

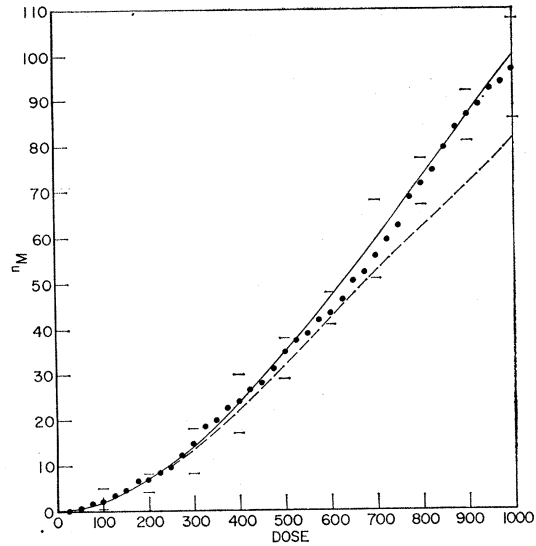


FIG. 3. Number of M centers as a function of dose for a two-dimensional model. The circles are the results of the Monte Carlo determination. The solid curve is the theoretical result. The dashed curve is square-law result based on the data of Fig. 2. The horizontal bars give the maximum range of the number of M centers at a given dose.

only if

$$\beta' = \beta. \quad (26)$$

It is clear from this result and also from the results discussed earlier in this section that the square-law relation does not necessarily hold if the F_2 model of the M center is correct. Additional conditions such as that given by Eq. (26) must be imposed.

From the fitting of the kinetic constants to the experimental data in Fig. 1, one sees that the probability β for destroying an F center is much greater than the probability γ for creating an F center. Equations (24), (25), and (26) imply that the probability of destroying a vacancy-electron complex is independent of whether the complex is isolated or associated with another complex. This seems physically reasonable, since the x-ray quanta have energies much larger than the binding energy of an M center relative to two isolated F centers.

Additional evidence for the destruction of F centers by x rays has recently been cited by Sonder and Sibley.² These authors also consider the exhaustion of necessary sites as a mechanism for saturation of F -center production, but conclude that this possibility is unimportant.

V. CONCLUSION

The principal point of this paper is that the square-law relation between F - and M -center concentrations during their production by x rays at low temperatures is not something that is automatically going to exist even if the F_2 model for the M center is correct. When the concentration of F centers is not a linear function of x-ray irradiation time, certain conditions on the rate equations for F and M centers must be satisfied if the

square law is to be valid. A mechanism in which color centers are not destroyed except by transformation to higher aggregates is shown to be inconsistent with the experimental data. Another mechanism involving both the creation and destruction of F and M centers solely by x rays is shown to be consistent with the square law if the probability of destroying a vacancy-electron complex is independent of whether the complex is isolated or associated with another complex. This mechanism is

consistent with experimental data presented on the production of F and M centers at liquid-nitrogen temperature by x rays in KCl.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Herbert Rabin for several helpful discussions. They also thank Mrs. B. W. Hennis and Mrs. C. G. Johnson for carrying out the Monte Carlo calculations.

Vibronic Spectra of $\text{SrF}_2:\text{Sm}^{2+}$ and $\text{BaF}_2:\text{Sm}^{2+}$

ISAAC RICHMAN

The Aerospace Corporation, El Segundo, California

(Received 29 July 1963; revised manuscript received 28 October 1963)

Recent work of Wood and Kaiser has yielded vibronic data on Sm^{2+} doped in two isomorphous crystals, SrF_2 and BaF_2 . The present work proposes a model using Born-von Karmann boundary conditions, which predicts the number of vibronic satellites and the $k=0$ selection rules. It is shown, however, that the $k=0$ selection rules are too restrictive to explain the vibronic spectrum and that to obtain a satisfactory explanation one must consider transitions involving vibrations away from $k=0$. The model, when such transitions are taken into account, is shown to be consistent with the observed data. It is proposed that one of the modes observed in the vibronic spectrum corresponds to vibrations of the transverse optical branch, a second to the longitudinal optical branch, and a third to transitions away from $k=0$ involving the Raman active branch. This model is able to qualitatively explain the differences observed in the two host lattices. It is contrasted with an XY_8 complex model, proposed by Axe and Sorokin to explain the same data. Raman scattering data have been obtained placing the F_{2g} mode (at $k=0$) at 280 cm^{-1} in SrF_2 and at 243 cm^{-1} in BaF_2 .

INTRODUCTION

THE spectra of lanthanide ions in crystals often display so-called vibronic satellites in addition to lines attributed to pure electronic transitions. These

vibronic lines are attributed to a simultaneous excitation of the lanthanide ion and a lattice vibration.¹ The evidence for such a conclusion is outlined in a recent publication² (hereafter referred to as RSW) and will not be covered here. What remains uncertain is the model appropriate to the analysis of such vibronic transitions. In this note it will be shown that a reasonable explanation of the data of Wood and Kaiser³ on Sm^{2+} in SrF_2 and BaF_2 is provided by the model of Born and von Karmann for the lattice modes, obtained in the manner of Hornig,⁴ and Winston and Halford.⁵ The application to vibronic transitions requires some modification of the methods of Hornig, and Winston and Halford, and these are outlined in RSW.

EXPERIMENTAL DATA

The fluorescence spectra of Sm^{2+} in SrF_2 and BaF_2 are given in Table I. The data are from Wood and Kaiser.³ The column labeled $\delta\nu$ gives the spacing of the vibronic satellites from its associated electronic transition. If the transition is electronic, then there is an e in this column. The labeling: "two phonon processes" indicates

TABLE I. Fluorescence spectra of Sm^{2+} in SrF_2 and BaF_2 .^a

SrF_2		BaF_2		SrF_2	
Energy (cm^{-1})	$\delta\nu$ (cm^{-1})	Energy (cm^{-1})	$\delta\nu$ (cm^{-1})	Energy (cm^{-1})	$\delta\nu$ (cm^{-1})
14 803		14 652	e	13 140	e
14 616	e	14 432	220	13 050	90
14 530	86	14 465	187	12 980	160
14 470	146	14 395	257	12 950	190
14 390	226	14 331	321	12 890	250
14 325	291			12 850	290
14 260	356			12 780	360
				12 580	560 ^c
14 353	e	14 374	e	12 550	590 ^d
14 125	228	14 186	188	12 520	620
14 060	293	14 118	256	12 470	670 ^e
13 955	358			12 450	690
13 964	e	13 943 ^b	e	12 350	e
13 870	94	13 755	188	12 276	74
13 800	164	13 689	254	12 246	104
13 750	214			12 146	204
13 680	284			12 096	254
13 625	339			12 016	334
13 581	e	13 620 ^b	e		
13 490	91	13 432	188		
13 450	131	13 364	256		
13 370	211				
13 290	291				
13 230	351				

^a The letter e means electronic transition.
^b Not observed but probably where indicated.
^c Two-phonon process: 2×280 .
^d Two-phonon process: $360 + 220$.
^e Two-phonon process: $360 + 290$.

¹ H. Ewald, Ann. Physik 34, 209 (1939).

² I. Richman, R. A. Satten, and E. Y. Wong, J. Chem. Phys. 39, 1833 (1963).

³ D. L. Wood and W. Kaiser, Phys. Rev. 126, 2079 (1962).

⁴ D. F. Hornig, J. Chem. Phys. 16, 1063 (1948).

⁵ H. Winston and W. Halford, J. Chem. Phys. 17, 607 (1949).