

AN ABSTRACT OF THE THESIS OF

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Title THERMODYNAMICS OF THE REACTION
BETWEEN F AND M CENTERS

Abstract approved [REDACTED]
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The thermal equilibrium between F centers and M centers was studied at temperatures of 60, 70, 90, and 110°C. The log of the absorbance/mm of the F band was plotted against that of the M band. Four straight lines, one for each temperature, were obtained. The slopes were approximately one-half, confirming van Doorn and Haven's model of the M center.

From the temperature dependence of M-center concentration and using van Hoff's equation, the thermodynamic functions for the process $2F = M$ were obtained. A graph of $\ln K$ versus $1/T$ gave $\Delta H^\circ = -4.03 \pm 0.12$ kcal (0.175 eV). The standard reaction potential was calculated for two commonly used reference functions from $\Delta \tilde{F}^\circ = RT \ln K$. For the reference function number of centers per cubic centimeter $\Delta \tilde{F}_{333}^\circ = 28.8 \pm 0.1$, $\Delta \tilde{F}_{343}^\circ = 29.7 \pm 0.1$, $\Delta \tilde{F}_{363}^\circ = 31.5 \pm 0.1$, and $\Delta \tilde{F}_{383}^\circ = 33.6 \pm 0.1$ kcal. From the definition of Gibbs free energy, $\Delta \tilde{S}^\circ$ was found to be -98 cal/deg. for all

temperatures of concern here. Using the mole fraction reference function, the standard reaction potentials were $\Delta\tilde{F}^{\circ}_{333} = -5.08 \pm 0.11$, $\Delta\tilde{F}^{\circ}_{343} = -5.19 \pm 0.12$, $\Delta\tilde{F}^{\circ}_{363} = -5.31 \pm 0.10$, and $\Delta\tilde{F}^{\circ}_{383} = 05.37 \pm 0.11$ kcal. The standard entropy changes were $\Delta\tilde{S}^{\circ}_{363} = 3.83 \pm 0.27$, and $\Delta\tilde{S}^{\circ}_{383} = 3.78 \pm 0.28$ cal/deg.

Other reported values for these functions are $\Delta H = 0.38$ ev and $\Delta S = 51$ cal/deg. An argument is presented against these values on the basis that the systems studied were in a steady state not in an equilibrium state. It is clear there was an entropy production and a free energy decrease, and hence the other reported values have no thermodynamic significance.

It is demonstrated that the standard entropy change, in the mole fraction reference system, should be $\Delta\tilde{S}^{\circ} = R \ln 6 = 3.56$ cal/deg which agrees with the experimental value. Equations for ΔS are obtained both on an experimental basis and a statistical basis. The ΔS 's obtained from these equations are in good agreement with each other.

The M band was found to be asymmetrical and is not well described by a single Gaussian shaped band. The M band was described to a fair degree of accuracy by using two Gaussian curves. One is used to describe the red side and one the violet side. An attempt to fit the M-band shape to a Poisson curve showed that the double-Gaussian fit is superior. The Gaussian constants for both

sides of the M band are tabulated for 77 and 298°K.

The M band was observed to change symmetry upon cooling from 298°K to 77°K. Although this inversion was not intensely studied, it is thought to occur near 200°K.

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F AND M CENTERS

by

JOHN DAVID ZAHRT

A THESIS

submitted to

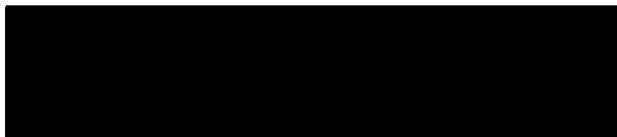
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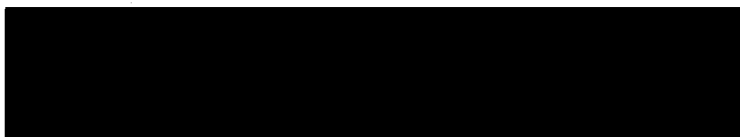
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THERMODYNAMICS OF THE REACTION BETWEEN F AND M CENTERS

I. INTRODUCTION

Alkali Halides

Pure alkali halides are transparent over a wide range of wavelengths, including the visible region of the spectrum. This wide range of transparency is bounded in the infrared region by a fundamental absorption associated with ion vibration. In KCl the edge of this fundamental absorption is near 70,900 millimicrons ($\text{m}\mu$). The transparency is bounded in the ultraviolet by fundamental electronic transitions from the valence band to exciton levels below the conduction band. This absorption edge is near 160 $\text{m}\mu$ in KCl.

The alkali halides, excluding RbCl, CsCl, CsBr, and CsI, crystallize into face-centered-cubic structures at normal temperatures and pressures. Single crystals of these materials are thus easily cleaved along the $\{100\}$ planes resulting in clean, smooth surfaces upon which to work.

F Centers

It has been known for nearly a century that an alkali-halide crystal heated in the presence of an alkali-metal vapor will become colored; it will absorb visible light. In past years it has been found

that these crystals can also be colored by high-energy photons, such as x rays, ultraviolet light, and gamma rays, and by bombardment with high-energy particles, such as neutrons and electrons. Electron injection in a crystal placed between a cathode and anode with high temperatures and electric fields can also be used as a coloration source. Heating a crystal in a vapor of halogen gas results in the formation of hole centers. All of these methods except the last produce a main absorption band which always appears at the same energy in a given crystal; the position of the absorption band is an inherent property of the crystal and not of the means of production. Among the various bands produced, this major absorption band has been labeled the F band, after the German word Farbe, meaning color.

de Boer (1) proposed a model for the center responsible for the F band which consists of an electron trapped at an anion vacancy. Since the anion vacancy has a positive charge associated with it, the F center is electrically neutral. The de Boer model is currently the accepted model and is not likely to be severely altered in the future.

The shape of the F band was first considered to be Lorentzian, later Gaussian, then double-Gaussian. One Gaussian shape describes the violet side of the band and a different one describes the red side. Most recently Markham (11) showed that the F band was Poissonian

(Pekarian) in shape at low temperatures and double-Gaussian at high temperatures. There is theoretical justification for the Poisson shape but not for the double-Gaussian. We shall be more interested in band shape later on when we discuss the shape of the M band.

Here we note that in an indirect way band shape is relevant to the determination of color-center concentration in a crystal.

Smakula (19) developed an equation based on classical dispersion theory for the number of noninteracting centers in a crystal (equation (1a)). The Lorentz shape is implicit in the derivation. According to Smakula, the concentration of centers is given by

$$Nf = \frac{9mc^2}{2e^2} \cdot \frac{n}{(n^2+2)^2} a_{\max} H, \quad (1a)$$

where N = concentration of absorbing centers

f = oscillator strength of absorbing center

n = index of refraction of the crystal

H = width of band at half its peak height

$a_{\max}$ = absorption coefficient, $(2.303/t) \log I_0/I$

I = transmitted light intensity

I_0 = incident light intensity

t = crystal thickness

and m , e , and c have their usual meanings. Numerically, Smakula's equation is

$$Nf = 1.29 \times 10^{17} \frac{n}{(n^2 + 2)^2} a_{\max} H. \quad (1b)$$

When H is given in electron volts and t is given in millimeters, N has the units centers/cubic centimeter. Refinements, including the use of Gaussian shape rather than Lorentzian shape, give

$$Nf = 0.87 \times 10^{17} \frac{n}{(n^2 + 2)^2} a_{\max} H. \quad (1c)$$

It is only necessary to measure N by a means not involving absorption spectroscopy to determine f for a given center in a given crystal. Experimentally this is readily done in various ways but in the case of f_F , the F-center oscillator strength, values have been obtained from 0.66 to 1.17. This is far outside of the precision expected. In KCl f_F is often taken as unity for simplicity, though the value of 0.81 obtained by Kleinschrod (8) and used by Konitzer and Markham (10) will be used in this work. Konitzer and Markham (10) have done a thorough study of the F band and found the following characteristic values for the pure F band in KCl. In Table 1, ϵ_v and ϵ_r correspond to photon energies at the half height on the violet and red side respectively.

Table 1. F band parameters in KCl.

Temperature ($^{\circ}\text{K}$)	$H(\text{ev})$	$\epsilon_v (\text{ev})$	$\epsilon_r (\text{ev})$	Position of Peak (ev)
78	0.193	2.408	2.215	2.303
300	0.336	2.407	2.071	2.226

The wavelength equivalent of the energy can be found by dividing 1239.5 by the energy in ev to obtain wavelength in mμ. Using $n = 1.49$ and the data cited above

$$N_F = 0.667 \times 10^{17} a_{\max} \quad (1d)$$

in KCl at 300°K. Since $N = C a_{\max} H$, only the constant C need be determined experimentally. A model of the system is necessary before f can be related to C. Thus the oscillator strength is not purely an experimentally determined number (17). It is here that the band shape influences the oscillator strength.

Secondary Centers

It has been found that the illumination of a crystal containing F centers with light of any wavelength contained in the F band causes a decrease in F-band absorbance. Associated with this decrease is a growth of absorption bands on the red side of the F band. In order of decreasing energy, these are the R_1 , R_2 , M, N_1 , and N_2 bands. For the M center (the center responsible for the M band) there have been found four bands corresponding to excitations from the ground state to excited states: the M_1 band between the R_2 and N_1 bands, the M_2 and M_3 bands under the F band, and the M_4 band under the R_1 band. We shall be concerned only with the M_1 band and will mean M to be synonymous with M_1 . R_1 and R_2 bands are likewise thought to be absorptions of the same center,

the F_3 of center.¹ The N_1 and N_2 bands however, may be due to two different configurations of an F_4 center (14).

M Centers

Molnar (12) discovered the M band in 1940. Seitz (18) proposed models for the R and M centers as early as 1946. These are diagrammed in Figure 1. All of the Seitz models lack cubic symmetry and have axes of symmetry lying in the $\langle 011 \rangle$ directions. Inui, et al. (5) made theoretical calculations on the Seitz M center and concluded that this model could account for the observed absorption band. Ueta (22) studied the dichroism of the M band and found that his observations agreed with the Seitz model and with Inui's calculations.

All of Seitz's models, lacking cubic symmetry, can be considered to be simple dipole oscillators with the dipole moment oriented along the line joining the negative ion vacancies. There are six possible orientations of $\langle 011 \rangle$ and in a normal crystal these

¹ Confusion may arise from the varied meaning of subscripts when applied to centers and bands. When we speak of F_i centers, the i refers to an aggregate of i F centers in the chemical sense. On the other hand, when we speak of the X_i bands, we are only systematizing the X bands by the index i . The i band designation, in general, tells us nothing of the center responsible for the band. For example the L_1 , L_2 , and L_3 bands are thought to correspond to excited states of the F center, whereas the centers responsible for the Z_1 , Z_2 , Z_3 , and Z_4 bands are not yet known.

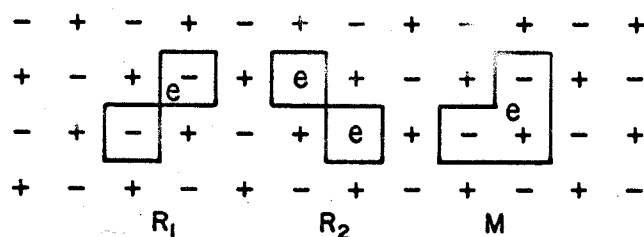


FIGURE 1. R and M centers after Seitz.

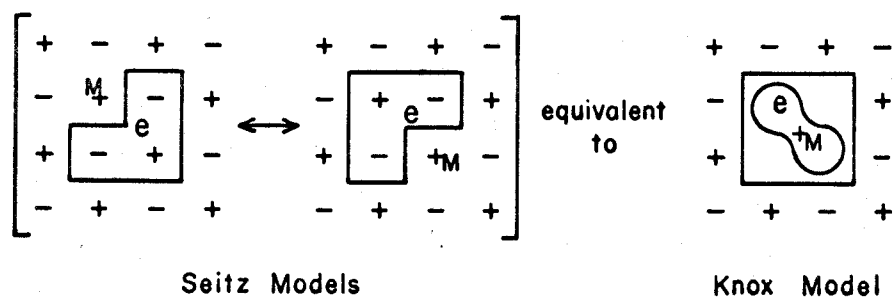


FIGURE 2. Knox model derived from resonance of two equivalent Seitz M centers.

six orientations should be equally occupied. The crystal is thus isotropic in M-band absorption. If the crystal is cooled down to liquid nitrogen temperature and irradiated with $[011]$ M-band light (electric-field vector pointing in the $[011]$ direction) on the (100) face, the M centers should be bleached as follows:

- a) those centers with $[011]$ orientation should be bleached by an amount x
- b) those centers with $[0\bar{1}1]$ orientation should not be bleached
- c) those centers lying in each of the remaining four $\langle 011 \rangle$ directions should be bleached by $x/4$ for each direction.

Experiments of this nature have been performed by Ueta (22) and Kanzaki (7) and the expected anisotropy confirmed. This experiment can not differentiate between one or another of the Seitz centers since they would all be expected to perform in this manner.

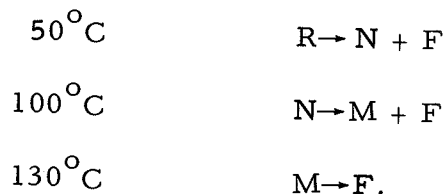
van Doorn and Haven (24) postulated a model composed of two F centers, one in a next-nearest-neighbor position to the other, for the M center. This model, called F_2 , is the same as Seitz's R_2 center. This proposal was the result of a study of the dichroism of both the absorption and the emission bands. The F_2 model, having inversion symmetry, should not possess a permanent dipole moment and thus not exhibit a linear Stark effect. The Seitz M center however, should possess a permanent dipole moment and should exhibit a linear Stark effect. Overhauser and Rüchardt (13)

performed an experiment using an applied field several hundred times that needed for the anticipated Stark effect and found none in either the M or the R bands. They concluded that both the M and the R centers possess inversion symmetry. Knox (9) then proposed a new model having inversion symmetry which kept the essential factors of the Seitz model. He considered a resonance of the Seitz M center between two configurations of the same orientation. This is diagrammed in Figure 2.

The results of further investigations have seemed to support the F_2 model. van Doorn (23) studied a supposed equilibrium between F and M centers at 697° and found the M center concentration to be proportional to the square of the F center concentration. Faraday, Rabin, and Compton (3) found a steady state while irradiating a crystal with x rays which also showed a quadratic relationship between F and M center concentration. Sonder (20) determined that the M center is not paramagnetic, which implies pairing of electrons. The F_2 model of the M center seems to account for all of the experimental data to date. Some of these data are unaccounted for by the Seitz or Knox model. More recently, a new theoretical discussion of the F_2 model of the M center by Evarestov (2) has given the energies for band maxima which are in good agreement with experimental data.

Exception must be made, however, to the thermal equilibrium

data obtained by van Doorn. Tomiki (21) has reported the following thermal decay scheme



The reactions are not meant to be stoichiometric as written. Yagi (25) has listed a similar decay scheme for photochemical transformations. It is contended that van Doorn did not study a true equilibrium between F and M centers at 697°C. van Doorn was probably "freezing-in" an equilibrium, associated with some temperature other than 697°C, during the quenching process.

It has been thought well worth while to repeat the van Doorn type of experiment. It will be demonstrated that a thermodynamic equilibrium does exist and the stoichiometric relationship between these two centers will be derived. Values for the various thermodynamic state functions will also be obtained.

The nature of the equilibrium experiment allowed a rather detailed study of the M-band shape. The M-band shape was analyzed several ways in a manner similar to that of Konitzer and Markham (10).

II. F AND M CENTER EQUILIBRIUM

Sample Preparation

All crystals used in this work were obtained from the Harshaw Chemical Co. These were additively colored by sealing the crystal and twice-distilled potassium in a pyrex tube and heating in a furnace. In general, the crystals were wrapped in aluminum foil. This process is described in more detail by Schulman and Compton (17). Crystals 1 and 2 were colored by H. Coker, 3 by F. Chapple, and 4 and 5 by the author. The density of coloration in Crystals 1 and 2 was shown to be homogeneous, by optical absorption measurements, to within 2%. Crystals 3, 4, and 5 were not measured quantitatively for homogeneity but appeared to be homogeneous on visual inspection.

Apparatus

The sample holder and cell were specially designed by this laboratory. The cell itself was made to be interchanged with the normal cell-holder of a Beckman model DU spectrophotometer. The cell and sample holder are schematically diagrammed in Figure 3. The cell was constructed from seven sections of brass and assembled in a sandwich-like manner and screwed together. The

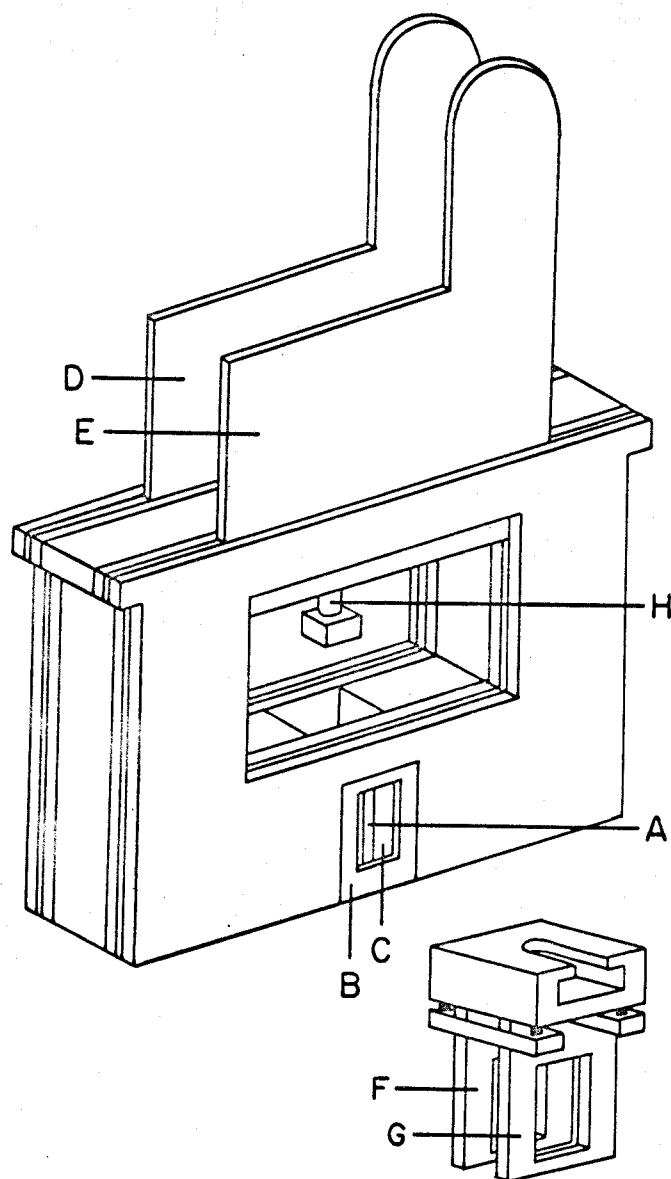


FIGURE 3. Schematic diagram of the cell and sample holder. A: slit; B and C: variable apertures; D and E: shutters; F and G: clamps for mounting the crystal; H: rod. Drawings are not to scale.

light from the spectrophotometer passed through the lower window (A), through the sample, and out the opposite side. There were two variable apertures (B and C) to adjust the dimensions of the light beam incident on the sample. The light entrance and exit holes could be closed off by the shutters (D and E) when the cell was to be moved from the dark room to the spectrophotometer.

The sample holder was also made of brass. The sample was placed between pieces F and G and four screws were tightened to keep the sample in place. The sample holder was mounted in the cell by a bayonet type mounting at the bottom end of rod H. The rod H could be rotated and because both the holder and receiver were square, the sample could be oriented two different ways in the light beam. The sample could be removed from the light beam simply by raising the rod. In this experiment, however, all measurements were made in the direction of short path length.

To attain equilibrium at high temperatures, the sample was placed in an aluminum well which was immersed in an oil bath. The bath was heated by a quartz heating element which was connected to a YSI model 72 proportional temperature controller. The bandwidth chosen was 0.2°C . The oil was kept in constant motion by the use of an electric stirrer. Heat conduction from the oil bath to the sample was good. Sample temperatures within one degree of the bath temperature were obtained within five minutes after immersion.

The sample equilibrium temperature was about 0.3°C lower than that of the bath. This was measured by means of a thermocouple inserted in a crystal.

Procedure

The crystal was removed from the pyrex tube in which it was colored, and under red light (a 25-watt tungsten bulb with a Kodak Series 1 filter) a sample was cleaved from the colored ingot. The sample was mounted in the sample holder and wrapped in several layers of aluminum foil. The foil-wrapped sample was then introduced into a furnace at 180°C for 20 minutes, 300°C for eight minutes, or 500°C^2 for 45 seconds to remove any F-aggregate (R, M, or N) or colloidal centers. The quench from these temperatures was made by placing the foil-wrapped holder, immediately after withdrawing it from the furnace, between two copper blocks and passing an air stream onto the foil. There was always some residual M band but never any observable R or N band. After the quench the foil was removed in the dark. There was no exposure of the sample to light from this time on, except during the actual spectrophotometric measurements. An initial spectrum was taken prior

²Sample 1 was the only sample subjected to heat treatment at 550°C . This was done to remove a colloidal absorption band.

to placing the sample and holder in the aluminum well and heating to the desired temperature. Spectra were taken at various time intervals depending on the sample and treatment temperature. When the absorbance was the same for two spectra, taken at different times, equilibrium was assumed to have been established. The temperature was then changed and the process was repeated. Quenches from the temperatures used in the study were made in a manner similar to that described above. The time required to quench a sample to near room temperature was approximately 20 seconds. This period was evidently too long for samples of high F-center concentration and this may account for some observed discrepancies. There was found no way to accelerate the cooling so that this source of error was not removed.

All optical absorption measurements for the equilibrium study were made by means of a Beckman model DU spectrophotometer at room temperature. The reference for absorption comparison was air.

Results

Equilibria were studied in the order 60° , 70° , 90° , 110° , 90° , 70° and 60° C. Figures 4 and 5 show the variation of the absorption coefficient at the peak of the M band, α'_M , with time for samples 1 and 2 (α'_M is 2.303 times the absorbance per millimeter

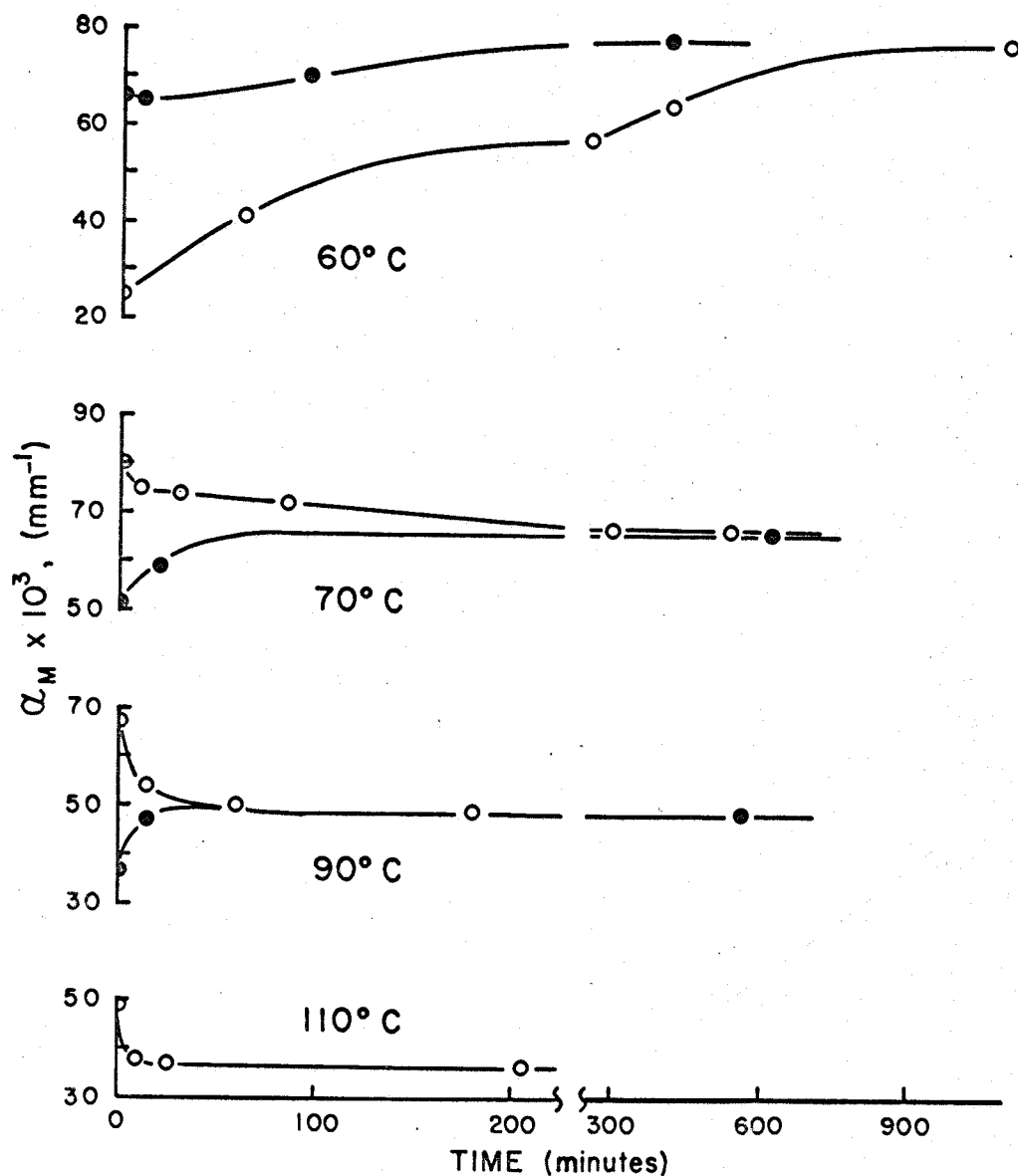


FIGURE 4. Growth and decay curves of the M-band at 60, 70, 90 and 110°C. (Sample I)

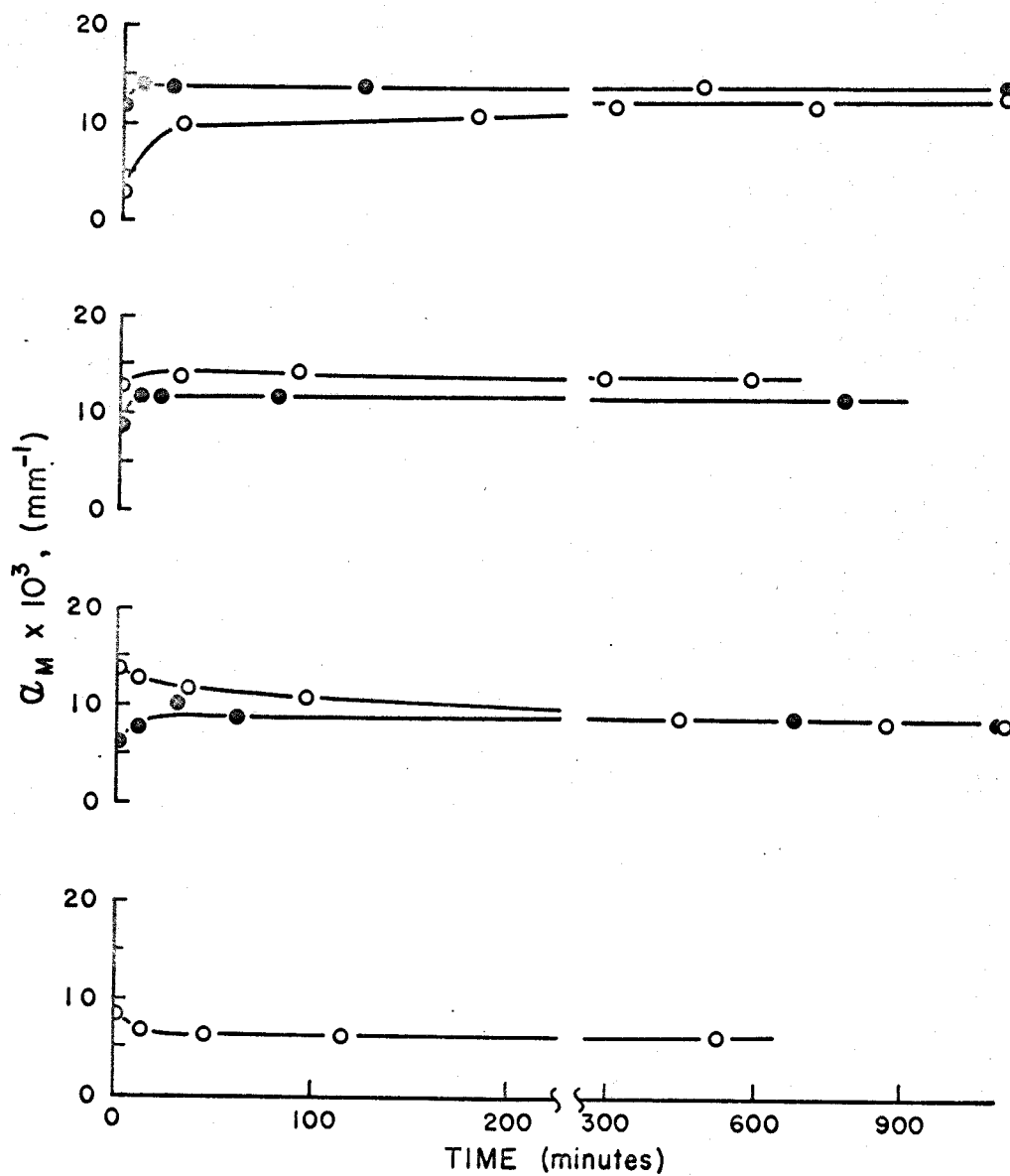


FIGURE 5. Growth and decay curves of the M-band at 60, 70, 90 and 110°C. (Sample 2)

of the M band). These graphs demonstrate the existence of a thermodynamic equilibrium; α'_M suffers no observable change at large times, and α'_M at a given temperature is the same whether the equilibrium is approached from over- or under-saturation with respect to M centers. For example, to obtain equilibrium at 70°C after attainment of equilibrium at 60°C we observe the M-center concentration to be over-saturated and M centers are destroyed. When the 70° equilibrium is approached from 90°C , M-center concentration is under-saturated and a growth of the M band is observed.

The rise in α'_M for crystal 2, on warming from 60° to 70°C is inexplicable.

We can write

$$xF = M \quad (2)$$

If the Seitz model is correct, x is one. If the van Doorn and Haven model (F_2 model) is correct, x is two. The equilibrium constant, K , can then be written as

$$K = \frac{[M]}{[F]^x} \quad (3)$$

where $[]$ denotes concentration. Taking logarithms

$$\log K = \log [M] - x \log [F] \quad (4a)$$

and rearranging

$$\log [F] = \frac{1}{x} \log [M] - \frac{1}{x} \log K \quad (4b)$$

A plot of $\log [F]$ versus $\log [M]$ will give a slope of $1/x$. Since

$$N = C a_{\max} H,$$

$$\log N_i = \log [i] = \log C_i H_i + \log a_{\max, i}, \quad (5a)$$

and we can rewrite equation (4b) as

$$\log a_F = \frac{1}{x} \log a_M + \frac{1}{x} (\log C_M H_M - \log K) - \log C_F H_F \quad (5b)$$

Now a plot of $\log a_F$ versus $\log a_M$ will give a slope of $1/x$. The results are shown in Figure 6 for the four temperatures. The curves were drawn to give the best fit by visual estimation. The numerical values of the slopes are tabulated in Table 2.

Table 2. Values of $1/x$ for 60° , 70° , 90° , and 110°C .

Temperature ($^\circ\text{C}$)	$1/x$
60	0.590
70	0.535
90	0.515
110	0.495
average	0.534
average deviation*	± 0.033

* The average deviation used was $a = \frac{\sum |d_i|}{n} / \sqrt{n(n-1)}$, where d_i is the deviation from the average of the i^{th} measurement and n is the number of measurements.

The value of x , corresponding to the reciprocal of the average value of $1/x$, is 1.88. This result confirms the van Doorn - Haven model of the M center.

It cannot be stated whether the apparent variation in $1/x$

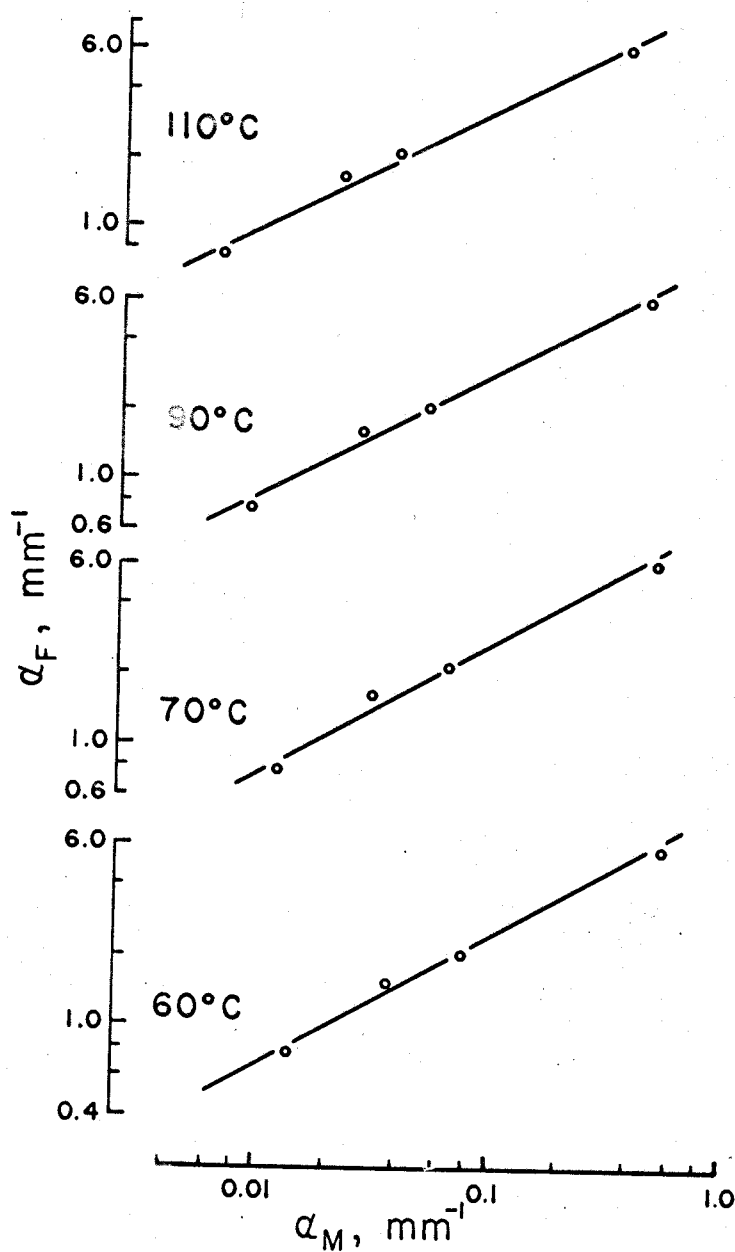


FIGURE 6. α_F versus α_M at 60, 70, 90 and 110°C. The slope gives $1/x$ in the equation $x F = M$. Note the discontinuities along the ordinate.

with temperature has any statistical significance. Sato and Nakano have observed this same temperature variation (16).

Thermodynamics

Number of Centers per Cubic Centimeter as a Reference Function

We define f_i , the fugacity of the i^{th} component, as

$$d\bar{F}_i = RT d \ln f_i \quad (6)$$

where $\bar{F}_i$ is the partial molar Gibbs free energy of the i^{th} component, R the gas constant, and T the absolute temperature. We also define the activity of the i^{th} component, a_i , by

$$a_i = f_i / f_i^0 \quad (7)$$

where f_i^0 is the fugacity of the i^{th} component in its standard state.

Integrating equation (6) we obtain

$$\bar{F}_i - \bar{F}_i^0 = RT \ln f_i / f_i^0 = RT \ln a_i. \quad (8)$$

For color centers in crystals, a convenient reference function is N_i , the number of i centers per cubic centimeter. The reference state is chosen such that Henry's law is obeyed, i. e. $N_i \rightarrow 0$. The standard state is a state in which $N_i = 1$ and in which Henry's law is obeyed. Henry's law is expected to hold at a concentration many orders of magnitude greater than $N_i = 1$, so that the standard state has the properties of the reference state. From equation (8) we can add an alternative definition of a_i , that is

$$\lim_{N_i \rightarrow 0} \frac{a_i}{N_i} = 1. \quad (9)$$

Considering the reaction

$$2F = M \quad (10)$$

we can write

$$(\bar{F}_M - 2\bar{F}_F) = \bar{F}_M^0 - 2\bar{F}_F^0 + RT \ln a_M - 2RT \ln a_F \quad (11)$$

or

$$\Delta \tilde{F} = \Delta \tilde{F}^0 + RT \ln \frac{a_M}{a_F^2}. \quad (12)$$

At equilibrium $\Delta \tilde{F} = 0$ and

$$\Delta \tilde{F}^0 = -RT \ln K \quad (13)$$

where $K = a_M / a_F^2$.

Utilizing a form of the Gibbs-Helmholtz equation,

$$\frac{\partial \Delta \tilde{F}^0}{\partial T} = \frac{\Delta \tilde{F}^0 - \Delta \tilde{H}^0}{T} = -\Delta \tilde{S}^0, \quad (14)$$

and substituting equation (13) we obtain

$$\frac{\partial \ln K}{\partial (1/T)} = \frac{-\Delta \tilde{H}^0}{R}. \quad (15)$$

It should be noted that the standard reaction potential $\Delta \tilde{F}^0$ and the standard partial molar entropy of reaction $\Delta \tilde{S}^0$ correspond to the reaction of two moles of F centers to give one mole of M centers at a concentration of one F center and one M center per cubic centimeter. To have a reaction actually proceed in such a manner as not to change the relative concentrations we should require a crystal of

very large dimensions. At the concentrations encountered here, the difference between $\Delta\tilde{H}^0$ and $\Delta\tilde{H}$ is negligible.

Since $K = N_M/N_F^2$ (we are working in concentration ranges dilute enough to assume activity as identical to number of centers per cubic centimeter) and $N_i = C A_i H_i / f_i$, we obtain

$$K = \frac{1}{C} \frac{A_M}{A_F^2} \frac{H_M}{H_F^2} \frac{f_F^2}{f_M} \quad (16)$$

With the refractive index equal to 1.49, C is 1.66×10^{17} . Taking $H_M = 0.107$ from this work, $f = 0.5$, and f_F and H_F from Konitzer and Markham (10) we obtain

$$K = 0.75 \times 10^{-17} \frac{A_M}{A_F^2} \quad (17)$$

where A_i is the absorbance per millimeter of the i^{th} center.

A graph showing the variation of $\log K$ with reciprocal temperature will give a straight line (over a small range of temperatures) with a slope of $-\Delta\tilde{H}^0 / 2.3 R$. This curve is shown in Figure 7. Table 3 gives the values of $\Delta\tilde{H}^0$ thus obtained.

The standard state functions $\Delta\tilde{F}^0$ and $\Delta\tilde{S}^0$ can then be calculated from equations (13) and (14). The numerical values are listed in Table 4.

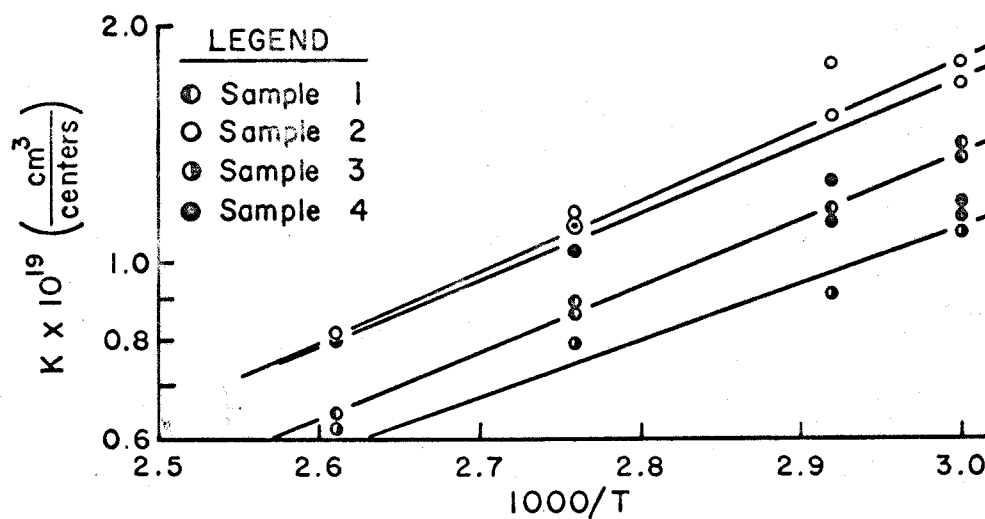


FIGURE 7. Equilibrium constant versus $1/T$. The slope is $-\Delta\tilde{H}^\circ/2.3R$. The reference function is centers/c.c..

Table 3. Values of K and $\Delta\tilde{H}^0$ from Figure 7.

Sample	$\Delta\tilde{H}^0$ (kcal)	$\Delta\tilde{H}^0$ (ev)	Temperature (°K)	$K \times 10^{19} \left(\frac{\text{cc}}{\text{center}} \right)^*$
1	-4.15	-0.180	333	1.38
			343	1.17
			363	0.87
			383	0.65
2	-4.06	-0.177	333	1.72
			343	1.65
			363	1.13
			383	0.81
3	-3.28	-0.143	333	1.09
			343	0.91
			363	0.72
			383	0.62
5	-3.88	-0.169	333	1.17
			343	1.19
			363	1.07
			383	0.80
average and deviation	$-4.03 \pm 0.12^+$		333	1.38 ± 0.22
			343	1.28 ± 0.23
			363	0.99 ± 0.13
			383	0.74 ± 0.10

* The K's listed for 333, 343, and 363°K for each sample are the average of two K's. The average K's are the average of all the K's, not just those listed.

+ This average does not include the value obtained from sample 3 which was greater than the average value minus four times the deviation obtained from the other three samples.

Table 4. $\Delta\tilde{F}^0$ and $\Delta\tilde{S}^0$ for the reaction $2F = M$.

Temperature $^{\circ}\text{K}$	$\Delta\tilde{F}^0(\text{kcal})$	$\Delta\tilde{S}^0(\text{cal/deg})$
333	28.8 ± 0.1	-98
343	29.7 ± 0.1	-98
363	31.5 ± 0.1	-98
383	33.6 ± 0.1	-98

A check on the sensitivity of $\Delta\tilde{F}^0$ on f_F showed that for a 25% variation in f_F there was only a 1% variation in $\Delta\tilde{F}^0$. There was essentially no variation in $\Delta\tilde{S}^0$.

Mole Fraction as a Reference Function

Although the above framework is a convenient one to use for color center work it does have the disadvantage of not being able to compare the state functions to those of common chemical reactions. With this in mind, the state functions using mole fraction as a reference function were calculated. Following an argument similar to that in the previous section K is found to be

$$K = \frac{X_M}{X_F^2} \quad (18)$$

where X_i is the mole fraction of the i^{th} center. Equations (13), (14), and (15) are still valid. Calculated data are tabulated in Table 5.

Table 5. Values of $\Delta\tilde{H}^0$, K , $\Delta\tilde{F}^0$, and $\Delta\tilde{S}^0$ for $2F = M$ with mole fraction as the reference function.

Sample	$\Delta\tilde{H}^0$ (kcal)	Temp($^{\circ}$ K)	$K \times 10^3$	$\Delta\tilde{F}^0$ (kcal)	$\Delta\tilde{S}^0$ (cal/deg)
1	-3.82	333	2.26	-5.11	3.57
		343	1.88	-5.15	3.58
		363	1.38	-5.22	3.58
		383	1.03	-5.29	3.58
		363	1.42	-5.24	3.64
		343	1.85	-5.14	3.55
		333	2.16	-5.08	3.48
2	-4.00	333	2.65	-5.22	3.90
		343	2.84	-5.42	4.37
		363	1.80	-5.41	4.10
		383	1.32	-5.48	4.07
		363	1.80	-5.41	4.10
		343	2.46	-5.33	4.11
		333	2.84	-5.26	4.02
3	-3.12	333	1.73	-4.96	3.06
		343	1.47	-4.97	3.07
		363	1.27	-5.16	3.41
		383	0.99	-5.26	3.50
5	-3.94	333	1.68	-4.92	3.00
		343	2.02	-5.20	3.73
		363	1.79	-5.40	4.07
		383	1.28	-5.45	3.99
		363	1.65	-5.34	3.91
		343	1.79	-5.11	3.46
		333	1.92	-5.01	3.27
averages and average deviations	-3.92 [*] ± 0.08	333	2.18 ± 0.38	-5.08 ± 0.11	3.47 ± 0.33
		343	2.04 ± 0.37	-5.19 ± 0.12	3.69 ± 0.35
		363	1.59 ± 0.21	-5.31 ± 0.10	3.83 ± 0.27
		383	1.16 ± 0.17	-5.37 ± 0.11	3.78 ± 0.28

* This average does not include the value obtained from Sample 3 which was greater than the average value minus four times the deviation obtained from the other three samples.

III. THE SHAPE OF THE M BAND

Although pure alkali-halide crystals are transparent between the infrared and near ultraviolet, there is nevertheless some loss of light intensity. This is caused by the reflecting and scattering of light from the crystal faces and some slight absorption by the crystal. To measure the absorption of a band we wish to separate the inherent absorption of the crystal from that of the absorbing centers. On continuous-scan spectra this inherent absorption is defined by the base line. On a point-by-point determination of the spectrum the base line is not well defined. It would facilitate matters if two or more points were located such that there was no absorption due to color center or impurity bands. In KCl, with only F and M centers present, points for determining the base line were chosen at 750, 1000, and 1100 $m\mu$. These three points, in general, described a straight line. The absorbance of the i^{th} center was found by subtracting from the peak absorbance the absorbance described by this line at the peak energy. In some colored samples these three points were not collinear and the straight line was drawn between the 750 $m\mu$ and 1100 $m\mu$ points. The non collinearity was attributed to the presence of the N band. Since the R and N bands encompass all of these points frequent checks were made to determine the presence of R and N bands, if indeed there were any.

The N bands were more prominent than the R bands.

Determination of the baseline led in turn to a study of the M-band shape. The analysis used here on the M band is similar to that used by Konitzer and Markham (10) on the F band.

The normalized Gaussian distribution, that is, for example, the absorbance as a function of energy ϵ , has the form

$$G = \frac{a}{\sqrt{\pi}} \exp \{ -a^2 (\epsilon - \epsilon_m)^2 \} \quad (19)$$

where a is a parameter related to the half width, H , and ϵ_m is the energy of the band maximum. Figure 8 shows a comparison of the M band at room temperature and a Gaussian curve with $a = 15.6$.

Agreement between these two shapes is good except near the tail of the band on the red side. If the log of relative absorbance is plotted versus $(\epsilon - \epsilon_m)^2$ we should expect a straight line with slope of $a^2/2.3$. When this is done as in Figure 9, two things should be noted. First the slope of the line for the red side of the band has quite a different value than that of the line corresponding to the violet side. Secondly, the line is not perfectly linear. These facts suggest that (a) we should use one Gaussian shape to describe the red side and one to describe the violet side and (b) our description of the M-band shape in terms of Gaussian curves will only be approximate.

For the M-band shape at room temperature a_r^2 was found to be $160 (\text{ev})^{-2}$. A measure of the asymmetry of the M band can be

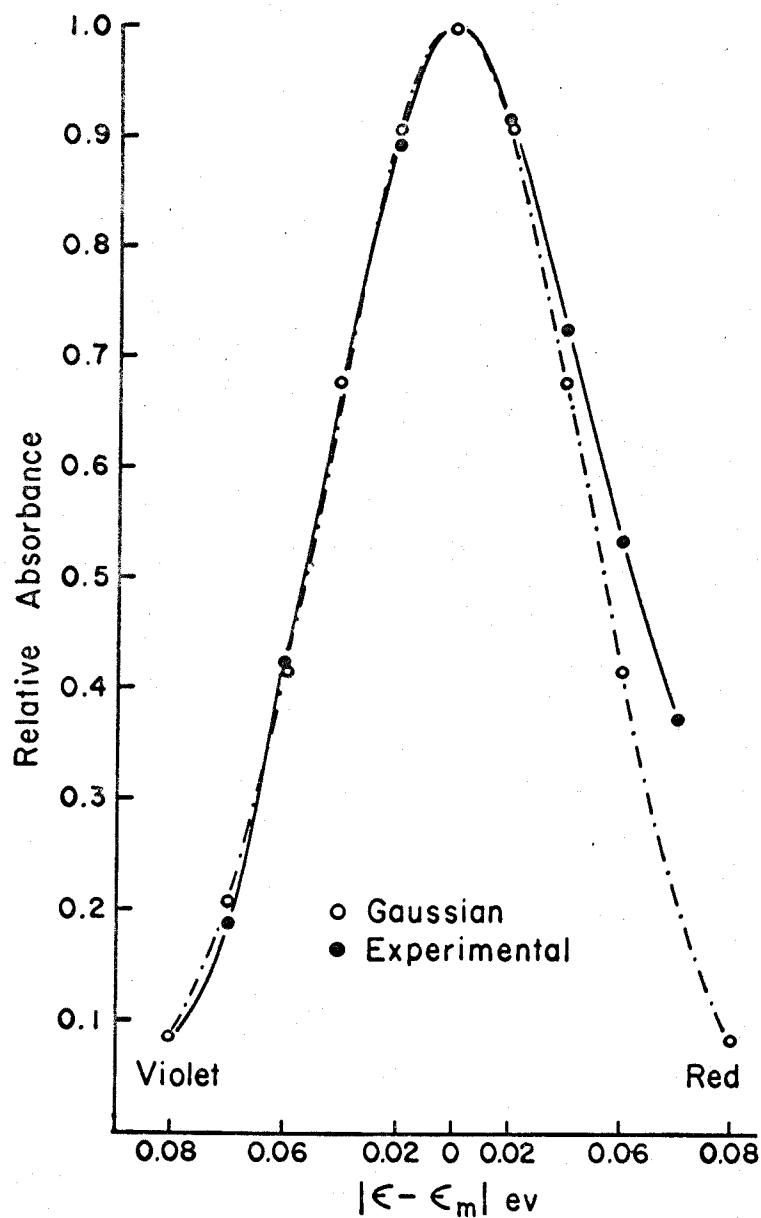


FIGURE 8. Comparison of M-band shape (—) against a Gaussian shape (---). Note the M-band asymmetry. Data was taken at 298° K.

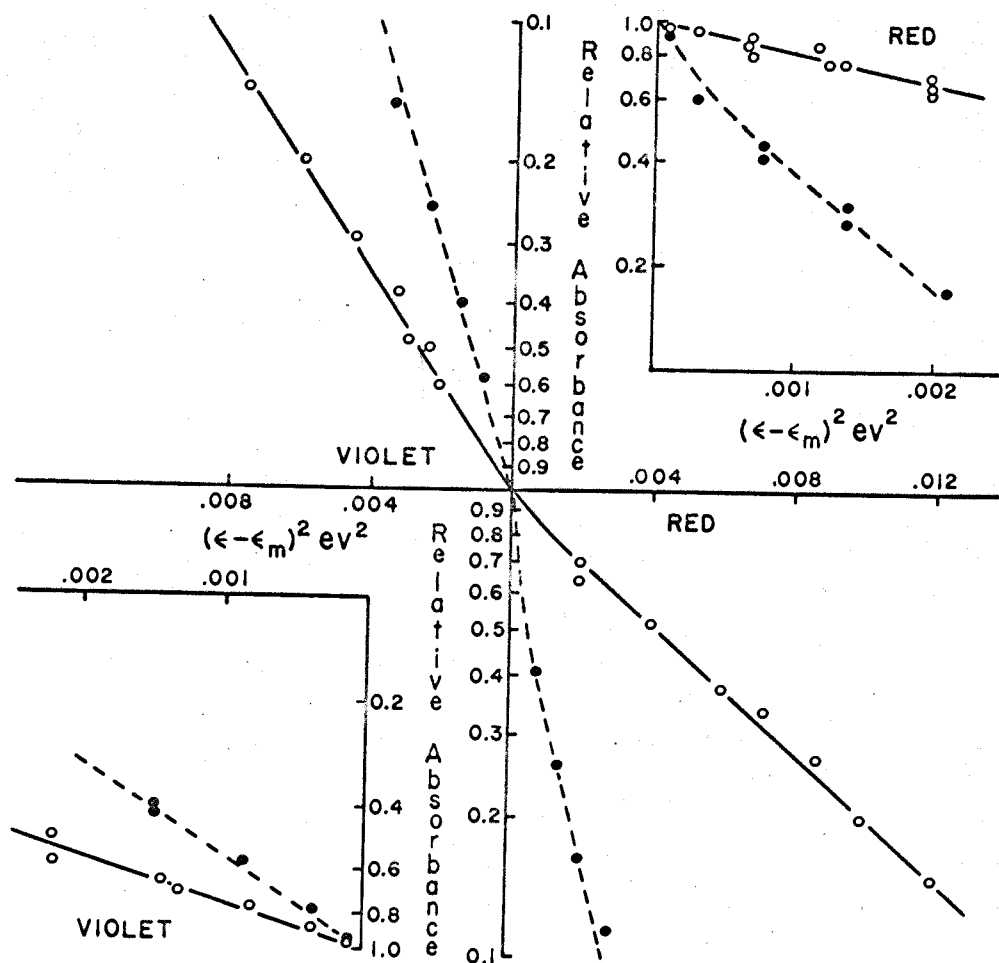


FIGURE 9. Graph of log (relative absorbance) versus $(\epsilon - \epsilon_m)^2$ for 77° K (---) and 298° K (—); this shows the asymmetry of the M-band and the utility of using two Gaussian curves to represent the M-band shape.

had by dividing G_v by G_r when these are evaluated at the same

$\epsilon - \epsilon_m$. These numbers and similar ones for liquid nitrogen temperatures are given in Table 6.

Table 6. Percent symmetry of the M band.

Temperature °K	$a_v^2(\text{ev})^{-2}$	$a_r^2(\text{ev})^{-2}$	$(\epsilon - \epsilon_m)^2(\text{ev})^2$	$G_v/G_r \times 100$
298	242	160	0.0005	96
			0.0010	92
			0.0020	85
			0.0030	78
77	580	715	0.0005	107
			0.0010	114
			0.0020	131
			0.0030	150

Near the maximum, $(\epsilon - \epsilon_m)^2 < 0.0003$, at liquid nitrogen temperatures, these parameters do not describe the red side. This is evident in Figure 9. Table 6 points out an interesting phenomenon; the M band changes symmetry between room temperature and liquid nitrogen temperature. On the basis of one spectrum taken at about 195°K it is estimated that the "inversion" temperature is near 200°K.

The M band in this sample was too small to obtain numerical data on a_v^2 and a_r^2 .

Although the double-Gaussian curve fits the experimental shape very well, there has not been put forth a theoretical justification for such a shape. Markham (11), using a synthesis of theories, showed

that the F band should be Poissonian (Pekarian) in shape. With this in mind, it was attempted to fit the M band to a Poisson curve.

The Poisson distribution is defined as

$$P(n) = e^{-\lambda} \lambda^n / n! \quad (20)$$

where λ is an arbitrary constant and n a positive integer. It is derived from the binomial distribution

$$B = \frac{m!}{(m-n)!n!} p^n q^{m-n} \quad (21)$$

as $m \rightarrow \infty$ and $mp = \lambda$. A glance at a Poisson curve indicates that it may fit the data very well since it is skewed to one side. A graphical comparison (Figures 10 and 11), however, shows that the Poisson curve does not fit the tails of the band any better than the single Gaussian.

All but two of the spectra used in the M-band analysis were taken on a Beckman model DK1 spectrophotometer. Most of these spectra and one of those taken on the model DU show evidence of a shoulder near 845 m μ . The position of the band seemed to be independent of temperature. It was graphically resolvable only at liquid nitrogen temperatures where it appeared Gaussian in shape. This may be a new band recently observed by Ring and Grossweiner (15). We do not believe that the band has origin in instrumental error, since it was observed with two instruments. Also, not all samples exhibited this band. It was observed in samples where the M band

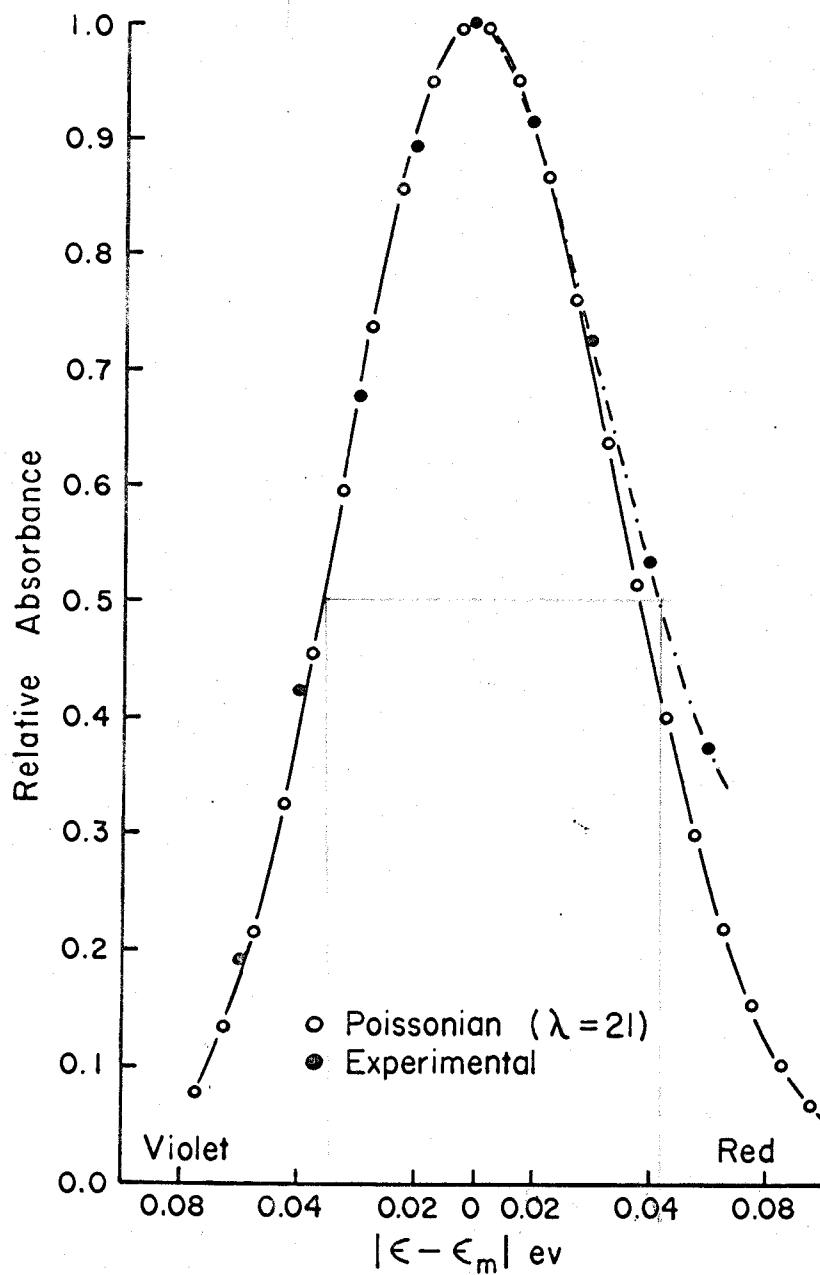


FIGURE 10. Comparison of M-band shape (---) against a Poissonian shape (—). Data was taken at 298° K.

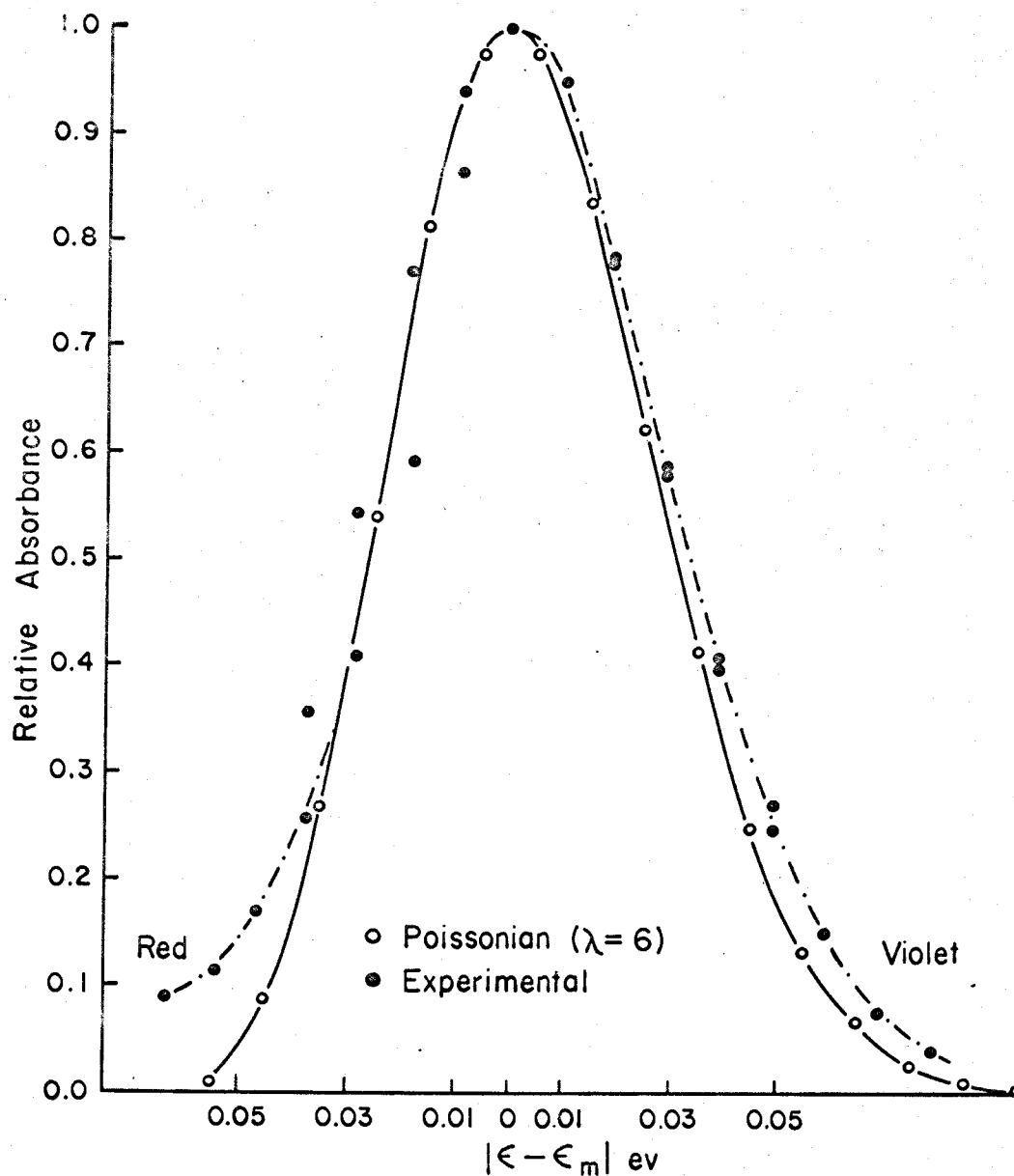


FIGURE 11. Comparison of M-band shape (---) against Poissonian shape (—). Data was taken at 77° K.

had been grown both by thermal means or by photochemical means.

There also seemed to be no relation between this band at 845 m μ and the R or N bands. A list of M band parameters found in this study are compiled in Table 7.

Table 7. M band parameters.

Temp. $^{\circ}\text{K}$	$\epsilon_v(\text{ev})$	$\epsilon_r(\text{ev})$	H(ev)
77	1.563	1.504	0.059
195	--	--	0.075
300	1.546	1.438	0.107

IV. DISCUSSION

Three other papers have been published in which values for $\Delta\tilde{H}^0$, K , and $\Delta\tilde{S}^0$ for the process $2F = M$ have been given. These are by van Doorn (23), Kalabukhov and Gorbenko (6), and Sato and Nakano (16).

van Doorn gives an approximate value for the heat of formation of the M center as 0.01 ev. This paper was not primarily concerned with the thermodynamics of the reaction $2F \rightarrow M$ and no data was presented. As has been mentioned before, we make objection to his claim of a thermal equilibrium at 697°C . An extrapolation of our data to 700°C indicates that there are essentially no M centers at this temperature. His data corresponded to an extrapolated temperature of about 300°C from our data. Even though he quenched the crystal within one second after removal from the furnace, it is reasonable to conclude that the quenched sample was representative of some intermediate temperature.

Kalabukhov and Gorbenko and Sato and Nakano worked with photochemically produced M centers and radiation induced F and M centers respectively. Kalabukhov and Gorbenko demonstrated a saturation of M centers and a steady state concentration of F centers and then calculated $\Delta H = 0.378$ ev. Their conclusion of M center saturation is in contradiction to Hirai (4) who demonstrated a decay

of M center concentration after rising to a maximum. Sato and Nakano recorded absorption immediately after removal of the sample from a gamma ray source. A quadratic relationship between M and F center concentrations was demonstrated. The value of $\ln K$ varied from -38 at 33°C to about -40 at 77°C. The enthalpy was found to be 0.38 ev and the entropy change was 51 cal /deg mole.

We take exception to both of these works on the basis that both papers deal with steady state concentrations, not equilibrium concentrations. In a steady state, properties of the system itself do not change with time but there is an irreversible flow of some quantity through the system. In the case of Kalabukhov and Gorbenko this quantity was F-band and light while for Sato and Nakano it was a gamma ray flux. Entropy is produced in an irreversible process and there is a corresponding free-energy destruction. We would thus not expect the thermodynamic values obtained in these experiments to correspond to those given in this work. On the other hand we do not mean to imply that the values of $\Delta H = 0.38$ ev and $\Delta S = 51$ eu have no significance. In fact, the agreement between these two groups indicate that there may be something significant in these quantities.

Let us now review the meaning of the numerical values obtained for the standard entropy change when mole fraction is the reference function. This is by definition the entropy change

observed when two moles of F centers at unit mole fraction are converted into one mole of M centers also at unit mole fraction. If we imagine a KCl lattice which has N_A potassium ions and N_A anion vacancies, and then we fill the N_A vacancies with N_A electrons (one per vacancy) we would have N_A F centers. Now we convert all of the F centers into M centers. We do this not by moving any F centers but simply by drawing boxes, each containing two F centers, around all of the F centers present. Although there are 12 ways to draw a box around any one F center to include another F center, there are only six possible orientations. We would expect the standard entropy change to be

$$\Delta \tilde{S}^0 = R \ln 6 = 3.58 \text{ eu} \quad (22)$$

This is in good agreement with the experimental values.

Consider now the free energy change when a crystal containing 10^{-5} mole fraction of both F and M centers reacts to give equilibrium concentrations of F and M centers. The value $x_i = 10^{-5}$ is chosen only for an example and has no special experimental or theoretical significance except that F center concentrations are often of this order of magnitude. By using

$$\Delta \tilde{F} = \Delta \tilde{F}^0 + RT \ln \frac{x_M}{x_F} \quad (23)$$

we obtain $\Delta \tilde{F}_{363} = 2.98 \text{ kcal/mole}$ and $\Delta \tilde{F}_{383} = 3.38 \text{ kcal/mole}$.

The positive $\Delta \tilde{F}$'s were expected since the concentration of M

centers is over-saturated at both 363 and 383°K.

Since

$$\frac{\partial \Delta \tilde{F}}{\partial T} = -\Delta \tilde{S} \quad (24)$$

$\Delta \tilde{S}$ is found to be about -20 eu.

Applying statistical mechanics we obtain the initial and final thermodynamic probabilities by Boltzmann statistics

$$W_i = \frac{N! 6^{N_M}}{N_F! N_M! (N - N_F - N_M)!} \quad (25)$$

$$W_f = \frac{N! 6^{N_M+1}}{(N_F-2)! (N_M+1)! (N - N_F - N_M + 1)!} \quad (26)$$

Since

$$\Delta S = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i} \quad (27)$$

$$\frac{\Delta S}{k} = \frac{6 N_F (N_F - 1)}{(N_M + 1) (N - N_F - N_M + 1)} \quad (28)$$

For $N \gg N_F \gg N_M \gg 1$, this reduces to

$$\Delta S = R \ln 6 + R \ln \frac{x_F^2}{x_M} \quad (29)$$

Substituting 10^{-5} for x_F and x_M we obtain $\Delta S = -19.2$ eu which is in good agreement with the experimental value of approximately -20 eu.

A calculation of $\Delta \tilde{S}^0$ for $2O \rightarrow O_2$ with the reference function of centers / cc gave $\Delta \tilde{S}^0 = -119$ eu. Other gas phase reactions would give similar results. Although the translational partition function was the primary contributor to this $\Delta \tilde{S}^0$, it is interesting

to note the similarity between this value and $\Delta\tilde{S}^0 = -98 \text{ eu}$ for $2F = M$ using number/cc as a reference function.

The location of the side band on the M band reported in this work agreed fairly well with the T_1 band reported by Ring and Grossweiner (845 $m\mu$ versus 836 $m\mu$). It seems to be stable at 110°C which is in agreement with the fact that the T_1 band is reported stable up to 140°C . If this is the reported T_1 band its corresponding center can be formed by strictly thermal means, and concurrent bleaching with both F and M light is not necessary.

V. SUGGESTIONS FOR FUTURE WORK

Thermodynamic functions for other color center reactions should be obtainable. For example the R center may be dependent on F and M center concentrations and a plot of α_R should give evidence for the construction of a model. The same experiment might also be done on the N centers but here the sample thickness may have to be increased.

A further study of the M band on theoretical grounds might give reasons for the shift in M-band symmetry near 200°K. The effect observed here might include more factors other than lattice vibration interactions which were used to describe the F band. Further work on the 845 m μ band is necessary to determine if this is the T_1 band, as observed by Ring and Grossweiner. Whether or not this is the case it would also be interesting to know what center is responsible for this absorbance.

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