

Absorption Band Shapes for the *F* Center and Thallium in KClC. C. KLICK, D. A. PATTERSON, AND R. S. KNOX\*  
*U. S. Naval Research Laboratory, Washington, D. C.*

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The shape of the optical absorption band has been measured for the *F* center in KCl and for  $Tl^+$  in KCl over a temperature range from 4°K to room temperature and over a range of absorption coefficients extending to  $10^{-4}$  of the peak value. No evidence is found that Urbach's rule applies to the absorption bands of these centers. For the *F* center in KCl it is possible to describe the long-wavelength side of the absorption band over the full range of absorption using configuration coordinate diagrams in which one of the approximations usually employed has been eliminated. It then becomes possible to determine the configuration coordinate diagram from absorption measurements alone. The configuration coordinate diagram determined in this way, however, fails to predict the *F*-center emission spectrum correctly. Several possible reasons for this failure are discussed.

## I. INTRODUCTION

IN a number of insulating solids the long-wavelength tail of the fundamental absorption edge may be described by an empirical equation proposed by Urbach<sup>1</sup> and frequently called Urbach's rule. If  $K$  is the optical absorption coefficient in the fundamental edge which varies with the frequency  $\omega$  of the light, the variation of  $K$  with both  $\omega$  and temperature  $T$  is given by

$$K = K_0 \exp[-\sigma(\hbar\omega_0 - \hbar\omega)/kT]. \quad (1)$$

$K_0$ ,  $\sigma$ , and  $\omega_0$  are constants chosen by curve fitting. Urbach's rule has been investigated in materials such as  $AgCl$ ,<sup>2</sup>  $CdS$ ,<sup>3</sup> and  $TlCl$ ,<sup>4</sup> but it is for the alkali halides in particular that this relationship has been found to be extraordinarily accurate.<sup>5-7</sup> Measurements on KI have shown that this relationship is obeyed over a range of seven decades in absorption coefficient.<sup>8</sup> The temperature dependence is also accurately given at room temperature and above, but deviations are found in low-temperature measurements.

There have been a number of attempts at developing a theory which will adequately explain Urbach's rule. Dexter<sup>8</sup> has explored the variation of the band-gap energy resulting from lattice vibrations. Agreement with experiment is found for only a relatively small range of absorption coefficients. Toyozawa<sup>9</sup> is able to reproduce the desired curve using the same model but assuming that in the tail of the absorption band only those modes of vibrations are important for which the band-gap energy varies as the square of the lattice displacement.

Hopfield<sup>10</sup> has suggested qualitatively that the absorption shape may arise from the thermal ionization of an intermediate low-energy exciton state. It has been pointed out by Eagles<sup>11</sup> that under some circumstances a configuration coordinate diagram for the excited state of a system may show a maximum near its center rather than a minimum and that this could lead to Urbach's rule. Finally, Redfield<sup>12</sup> has suggested that the vibration of lattice ions will lead to local electric fields which will alter the absorption edge by the mechanism of Franz and Keldysh<sup>13</sup> and that this might also lead to the observed variation of absorption coefficient. It is apparent that there is not yet general agreement as to the mechanism giving rise to Urbach's rule.

The addition of impurities to insulating solids frequently produces an optical absorption band in a previously transparent region of the spectrum. Two methods for dealing with such absorption bands have been developed. One is the configuration coordinate diagram approach which assumes that the center interacts primarily with its nearest neighbors.<sup>14</sup> This approach is most appropriate for highly localized centers. The other is the continuous dielectric model which treats the center as interacting with the whole phonon field of the solid, and is more appropriate for diffuse centers.<sup>15</sup> Methods for applying this model to localized centers have been discussed by Markham.<sup>16</sup> Both models give the band shape as approximately Gaussian and both give the same functional dependence of bandwidth on temperature. These predictions have been verified for a number of systems.

The situation has been complicated by recent measurements on bands due to small concentrations of

\* Present address: University of Rochester, Rochester, New York.

<sup>1</sup> F. Urbach, *Phys. Rev.* **92**, 1324 (1953).

<sup>2</sup> F. Moser and F. Urbach, *Phys. Rev.* **102**, 1519 (1956).

<sup>3</sup> D. Dutton, *Phys. Rev.* **112**, 785 (1958).

<sup>4</sup> S. Tutihasi, *Phys. Chem. Solids* **12**, 344 (1960).

<sup>5</sup> W. Martienssen, *Phys. Chem. Solids* **2**, 257 (1957).

<sup>6</sup> U. Haupt, *Z. Physik* **157**, 232 (1959).

<sup>7</sup> K. Kobayashi and T. Tomiki, *Phys. Chem. Solids* **22**, 73 (1961).

<sup>8</sup> D. L. Dexter, *Nuovo Cimento Suppl.* **7**, 245 (1958).

<sup>9</sup> Y. Toyozawa, *Progr. Theoret. Phys. (Kyoto)* **20**, 53 (1958); **22**, 445 (1959); **26**, 29 (1961); *Progr. Theoret. Phys. (Kyoto) Suppl. No. 12*, 111 (1959).

<sup>10</sup> J. J. Hopfield, *Phys. Chem. Solids* **22**, 63 (1961).

<sup>11</sup> D. M. Eagles, *Phys. Rev.* **130**, 1381 (1963).

<sup>12</sup> D. Redfield, *Phys. Rev.* **130**, 916 (1963).

<sup>13</sup> W. Franz and L. V. Keldysh, *Zh. Eksperim. i Teor. Fiz.* **33**, 994 (1957) [English transl.: *Soviet Phys.—JETP* **6**, 763 (1958)].

<sup>14</sup> For a review of this subject see C. C. Klick and J. H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. V, p. 97.

<sup>15</sup> For a summary of this approach see S. I. Pekar, *Untersuchungen über die Elektronentheorie der Kristalle* (Akademische Verlagsgesellschaft, Berlin, 1954).

<sup>16</sup> J. J. Markham, *Rev. Mod. Phys.* **31**, 956 (1959).

KBr or KI in KCl.<sup>7,17,18</sup> In these cases Urbach's rule again appears to apply on the long-wavelength side of the band. The situation has been most extensively investigated by Mahr<sup>18</sup> for the KCl:KI case. He finds that the iodide absorption band appears Gaussian in shape for a variation of a decade in absorption coefficients about the peak, but takes the form of Urbach's rule in the range below about  $10^{-2}$  of the peak value.

Since Urbach's rule has been observed in some impurity centers, it is of interest to find out if this rule applies to impurity centers of other types as well. The principal purpose of the present paper is to explore the general applicability of Urbach's rule by measuring band shapes for two widely investigated and well-understood impurity centers: the *F* center in KCl and  $Tl^+$  in KCl.

## II. *F* CENTER IN KCl

The band shape of the *F* center in KCl was measured at liquid-helium temperature by mounting commercial<sup>19</sup> crystals of KCl in a Dewar, cooling with liquid helium, x raying with 50-kV x rays, and measuring the optical absorption without warm up. Since it was desired to measure the absorption spectrum over a range of  $10^4$  in transmission, special precautions were necessary. No additional absorption bands on the long-wavelength side of the *F* band could be tolerated. The *M* and *R* bands were kept to negligible values by x raying at low temperature for periods of an hour or less. The *K* band appears on the short-wavelength side of the *F* band under all conditions, making that wavelength range unsuitable for the present purposes. Measurements at room temperature and liquid-nitrogen temperature were made by x raying KCl:H at room temperature. This material is known to be free of *M* and *R* bands

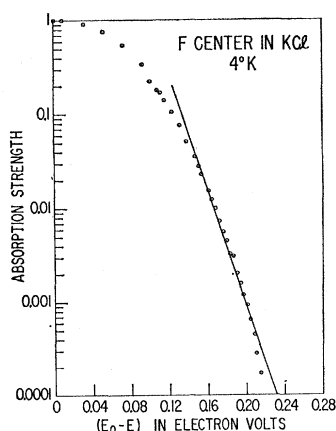


FIG. 1. The absorption coefficient, normalized to unity, of the *F* center in KCl at 4°K, is plotted as a function of the difference in energy from the peak of the band on the long-wavelength side. A straight line on this plot is what would be expected for Urbach's rule as given in Eq. (1).

<sup>17</sup> H. Mahr, Phys. Rev. **122**, 1464 (1961).

<sup>18</sup> H. Mahr, Phys. Rev. **125**, 1510 (1962).

<sup>19</sup> Principally from Harshaw Chemical Company.

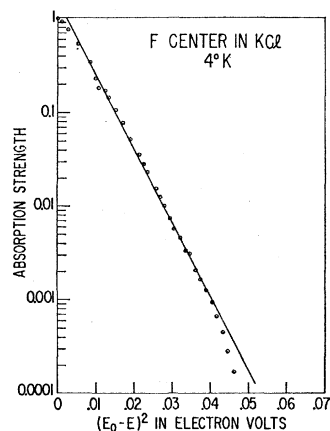


FIG. 2. The absorption coefficient, normalized to unity, of the *F* center in KCl at 4°K, is plotted as a function of the square of the difference in energy from the peak of the band on the long-wavelength side. A straight line on this plot represents a Gaussian curve.

under these conditions.<sup>20</sup> Absorption measurements were made with a Cary model 14 spectrophotometer using both the regular slidewire and a special slidewire which extends the sensitivity range by a factor of 10. Baseline runs were taken with the crystal in the Dewar before x raying so that accurate subtractions could be made. Also, measurements were sometimes made for two different x-ray exposures and were fitted together in the overlapping region. In Fig. 1 and Fig. 2 the absorption measurements, normalized to unity, are plotted for the liquid-helium data. Figure 1 shows the logarithm of this "absorption strength" as a function of  $(E_0 - E)$  where  $E_0$  is the energy of the peak of the band. If Urbach's rule were obeyed, the points should fall on a straight line for some portion of this plot. It is seen that for about a decade the data fall pretty well on a straight line, but then fall below the line. In Fig. 2 the same data are plotted as a function of  $(E_0 - E)^2$  which should give a straight line if the absorption band is Gaussian. Here the fit is seen to be considerably better, showing a straight-line dependence for about three decades. But even here the points at the peak of the curve and those at the end deviate. At the long-wavelength end the observed data are at lower values of absorption strength than the Gauss curve; this is opposite to the results of Mahr for KCl:KI who found that the experimental points giving rise to Urbach's rule fell above the Gaussian curve. It is obvious from these figures that an Urbach's rule relationship does not describe the *F* center in KCl at low temperatures. While a Gaussian curve is a better fit, it too shows deviations from the experimental points. The prediction of a Gaussian band shape on the configuration coordinate model involves several simplifying assumptions. It is now of interest to determine whether or not the

<sup>20</sup> H. W. Etzel (private communication).

elimination of some of these approximations will improve the agreement between theory and experiment.

Figure 3 illustrates the usual configuration coordinate diagram. The total energy of the system is plotted on the ordinate and the abscissa specifies some generalized coordinate  $X$ . There are two parabolic curves, one for the ground state of the system and the other for an excited state. This describes a simple harmonic oscillator with force constants  $K_g$  and  $K_e$  for the ground and excited states, respectively. The minima of the two states are displaced in energy by  $E_0$  and in coordinate by  $X_0$ . Transitions between the curves are vertical in accord with the Frank-Condon principle. This model allows for a simple description of the Stokes shift of emission and the origin of broad absorption and emission bands. When quantitative applications are desired, several further assumptions are introduced. One is that the primary mode of lattice vibration influencing bandwidth is the symmetrical or "breathing" mode since that causes the largest variation in the energy of the

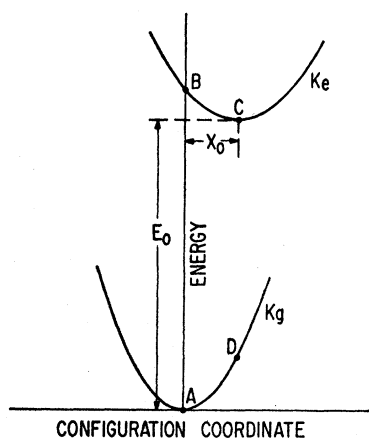


FIG. 3. A schematic configuration coordinate diagram in which the energy of the system is plotted as a function of some coordinate. The lower curve represents the ground state of the system characterized by a force constant  $K_g$ ; the upper curve is an excited state with force constant  $K_e$ . The minima of the curves are separated in energy by an amount  $E_0$  and in coordinate by an amount  $X_0$ .

state. Considering this mode alone, the abscissa can be interpreted physically as the distance from the center to its nearest neighbors. In addition, the spectra at low temperatures require the introduction of quantum-mechanical effects. This is usually done by assuming that the initial state of the system (the ground state for absorption measurements) is quantized but that the final state is a classical continuous curve since the transition is to a region many vibrational levels above the minimum of the final state.

In the case of absorption transitions at very low temperatures, only the lowest vibrational level will be populated so that the energy of the ground state above the classical minimum is simply the zero-point energy

$$E_g = \hbar\omega_g/2,$$

and the excited state, treated classically, has an energy

$$E_e = E_0 + (X - X_0)^2 K_e/2.$$

The energy of the absorption transition as a function of  $X$  is then

$$E_a(X) = (E_0 - \hbar\omega_g/2 + K_g X_0^2/2) - (K_e X_0)X + (K_e/2)X^2. \quad (2)$$

It has previously been customary to drop the last term in this equation since the range of values over which  $X$  is taken is usually small.<sup>21</sup>

The probability of an absorption transition as a function of  $E$  is given by<sup>22</sup>

$$P(E_a) = (K_g/2\pi kT^*)^{1/2} \times \exp(-K_g X^2/2kT^*) (dX/dE_a), \quad (3)$$

where  $T^*$ , an effective temperature, is given by

$$T^* = (\hbar\omega_g/2k) \coth(\hbar\omega_g/2kT).$$

Substituting for  $dX/dE_a$  from Eq. (2) and taking the low-temperature limit, one obtains

$$P(E_a) = [K_e(X - X_0)]^{-1} (K_g/\pi\hbar\omega_g)^{1/2} \times \exp(-K_e X^2/\hbar\omega_g). \quad (4)$$

In the usual approximation mentioned above, the terms before the exponential are constants. As a result  $P(E_a)$  is then found to be Gaussian. If, instead, the full form of Eqs. (2) and (4) are used, a modified Gaussian will result. The procedure used here was to solve Eq. (2) for  $E_a$  as a function of  $X$  and solve Eq. (4) for  $P(E_a)$  as a function of  $X$ . Then  $P(E_a)$  can be plotted as a function of  $E_a$ . In practice, this appeared to be more convenient than the complications arising from eliminating  $X$  between Eqs. (2) and (4).

To describe configuration coordinate diagrams in this model, four constants  $K_g$ ,  $K_e$ ,  $X_0$ , and  $E_0$  are required. The mass of the vibrating system  $M$  does not effect the predicted optical properties as long as it is the same in both the ground and excited state. It is customary, considering the breathing mode as predominant, to take the mass to be the sum of the masses of the nearest neighbors. Since there are four constants to be evaluated, a minimum of four experimental facts are needed. In the usual approximation there are only three available from absorption measurements alone. These are, using energies in electron volts and distances in angstroms: the peak position of absorption given by

$$E_{\max} = E_0 + K_e X_0^2/2, \quad (5)$$

the half-width of the absorption band at low temperatures given by

$$W_0 = [(4 \ln 2)(\hbar\omega_g/K_g)]^{1/2} K_e X_0, \quad (6)$$

<sup>21</sup> An exception is found in Ref. 8 where some of the results of including this term are investigated.

<sup>22</sup> F. E. Williams and M. H. Hebb, Phys. Rev. **84**, 1181 (1951).

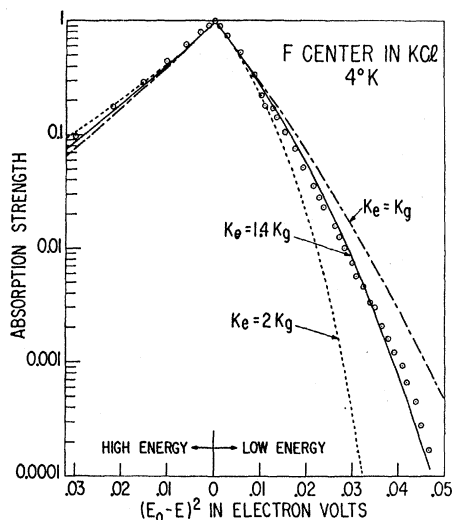


FIG. 4. The relative absorption strength of the  $F$  center in KCl at  $4^\circ\text{K}$  is plotted as a function of the square of the energy deviation from the peak. The best fit on the long-wavelength side is found for  $K_e = 1.4 K_0$ . On the short-wavelength side, the  $K$  band overlaps the  $F$  band making comparisons difficult.

and the variation of half-width with temperature given by

$$W = W_0 [\coth(\hbar\omega_0/2kT)]^{1/2}. \quad (7)$$

Since similar additional data are available from luminescence, it has been customary to derive the constants of the curves using both absorption and emission data. For reasons which will be described later, an effort was made to derive the constants for the  $F$ -center case from absorption measurements alone. This was accomplished by employing Eqs. (5), (6), and (7) and using a variable  $(K_e/K_0)$ . Equations (2) and (4) are solved parametrically in  $X$  and a family of curves plotted for various values of  $(K_e/K_0)$ . By fitting of experimental data on the variation of absorption strength with energy, the correct value of  $(K_e/K_0)$  may be obtained.

This procedure is illustrated in Fig. 4 for the  $F$  center in KCl. The circled points give the experimental data normalized to unity at the peak. Curves are computed for  $K_e$  equal to  $K_0$ ,  $1.4 K_0$ , and  $2 K_0$ . There are a number of features to be observed in this figure. First, using the more exact form of Eqs. (2) and (4) does lead to a slowly perturbed Gaussian curve. For measurements near the peak of the curve, this perturbation will have little effect but it will be quite important in the wings. Second, the experimental points on the low-energy side of the  $F$  band follow the computed curve for  $K_e = 1.4 K_0$  over four decades in absorption constant within the precision of the measurement. On the high-energy side, the overlapping of the well-known  $K$  band raises the experimental points above those computed. Third, the curves are not symmetrical about the peak. This has

been observed before<sup>23-25</sup> and has usually been taken care of empirically by the "double Gaussian" method, that is, by approximating the curve with two straight lines of different slopes. One sees here that this asymmetry phenomenon is accurately described without additional assumptions when the more exact equations are used. This result had been foreseen by Dexter.<sup>8</sup>

Curves similar to those shown in Fig. 4 may also be obtained using the continuous dielectric model. A good approximation at low temperatures<sup>15</sup> is that the absorption strength is proportional to  $(S^P/P!)$ . Here  $S$  is the number of phonons created at the peak of the absorption band and may be typically near 20 for the  $F$  center;  $P$  varies above and below  $S$  giving rise to the absorption band.<sup>26</sup> There are a variety of experimental results which argue that this model is inappropriate for the  $F$  center.<sup>14</sup> One of these is that the half-widths of absorption and emission spectra are not always identical as this model would predict. Another is that  $\omega_g$  and  $\omega_e$  can be obtained from the temperature variation of the bandwidth of the absorption and emission bands. When obtained, these are not identical and both differ from the longitudinal optical frequency of the lattice which is the predicted value. Fowler and Dexter<sup>27</sup> have also raised objections to the use of this model for the  $F$  center on the basis of an analysis of its theoretical foundations. For these reasons no detailed attempt was made to compare the results of Fig. 4 with the predictions of this model.

The configurational coordinate equations used in treating the data of Fig. 4 were derived for the low-temperature limit. At sufficiently high temperatures, enough vibrational levels of the ground state will be excited so that this state may also be described by a classical curve. For the  $F$ -center absorption in KCl where the effective temperature  $T^*$  is  $71^\circ\text{K}$  when the actual temperature is  $0^\circ\text{K}$ , room temperature should be sufficiently high for this approximation. Support for this view comes from the observation that at room temperature it is found experimentally that the half-width varies as  $T^{1/2}$  which is the classical limit.<sup>24</sup> In this high-temperature approximation the ground-state curve is given as

$$E_g = K_g X^2/2. \quad (8)$$

The energy of the absorption transition as a function of  $X$  then becomes

$$E_a(X) = (E_0 + K_e X_0^2/2) - (K_e X_0)X + (K_e - K_g)X^2/2 \quad (9)$$

<sup>23</sup> R. V. Hesketh and E. E. Schneider, *Phys. Rev.* **95**, 837 (1954).

<sup>24</sup> G. A. Russell and C. C. Klick, *Phys. Rev.* **101**, 1473 (1956).

<sup>25</sup> J. D. Konitzer and J. J. Markham, *J. Chem. Phys.* **32**, 843 (1960).

<sup>26</sup> We are indebted to Professor H. Mahr of Cornell University for sending us machine calculations of the more exact expression for the band shape using this model. At low temperatures the approximate value appears to be quite accurate for the range of practical interest.

<sup>27</sup> W. B. Fowler and D. L. Dexter, *Physica Stat. Solidi* **2**, 821 (1962).

and the probability of an absorption transition becomes

$$P(E_a) = [-K_e X_0 + (K_e - K_g)X]^{-1} (K_g/2\pi kT^*)^{1/2} \times \exp(-K_g X^2/2kT^*), \quad (10)$$

where  $T^*$  approaches  $T$  closely. For the *F* center in KCl at room temperature, the deviation between  $T$  and  $T^*$  is 2%.

If one now uses the constants of the configuration coordinate curves determined by fitting the low-temperature data of Fig. 4 and inserts these constants into Eqs. (9) and (10), it is possible to compute the shape of the absorption band at room temperature and compare this with experiment. This is done in Fig. 5. Here again there is a good fit of the computed curve for 293°K and the experimental points over three decades on the long-wavelength side, and once again the *K* band interferes with the short-wavelength measurements.

In Fig. 5 are also shown some experimental points taken at 77°K along with computed curves using both the low-temperature approximation and the high-temperature approximation but using the effective temperature 98°K in both cases. As might be expected, neither approximation is adequate at this temperature and the experimental points fall between the two computed curves. A more exact calculation would involve computing  $P(E_a)$  for each of a number of ground-state vibrational levels, weighting these by the Boltzman distribution for the temperature involved, and then summing the result.

From the results of Figs. 4 and 5 it appears that configuration coordinate curves may be used to describe the *F*-center absorption band with high accuracy over

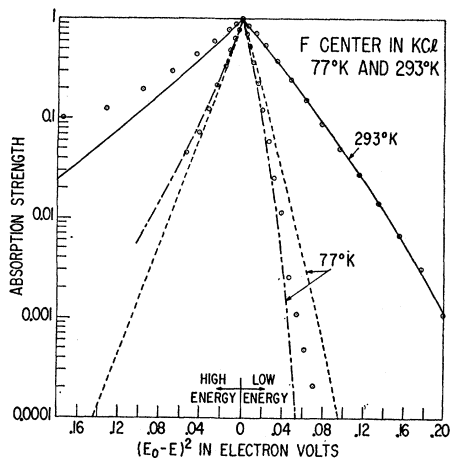


FIG. 5. The circled points show experimental values for the absorption strength of the *F* center plotted as a function of the square of the deviation of energy from the peak. Data are given for measurements at 77 and 293°K. The solid curve is computed from configuration coordinate curves determined from low-temperature data. The 77°K data falls between the curve predicted on the low-temperature approximation (long dash-short dash curve) and that predicted using the high-temperature approximation (dashed curve).

TABLE I. Constants for KCl *F*-center configuration coordinate curves.

	Lüty and Gebhardt	Present work
$K_g$	8.42 eV/Å <sup>2</sup>	8.42 eV/Å <sup>2</sup>
$K_e$	7.18 eV/Å <sup>2</sup>	11.79 eV/Å <sup>2</sup>
$X_0$	0.374 Å	0.217 Å
$E_0$	1.816 eV	2.041 eV
$M_e/M_g$	0.42	assumed 1.0

a wide range of absorption coefficients and temperatures. The constants evolved for the *F*-center configuration coordinate curves are given in Table I along with those obtained recently by Lüty and Gebhardt.<sup>28</sup> The present work uses absorption data only; Lüty and Gebhardt used both absorption and emission data. It is apparent that these two sets of curves do not agree and that each fails to describe some experimental data. If one uses the constants derived in the present work to predict the *F*-center emission band, a peak at 1.852 eV with low-temperature half-width 0.112 eV is obtained. For KCl the *F*-center emission has been measured at 1.238 eV with a low-temperature half-width of 0.248 eV. Thus, while the present work seems to be able to describe the absorption curves over a wide range of absorption coefficients and temperatures, it fails to describe the emission processes. On the other hand, the constants derived by Lüty and Gebhardt, using emission as well as absorption data, describe most of the experimental data very well; but if one uses their value of  $K_e=0.85 K_g$ , it is apparent from Fig. 4 that agreement with the long-wavelength side of the *F* band would be very poor. It is not yet clear why each of these descriptions, which fits some set of data quite well, does not describe the remainder. Two possible sources of difficulty will be discussed here, but these may not exhaust the possibilities.

One possible difficulty is that emission from the *F* center does not occur from the same excited-state level involved in absorption. The oscillator strength for *F*-center absorption is close to unity indicating that an allowed transition is involved in absorption; but the measurements of Swank and Brown<sup>29</sup> show that the decay time of *F*-center emission in KCl is  $0.59 \times 10^{-6}$  sec which is considerably longer than expected for an allowed transition. Fowler and Dexter<sup>30</sup> find a discrepancy by a factor of 12 if the wave function of the excited state of the *F* center were the same before and after relaxation. It is not clear whether relaxation effects in the excited state, which alter the wave function, are sufficiently pronounced to account for this factor of 12. Another possible explanation of the long decay time is that there exists a metastable level between the *F*-center ground state and the state to which

<sup>28</sup> F. Lüty and W. Gebhardt, Z. Physik **169**, 475 (1962).

<sup>29</sup> R. K. Swank and F. C. Brown, Phys. Rev. Letters **8**, 10 (1962).

<sup>30</sup> W. B. Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1962).

absorption transitions are made. After absorption of light the  $F$  center might decay to this metastable level and the observed luminescence might arise from a transition from this level to the ground state. Fowler and Dexter<sup>30</sup> present qualitative arguments against the occurrence of such a level below the level involved in absorption and Wood<sup>31</sup> fails to find it in computations of the  $F$  center in LiCl. Should it turn out that the emission does arise from a metastable level, all the configuration coordinate diagrams derived using both absorption and emission data<sup>24,28</sup> would be invalid.

On the other hand, if the same two energy states are involved in absorption and emission, then one might look to the Jahn-Teller effect for an explanation of the difficulties seen in the configuration coordinate diagrams. Wood and Korringa<sup>32</sup> have calculated the equilibrium position of the ions surrounding an  $F$  center in LiCl when the  $F$  center is in the excited state. They find that the two ions along the symmetry axis of the electronic distribution are displaced outward by 16% of the interatomic distance while the other four nearest neighbors are displaced inward by 6%. Such a distortion would not be accurately described by the usual configuration coordinate diagram which uses an average distance as a parameter and this may be a source of some of the observed difficulty.

Another complication which might arise is the need to consider explicitly two different types of vibrational modes, one which is important for the center in its electronic ground state, and the other which is important for its excited state. Such considerations form the basis of an analysis by Lüty and Gebhardt,<sup>28</sup> who characterize the different vibrations in the ground and excited electronic states by using different oscillator masses as well as different force constants. This technique is useful in that one often finds that different normal modes behave as though different total masses were involved in a simple harmonic motion. Lüty and Gebhardt assume that the vibrations in the ground electronic state are totally symmetric about the  $F$  center but that those of the excited electronic state correspond to the distortion symmetry computed by Wood and Korringa. Using an oscillator mass in the excited state which is 0.42 times that of the ground state, Lüty and Gebhardt are able to explain their  $F$ -center absorption and emission data with the use of a single configuration coordinate. We believe that such a description is not internally consistent, however, since the vibrations in the excited state involve an entirely different configuration coordinate from that in the ground state and one cannot place both on the same diagram. Referring to Fig. 3, let us assume that the ground-state curve corresponds to a high-symmetry mode ( $q_1$ ) but that the excited state involves a mode of lower symmetry ( $q_2$ ). Consider now a center which absorbs light ( $A \rightarrow B$ ),

relaxes by emitting phonons ( $B \rightarrow C$ ), and finally emits light ( $C \rightarrow D$ ). The point  $D$  then corresponds to the ground electronic state of the system with a distribution of ions having not a  $q_1$ -like distortion but a  $q_2$ -like distortion. However, in principle the point  $D$  can be reached thermally from  $A$  and therefore corresponds to a  $q_1$ -like distortion. In this picture, then, the description of point  $D$  is not logically consistent. The introduction of an additional type of normal coordinate necessitates the development of a more complex configuration coordinate diagram, in particular, one with at least two configuration coordinate axes. In such a theory, the parabolas of Fig. 3 would become paraboloids.

To summarize, the failure of a configuration coordinate diagram to describe all the  $F$ -center optical properties may be due to an assumption that this is a two-level system when it may turn out to be a three-level system; or it may indicate that this very simple model is unable to describe more complex properties such as those arising from the Jahn-Teller effect.

### III. KCl:Tl

Absorption measurements were made at 4 and 77°K of the "A" band absorption<sup>33</sup> of KCl:Tl which occurs at 2470 Å. The crystals used had a concentration of approximately 300 parts per million of Tl. Measurements were made on two crystals differing in thickness by a factor of 10 and the over-all curve was obtained by combining the measurements from these specimens. The results, normalized to unity, for the 4°K measure-

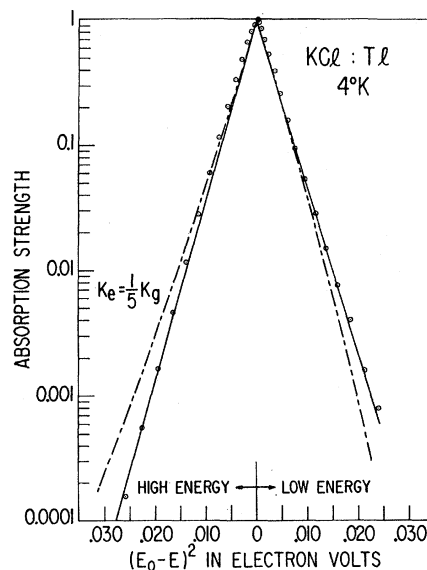


FIG. 6. The absorption strength, normalized to unity, of the  $A$  band in KCl:Tl at 4°K is plotted as the square of the difference in energy from the peak of the band. The solid curve represents a Gaussian curve drawn through the points. The dashed curve is the result of a configuration coordinate-diagram analysis assuming  $K_e = 0.2 K_g$ .

<sup>31</sup> R. F. Wood, Phys. Rev. Letters **11**, 202 (1963).

<sup>32</sup> R. F. Wood and J. Korringa, Phys. Rev. **123**, 1138 (1961).

<sup>33</sup> F. Seitz, J. Chem. Phys. **6**, 150 (1938).

ment are shown in Fig. 6 where the logarithm of the absorption strength is plotted as a function of the square of the energy difference from the peak. Here again it is seen that straight lines, corresponding to Gaussian curves, are a reasonably accurate fit. There seems to be little evidence that the curve is shifting over into an Urbach's rule type of plot.

There are a number of interesting features connected with Fig. 6. One is that the experimental points fall above the straight line on the high-energy side of the curve, possibly indicating that there is more than one absorption band in this wavelength region. Other evidence pointing to complexities in the  $A$  band is found in the asymmetrical band shape at room temperature,<sup>34</sup> separate excitation bands for the 3050 and 4750 Å emissions in the  $A$ -band region,<sup>35,36</sup> and temperature-dependent band shapes and oscillator strengths which appear in the  $A$ -band region for many thallium-activated alkali halides.<sup>37</sup> Another interesting feature of Fig. 6 is that there does not appear to be any pronounced asymmetry about the peak position of the absorption band as there is in the  $F$ -center results of Fig. 4. Finally, the dashed curve of Fig. 6 shows an attempt to fit configuration coordinate diagrams to the experimental points using a value of  $K_e = 0.2 K_0$ . Even with such a small value, the fit is poor and it is clear that the agreement would improve as the ratio approaches zero. This makes it impossible to attempt to analyze this data in the way that was done for the  $F$  center. Previous attempts to determine configuration coordinate diagrams for KCl:Tl<sup>36,38</sup> have also not been completely successful.<sup>39</sup> For a variety of reasons, then,

it does not seem possible to learn much more about this system except that its absorption band shape is closely Gaussian on the long-wavelength side.

The  $C$  band of KCl:Tl at 1950 Å failed to show any regularity when investigated at 4°K. The complexity of this band has long been apparent. It is known, for instance, that the width of the band is a function of the thallium concentration.<sup>40</sup>

#### IV. SUMMARY

Absorption measurements for the  $F$  center in KCl and thallium in KCl fail to show any evidence that these bands follow Urbach's rule at low-absorption coefficients. If they do so at all, it must be at absorption coefficients lower by an order of magnitude than were found by Mahr for KCl:I. This result would seem to reduce the likelihood that Urbach's rule has a broad general applicability not only to optical transitions in pure solids but to transitions arising from imperfections as well. While it is not yet clear what the parameters are that lead to Urbach's rule, it may be significant that highly localized centers such as Tl<sup>+</sup> and the  $F$  center do not follow the rule, while excitons and other transitions close in energy to the band gap do follow it.

In the case of the  $F$  center in KCl, configuration coordinate diagram analysis is able to account for the band shape over a range of four decades in absorption coefficient. This analysis also permits one to obtain constants for the curves from absorption measurements alone. Curves obtained in this way, however, fail to predict the observed  $F$ -center emission spectrum. Two possible reasons for this failure are noted: one is that the  $F$  center may really be a three-level rather than a two-level system; the other is that relaxation effects in the excited state, which are not included in the simple model, have an important bearing on the emission spectrum.

<sup>34</sup> P. D. Johnson and F. J. Studer, Phys. Rev. **82**, 976 (1951); D. A. Patterson, *ibid.* **112**, 296 (1958).

<sup>35</sup> K. H. Butler, J. Electrochem. Soc. **103**, 508 (1961).

<sup>36</sup> D. A. Patterson and C. C. Klick, Phys. Rev. **105**, 401 (1957).

<sup>37</sup> R. Edgerton and K. Teegarden, Phys. Rev. **129**, 169 (1963).

<sup>38</sup> F. E. Williams, J. Chem. Phys. **19**, 457 (1951).

<sup>39</sup> R. S. Knox and D. L. Dexter, Phys. Rev. **104**, 1245 (1956).

<sup>40</sup> W. Koch, Z. Physik **57**, 638 (1929).