

Configuration Coordinate Curves for *F*-Centers in Alkali Halide Crystals*

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Measurements have been made of the *F*-center absorption band in KCl, KBr, KI, NaCl, and LiF in the range from 4°K to 300°K. Analysis of these data shows that the important ionic vibrational frequency influencing the *F*-center is considerably lower than that of the lattice, indicating that a configuration coordinate curve model may be the appropriate one to use, rather than the continuous dielectric model. Using the peak of the *F*-center emission bands as determined by Botden, van Doorn, and Haven, and the present absorption data, configuration coordinate curves are computed for the ground and excited state curves of *F*-centers in KCl, KBr, KI, and NaCl. Using these curves, predictions of the emission bandwidths are found to be in agreement with experiment except for the case of KCl. The low efficiency of *F*-center luminescence may be understood by applying the criterion for luminescence proposed by Dexter, Klick, and Russell to these configuration coordinate curves.

I. INTRODUCTION

THE *F*-center in alkali halides¹ is believed to consist of an electron trapped at a negative ion vacancy. It has been widely investigated for many years and is probably the best understood imperfection in the field of solids. Properties of the *F*-center such as absorption, thermal and optical bleaching, photoconduction, and magnetic susceptibility appear to be understood in at least a qualitative fashion. Also, the model has been investigated theoretically as an impurity imbedded in a static dielectric, and the wave functions thus obtained have given reasonably correct values for the position of the *F*-band absorption and its absorption strength.

It has generally been anticipated that, after absorption of light, the *F*-center would return to its ground state by emission of light. It was also anticipated that the efficiency of this process would be high if measured at sufficiently low temperatures.² An investigation by Klick³ of the luminescence of the *F*-center in LiF and KCl over the wavelength range from the *F*-center absorption band to 25 000 Å indicated that the efficiency at 4°K was less than 3% over most of this range. Botden, van Doorn, and Haven⁴ found that by quenching additively colored crystals of KCl, KBr, KI, NaCl, and RbCl from high temperatures to that of liquid nitrogen they were able to obtain luminescence which they attributed tentatively to *F*-centers. The efficiency was estimated to be of the order of 1%. The conclusion appears to be that a large fraction of *F*-centers return to their ground state by some radiationless process.

Huang and Rhys⁵ and Pekar⁶ have extended the *F*-center theory to include the interaction of the *F*-center with the vibrational phonons of the lattice at large distances from the center. On the basis of this dissipation mechanism the ratio of the probability of a radiative transition to a radiationless transition was computed to be 10^{18} for the *F*-center in KBr at 20°K, in striking contrast to the value of 10^{-2} observed experimentally at even lower temperatures. Markham⁷ and Meyer⁸ have suggested that a less approximate treatment might reduce the computed ratio to that observed. More detailed calculations,⁹ however, still leave a discrepancy of a factor of 10^9 in most cases.

In contrast to the methods which treat the lattice as a continuous dielectric, there is the configuration coordinate curve approach which takes into account the interaction of a center and its neighboring ions or atoms. Configuration coordinate curves, introduced by von Hippel¹⁰ and Seitz¹¹ have long been used in a qualitative way for describing optical processes occurring at a center. An important additional observation is due to Schön¹² who suggested that the broad-band low-temperature absorption and emission spectra¹³ arose from the zero-point vibrational energy of the center. Williams¹⁴ made a detailed computation of the configuration coordinate curves for thallium in potassium chloride, using the distance from the thallium to the neighboring chlorine ions as the coordinate. Using these curves and treating the center quantum mechanically as a simple harmonic oscillator, Williams was able to compute the position and band width of both the

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¹ See F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954) for a comprehensive review of the properties of color centers.

² N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), pp. 136, 222.

³ C. C. Klick, *Phys. Rev.* **94**, 1541 (1954).

⁴ Botden, van Doorn, and Haven, *Philips Research Repts.* **9**, 469 (1954).

⁵ K. Huang and A. Rhys, *Proc. Roy. Soc. (London)* **A204**, 406 (1950).

⁶ S. I. Pekar, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **20**, 510 (1950); **22**, 641 (1952).

⁷ J. Markham, *Phys. Rev.* **91**, 1277 (1953).

⁸ H. J. G. Meyer, *Physica* **20**, 181 (1954).

⁹ H. J. G. Meyer, *Physica* **20**, 1016 (1954).

¹⁰ A. von Hippel, *Z. Physik* **101**, 680 (1936).

¹¹ F. Seitz, *Trans. Faraday Soc.* **35**, 79 (1939).

¹² M. Schön, *Ann. Physik*, Series 6, **3**, 343 (1948).

¹³ C. C. Klick, *J. Phys. Chem.* **57**, 776 (1953).

¹⁴ F. E. Williams, *J. Chem. Phys.* **19**, 457 (1951); *J. Phys. Chem.* **57**, 780 (1953).

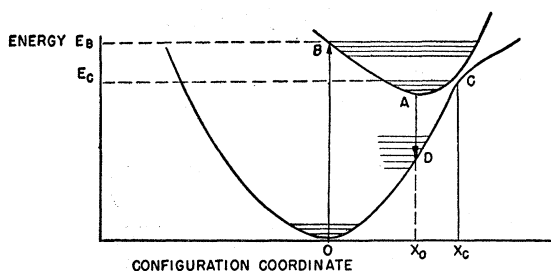


FIG. 1. Schematic illustration of a radiationless transition according to Dexter, Klick, and Russell.

thallium emission and absorption bands as a function of temperature with considerable accuracy. It has also been shown that by using the same model, configuration coordinate curves may be computed from experimental data¹⁵ and this has been done for manganese in zinc silicate.¹⁶ Some of the approximations involved in the configuration coordinate curve method are discussed by Williams and Hebb¹⁷ and by Lax.¹⁸ On the basis of this model Dexter, Klick, and Russell¹⁹ have proposed a mechanism for radiationless transitions which is illustrated in Fig. 1. If the intersection point, *C*, of the ground and excited states of a center is at lower energy than the point, *B*, on the excited-state curve to which transitions are made, then in approaching its new equilibrium after absorption of light, the system may find itself in the vicinity of *C* for a time long enough for transitions to the ground state to be made without radiation.

In general, the configuration coordinate model should be applicable in cases where the wave functions of the center are highly localized while the continuous dielectric model should be preferable in cases where the wave functions are spread out. It is not clear which model is the more accurate for the *F*-center, and the first problem is to decide this point experimentally. Having settled on a model, the problem will then be to attempt to examine the luminescence behavior of the *F*-center on the basis of this model.

It is possible to decide between these models in a rather direct way by observing the absorption band of the *F*-center as a function of temperature. Both models predict that the width of the band at half-maximum, ΔE , is given by

$$\Delta E = A [\coth(h\nu_0/2kT)]^{\frac{1}{2}}, \quad (1)$$

where *A* is a constant, *h* is Planck's constant, *k* is Boltzmann's constant, and *T* is the temperature in degrees absolute. In this expression ν_0 is the vibrational frequency which influences the center in its ground state. The continuous dielectric model would specify

¹⁵ C. C. Klick, *Phys. Rev.* **85**, 154 (1952).

¹⁶ C. C. Klick and J. H. Schulman, *J. Opt. Soc. Am.* **42**, 910 (1952).

¹⁷ F. E. Williams and M. H. Hebb, *Phys. Rev.* **84**, 1181 (1951).

¹⁸ M. Lax, *J. Chem. Phys.* **20**, 1752 (1952).

¹⁹ Dexter, Klick, and Russell, *Phys. Rev.* **100**, 603 (1955).

that ν_0 be the frequency of the longitudinal optical vibrational modes of the lattice while on the configuration coordinate model the frequency necessary to fit experimental data would be characteristic of vibrations near the center and in general would be different from the lattice frequencies. Experiments were carried out, then, to determine the variation of the width of the absorption band as a function of temperature with sufficient precision to establish the validity of the functional form of Eq. (1) and to determine ν_0 for the *F*-center.

II. EXPERIMENTAL RESULTS

Figure 2 is a schematic drawing of the low-temperature Dewar used in these experiments. It was designed to hold a crystal sample at any temperature between 4°K and room temperature for a time sufficiently long so that an absorption curve might be taken for the *F*-center. This measurement took between five and ten minutes, and in that time the temperature variation was $\pm 1^\circ\text{K}$ for the worst case. Temperature control at low temperatures was obtained by varying the pumping speed on the charcoal container which varied the desorption rate of helium, and by varying the energy supplied to the heater. At higher temperatures, cooling was accomplished by circulating precooled helium gas through the charcoal container to offset the heat input to the system. The temperatures were measured by using a platinum resistance thermometer and a calibrated carbon resistor,²⁰ both of which were placed close to the samples.

Optical absorption measurements were made with a

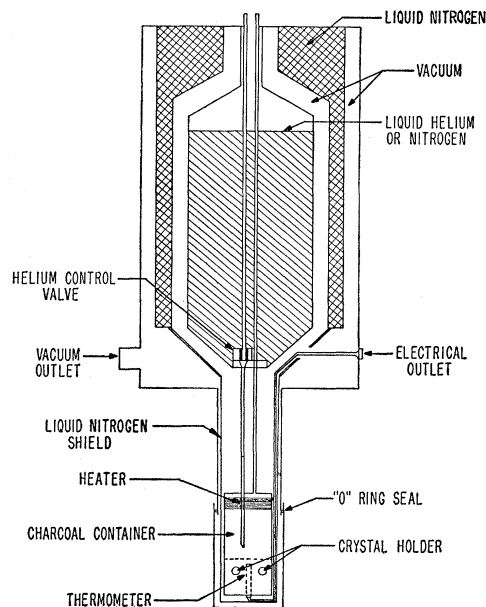


FIG. 2. Schematic drawing of low-temperature Dewar.

²⁰ J. R. Clement and E. H. Quinell, *Rev. Sci. Instr.* **23**, 213 (1952).

Beckman Model DU Spectrophotometer. Two crystals of the same material and approximately the same thickness were placed in the two crystal-holder positions shown in Fig. 2. One crystal, however, contained *F*-centers. A mirror system was used to transmit the optical beam first through one crystal and then through the other so that the absorption of the *F*-band could be determined directly.

Measurements were made on the *F*-bands in KCl, KBr, KI, NaCl, and LiF. In all cases single crystals grown by the Harshaw Chemical Company were used. KCl and KBr were additively colored at 650°C and after being cleaved to size, the samples were heated to 500°C for 35 minutes, quenched to room temperature, and kept in the dark until the optical absorption measurements were made. NaCl, KI, and LiF were colored by exposure to gamma rays from Co⁶⁰. A dosage from 12 to 48 megareöntgens was used and the high energy of the gamma rays (1.2 Mev) insured essentially uniform coloration of the samples. The samples were kept in the dark to prevent formation of the *K*-band.²¹ In addition it was necessary to store KI at 77°K to prevent the rapid bleaching of the *F*-band observed in this material at room temperature.

Both the configuration coordinate model¹⁵ and the continuous dielectric model¹⁸ suggest that, to a first approximation, the absorption and emission bands of simple centers are Gaussian in shape. Possible deviations from a Gaussian shape are discussed by Dexter.²² Hesketh and Schneider²³ have shown that the absorption curve of the *F*-center can be fitted by an expression of the form

$$\alpha = \alpha_0 \exp[-a(h\nu - h\nu_0)^b], \quad (2)$$

where α is the coefficient of absorption, α_0 and a are constants, b is a constant which should be 2 for the

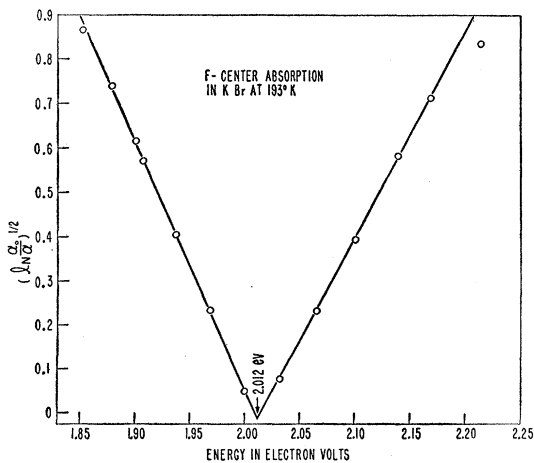


FIG. 3. Method used to determine the peak of the *F*-center absorption band.

²¹ H. W. Etzel and F. E. Geiger, Jr., Phys. Rev. **96**, 225 (1954).
²² D. L. Dexter, Phys. Rev. **96**, 615 (1954).
²³ R. V. Hesketh and E. E. Schneider, Phys. Rev. **95**, 837 (1954).

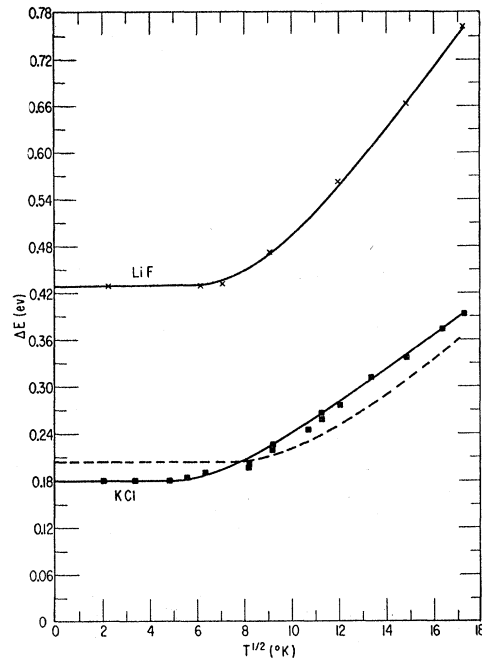


FIG. 4. Variation of the width of the *F*-band in KCl and LiF at half-maximum as a function of temperature. The solid curves are the best fits to the experimental points using Eq. (1) and choosing $\nu_0 = 2.6 \times 10^{12}$ for KCl and $\nu_0 = 4.1 \times 10^{12}$ for LiF. The dashed curve illustrates an equation given by Meyer for KCl.

curve to be Gaussian but which has been found to be 2.0 on the high-energy side and from 2.5 to 2.8 on the low-energy side of the *F*-band, h is Planck's constant, ν is the frequency of light at which α is measured, and ν_0 is the frequency of the peak of the absorption curve. By plotting $(\ln \alpha_0 / \ln \alpha)^{1/b}$ as a function of $h\nu$, it is possible to obtain high precision in the determination of both the peak position of the absorption and the width of the curve at half the maximum. A plot of this sort, which assumes the curve to be Gaussian, but allows the constant a to vary from one side of the band to the other, is shown in Fig. 3 for the *F*-center in KBr taken at 193°K. Measurement errors are estimated to be ± 0.001 eV for the peak position and ± 0.005 eV for the width of the absorption curves.

The variation of the *F*-band width with temperature is plotted in Figs. 4 and 5 for various alkali halides and an equation of the form of Eq. (1) is fitted to the points by choosing ν_0 . In these figures the abscissa is given as $T^{1/2}$ in order to show the approach at high temperature to the $T^{1/2}$ dependence of the width of the absorption curve. From these data it is apparent that it is the deviation from the $T^{1/2}$ dependence that determines ν_0 , and for this reason the low-temperature points are the most significant ones.

Figure 6 shows the variation in peak position of the *F*-band as a function of temperature for KCl, KBr, KI, and NaCl. Results on LiF are not included because of the relatively large experimental errors in this case.

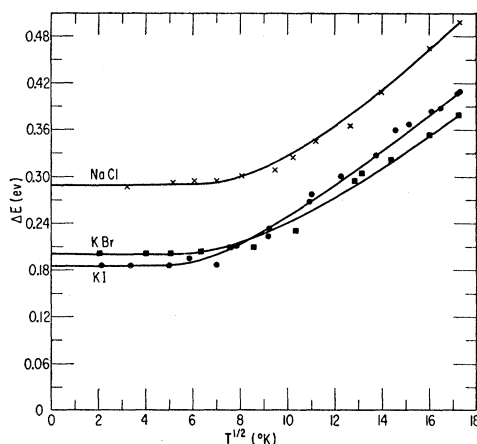


FIG. 5. Variation of the width of the F -band in NaCl, KBr, and KI at half-maximum as a function of temperature. The curves are the best fits to the experimental points using Eq. (1) and choosing $\nu_0 = 4.4 \times 10^{12}$ for NaCl, $\nu_0 = 2.6 \times 10^{12}$ for KBr, and $\nu_0 = 3.6 \times 10^{12}$ for KI.

The data follow that of Pohl²⁴ in general but cover the low-temperature region in somewhat greater detail.

III. CONTINUOUS DIELECTRIC MODEL VS CONFIGURATION COORDINATE MODEL

Examination of the experimental results on band-width measurements, given in Figs. 4 and 5, shows that a relation of the form given in Eq. (1) describes the results within the limits of experimental error. Therefore it appears to be a good approximation to consider the center as interacting with an ionic vibration of a single frequency rather than a spectrum of frequencies.

It is then of interest to examine whether this frequency is characteristic of the unperturbed lattice, as assumed in the continuous dielectric model, or is different as would in general be the case if the configuration curve model were applicable. The longitudinal optical vibrational frequencies, ν_0 , of the ionic lattices are obtained from the transverse vibrational frequencies, ν_t , by the use of the relation of Lyddane, Sachs, and Teller²⁵:

$$\nu_0 = \nu_t (\epsilon_s / \epsilon_0)^{1/2}, \quad (3)$$

where ϵ_0 and ϵ_s are the "high-frequency" and static dielectric constants respectively. The transverse frequency ν_t corresponds to the peak of the infrared absorption. In some cases this is not known directly but the restrahl frequencies, ν_R , are known. An approximation to ν_t is then made by using

$$\nu_t = A \nu_R, \quad (4)$$

where the constant, A , is determined from transmission and restrahl measurements on other alkali halides to be approximately 0.90. Table I compares the values of

ν_0 obtained by using Eq. (3) with the experimentally obtained ν_R . For KCl, KI, and NaCl the infrared absorption peak is known; for KBr and LiF only the restrahl frequency is known. It is apparent that ν_0 differs from ν_R by a factor of approximately 2 or more, except for the case of KI where the factor is reduced to 1.1.

These results seem to indicate, then, that the F -center is influenced primarily by the vibrations of its nearest neighbors. In general it would be expected, because of the "softness" of the F -center, that the vibrational frequencies of ions surrounding it would be less than that of normal ions so that on the configuration coordinate model ν_0 should be less than ν_R . Table I indicates that this is the case.

An additional argument can be advanced from the calculations of Huang and Rhys.⁵ To account for the experimentally observed width of the F -band in KBr at 20°K, they computed that an average value of 22.4 vibrational quanta were given to the lattice in the transition corresponding to optical absorption. However, using Simpson's model of the F -center in NaCl,²⁶ they calculated only 3.6 vibrational quanta. This calculation might be taken to indicate that the continuous dielectric model used by Huang and Rhys describes a relatively minor interaction of the F -center.

Meyer⁹ has examined some of the older work of Mollwo²⁷ and has attempted to fit band widths to an equation of the form of Eq. (1) using the longitudinal optical frequencies of the lattice. To fit the points, he arbitrarily introduces a constant C so that the equation

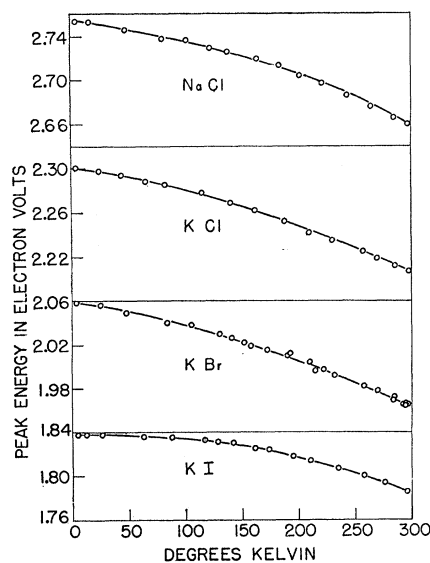


FIG. 6. Variation of the peak of the F -center absorption band with temperature for NaCl, KCl, KBr, and KI.

²⁴ R. W. Pohl, Proc. Roy. Soc. (London) **49** (extra part), 3 (1937).

²⁵ Lyddane, Sachs, and Teller, Phys. Rev. **59**, 673 (1941).

²⁶ J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

²⁷ E. Mollwo, Z. Physik **85**, 56 (1933).

becomes of the form

$$\Delta E = A \left(\coth \frac{h\nu_0}{2kT} + C \right)^{\frac{1}{2}}, \quad (5)$$

where ν_0 is taken to be the lattice frequency. In this older experimental work, however, there are very few data taken in the low-temperature range and, as has been shown before, this is the crucial region for the determination of ν_0 . In Fig. 4 the dashed curve is a plot of Eq. (5) for KCl *F*-centers using the constants given by Meyer. It is apparent that this curve is not a good fit to the experimental points.

IV. COMPUTATION OF CONFIGURATION COORDINATE CURVES

The continuous dielectric model appears to be inadequate to describe the optical properties of the *F*-center. In this section, therefore, the configuration coordinate model will be applied to the *F*-center and the ground and excited state energy curves will be computed. The accuracy of this treatment can be evaluated by comparing the predictions of the model with experiment.

Experimental data are used to evaluate the configuration coordinate curves, following the methods described by Klick.¹⁵ It is assumed that there is a single ground state for the *F*-center and that the energy curves are parabolic so that the center acts as a simple harmonic oscillator in either state. The mass of this oscillator is taken to be the sum of the masses of the six nearest positive ions. In KCl:Tl, Williams¹⁴ has shown that the effective mass is larger than this sum by a factor of 1.2. In most applications of these curves, the specific assumption on the mass is not critical. It is also assumed that the only mode of oscillation of importance for the center is the radial in-phase motion of the six nearest positive ions. This assumption is justified on the basis that changes in energy of the center are much greater for the radial in-phase oscillations than for other allowed modes of oscillation. The state from which an optical transition starts is treated quantum mechanically while the final state is treated classically if the region of the curve to which transitions are made is many vibrational quanta above the minimum of the curve. This procedure can be justified by using the Bohr correspondence principle, and has been discussed in detail by Williams and Hebb¹⁷ and by Lax.¹⁸ Finally,

TABLE I. Longitudinal optical vibrational frequencies of the lattice (ν_0) and experimentally determined vibrational frequencies of the *F*-center (ν_g) for various alkali halides.

	ν_0	ν_g
KCl	6.3×10^{12}	2.6×10^{12}
KBr	4.7×10^{12}	2.6×10^{12}
KI	4.0×10^{12}	3.6×10^{12}
NaCl	7.8×10^{12}	4.4×10^{12}
LiF	22.3×10^{12}	4.1×10^{12}

it is assumed that the transition probability between the states is independent of the value of the coordinate at which the transition is made. Dexter²² has investigated this point and estimated the corrections to be made to the shapes of the emission and absorption bands.

The configuration coordinate curves are then given by four constants: k_g , k_e , X_0 , and U_0 . The k 's are force constants for the ground and excited states respectively and the X_0 and U_0 are the separation of the minima of the curves in coordinate and energy. In this treatment the abscissa X is the variation in distance from the center of the *F*-center to the center of one of the nearest neighbor ions; the origin for this coordinate is taken as the minimum of the ground-state curve. Both the electronic and ionic energy of the system are included in the energy plotted as the ordinate of these curves. The origin in energy is also taken at the minimum of the ground state curve.

Experimental data such as that of Figs. 4 and 5 are used to determine ν_0 , which is simply related to k_g by

$$k_g = 4\pi^2\nu_0^2M, \quad (6)$$

where M is the mass assigned to the center. It can also be shown¹⁵ that the width at half-maximum of the absorption band at absolute zero is

$$\Delta E_{\text{abs}}(0^\circ\text{K}) = 1.355 \times 10^{-13} (\nu_0/k_g)^{\frac{1}{2}} k_e X_0. \quad (7)$$

The peak of the absorption band at absolute zero will be given by

$$E_{m \text{ abs}}(0^\circ\text{K}) = U_0 + \frac{1}{2}k_e X_0^2 - \frac{1}{2}h\nu_0. \quad (8)$$

In addition to Eqs. (6), (7), and (8), a fourth independent equation is necessary to determine the four constants of these curves. Following a suggestion by Lax,²³ a careful attempt was made to use the variation in peak position of the *F*-band absorption with temperature and relate it to the constants of the curve. The expression which evolves is

$$\left. \frac{\partial E_m}{\partial T} \right|_P + \frac{3\alpha_F k_g}{4\pi R \eta} \left. \frac{\partial E_m}{\partial P} \right|_T = \frac{-h^2\nu_0^2}{4k} \times \left\{ \frac{k_e - k_g}{2k_g} \right\} \frac{\coth^2(h\nu_0/2kT)}{T^2}, \quad (9)$$

where η is defined by

$$V_m = (4/3)N_0(r_+^3 + r_-^3)\eta,$$

and V_m is the molar volume of the host lattice, N_0 is Avogadro's number, r_+ and r_- are the radii of the positive and negative ions of the host lattice, α_F is the coefficient of thermal expansion of the *F*-center, and R is the radius of the *F*-center. By using the variation of the absorption band with pressure determined by

²³ M. Lax, Office of Naval Research Technical Report No. 5, Project No. NRO 17-419 (unpublished).

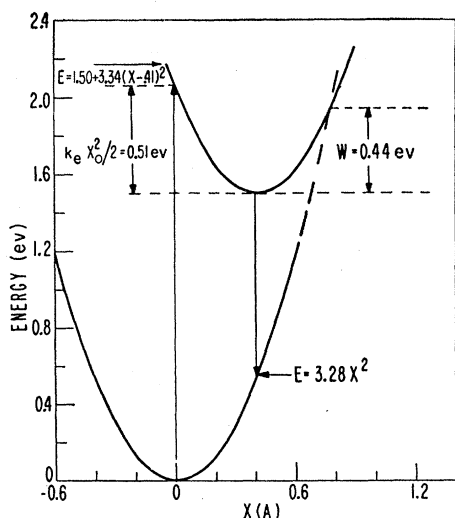


Fig. 7. Configuration coordinate curves for the F -center in KBr.

Jacobs,²⁹ it is possible to use Eq. (9) if the ratio α_F/R is known. Since neither is known it is possible to assume that α_F is the same as the linear coefficient of thermal expansion of the host lattice and that R is equal to the radius of the missing negative ion. With these assumptions, constants for the configuration coordinate curves of the F -center in KCl have been computed. In this case, however, a variation of a factor of 2 in k_e occurs for a variation of α_F/R by a factor of 1.2. This procedure for determining the fourth equation was abandoned in this case as being too sensitive to the choice of the unknown constants.

A fourth equation was obtained, instead, by using the emission data of Botden, van Doorn, and Haven⁴ on additively colored and quenched crystals. By arguments similar to that used in obtaining Eqs. (7) and (8), the peak of the emission spectrum at low temperatures is given by

$$E_{m \text{ emis}}(0^\circ\text{K}) = U_0 - \frac{1}{2}k_g X_0^2 + \frac{1}{2}h\nu_e, \quad (10)$$

and the low-temperature emission band width is

$$\Delta E_{\text{emis}}(0^\circ\text{K}) = 1.355 \times 10^{-13} (\nu_e/k_e)^{1/2} k_g X_0. \quad (11)$$

Equations (6), (7), (8), and (10) were then used to compute the configuration coordinate curves for the F -center in KCl, KBr, KI, and NaCl. Figure 7 illustrates the results for KBr. Emission data is not available for LiF so that only the ground state and slope of the excited-state curve at $X=0$ are known in this case.

The results of the configuration coordinate calculations are given in Table II; in this table energy is given in electron volts and distance in angstroms. The values of $k_e X_0^2/2$ give the energy of the point on the excited state curve to which transitions are made in absorption above the minimum of that curve and W is the height of the "intersection" of the ground- and excited-state

curves above the minimum of the excited state curve as shown in Fig. 7.

By using these configuration coordinate curves, it becomes possible to predict the width at half-maximum of the emission band. This value, ΔE_{ec} , may be compared with the value, ΔE_{exp} , obtained by Botden, van Doorn, and Haven from experiment. These values are given in the last two columns of Table II. For NaCl, Botden, van Doorn, and Haven report a double peak at low temperature; the half-width given in Table II corresponds to the longer wavelength emission band obtained by analyzing the emission into two overlapping bands.

DISCUSSION

It is interesting to compare the widths of the emission spectra derived from the configuration coordinate curves and from experiment. For KBr and KI the agreement is reasonably good. In NaCl agreement is found if the observed emission is separated into two bands. A distinct double-peaked emission is not always found in NaCl, however, so that the emission may be influenced by such factors as the size of the crystal or the rate of quenching. In KCl the observed emission is distinctly wider than that predicted from the curves. Here too there may be overlapping bands since a crystal allowed to stand at room temperature for 15 hours and then cooled to 77°K has emission peaks at 1.08 μ and 1.23 μ . The shorter wavelength band overlaps the 1.00- μ band found by quenching directly to 77°K, and if there is a sizeable amount of the 1.08 μ band introduced in the rapid quenching case, the observed emission would be broadened. In general, then, the results indicate that the luminescence observed by Botden, van Doorn, and Haven is from F -centers and that the configuration coordinate model accounts for both absorption and emission.

It is also interesting to note from Table II the closeness of the values of k_g and k_e in each case. This is rather surprising since for KCl:TI the ground-state stiffness is greater than that of the excited state by a factor of two. It appears from these values that the vibration of the center is rather weakly dependent on the state of excitation of the electron. For the case of the F -center, X_0 is positive, as shown by the pressure data of Jacobs,²⁹ indicating an expansion of the F -center as the electron is excited. This is contrary to the rather surprising negative values of X_0 for the case of KCl:TI where the center diminishes in size when the electron on the thallium ion is excited. The values of X_0 are

TABLE II. Constants of the configuration coordinate curves for the F -center in various alkali halides.

	k_g (ev/Å ²)	k_e (ev/Å ²)	X_0 (Å)	U_0 (ev)	$k_e X_0^2/2$ (ev)	W (ev)	ΔE_{exp} (ev)	ΔE_{ec} (ev)
KCl	6.50	6.56	0.42	1.75	0.56	0.51	0.26	0.19
KBr	6.56	6.68	0.41	1.50	0.51	0.44	0.19	0.18
KI	12.44	12.44	0.28	1.35	0.49	0.35	0.17	0.20
NaCl	10.94	11.42	0.37	1.96	0.80	0.59	0.27	0.27

²⁹ I. S. Jacobs, Phys. Rev. **93**, 993 (1954).

slightly larger in all cases for the F -center than for the thallium activated KCl as might be expected.

From the work of Botden, van Doorn, and Haven it appears that only by immediately quenching to very low temperatures is it possible to produce the luminescence which they attribute to the F -center. It is possible that if the crystals are left at higher temperatures some type of migration occurs which puts the centers at positions where their emission is quenched. This does not seem to materially alter the absorption spectrum in most materials. A similar phenomenon has been reported by Schulman, Ginther, and Klick³⁰ for lead in NaCl. From this one might conclude that only in crystals quenched rapidly to very low temperatures do the F -centers exist in a completely random distribution.

Examination of Table II shows that in each case the intersection of the curves occurs at an energy, W , less than the energy of the point to which transitions are made, $keX_0^2/2$. On the criterion for luminescence proposed by Dexter, Klick, and Russell,¹⁹ it would be expected that the efficiency of luminescence would be small, and this is in accord with the measurements of Klick³ and of Botden, van Doorn, and Haven.⁴

³⁰ Schulman, Ginther, and Klick, *J. Opt. Soc. Am.* **40**, 854 (1950).

SUMMARY

This work appears to have shown that the continuous dielectric model is not a satisfactory approximation, but that the configuration coordinate model adequately describes the absorption and emission properties of F -centers in alkali halides. A quantitative determination of configuration coordinate curves for both the ground and excited states of the F -center has been made for KCl, KBr, KI, and NaCl. The ground-state curve has been determined for LiF. In addition to showing how the F -center interacts with its neighboring ions, these curves have led to a simple explanation of one of the most puzzling aspects of the F -center: the low efficiency of F -center luminescence.

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Levels of Al^{25} from the $Mg^{24}(p,\gamma)Al^{25}$ Reaction

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At the 222-kev resonance in the reaction $Mg^{24}(p,\gamma)Al^{25}$, a 2.05 ± 0.02 -Mev gamma ray in cascade with one of 0.454 ± 0.005 Mev, and a 1.56 ± 0.03 -Mev gamma ray in cascade with one of 0.97 ± 0.03 Mev have been observed. The intensities of the 2.05, 1.56, and 0.97-Mev gamma rays are in the ratio of 100:14:5. The 2.05-Mev gamma rays have a thick target yield of $(1.0 \pm 0.5) \times 10^{-11} \gamma/p$, and exhibit an isotropic angular distribution with respect to the bombarding beam. The width at half-maximum of the resonance is less than 2 kev. The level in Al^{25} formed at the 222-kev resonance has an energy of 2.50 ± 0.02 Mev, and a spin and parity of $\frac{1}{2} \pm$ or $\frac{3}{2} +$, with the latter being a less probable assignment.

INTRODUCTION

A RESONANCE in the reaction $Mg^{24}(p,\gamma)Al^{25}$ at a bombarding energy of 222 ± 1 kev was first observed by Tangen *et al.*^{1,2} In the present experiment, the gamma-ray spectrum from this reaction was examined with a NaI(Tl) crystal and the following quantities measured: the energies of the gamma rays, the components in coincidence, their relative intensities, and the angular distribution of one of the gamma rays.

The low-lying levels of Al^{25} have been examined pre-

viously by Goldberg³ through the reaction $Mg^{24}(d,n)Al^{25}$, and by Casson⁴ using the reaction $Mg^{24}(p,\gamma)Al^{25}$.

Casson used a one-inch cube of NaI(Tl) to examine the gamma spectrum. His proton beam ranged between 6 and 12 microamperes. Since the yield of this reaction is low, he used an arrangement which allowed the crystal to be moved to within 3.5 mm of the target to obtain an adequate counting rate. With such a geometry, there is a high probability that two gamma rays in cascade will enter the crystal simultaneously. The crystal then responds as if a gamma ray with an energy equal to the sum of the two in cascade had entered. It is believed that the 2.35-Mev gamma ray

¹ R. Tangen, *Kgl. Norske Videnskab. Selskabs, Fork. Skrifter*, No. 1 (1946).

² Grottdal, Lönsjö, and Tangen, *Phys. Rev.* **77**, 296 (1950).

³ E. Goldberg, *Phys. Rev.* **89**, 760 (1953).

⁴ H. Casson, *Phys. Rev.* **89**, 809 (1953).