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Luminescence of *F* Centers in Alkali Halides under Hydrostatic Pressure*

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F-center luminescence spectra have been measured at 78°K in NaCl, KCl, KBr, KI, RbCl, and CsBr under hydrostatic pressure to 3.5 kbar. From a comparison between the shift of the emission peak with pressure and the shift with temperature, it is concluded that most of the latter arises from the electron-lattice interaction and not from thermal expansion. This is the opposite of the conclusion for *F*-center absorption, for which thermal expansion dominates the temperature coefficient of the peak energy. The halfwidth of the function $W(E)$, the probability per unit time of emitting a photon with energy between E and $E+dE$, does not vary with pressure in NaCl, KCl, and RbCl, but the half-width of the "shape function," $E^{-3}W(E)$, changes with pressure. This is interpreted as meaning that for *F*-center emission, it is more suitable to make the Condon approximation on the momentum operator than on the position operator. Lifetime measurements in KCl under pressure at 15 and 78°K give the pressure derivative of the thermal ionozation energy of the relaxed excited state of the *F* center in KCl, $+19\times10^{-6}$ eV bar^{-1}. The pressure coefficients of a few *K*- and *L*-band peaks have been determined. These provide additional evidence that the final states in the *L*-band transitions are not similar to those for *F*- and *K*-band transitions. The *K* band in RbCl changes shape with pressure. The F_A-band splitting has been found to increase with pressure in KCl:Na. The *F*-center emission in KBr under pressure has been found to have two components, and the excitation spectrum has two peaks, the *F* band and a peak very close to the K' band previously found in absorption at much higher pressures. Emission data at 12°K on diverse samples of additively colored KBr strongly suggest that there are two components to the normal *F*-center luminescence in KBr with no applied pressure.

INTRODUCTION

THE *F* center in alkali halides has been the subject of intensive study for several decades. The model for this center, an electron trapped at a halogen vacancy, is widely accepted, and electron wave functions for the ground and first excited state have been calculated many times from several viewpoints. It is known that the *F*-center electron interacts strongly with the vibrating lattice, but a detailed theoretical picture of this interaction is not yet at hand. In his recent book, Markham[1] has listed a number of experimental manifestations of the electron-lattice interaction. Those of concern to us here are the broadening of the absorption and emission bands with increasing temperature, and especially the shifts of the absorption and emission band peaks to lower energy with increasing temperature. A theory of the electron-lattice interaction for *F* centers ultimately should yield these quantities.

As the temperature of the crystal increases, the lattice vibrations increase in amplitude and the crystal expands. The expansion of the crystal will shift the energy levels of the *F*-center electron through changes in the static potential, and it will change lattice vibrational frequencies. The effects of thermal expansion should be separated from those of the vibrating lattice when comparing observed temperature effects with theory. The application of hydrostatic pressure enables one to duplicate the effects of thermal expansion without measurably altering, in our problem, the amplitudes of the lattice vibrations. Thus one can determine separately, from measurements at several temperatures and pressures, the effects of lattice vibrations and crystal volume on various *F*-center parameters.

Jacobs[2] was the first to study the *F*-center absorption in alkali halides under pressure. Subsequent work by Drickamer and co-workers[3,4] at much higher pressures is summarized in a review by Drickamer.[5] Fitchen[6,7] more recently studied the production, by ionizing radiation, of *F* centers in crystals under pressure. In the course of that work, he repeated the measurements of Jacobs at several lower temperatures. We have repeated the work of Jacobs and have made measurements of the peak position, half-width, excitation spectrum, and lifetime of *F*-center luminescence under pressure. We also have examined the *K* and *L* bands under hydrostatic pressure. Our pressures in all cases are far lower than those of Drickamer and co-workers, and give rise to changes in the lattice parameter of less than 2%.

EXPERIMENTAL

Crystals from various sources (Harshaw, Korth, and Optovac) were additively colored, usually by the method of Van Doorn.[8] Just prior to use they were quenched under safelight from about 1 min at the

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[1] J. J. Markham, *F-Centers in Alkali Halides* (Academic Press Inc., New York, 1966).

[2] I. S. Jacobs, Phys. Rev. **93**, 993 (1954).

[3] W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids **5**, 328 (1958).

[4] R. A. Eppler and H. G. Drickamer, J. Chem. Phys. **32**, 1418 (1960).

[5] H. G. Drickamer, Solid State Phys. **17**, 1 (1965).

[6] D. B. Fitchen, Ph.D. thesis, University of Illinois, Urbana, Illinois, 1962 (unpublished).

[7] D. B. Fitchen, Phys. Rev. **134**, A1599 (1964).

[8] C. Z. van Doorn, Rev. Sci. Instr. **32**, 755 (1961).

temperature of coloration and kept in the dark until measurements were made at liquid-nitrogen temperature. M bands were always very small, if detectable.

The high-pressure cell was similar to that of Fitchen[9] but was made of Almar 300 steel and had two sapphire windows 9.5 mm diam by 9.5 mm in length. The aperture in the plug was 4.8 mm in diam and the drive nuts had conical holes of 16° included angle, reducing the aperture of the luminescence apparatus from that normally employed. The pressure fluid was helium. Pressures to 6 kbar were occasionally used, but typical runs spanned the range from 1 to 3.5 kbar. The pressure was measured on a 75 000 psi Astra bourdon gauge (accuracy of $\pm\frac{1}{4}\%$) or a manganin resistance wire calibrated with the bourdon gauge and extrapolated linearly to 100 000 psi. In a typical run at liquid-nitrogen temperature the pressure was cycled. Limited data were taken at liquid-helium temperature because the helium pressure fluid froze, and the temperature of the cell and cryostat had to be raised to about 30°–40°K before the pressure could be changed, necessitating recooling to liquid-helium temperature for each pressure change. At liquid-nitrogen temperature the pressure was truly hydrostatic. At liquid-helium temperature the pressure was nearly hydrostatic because of the large compressibility of solid helium.

Absorption measurements were made on a Cary 14R spectrophotometer. Emission was excited by a 1 kW mercury arc or a 150 W xenon arc through Jena OG-1 and KG-3 filters and an aqueous solution of Cu_2SO_4. The exciting light transmitted by the crystal was filtered out by two Jena UG-8 or RG-10 filters at the monochromator entrance slit. (With this pressure cell, the exciting light was directed toward the analyzing monochromator.) The monochromator was a Bausch and Lomb 250-mm focal length grating monochromator. A cooled PbS cell and synchronous amplifier were used. The response of the detection system was calibrated by replacing the luminescent crystal by an uncolored crystal and focusing a tungsten filament at a known temperature on this crystal.[10] The data were then corrected to give ordinates proportional to photons emitted per unit energy interval.

Lifetimes were measured using a lamp designed by Swank[11] to excite the F centers through OG-1 and KG-3 filters. An Amperex 150-CVP photomultiplier viewed the emission through a UG-8 or RG-10 filter. The luminescent decays were measured from a photograph of the oscilloscope trace. The flashlamp characteristic decay time as measured by our system was 0.05 μsec. This probably indicates the characteristic response time of our system, and it is adequately short for this work.

The rms scatter in the points on a plot of peak energy versus pressure was only a few percent about a straight line through the data. Sample-to-sample variations of 5 to 10% occurred, however, and this is the best estimate of the errors. The half-widths could be measured to within a few percent and they, too, showed very little scatter for a given sample. Errors in the shifts of the K and L bands are much larger and hard to estimate, for they arise from shifts in the baseline due to overlapping bands. We assume our results for these bands are good to within 30%, which is sufficient accuracy for our purposes. In all measurements, errors arising from temperature drift of the sample are negligible.

METHOD OF DATA PRESENTATION

A plot of peak absorption or emission energy versus pressure yields a straight line in the pressure range we use. Its slope, $(\partial E/\partial P)_T$, can be converted to $(\partial \ln E/\partial \ln a)_T$, where a is the lattice parameter, using the bulk compressibility. At pressures exceeding 5 kbar, a plot of E versus P for the F-band absorption peak begins to curve.[3,4] If the pressure-dependent compressibility is used, a plot of $\ln E$ versus $\ln a$ is straight over a larger range of pressure than is one of E versus P, but even it exhibits curvature above about 10 kbar.[3,4] The values of $(\partial E/\partial P)_T$ vary by more than a factor of two between F-band absorption in LiF and in KI while those of $(\partial \ln E/\partial \ln a)_T$ vary by less than 50%. Both $(\partial E/\partial P)_T$ and $(\partial \ln E/\partial \ln a)_T$ are independent of temperature to within about 5%, provided in $(\partial \ln E/\ln a)_T$ one uses the temperature-dependent peak energy and compressibility.[12]

Similar considerations obtain for F-center emission, although the temperature dependence of the pressure and volume derivatives is hard to test in the limited temperature range available. For the purposes at hand, a choice between $(\partial E/\partial P)_T$ and $(\partial \ln E/\partial \ln a)$ is not important.[13,14] We have chosen to display the former

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[9] D. B. Fitchen, Rev. Sci. Instr. **34**, 673 (1963).

[10] There is an error in this calibration technique which is unavoidable and difficult to estimate. It arises from the nonuniformity of the light beam. The light from the crystal and from the tungsten filament is distributed differently across the grating and across the PbS cell. Moreover, each beam may be slightly polarized in a different fashion. All of these lead to different spectral-dependent efficiencies of the monochromator and detector for the two sources. Masking different parts of the grating while using the tungsten filament gave correction curves that agreed to within 1% except in small wavelength regions where 5–8% differences were found. To reduce such errors, our tungsten filament was imaged on an uncolored crystal in such a fashion as to fill the area of the crystal, instead of being imaged directly on the entrance slit. We believe that discrepancies in F-center emission band shape parameters reported by different investigators arise from such errors in calibration.

[11] R. K. Swank, Ph.D. thesis, University of Illinois, Urbana, Illinois, 1962 (unpublished).

[12] D. B. Fitchen, (private communication).

[13] In studies of the optical and electrical properties of semiconductors, it has been found that the pressure derivatives of band gaps, $(\partial E/\partial P)_T$, exhibit values characteristic of the symmetries of the band edge wave functions, but independent of the nature of the atoms, for semiconductors with the diamond and zinc blende structures (Ref. 14). There is little correlation of $(\partial E/\partial V)_T$ or $(\partial \ln E/\partial \ln a)_T$ with the symmetries of the band edges.

[14] W. Paul, J. Appl. Phys. Suppl. **32**, 2082 (1961).

in most cases. For our pressure range there is negligible pressure dependence in the compressibility.

The luminescence data can be described in two ways, both existing in the literature [15–17]: as $W(E)$, the probability per unit time of emitting a photon with energy between E and $E+dE$; and as $S(E)$, a shape function defined as $E^{-3}W(E)$. We point out below that an alternate definition of $S(E)$ in terms of $W(E)$ is probably better for describing F-center emission. In the derivation[18–20] of the expressions for the absorption coefficient and spontaneous emission probability there appears the square of the matrix element of the electron momentum operator between initial and final states, $\mathbf{p}_{if}$. The states here include the lattice states, and the electronic wave function has lattice coordinates as parameters. If states i and f are eigenstates, then,

$$\mathbf{p}_{if}=im\omega_{if}\mathbf{r}_{if}, \tag{1}$$

where $\hbar\omega_{if}$ is the energy difference between the two states and $\mathbf{r}_{if}$ is the matrix element of the electron position vector. The matrix element $\mathbf{r}_{if}$ or $\mathbf{p}_{if}$ is factored into an electronic part and a lattice "overlap integral." The former, a function of the lattice coordinates, usually is assumed independent of the lattice coordinates, or else an average value is used. In either case it is replaced by a constant. This is the Condon approximation. In most derivations $\mathbf{r}_{if}$ is the matrix element on which the Condon approximation is invoked. The following results then obtain for the absorption coefficient at energy E, $\mu(E)$, and the spontaneous emission rate per unit energy interval, $W(E)$[19]:

$$\mu(E)=\left(\frac{\mathcal{E}_{\text{eff}}}{\mathcal{E}_0}\right)^2\frac{4\pi^2e^2N}{3nch}|\langle\mathbf{r}_{if}\rangle_{\text{av}}|^2ES(E) \tag{2}$$

$$W(E)=\left(\frac{\mathcal{E}_{\text{eff}}}{\mathcal{E}_0}\right)^2\frac{4e^2n}{3\hbar^4c^3}|\langle\mathbf{r}_{if}\rangle_{\text{av}}|^2E^3S'(E), \tag{3}$$

where S and S' are shape functions, and are integrals of products of lattice wave functions. The first factor in (2) and (3) is a local field correction. n is the refractive index. N is the density of centers. An average matrix element is used. If, instead, one makes the Condon approximation on $\mathbf{p}_{if}$, the energy dependence becomes

$$\mu(E)=\left(\frac{\mathcal{E}_{\text{eff}}}{\mathcal{E}_0}\right)^2\frac{4\pi^2e^2\hbar N}{3ncm^2}|\langle\mathbf{p}_{if}\rangle_{\text{av}}|^2E^{-1}S(E) \tag{4}$$

$$W(E)=\left(\frac{\mathcal{E}_{\text{eff}}}{\mathcal{E}_0}\right)\frac{4e^2n}{3\hbar^2m^2c^3}|\langle\mathbf{p}_{if}\rangle_{\text{av}}|^2ES'(E), \tag{5}$$

TABLE I. F-band absorption peak pressure shifts in 10^{-6} eV/bar.

	This work	Ref. 2	Refs. 6, 7, 12	Ref. 21
LiF	7.7		8.7	
NaF	8.1		8.7	
NaCl	16.4	16.7	14.9	
KCl	13.2	14.4	12.7	
KBr	16.2	13.6	15.5	
KI	18.6	17.6		
RbCl	12.2	13.7		15.3
RbBr	16.0			18.3
CsCl		10.8	9.8[a]	
CsBr	14.4		~10	

[a] Low-energy component.

where S and S' are the same as in Eqs. (2) and (3). Now in studies of the electron-lattice interaction the problem is to calculate $S(E)$ and $S'(E)$. The differences between $S(E)$, $ES(E)$ and $E^{-1}S(E)$ are not very great and, as others do, we report our results as $\mu(E)$. The parameters associated with curves fitted to $W(E)$ and to $E^{-1}W(E)$ are similar, but Gebhardt and Kühnert[16,17] have shown that the difference in the shapes of $W(E)$ and $S'(E)=E^{-3}W(E)$ is significant. If one studies the temperature dependence of the halfwidths of $W(E)$ and $S'(E)$, one gets quite different parameters. We have plotted our emission data as $W(E)$ and as $S'(E)=E^{-3}W(E)$. We find the former curves have half-widths that are independent of pressure while the half-widths of the latter change with pressure at a rate of about one-sixth the pressure shift of the emission peak. The signs of these changes are not the same in all alkali halides. Thus a simpler description of emission spectra is given by $W(E)$ compared to $E^{-3}W(E)$. This can mean that if the Condon approximation is valid for F-center emission, it is for the momentum matrix element, and the better shape function to use is $E^{-1}W(E)$ instead of $E^{-3}W(E)$. All of our results here are reported as $W(E)$, which is similar to $E^{-1}W(E)$.

RESULTS

1. F-Band Absorption

Table I shows our values of $(\partial E/\partial P)_T$ obtained at 78°K along with those of Jacobs[2] at 300°K, of Fitchen[6,12] (several temperatures), and of Knof and Maisch[21] at 300°K. The agreement of our values with those of Fitchen is satisfactory. We observe, as did Jacobs, that the half-width of the F band does not change with pressure to within 5%.

We have chosen to analyze our results in a way that is different from that of Jacobs, but our conclusions will be qualitatively the same as his. We write

$$\left(\frac{\partial E}{\partial T}\right)_P=\left(\frac{\partial E}{\partial T}\right)_V-\frac{3\alpha}{K}\left(\frac{\partial E}{\partial P}\right)_T. \tag{6}$$

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[15] F. Lüty and W. Gebhardt, Z. Physik **169**, 475 (1962).

[16] W. Gebhardt and H. Kühnert, Phys. Letters **11**, 15 (1964).

[17] W. Gebhardt and H. Kühnert, Phys. Status Solidi **14**, 157 (1966).

[18] J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).

[19] D. L. Dexter, Solid State Phys. **6**, 355 (1958).

[20] M. H. L. Pryce, in *Phonons in Perfect Lattices and in Lattices with Imperfections*, edited by R. W. H. Stevenson, (Oliver & Boyd, Edinburgh, 1966) p. 403.

[21] H. Knof and W. G. Maisch, J. Phys. Chem. Solids **24**, 1625 (1963).

$(\partial E/\partial T)_P$ and $(\partial E/\partial P)_T$ are the observed temperature and pressure coefficients of the absorption peak. α is the linear thermal expansion coefficient and K is the isothermal compressibility. (3α is the isobaric volume thermal expansion coefficient.) Thus the observed temperature coefficient, $(\partial E/\partial T)_P$, is written as a sum of two terms. One, $(\partial E/\partial T)_V$, is volume independent and represents the electron-lattice contribution to $(\partial E/\partial T)_P$ while the last term in Eq. (6) represents the part of $(\partial E/\partial T)_P$ due to thermal expansion. Thermal expansion has two effects. The static potential seen by the electron changes with lattice parameter, and the lattice vibrational frequencies change. The latter effect is negligible for F-center absorption, for an appreciable change with volume of the frequencies of the important vibrational modes would cause the absorption band width to vary with pressure, and it would cause $(\partial E/\partial P)_T$ to vary with temperature, neither of which is observed.

Equation (6) is appropriate for energy levels and differences between energy levels in a perfect crystal. Its use for energy levels at defects may be questioned, for K and α are not defined in such cases. We use bulk values of α/K with the view that only the interionic spacing of the perfect crystal has any significance, there being a variety of interionic spacings for ions at various distances from the vacancy. This assumption seems reasonable in view of the fact that there is a fairly good correlation of the F-band peak energy with the bulk lattice parameter, the Mollwo-Ivey rule.[1] (Jacobs discussed "local" values of α and K but used bulk values of α/K in his analysis.[2]) We use bulk values of α/K for both emission and absorption, with better justification for the former. There is lattice relaxation between emission and absorption,[22,23] which produces a more diffuse F-center electron prior to emission. The electron then samples more of the lattice and less of the vacancy.

All of the parameters in (6) except $(\partial E/\partial P)_T$ vary with temperature. α and $(\partial E/\partial T)_V$ both go to zero at 0°K. We have chosen to evaluate (6) at room temperature where all the parameters are known. Experimental data of E versus T are accurately fitted[24] by an expression $E_0 - B\coth(T_0/T)$,[25,26] and the parameters have been evaluated for many alkali halides by Gebhardt and Kühnert.[16] We obtain $(\partial E/\partial T)_P$ by evaluating the derivative of $-B\coth(T_0/T)$ at 300°K. Table II shows the three terms in Eq. (6) for F-center absorption.[27-35]

TABLE II. Components of F-absorption band peak temperature derivatives.

	$\left(\frac{\partial E}{\partial T}\right)_P$ [a] $(10^{-4}$ eV/°K)	$\frac{3\alpha}{K}\left(\frac{\partial E}{\partial P}\right)_T$ [b] $(10^{-4}$ eV/°K)	$\left(\frac{\partial E}{\partial T}\right)_V$ $(10^{-4}$ eV/°K)
LiF	-6.0	$+5.0$	-1
NaF	-4.4	$+4.1$	-0.3
NaCl	-4.3	$+5.2$	$+0.9$
KCl	-3.7	$+2.5$	-1.2
KBr	-3.5	$+3.1$	-0.4
KI	-3.7	$+2.7$[c]	-1.0
RbCl	-2.8	$+1.9$[d]	-0.9
CsCl	~ -3.9	$+2.4$[e]	-1.5
CsBr	~ -3.4	$+3.0$[f]	-0.4

[a] All coefficients are evaluated at 300°K except those with ∼, which are estimates based on the shift of the peak between 78 and 300°K. Their magnitudes may be underestimated.
[b] Unless noted, K data are isothermal values computed in Ref. 27 from the adiabatic elastic constants of Ref. 28. α data are from Ref. 29.
[c] Reference 30.
[d] Reference 31.
[e] References 32 and 33.
[f] References 34 and 35.

It is easy to see that thermal expansion gives rise to most of the shift of the absorption peak with temperature. This was Jacobs's conclusion also.[2] From Table II one can see that about 65–90% of $(\partial E/\partial T)_P$ arises from thermal expansion while Jacobs concluded that this figure should be about 95%. An estimate of the uncertainty in $(\partial E/\partial T)_V$ is about ±0.3 of the units used in Table II. However, we suspect that $(\partial E/\partial T)_V$ should be negative in most cases, and the positive value found for NaCl may be a better indication of the errors encountered.

The fitting of E versus T to a hyperbolic cotangent has theoretical basis if one assumes that E varies with T because of the electron-phonon interaction.[18] We have just seen that thermal expansion produces the larger contribution to $(\partial E/\partial T)_V$. Konitzer and Markham[25] have produced a good fit of E versus T for the F-band peak in KCl with the function $E_0 - \mathrm{B}\coth(71°\mathrm{K}/T)$, where 71°K is the characteristic temperature T_0 obtained by fitting the half-width versus T to the function $[\coth(T_0/T)]^{1/2}$. Gebhardt and Kühnert[16] have done the same for other alkali halides. If thermal expansion dominates $E(T)$, as good a fit should be obtained by fitting to $E_0 - D'[a(T) - a(0)]$ where a is the lattice parameter and D' is a constant. Rather than use detailed data on the thermal expansion coefficient $\alpha(T)$, we have made use of the Grüneisen relation for α,

$$\alpha(T) = \gamma K(T) C_v(T) / 3V(T), \qquad (7)$$

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[22] W. B. Fowler, Phys. Rev. **135**, A1725 (1964).

[23] R. F. Wood and H. W. Joy, Phys. Rev. **136**, A451 (1964).

[24] We believe there is no theoretical justification for fitting the position of the absorption peak to this function because thermal expansion dominates $(\partial E/\partial T)_P$, but because the fit is so good, we do so to obtain values of $(\partial E/\partial T)_P$.

[25] J. D. Konitzer and J. J. Markham, J. Chem. Phys. **32**, 843 (1960).

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[27] M. P. Tosi, Solid State Phys. **16**, 1 (1964).

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[31] F. A. Henglein, Z. Elektrochem. **31**, 424 (1925).

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[33] J. W. Menary, A. R. Ubbelohde and I. Woodward, Proc. Roy. Soc. (London) **A280**, 158 (1951).

[34] B. J. Marshall, Phys. Rev. **121**, 72 (1961).

[35] R. S. Krishnan, Proc. Phys. Soc. (London) **69B** 679 (1956).

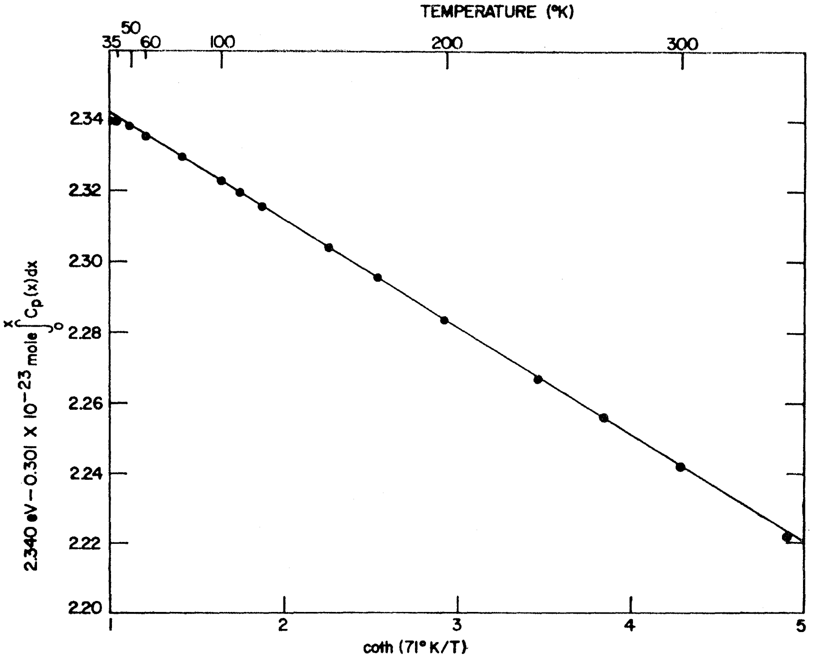

Fig. 1. A plot of 2.340 eV -0.301×10^{-23} mole $\int_0^x C_p(x)dx$ versus coth $(71°\text{K}/T)$. $x=T/230°\text{K}$. The ordinate is the position of the peak of the F band in KCl as a function of temperature if thermal expansion causes the shift in peak position ($230°\text{K}=\theta_D$). The abscissa is proportional to the peak position of the F band if the interaction with one lattice mode with a characteristic temperature of 71°K causes the shift. With the precision to which the peak position can be measured, the points fall on a straight line and either function, or a linear combination of both, will describe the peak position.

where the Grüneisen constant γ, the compressibility K, and the volume V have temperature variations that are small compared to that of the specific heat C_v. Hence, we expect E to vary as

$$E_0-D\int_0^T C_v(T)dT\,,$$

i.e., to depend on the Debye heat content of the crystal.

We have evaluated this expression using a Debye specific heat with $\Theta_D=230°\text{K}$ (KCl) for comparison with the hyperbolic cotangent. The result is shown in Fig. 1. There is a good straight line fit except at temperatures below about 30°K where E is essentially temperature-independent. Similar results are obtained for KBr, KI, RbCl, and NaCl.

The successful fitting of E versus T with a coth plot does not prove that the temperature shift of the peak

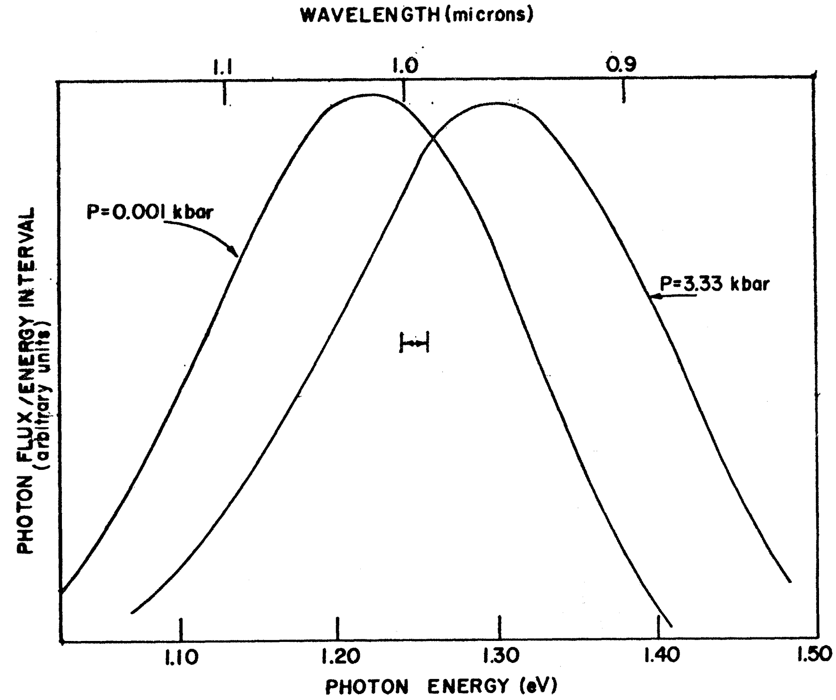

Fig. 2. F-center emission probability $W(E)$ in KCl at 80°K at pressures of 0.001 kbar and 3.33 kbar. The spectral band pass is indicated by the arrows.

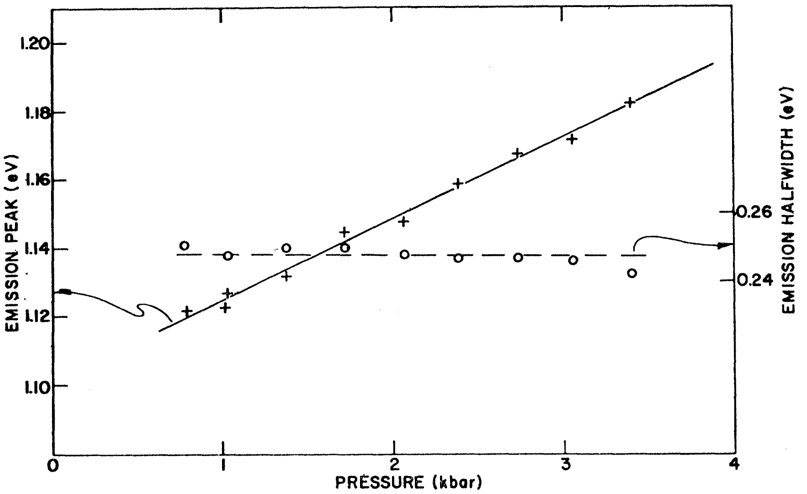

FIG. 3. Position of the peak of the emission probability $W(E)$, and its half-width versus pressure for F centers in in RbCl at 80°K.

energy arises from the electron-lattice interaction. Equally good success is achieved with a plot against a Debye heat content curve indicating the shift in E due to thermal expansion. Our (and Jacobs's) interpretation of the pressure data indicates that the latter is the better approximation. We should mention here that the above relation between the position of the absorption peak and the Debye heat content arises from thermal expansion, not from the electron-lattice interaction as for some electronic transitions at impurities, e.g., Cr^{3+} in MgO.[36]

2. *F*-Center Emission

Figure 2 shows the F-emission band, $W(E)$, of KCl versus pressure. The peak heights and integrated areas seem to change with pressure, but this arises from the pressure shift of the absorption band, producing more or less efficient excitation with the fixed spectrum of exciting radiation. Figure 3 shows the peak position and half-width of the emission band of RbCl versus pressure. The half-width of $W(E)$ is independent of pressure for RbCl, KCl, NaCl, and CsBr. We assume this is the normal behavior for F-center emission. The emission half-widths in KBr and KI broaden with pressure. This behavior is considered anomalous and will be discussed later. The shape function $E^{-3}W(E)$ has a peak shift with pressure that is about 20% greater than that for $W(E)$ for all salts examined. The half-width of $E^{-3}W(E)$ changes with pressure, increasing in some alkali halides and decreasing in others at a rate of about one-sixth $(\partial E/\partial P)_T$.

TABLE III. F-emission band peak pressure shifts in 10^{-6} eV/bar.

NaCl	9.8
KCl	19.8
KBr	splits[a]
KI	20.4[b]
RbCl	22.2
CsBr	24.3

[a] Main component ~25, new high-energy component ~17.
[b] Unresolved splitting suspected.

Table III lists the values of $(\partial E/\partial P)_T$ found for F-center emission, usually at 78°K. Note that they are larger than the corresponding values for F-center absorption by from 10 to 80%, except for NaCl. They also have the same signs as $(\partial E/\partial P)_T$ in absorption, in disagreement with the prediction of Alers and Dolecek[37] based on a single configuration-coordinate model. Table IV lists the terms in Eq. (6). $(\partial E/\partial T)_P$ was evaluated in the same manner as for absorption.[38] In emission $(\partial E/\partial T)_P$ is larger than in absorption by factors of from 3 to 5. The pressure shift increase is less than a factor of two. As a result, the electron-lattice interaction is the larger contributor to $(\partial E/\partial T)_P$, giving from 63 to 82% of the total. This is just the opposite of the absorption case.

TABLE IV. Components of F-emission band peak temperature derivatives.

	$\left(\frac{\partial E}{\partial T}\right)_P$ (10^{-4} eV/°K)	$\frac{3\alpha}{Tc}\left(\frac{\partial E}{\partial P}\right)_T$[a] ($10^{-4}$ eV/°K)	$\left(\frac{\partial E}{\partial T}\right)_V$ (10^{-4} eV/°K)
NaCl	−17.1	3.1	−14.0
KCl	−18.4	3.7	−14.7
KBr	−12.9	4.8[b]	−8.1
KI	−10.8	2.8[c]	−8.0
RbCl	−11.0	3.4	−7.6
CsBr	d	5.0	

[a] K and α data are from sources listed in Table II.
[b] Main component.
[c] Unresolved splitting suspected.
[d] See Sec. 5.

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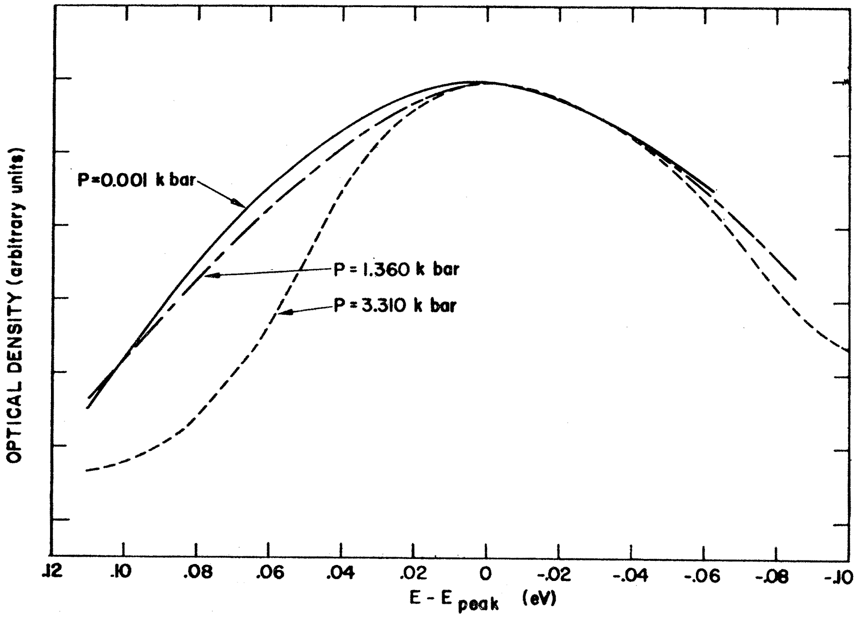

FIG. 4. Shape of the K absorption band in RbCl at 80°K at several pressures. These curves have been shifted horizontally and vertically to make their peaks coincide, emphasizing the shape changes. The peaks actually shift to higher energy with increasing pressure.

We do not have a large enough temperature range available to determine whether $(\partial E/\partial P)_T$ for emission is temperature-independent. However, since $W(E)$ is pressure-independent, the frequencies of the lattice modes important for F-center emission do not vary much with pressure. Using the pressure shift of the long wavelength longitudinal optical mode in NaF,[39] we estimate the half-width of $W(E)$ would decrease by about 0.1 to 0.2% as the pressure increases to 5 kbar. This is too small to measure directly.

3. K- and L-Band Absorption

The K band is a shoulder on the high-energy side of the F band, well-resolved at low temperatures in RbCl and KBr. A recent interpretation[40,41] attributes the K band to transitions of the F-center electron to excited states higher than the first excited state, including continuum (conduction band) states. In densely colored crystals three or four bands, the L bands, are observed at even higher energies[42] and in KCl these have been shown to originate from the F-center ground state,[43–46] with the final states not known.

TABLE V. F-, K-, and L-band peak pressure shifts in 10^{-6} eV/bar.

	F	K	L_1	L_2	L_3
KCl	13.2	10	-2 to $+2$	11.4	
KBr	16.2		2		4
RbCl	12.2	13[a]	-4 to -6	0 to 3	6
CsBr	14.4		-1 to $+1$		4

[a] Shape changes. See Fig. 4.

The pressure shifts of these bands are difficult to obtain reliably because of their poor resolution and the pressure shift of the underlying background. Those we have been able to obtain are shown in Table V. The K band not only shifts but changes shape as shown in Fig. 4. The various curves in Fig. 4 have been shifted to have a common peak to emphasize the shape changes. The peak actually shifts according to Table V. The peak heights change as well, but we cannot tell whether this is a genuine change of the K-band peak absorption coefficient or a result of the shifting F-band shoulder which lies underneath.

Any potential well model (see later) predicts positive values of $(\partial E/\partial P)_T$ provided the well depth increases with pressure no faster than the square of the well radius decreases. In these models the zero of energy, assumed independent of pressure, is the bottom of the conduction band. On this basis the wide variation of the values of $(\partial E/\partial P)_T$ for the L bands indicates that the final states for these transitions do not lie in the potential well. This is not in accord with the suggestion of Hall[47] that these transitions are $1s$-$2pF$ center transitions with the emission of several phonons, for in that event the values of $(\partial E/\partial P)_T$ would be nearly alike for F and L bands in any one crystal. If the final states for the L-band transitions are localized resonant states

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within the conduction band[48] or are states associated with conduction-band minima other than the lowest,[46,49] then the values of $(\partial E/\partial P)_T$ of those regions of the band structure with respect to the lowest conduction-band minimum must be added to any shifts computed for levels within a well. This is indicated schematically in Fig. 5. Since it is known that some regions of the conduction band in zinc blende-structured semiconductors shift toward and some shift away from the valence band maximum upon application of pressure,[14] it is possible to conceive of negative values of $(\partial E/\partial P)_T$ for L bands arising in this fashion. We shall defer a discussion of the K band shape changes till later in this paper.

Wood[50] has calculated a number of energy levels for the F center in LiCl which could account for the L bands. All of these are below the conduction band minimum but may ionize upon lattice relaxation. It remains to be seen whether the effects of ion cores could give $(\partial E/\partial P)_T<0$ for some transitions.

4. *F*-Center Lifetimes

The lifetime τ for luminescence of the excited F center is given by[51]

$$\tau^{-1}=\tau_R^{-1}+\nu_0\exp(-\Delta E/kT). \tag{8}$$

τ_R is the radiative lifetime, and the second term is the rate of thermal ionization of the excited F center. ΔE is the thermal ionization energy of the relaxed excited F center and ν_0 is a constant. At sufficiently low temperatures, $\tau=\tau_R$ and

$$\tau^{-1}=\tau_R^{-1}=\int_0^\infty W(E)dE, \tag{9}$$

the integrated area under a luminescence spectrum as in Fig. 2 but at a lower temperature. We do not know $W(E)$ because of the unknown and pressure-dependent efficiency of the excitation and collection of emitted photons.

For KCl at 15°K $(\partial\ln\tau/\partial P)$ was found to be $(-31\pm4)\times10^{-6}$ bar^{-1} (see Fig. 6.). The errors in τ and its pressure derivatives are statistical.

Knowing $(\partial\ln\tau_R/\partial P)_T$ as the measured value of $(\partial\ln\tau/\partial P)_T$ at low temperature, we can measure $(\partial\ln\tau/\partial P)_T$ at liquid-nitrogen temperature to get $(\partial\Delta E/\partial P)_T$. This involves taking the derivative of (8) with respect to pressure and neglecting $(\partial\nu_0/\partial P)_T$. The values of τ_R, ν_0, and ΔE must be known, and these were obtained from Brown and Swank.[51] Our value of τ_R was 0.77 μsec, in good agreement with theirs. For KCl we find $(\partial\ln\tau/\partial P)_T=(-11\pm1)\times10^{-6}$ bar^{-1} at 80°K which leads to $(\partial\Delta E/\partial P)_T=+19\times10^{-6}$ eV/bar. (The error in the latter quantity is large, at least 20% from our measurements and unknown amounts from errors in ν_0 and ΔE.) The positive sign means that the relaxed excited state drops further below the conduction band, taken to be the zero of energy, as the crystal volume is decreased. One cannot use this value and the pressure shift of the emission peak to get the pressure shift of the electronic state just after emission, for ΔE is a thermal excitation energy, and the emission peak is an optical transition energy.

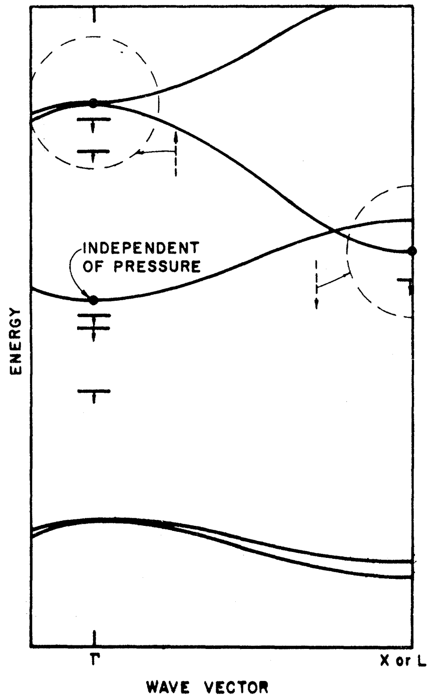

FIG. 5. Schematic indication of possible pressure shifts of localized states at anion vacancies in an alkali halide. Three conduction-band minima are indicated by heavy dots. Localized levels caused by the vacancy potential are indicated by short lines. Upon applying pressure these levels shift with respect to the nearest band edge by amounts shown by solid arrows. These shifts arise from changes in the potential of the vacancy upon compression. Upon applying pressure, the band edges shift with respect to each other. We take one edge fixed as indicated. These shifting edges carry the localized levels with them according to the dotted arrows. With respect to the lowest conduction-band edge, any one localized level shifts by the sum of its solid and dotted arrows.

5. Anomalous Emission Spectra

Figure 7 shows the luminescence spectrum of KBr at 78°K as a function of pressure. The band seems to split, with the new high-energy component growing stronger as the pressure increases. The splitting is not resolved much better at 15°K (Fig. 8). In KI we cannot resolve two bands, but the width of the emission spectrum increases with pressure. The two bands in KBr overlap so severely that we could not run separate excitation curves for each band. Figure 9 shows a

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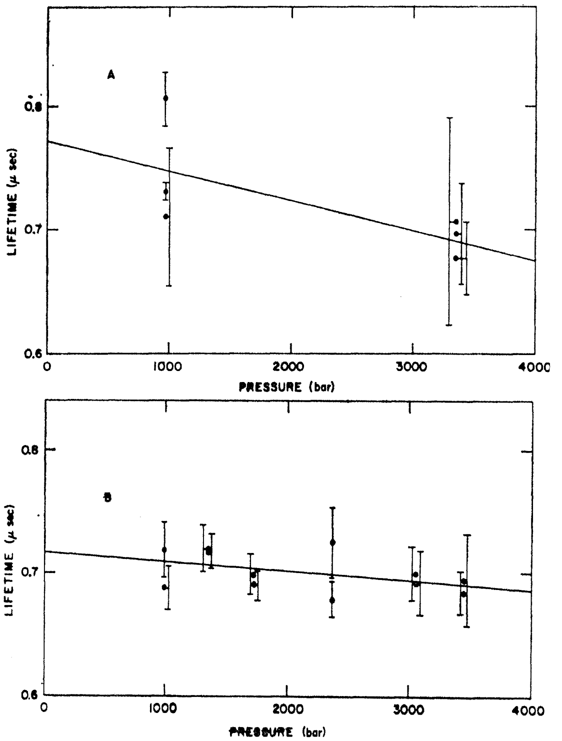

FIG. 6. *F* center lifetime in KCl versus pressure. A: 15°K, B: 80°K The errors indicated are the standard deviations of the data, read from an oscilloscope photograph, about an exponential decay with the indicated time constant.

normal excitation curve (RbCl) under high pressure and the excitation curve for KBr. It is clear that there is a second excitation peak on the high-energy side of the *F*-band peak in KBr. This peak is too low in energy to be the *K*-band peak, and it may be too low in energy to be the "1*s*-3*p*" transition of the *F* center.[40] This excitation peak lies very close to the *K′*-band peak observed by Maisch and Drickamer.[3] We examined the *F*-absorption band of KBr under pressure at 78°K and found no evidence of any new absorption in this region to pressures of 4 kbar. Attempts to measure excitation curves for KI under pressure were unsuccessful due to inadequate sensitivity.

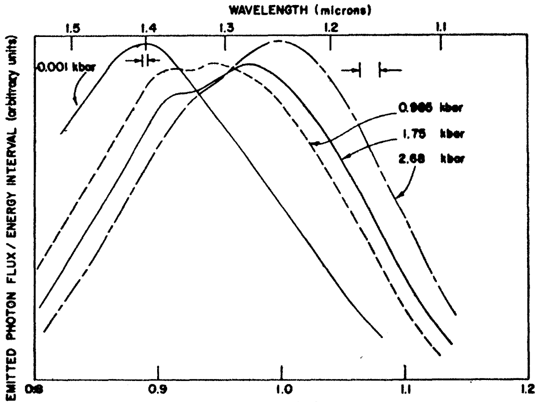

FIG. 7. *F*-center emission spectrum in KBr at 80°K at several pressures. The larger spectral bandpass (arrows) refers to all high-pressure measurements.

The *K′* band was observed by Maisch and Drickamer[3] to grow at the expense of the *F* band when the pressure reached about 8 kbar. Between 8 and 12 kbar the relative oscillator strengths, $f_F/f_{K'}$, went from 10/1 to $\frac{1}{10}$ although there were no anomalously large shifts in peak energies. Both bands were bleached by irradiation in either band at room temperature. The *K′* band was found in several alkali halides, but it appeared at lowest pressures (8 kbar) in KBr and next-lowest (17 kbar) in KI. (It was reported present at 1 atm in CsCl and CsBr, but it is not clear that it is the same band.)[52,53] It seemed to correlate with the proximity of an fcc-sc phase transition, but a *K′* band is not found in RbCl[7,21] or RbBr[21] which undergo this transition at lower pressures than KBr or KI, nor in CsI[21] which is sc. Maisch and Drickamer[3] observed that the *K′* band may be associated with the propagation of shear strain in the crystal. However, we seem to observe the *K′* band by excitation of luminescence under smaller, purely hydrostatic pressures, ruling out shear strain as the source of this band. An alternative source does not present itself. The *K′* band has a pressure coefficient that is positive[3] (except in CsBr where it is zero), similar to that of the *F* and *K* bands and unlike those of the *L* bands. This indicates that the *K′*-band final state is probably in the *F*-center potential well. There are no data yet at 10–15 kbar at temperatures other than 300°K so one cannot say that the final state is *s*-like or *d*-like with *p* components mixed in by lattice vibrations.[50]

Figure 8 also shows the emission spectrum of *F* centers in KBr at 12°K and atmospheric pressure. Two types of monochromators, prism and grating, were used to disperse the emission although the same cooled PbS detector was used with each. The correction curves for the monochromator transmission and dispersion are dissimilar, but the small structure is nearly the same in both cases. Moreover, we observe no structure in emission bands of other alkali halides which fall in this region. The structure is probably the same as that seen when pressure is applied. There apparently are two unresolved emission peaks at 78°K and 1 atm which separate and change in relative area as the pressure is increased. This is not believed to be an impurity effect. Curves like those of Fig. 8 were obtained on Korth KBr colored by the van Doorn method and on zone-refined KBr colored with triply-distilled potassium in a Pyrex tube. [The change in relative heights of the two components at high pressure as the temperature is lowered from 78°K (Fig. 7) to 15°K (Fig. 8) may be spurious.]

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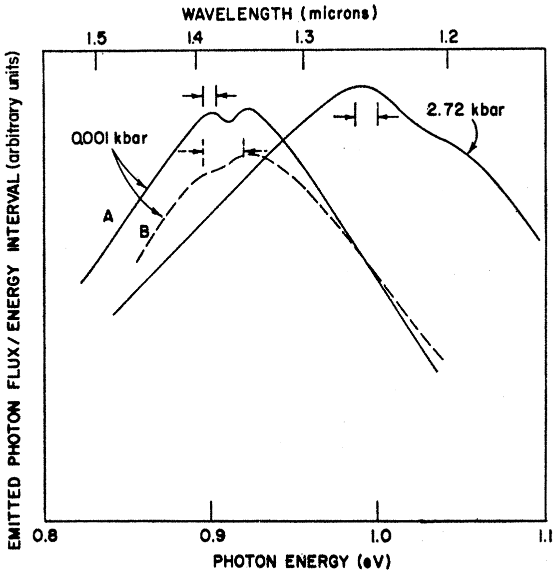

FIG. 8. *F*-center emission spectrum in KBr at 12°K at two pressures. The emission was measured using two different types of monochromator. Curve A was taken using a Bausch and Lomb 250-mm focal length grating monochromator. Curve B was found with a Perkin-Elmer 98-prism monochromator having a larger spectral bandpass indicated by arrows.

Lifetime measurements were made as a function of pressure to see whether there were two different decay times involved in KBr. At 78°K we found $\tau=0.97$ μsec, in good agreement with Brown and Swank.[51] As the pressure increased, the decay time shortened, as in KCl, but the data fitted a single exponential decay as well at high pressure as at low. $(\partial \ln\tau/\partial P)_T$ was -13×10^{-6} bar^{-1}. At 15°K considerable difficulty was encountered. In several cases we did not observe luminescence, and in others there was an increase in emission intensity after the exciting flash was over, followed by a decay which was not as good a fit to an exponential as was that at 78°K. This decay had a characteristic time of ~0.6 μsec, shorter than that at 78°K. Brown and Swank's data[51] yield an expected decay time of 1.1 μsec at low temperature, but they did not actually measure luminescent decay times at very low temperatures. The lifetime of *F* centers in KI could not be observed in our pressure cell because the excitation and emission were at too long wavelengths to give an adequate signal from the photomultiplier.

We must conclude that KBr and KI are in some sense anomalous. It appears that two excited states contribute to the emission and that one of these is populated by K'-band absorption (at least in KBr). Whether these are $3p$-like states or not is an open question. Our main purpose in displaying Fig. 8 is to encourage the repetition of this measurement in another laboratory to verify the structure. Another mystery is how the K' band can be seen so easily in the excitation spectrum (Fig. 9) when it is not resolved in absorption.

CsBr is anomalous as well although here we believe crystal purity plays a role. Although a band similar to the K' band is observed at 1 atm, the emission band is simple. An excitation curve taken at 15°K at 2 kbar was identical to one at 15°K with no pressure applied. No K' excitation peak appeared. The odd behavior is that $(\partial E/\partial T)_P$ for emission is roughly zero although there is an appreciable pressure shift. Taken at face value this means that $(\partial E/\partial T)_V$ is $+5\times10^{-4}$ eV/K°, instead of from -11 to -16×10^{-4} eV/K° for other alkali halides. However, in several crystals of CsBr we have found much smaller values of $(\partial E/\partial P)_T$ than the value reported in Table III, in one case about one-

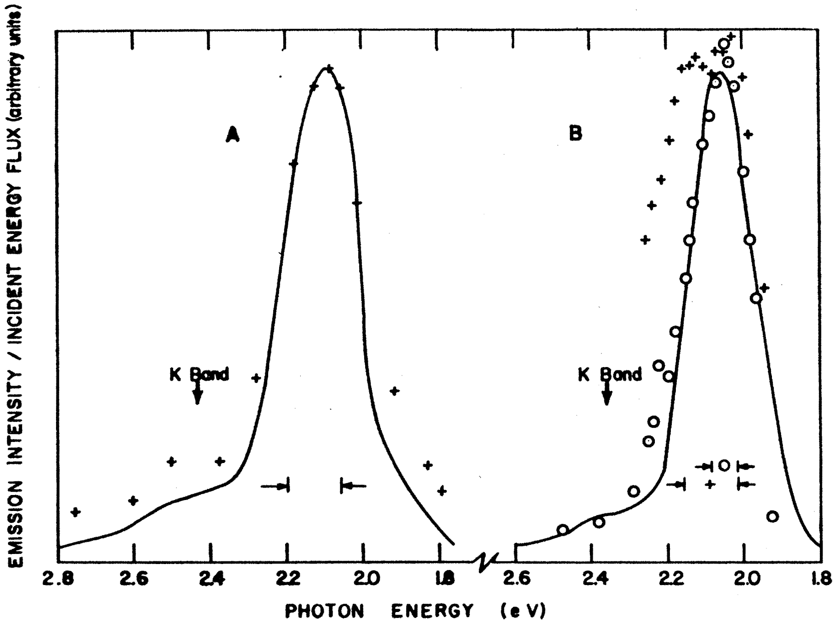

FIG. 9 Excitation spectra for *F* centers in RbCl at 80°K, 2.72 kbar (curve *A*), and in KBr at 80°K, 3.75 kbar (crosses) and at 12°K 0.001 kbar (circles) (B). The solid lines are absorption spectra at 80°K, normalized to match the excitation spectra. The indicated spectral bandpasses refer to the excitation spectra.

half the value reported and in another, less than one-tenth. In all of these crystals the emission peak energy and half-width were the same.

6. Microscopic Models

We report here the failure of simple microscopic models to account for the observed pressure shifts. Jacobs[2] obtained qualitative agreement between $(\partial \ln E/\partial \ln a)_T$ for the F band and that calculated for a simple square well of radius R and depth C/R. C was adjusted to give the proper energy for the $1s$-$2p$ transition, and R varied with pressure at about twice the rate that the lattice parameter varied, i.e., the F-center square well was about twice as compressible as the lattice. However, this model gives unreasonably high values for the K-band peak energy if it is assumed that the K band results from $1s$-np transitions with $n>2$. However, despite the high value of the $1s$-$3p$ transition energy, its pressure shift, under Jacobs's assumptions, is of the correct sign and order of magnitude.

Smith and Spinolo[40,41] have used a square well with a Coulomb tail to calculate the shape of the K band in RbCl, and Fowler[22] has used a similar model for F-center absorption and emission NaCl. The Coulomb tail is a potential $-e^2/(\epsilon_{\rm eff}r)$ where $\epsilon_{\rm eff}$ is an effective dielectric constant. If we use hydrogenic variational wave functions and vary only the well depth ($\propto R^{-1}$) and radius R by letting R vary twice as fast with pressure as a does, using Smith and Spinolo's values for RbCl, we find that the values of $(\partial E/\partial P)_T$ are reduced by a factor of 20 from the square well case, giving poorer agreement with experiment. If $\epsilon_{\rm eff}$ is allowed to vary with pressure as the optical dielectric constant,[54,55] there is insignificantly small improvement, while if it varies as the static dielectric constant, ϵ_0[56] $(\partial\epsilon_0/\partial P<0)$, the calculated values of $(\partial E/\partial P)_T$ have the wrong sign for the F band.

The point-ion model[57,58] comes much closer to giving $(\partial E/\partial P)_T$ for the F band, but $3p$-like levels to represent the K band have not yet been calculated. The point-ion model ignores the ion cores and gives F-center transition energies which agree approximately with the "Ivey law," $E\propto a^{-1.84}$ where a is the lattice parameter. On the basis of this experimental "law" one expects $(\partial \ln E/\partial \text{ in } a)_T$ to be -1.84 for all alkali halides. The point-ion calculations give some departure from this prediction for crystals of small a. However, the experimental facts are that upon varying a by applying pressure, $(\partial \ln E/\partial \ln a)$ is from -3.1 to -4.2 in several alkali halides,[4] being -3.6 in KCl.[12] If, instead, one varies the lattice parameter by changing the temperature, one gets $(\partial \ln E/\partial \ln a)_P=-4.7$ at 300°K for KCl. Disagreement with the Ivey rule is worse if one uses a form that is in better accord with experiment: $E\propto a^{-n}$ where n has the value 1.682 for Li-halides, 1.637 for Na-halides, and 1.552 for K-halides,[59,60] predicting $(\partial \ln E/\partial \ln a)=-1.55$ for KCl. Considerations of "local compressibility" do not enter, for a is the bulk lattice parameter, not the distance of an F-center nearest neighbor from the center of the vacancy. Despite the discrepancy of a factor of two or three, the point-ion model, as used by Gourary and Adrian, at least gives the right order of magnitude for the pressure coefficient of the F-absorption band. More recent work by Kübler and Friauf[61] indicates that improving the point-ion model by including a nonspherical term in the potential tends to spoil agreement with experiment, but the inclusion of ion core effects by the introduction of pseudopotentials tends to restore agreement.

Clearly, it is expecting too much of a simple model to produce derivatives of energy differences correctly as well as the energy differences themselves. For example, in the semicontinuum model,[22,40] if the effective dielectric constant, which hides a number of effects, were to tend more toward the static value as the pressure increases, one would have $(\partial\epsilon_{\rm eff}/\partial P)_T>0$ even though $(\partial\epsilon_0/\partial P)_T<0$. If justifiable, such an effect would tend to produce better agreement with experiment than we have found.

Continuum models should suffice for the relaxed excited F center. We have taken Fowler's potential[22] for the relaxed excited F center in NaCl and have allowed R to vary, again at twice the rate that the lattice parameter would vary with pressure. We have also allowed the dielectric constant to vary in different amounts. Using $1s$ and $2p$ hydrogenic wave functions we found that the $2p$ level drops with pressure with respect to the conduction band (if the static dielectric constant pressure derivative is used) at about one-tenth the observed $(\partial\Delta E/\partial P)_T$ for KCl. The $1s$ level drops more rapidly, an effect due to $(\partial\epsilon/\partial P)_T$, and a positive value of $(\partial E/\partial P)_T$ is predicted for emission, but it is about one-tenth of that observed. A simple effective mass model for the relaxed $2p$ state in KCl gives $(\partial\Delta E/\partial P)_T=-0.8\times10^{-6}$ eV bar^{-1} for $m^*=1$, assuming m^* does not change with pressure and using the static dielectric constant. Again the sign is correct, but the magnitude is too small.

There were also small changes in oscillator strengths for absorption. Using Smith and Spinolo's parameters for RbCl, the $1s$-$2p$ oscillator strength was calculated to decrease 2% between 0 and 5 kbar while that of the $1s$-$3p$ transition lost 6% of its value, keeping ϵ fixed. If experimental values of $(\partial\epsilon_0/\partial P)_T$ were used, these

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changes were a 12% decrease and a 6% increase, respectively. In this connection, the shape change of the *K* band (Fig. 4) can be interpreted either as a decrease in oscillator strength of the 1*s*-continuum transitions with respect to those of the 1*s*-*np* (the opposite of the calculated result, assuming an *f* sum rule), or as a larger shift of the 1*s*-*np* transition energies with pressure than of the 1*s*-continuum energies. The latter is in qualitative agreement with some potential-well calculations, for the 1*s* level drops with pressure, while the 3*p* level sometimes rises toward the fixed conduction-band minimum, depending on the value of $(\partial\epsilon/\partial P)_T$ used.

In short, no simple potential-well model seems to account even qualitatively for all the features of the data. In all of these models we have taken the zero of energy to be the conduction-band minimum. This is why we calculate a shift in the ground-state energy that is linear with pressure. The energy of the ground state, an equilibrium state, should vary quadratically with pressure if the zero of energy is taken at infinity.

7. F_A Band

We have examined the pressure shift of the two absorption bands present with F_A centers present. F_A centers are believed to be *F* centers having an impurity alkali ion[62–65] as one of the six nearest alkali ions. Generally, these are smaller alkali impurities. In our case we examined KCl+NaCl.

An F_A band was produced in KCl:Na in the pressure cell. The crystal was then cooled to 80°K and irradiated with 100-oriented *F*-band light. By examining the pressure shifts of the dichroic spectrum, $\mu_{100}-\mu_{010}$, we could eliminate the effects of the pressure shift of the *F* band, which overlies the higher energy F_A transition (F_{A2}) in the μ_{100} and μ_{010} spectra separately. The low-energy F_A band (F_{A1}) shifts at a rate $(\partial E/\partial P)_T = 10\times10^{-6}$ eV bar^{-1} and the F_{A2} band has $(\partial E/\partial P)_T = (14-15)\times10^{-6}$ eV bar^{-1}, the latter about equal to the *F*-band shift. The latter result is expected since the wave functions involved in the higher-energy transition are probably quite similar to *F*-center wave functions.

The splitting of the F_A-center peaks increases with pressure at a rate of about 4 to 5×10^{-6} eV bar^{-1}. There have been no calculations published on F_A centers. Clearly a potential-well model is inadequate, and one must consider the difference between the impurity cores and those of the host alkali ions. ENDOR measurements[66] indicate that in the F_A center in KCl:Li, the Li^+ ion lies further from the vacancy center than do the five K^+ ions by an amount difficult to estimate. This further complicates future calculations. The fact that the F_A-band splitting increases with pressure in KCl:Na simply means that the effect of the perturbation caused by the K^+-Na^+ ion differences increases with pressure. The perturbation in the Hamiltonian need not increase with pressure if the *F*-center electron wave functions in the alkali ion cores become sufficiently larger with increasing pressure.

SUMMARY

An important conclusion of Jacobs[2] was that most of the temperature shift of the *F*-absorption band peak arises from thermal expansion and very little (~5%) from the electron-lattice interaction. We feel that this important conclusion has been ignored in the intervening years. By analyzing our data somewhat differently, we reach the same conclusion although we believe the electron lattice interaction to be responsible for more than 5% (about 30%) of the absorption peak shift. We find from our luminescence studies that most (60–80%) of the emission peak temperature shift arises from the electron-lattice interaction even though the magnitude of the thermal expansion contribution is larger for emission than absorption.

We also find that the simple microscopic *F*-center models extant cannot account quantitatively for the observed pressure shifts of the *F*-center absorption and emission peaks. Our measurements on the shifts of the *K* and *L* bands with pressure indicate that the final states for the *L* transitions are not bound in the potential well of the vacancy in the usual sense. Finally, from measurements of the lifetime of excited *F* centers in KCl, we have obtained a rough value for the pressure derivative of the thermal ionization energy of the relaxed excited *F* center.

In the course of the luminescence measurements we have obtained luminescence from a new band in KBr, apparently the *K′* band discovered by Maisch and Drickamer.[3] This band seems to arise from the *F*-center electron, and its luminescence is detectable at 1 atm pressure even though we cannot observe any *K′* band in absorption in our range of pressures. A similar occurence may take place in KI.

ACKNOWLEDGMENTS

The authors wish to thank Professor C. A. Swenson for considerable advice on high pressure techniques, Professor F. C. Brown for drawings of the fast light source used, Professor R. J. Maurer for a zone-refined crystal of KBr, and Dr. W. Gebhardt for a copy of his paper. A beneficial conversation with Professor J. J. Markham and correspondence with Professor W. B. Fowler, Professor D. Y. Smith, Professor D. B. Fitchen and Dr. H. Kühnert are acknowledged.

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