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Pressure Shift of the F Band in Alkali Halides: Ion-Size Effects*

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The coupling of the F-band transition energy to cubic strain has been determined from hydrostatic-pressure measurements (0–8 kbar at 78°K) in several of the less common alkali halides. Whereas in most cases the F band shows a strong dependence on lattice volume, consistent with the Mollwo-Ivey relation, the shift is found to decrease unexpectedly for those alkali halides which have large alkali ions and small halogen ions. In the most extreme case, CsF, the shift has the opposite sign. These results are compared with previous experimental and theoretical evidence for the volume dependence of the F center. A simple model which takes some account of the finite size of the ions neighboring the vacancy is able to explain not only this new pressure behavior, but also the deviation from the Mollwo-Ivey relation and the large uniaxial stress splitting found for these alkali halides.

I. INTRODUCTION

It is often assumed that certain characteristic features of the F center are qualitatively similar from one alkali halide to another. For instance, a strong dependence of the F-band transition energy on lattice volume has been assumed to be a common property.[1] In this paper, we report new measurements of the shift of the F band under hydrostatic pressure in some of the less common alkali halides and show that the shift varies in size and actually reverses sign in the most extreme case, CsF. We attribute this new variation to ion-size effects in the volume dependence of the F-band peak position.

Several authors, most recently Smakula,[2] have sought correlations between the spectral position of the F band in different alkali halides and the properties of the host lattice. The most successful correlation—that $\lambda_m \propto d^2$ for alkali halides with the NaCl structure—was first noted by Mollwo[3] in 1931, and was later refined to $\lambda_m = \lambda_0 d^{1.84}$ by Ivey.[4] Here, λ_m is the wavelength of the peak of the F band, and d is the interionic distance. This relation was shown to hold also for mixed crystals.[5] Although the agreement is only rough, it was inferred that this empirical Mollwo-Ivey relation reveals the volume dependence of the F-center transition energy.

There is some theoretical support for this conclusion. For instance, the simplest possible model treats the F center with its electron trapped at a negative-ion vacancy as a finite square well with two bound states. As the radius of this well is varied, the transition energy between the states will vary in qualitatively the same way as the Mollwo-Ivey relation predicts.[6] Gourary and Adrian[7] have shown that a point-ion potential model also predicts a similar dependence on interionic distance. Recently, Wood[8] has attempted to refine the theoretical treatment of the volume dependence by taking into account the electronic structure of the neighboring ions.

It is also possible to measure the dependence on lattice volume directly, by subjecting a crystal containing F centers to hydrostatic pressure. The pressure shift at room temperature has been measured by Jacobs[6] to 5 kbar, by Maisch and Drickamer[9] and Knof and Maisch[10] to about 50 kbar, and by Eppler and Drickamer[11] to pressures as high as 165 kbar in various alkali halides. Shifts at low temperatures have been measured for the most common alkali halides by Fitchen[12] and by Brothers and Lynch.[13] In every case, the changes in wavelength at low pressures were two or three times as large as those predicted by the Mollwo-Ivey relation. This stronger dependence on lattice constant has been explained as an indication of greater local compressibility at the F center because of relaxation of the surrounding ions into the vacancy.[6] At the higher pressures used by Drickamer and his collaborators, this discrepancy decreased, presumably because the local compressibility approached that of the bulk lattice.[14]

That deviations in local compressibility could not be the complete explanation for pressure-shift discrep-

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ancies was indicated when a pressure shift of the opposite sign was found in the course of a detailed study of the *F* center in CsF.[15] To see if we could find some systematic variation with which to understand this anomaly, we have measured the hydrostatic pressure shift of the *F* band in many of the less common alkali halides. Most of the measurements were made at liquid-nitrogen temperature in the range 0–8 kbar. The results, expressed as a strain shift $(\Delta E/E_0)/(\Delta a/a_0)$ or $\partial \ln E/\partial \ln a$, are independent of temperature and show a marked decrease in magnitude as the relative size of the anion decreases through the series, until the effect changes sign for CsF with its extreme ion-size ratio.

In the latter part of the paper, we compare the pressure results with other evidence for the volume dependence of the *F* center and with its uniaxial stress behavior. We suggest qualitatively how ion-size effects can account for the observed variation, using a simple semicontinuum model which takes into account the finite size of the ions neighboring the vacancy.

II. EXPERIMENTAL PROCEDURES

The alkali-halide crystals studied were obtained from the following sources: Harshaw Chemical Company—LiF, NaF, NaCl, NaI, KF, KCl, KBr, CsBr, and CsI; Semi-Elements, Inc.—LiCl, LiBr, KF, RbBr, RbI, and CsF; Naval Research Laboratory—RbF. Samples were cleaved, or ground and polished, to a thickness of a few millimeters. Deliquescent crystals were prepared and mounted in a dry-nitrogen atmosphere in a dry box. Most samples were colored by x irradiation, usually at room temperature, using unfiltered radiation from a tube operated usually at 120 kV and 10 mA. LiBr was x irradiated at dry-ice temperature because its *F* band is unstable at room temperature. Some crystals, particularly those which could not be colored easily by x rays (RbBr, RbI, CsI), were colored electrolytically[1] in a dry-nitrogen atmosphere. These crystals were later annealed and quenched in the dark to remove aggregate centers. Attempts to color LiI were unsuccessful because of extreme handling difficulties.

Coloration was controlled to produce *F*-band optical densities of order unity at liquid-nitrogen temperature, with negligible *M*- and *R*-band densities. The *F*-center densities were estimated to be of the order of 10^{16} cm^{-3}, using Smakula's formula.[1]

The colored samples were mounted in an optical pressure cell described elsewhere.[16] The cell was soldered directly to the cold finger of a small metal cryostat which was inserted in the sample compartment of a Cary 14R spectrophotometer. Helium gas was used to apply hydrostatic pressure in the range 0–8 kbar and was delivered through small-diameter tubing from a remote gas-pressure system. Pressures were measured in a room-temperature manganin gauge cell coupled to the optical cell. The manganin wire was assumed to have a linear variation of resistance with pressure in this range and was calibrated at the freezing pressure of mercury at 0°C (7566 bar).[17]

Nearly all the measurements reported here were performed at liquid-nitrogen temperature. The principal advantage of the low temperature was the smaller half-width of the *F* band at 78°K and the smaller overlap of other absorption bands. In addition, some of the *F* bands were quite unstable at room temperature. Because of leakage past the sapphire windows at low pressures and low temperatures, no measurements were made in the range 0–2.5 kbar at 78°K, except at the end of each run when zero-pressure data were recorded. No hysteresis was apparent upon increasing or decreasing pressure.

III. RESULTS AND ANALYSIS

In this experiment we studied the effect of pressure on the position of the *F*-band peak. A result typical of most of the *F* bands is shown in Fig. 1(a). Our criterion for determining the peak wavelength was to extrapolate the midline of the band to the band peak. The midline was drawn through the mean wavelength midpoints determined at several heights on the *F* band, and corrected for any linear slope in the background because of reflection loss or window absorption. The background was measured directly in a few cases, using an uncolored sample, and was found to be small and quite insensitive to pressure.

In nearly all cases, the shape and half-width of the *F* band appeared to be independent of pressure within our measuring uncertainty in this pressure range, although this was not investigated in detail. This result is consistent with the 1 or 2% increase in width expected in this range[6] and the 10% broadening observed at 50 kbar.[9] Consequently, the shape and slope of the midline usually did not change with pressure.

Since the *F* band in CsF has a well-resolved triplet structure (because of the combined effect of spin-orbit coupling and a Jahn-Teller effect[15,18]), a different procedure was followed with it. The pressure shift was determined by superimposing traces at different pressures and measuring the wavelength displacement. In addition to causing a small red shift, pressure also caused a slight distortion of the band shape and an apparent decrease of about 25% in the area under the *F* band at 7 kbar, as shown in Fig. 1(b).

In two other cases, the shape of the *F* band changed perceptibly. In LiCl [Fig. 1(c)], the band appeared to broaden and become flat-topped, possibly indicating the presence of two different bands. In LiBr [Fig. 1(d)],

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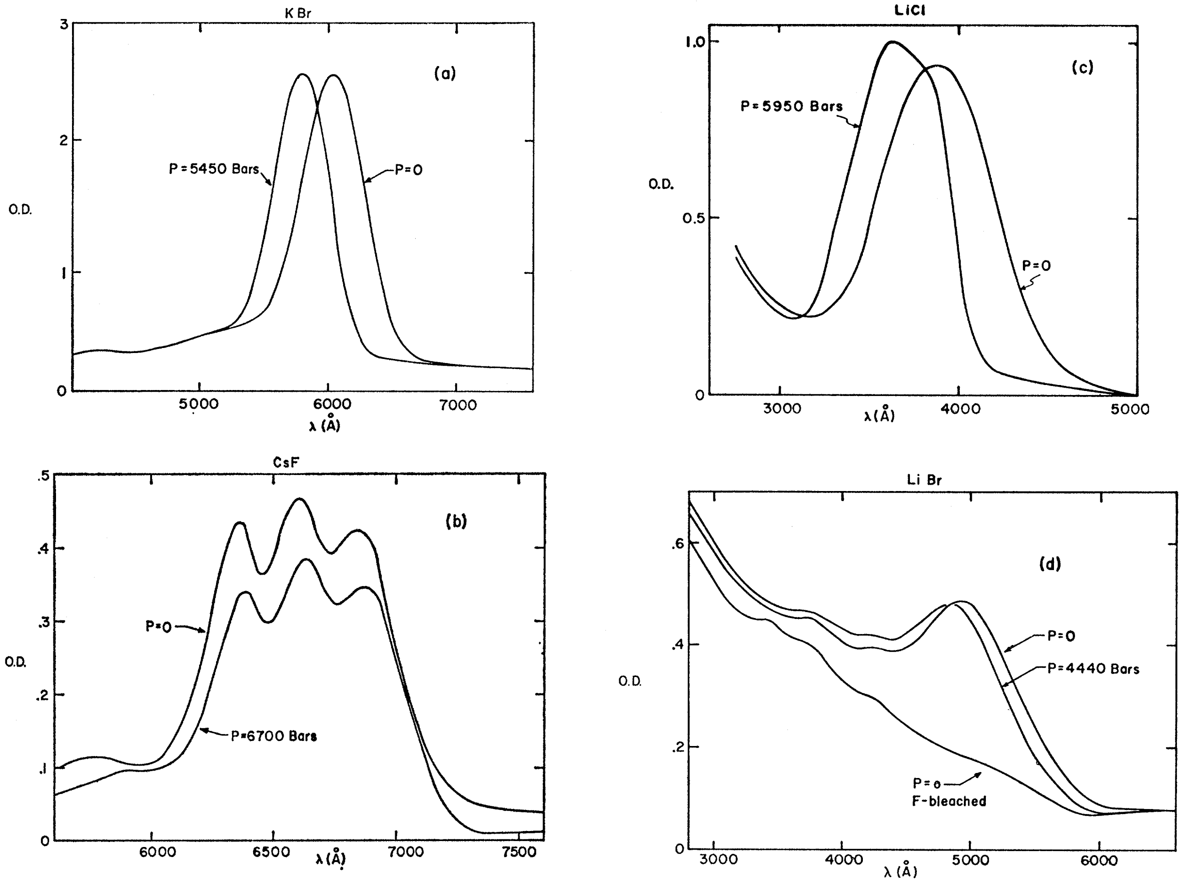

FIG. 1. Effect of hydrostatic pressure on several F bands at 78°K. (a) KBr, (b) CsF, (c) LiCl, (d) LiBr.

there were serious background complications, and only a weak F band could be produced. Furthermore, the band position at zero pressure depended strongly upon details of sample preparation, and therefore the given value must be considered questionable.

We list in Table I for each of the F bands studied the zero-pressure position at 78°K and the pressure coefficent $(\partial E/\partial p)_T$. Since the shift is not quite linear with pressure, the value quoted was determined by extrapolating to zero pressure. Jacobs's values[6] for pressure shifts of F bands in other alkali halides are given in parentheses.

The results appear to be nearly independent of the method used to produce the F centers, although there are variations from sample to sample which are larger than the measuring uncertainty of about 3%. For instance, we have measured pressure shifts at 78°K for KBr crystals colored by x irradiation at liquid-nitrogen and room temperature and by electrolytic coloration. Brothers and Lynch[13] have measured shifts at 78°K for KBr crystals colored by additive coloration and by x irradiation at room temperature. These results are listed together in Table II. We have not been able to correlate the small variations with any particular parameter. We consider the results given in Table I to be sample-independent to within about 10%, except where otherwise indicated. The smaller error estimates given are simply estimates of the precision of our measurement.

A quantity of more basic interest is the fractional energy change per unit strain. Jacobs[6] first showed that a plot of log E versus log a is almost exactly linear in this range of pressure, implying a strain dependence of the form

$$E=Ca^{-n}, \tag{1}$$

where E is the energy of the F-band peak and a the bulk-lattice constant, and where n and C depend on the particular alkali halide. The exponent n is directly related to the coefficient B_1 defined by Schnatterly[19] as the cubic-strain coupling coefficient of the F-band transition:

$$n=-(\partial \ln E/\partial \ln a)_T=B_1/\bar{E}. \tag{2}$$

We have estimated the change in lattice constant from the relation $-da/a_0=[K(p,\ T)/3]\ dp$, where $K(p,\ T)$ is an estimated value for the isothermal bulk compressibility at the measuring pressure and temperature. In a few cases, the compressibility at 78°K

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[19] S. E. Schnatterly, Phys. Rev. **140**, A1364 (1965).

TABLE I. Pressure shift of the *F* band in alkali halides.

Alkali halide	$(E_0)_{78°\mathrm{K}}$ (eV) $p=0$	$(\partial E/\partial p)_{78°\mathrm{K}}$ (μeV/bar) $p=0$	$-(\partial \ln E/\partial \ln a)_T$
LiF	5.12	8.9 ± 0.5	3.61 ± 0.15
NaF	3.74	9.1 ± 0.3	3.51 ± 0.10
KF	2.85	3.2 ± 0.1	2.23 ± 0.10
RbF	2.41	6.2 ± 0.3	2.10 ± 0.10
CsF	1.88	-1.2 ± 0.2	$-0.5\ \pm0.1$
LiCl	3.27	11.2 ± 0.3	3.44 ± 0.10
NaCl	2.75	15.9 ± 0.5	4.56 ± 0.15
KCl	2.30	13.7 ± 0.4	3.30 ± 0.10
RbCl	2.30[b]	(12.0 ± 1.0)[c]	$(3.4\ \pm0.1)$[c]
CsCl[a]	2.14[b]	(9.5 ± 1.0)[c]	$(2.8\ \pm0.2)$[c]
LiBr	1.23	9.2 ± 0.6	$3.0\ \pm0.2$
NaBr	2.36[b]	(10.8 ± 0.7)[c]	$(2.6\ \pm0.2)$[c]
KBr	2.09	16.0 ± 0.5	3.74 ± 0.15
RbBr	1.84	15.0 ± 0.4	3.38 ± 0.10
CsBr[a]	1.98	10.8 ± 0.6	2.85 ± 0.15
LiI	...	...	...
NaI	2.08	20.1 ± 0.5	4.44 ± 0.10
KI	1.84[b]	(14.1 ± 0.4)[c]	$(3.7\ \pm0.1)$[c]
RbI	1.70	18.3 ± 0.5	3.66 ± 0.10
CsI[a]	1.65	11.6 ± 0.8	$2.9\ \pm0.2$

[a] Simple-cubic structure.
[b] W. D. Compton and H. Rabin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 121.
[c] At 300°K [I. S. Jacobs, Phys. Rev. 93, 993 (1954)].

can be determined from ultrasonic measurements of the adiabatic elastic constants. Rather than use these, we have chosen to determine $K(p,\ 78°)$ from room-temperature data in the following arbitrary but uniform way. Tosi[20] has tabulated the isothermal compressibility K_0 and its measured or estimated pressure and temperature derivatives at room temperature for all the alkali halides, in a recent review article. We use these values exclusively to get $\Delta a/a_0$, using

$$-\frac{\Delta a}{a_0}\simeq\tfrac{1}{3}K_0\left[1-\frac{1}{K_0}\left(\frac{\partial K}{\partial T}\right)_p\times(150°\mathrm{K})\right]\times\left[1-\frac{1}{2K_0}\left(\frac{\partial K}{\partial p}\right)_T p\right]p. \qquad (3)$$

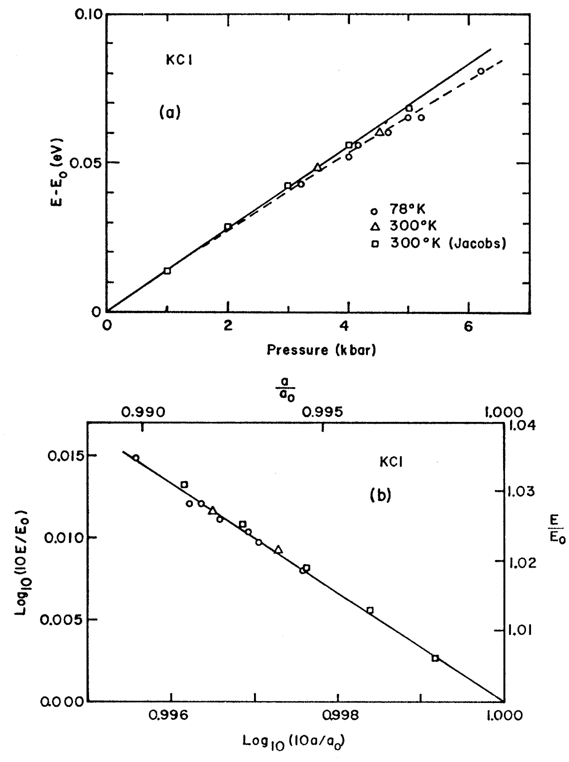

FIG. 2. (a) Pressure shift and (b) volume shift of the *F* band in KCl. Room-temperature values are from Fitchen (Ref. 12) and Jacobs (Ref. 6). The dashed curve in (a) represents the solid line in (b).

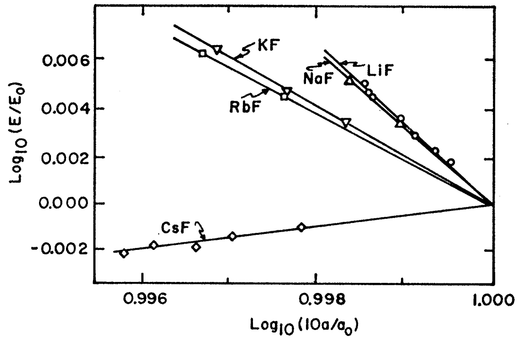

FIG. 3. Volume shifts of the *F* band at 78°K in the alkali fluorides.

We make the temperature correction assuming that the compressibility depends mainly on volume, and use a constant factor of 150°K instead of 220°K to account roughly for the reduction in thermal-expansion coefficient at low temperatures. The additional assumption that the pressure derivative is nearly temperature-independent is borne out by the ultrasonic measurements. While this procedure is rather arbitrary, the errors introduced are usually no larger than some of the other uncertainties in the results.

Both the pressure shift $(\partial E/\partial P)_T$ and the volume shift $(\partial \ln E/\partial \ln a)_T$ are practically independent of temperature, as indicated for KCl in Fig. 2. Our low-temperatures results for KCl, KBr, and NaCl can thus be compared with Jacobs's earlier room-temperature results. The results agree within about 7%.

TABLE II. Pressure shifts in KBr for *F* Bands produced in different ways.

Coloration method	Measurement temperature (°K)	$(\partial E/\partial P)_T$($\mu$eV/bar)
x rays at 78°K[a]	78	15.6
x rays at 300°K[b]	78	15.3
x rays at 300°K[c]	300	15.0
Electrolytic[d]	78	16.5
Additive[b]	78	16.2
Additive (requenched)[b]	78	15.9

[a] Fitchen (Ref. 12).
[b] Lynch (private communication).
[c] Jacobs (Ref. 6).
[d] This work.

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[20] M. P. Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 44.

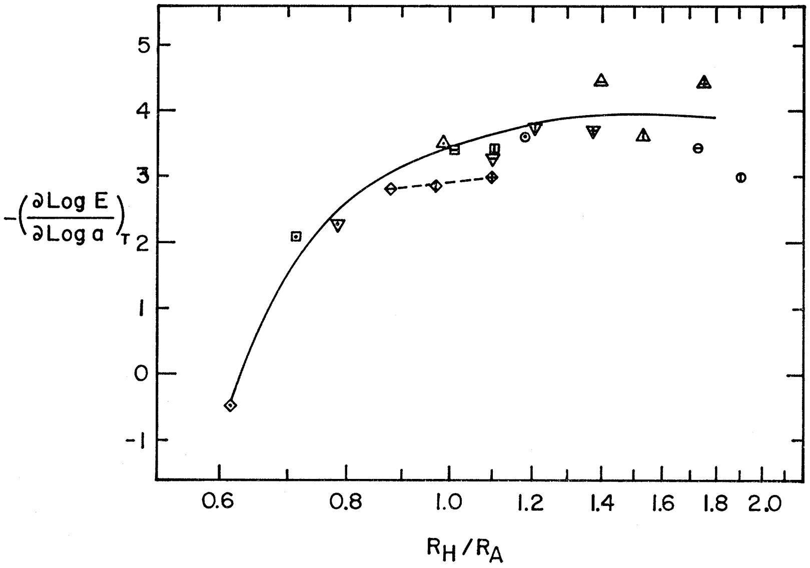

FIG. 4. Variation of the volume shift of the F band in alkali halides as a function of the ratio of halide-ion radius to alkali-ion radius. See Fig. 5 for key to symbols.

Values of the pressure shift for different alkali halides cover a wide range because they depend on compressibility, but in previous studies the volume shift was found to have nearly the same value (~3–4) for each of the common alkali halides measured. When the less common compounds are included, we find, instead, a significant variation in the volume shifts. For instance, the volume shifts of the F band in all five alkali fluorides with the NaCl structure are plotted in Fig. 3. The monotonic decrease in the slope $-(\partial \ln E/\partial \ln a)_T$ suggests that the relative size of the alkali and halogen ions is important. To demonstrate this ion-size dependence, we plot in Fig. 4 the coefficient $-(\partial \ln E/\partial \ln a)_T$ versus the ion-radius ratio R_H/R_A for all the alkali halides which have been measured. We take for the halide- and alkali-ion radii R_H and R_A the values listed by Gourary and Adrian[7] from maps of the electron density measured in x-ray diffraction studies of LiF and NaCl. The ratios R_H/R_A do not differ substantially from those of other more conventional radii, except that they are generally smaller. We are interested only in the trend of values.

IV. DISCUSSION

With the results reported here, the F-band pressure shifts are now known for all of the twenty alkali halides except LiI. The behavior shown in Fig. 5 can be summarized as follows: All but three of the alkali halides with the NaCl structure have a shift $-(\partial \ln E/\partial \ln a)_T$ lying in the range 3.0 to 4.4; the three alkali halides with the CsCl structure (CsCl, CsBr, and CsI) have shifts of about 2.8; and the three alkali halides with the smallest ion-size ratio (CsF, RbF, and KF) have smaller shifts. In this section, we consider possible explanations for this behavior.

As mentioned earlier, there are quite definite predictions for the volume dependence of the F-band energy. The Mollwo-Ivey relation, based on the empirical correlation between F-band position and interionic distance shown in Fig. 5, implies a shift

$$-(\partial \ln E/\partial \ln a)_{T,P} \simeq 1.8. \qquad (4)$$

Theoretical estimates based on the point-ion model[7,8] and on an extended-ion model[8] also predict a comparable shift

$$-(\partial \ln E/\partial \ln a)_{\text{theor}} \simeq 1.5. \qquad (5)$$

However, the shift derived from the pressure behavior is in most cases twice this size, as noted by Jacobs.[6] He proposed the following explanation for the enhanced pressure shift.

A. Local Compressibility

Assume that the dominant dependence of the F-band energy is on the distance R of the first-neighbor ions from the center of the vacancy after relaxation has taken place. Then the pressure shift can be written as

$$(\partial \ln E/\partial \ln a)_T = (\partial \ln E/\partial \ln R)_T (\partial \ln R/\partial \ln a)_T. \qquad (6)$$

The term $(\partial \ln R/\partial \ln a)_T$ measures the ratio f of the local compressibility at the F center to the bulk compressibility of the lattice. If we assume that the dependence of energy on nearest-neighbor distance is given correctly by the Mollwo-Ivey relation or the theoretical estimates, then the pressure shift implies that the local compressibility is greater than the bulk compressibility by a factor of about 2.

It is not difficult to understand why this ratio could be greater than unity, since there is no ion-core repulsion at the vacancy. Jacobs showed that even the simplest model of a spherical cavity of radius R in an elastic continuum predicts about a twofold enhancement in radial strain under hydrostatic pressure.

Benedek and Nardelli[21] arrive at a similar conclusion from their analysis of the recent data on Raman scattering at *F* centers. They estimate that there is a local reduction in force constants in the neighborhood of the *F* center which amounts to 60% in KCl and 80% in NaCl.

There is also some recent experimental evidence of a different sort which supports this hypothesis. Blum[22] has measured the pressure variation of the isotropic hyperfine splitting in the ESR spectrum of the *F* center in LiF. This provides an independent estimate of the local compressibility at the *F* center, since Gourary and Adrian[7] have estimated theoretically the splitting as a function of nearest-neighbor distance. Blum's results imply an enhancement factor for the local compressibility of $f_{\mathrm{ESR}}\approx 1.6$ with an uncertainty of about 50% in the experimental measurements as well as in the theoretical prediction. If we take our pressure shift result for LiF, $-(\partial \ln E/\partial \ln a)_T=3.6$, and assume that $-(\partial \ln E/\partial \ln R)_T\approx 1.8$, then the corresponding optical value is $f_{\mathrm{opt}}\approx 2.0$.

Jacobs used the same argument to explain the smaller pressure shift observed in the CsCl structure. Since this is a more closely-packed structure, the nearest-neighbor ions cannot move as far into the vacancy before significant overlap occurs. Hence the smaller shift ($\sim$2.8) is presumably due to a smaller value for f.

However, this does not appear to be the source of the anomalous *F*-band shifts in the crystals with small ion-size ratio. Although these have large nearest-neighbor ions and a small vacancy, so that f is probably somewhat reduced, it seems unlikely that the local compressibility would be less than the bulk compressibility or of opposite sign. Instead, the reduced shifts in these cases must reflect some other dependence of the *F*-band energy not normally apparent.

B. Electron-Phonon Interaction

One other dependence, suggested by theories of the electron-phonon coupling at an *F* center, was used by Jacobs[6] to account for the difference between the pressure and temperature shifts of the *F* band. This involves the effect of changes in frequency of the coupled-lattice modes when the *F* center changes its electronic state. It introduces an intrinsic temperature shift proportional to the degree of thermal excitation of these modes, in addition to the dominant shift due to thermal expansion. In the simplest approximation, where the *F* center is assumed to couple to a single mode of frequency ω, the transition energy can be written as

$$E=E(R)-b<2n+1>. \qquad (7)$$

In this expression, $E(R)$ represents the dependence on interionic distance discussed in the preceding section,

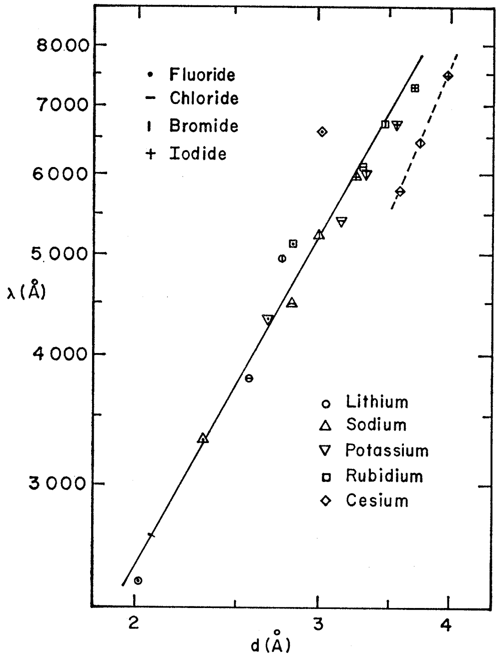

FIG. 5. The spectral position of the *F* band in alkali halides as a function of interionic distance. The solid line is the Mollwo-Ivey relation $\lambda_m=703d^{1.84}$, where λ_m and d are both in Å. The dashed line connects the values for the three alkali halides with cesium-chloride structure.

b is a coupling constant proportional to the frequency shift, n is $[\exp(\hbar\omega/kT)-1]^{-1}$, and the phonon energy $\hbar\omega$ can be approximated roughly by the Debye temperature $k\Theta$. In the high-temperature limit, Eq. (7) becomes

$$E=E(R)-bT/\Theta. \qquad (8)$$

Jacobs argues that this extra term is responsible for about 30% of the temperature shift $-(\partial \ln E/\partial \ln a)_p$ but less than five percent of the pressure shift $-(\partial \ln E/\partial \ln a)_T$. The latter contribution comes from the change in vibrational frequency Θ with volume. If we assume that the coupling parameter b might also vary, then the full expression for the pressure shift would be

$$-\left(\frac{\partial \ln E}{\partial \ln a}\right)_T=-\left[\left(\frac{\partial \ln E}{\partial \ln R}\right)_T\left(\frac{\partial \ln R}{\partial \ln a}\right)_T+\frac{bT}{\Theta E}\left(\frac{\partial \ln \Theta}{\partial \ln a}\right)_T-\frac{T}{\Theta}\left(\frac{\partial \ln b}{\partial \ln a}\right)_T\right]. \qquad (9)$$

The last term would decrease the size of the pressure shift. However, if this were the dominant term for CsF at 78°K, it would imply a strong temperature dependence of the pressure shift. It would also imply a larger than usual temperature shift for this *F* band, whereas its position is observed to be quite independent of temperature. We conclude that the electron-phonon interaction is not the cause of the anomalous shifts.

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[21] G. Benedek and G. F. Nardelli, Phys. Rev. **154**, 872 (1967).
[22] H. Blum, Phys. Rev. **140**, A1998 (1965).

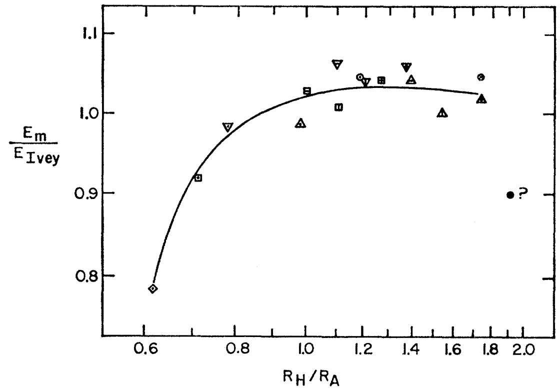

FIG. 6. Deviations from the Mollwo-Ivey relation as a function of ionic-radius ratio.

C. Finite Ion Size

The most likely cause of the anomalous behavior appears to be an extra dependence of the transition energy on the relative size of the nearest-neighbor ions. This is suggested empirically by the variation with ionic-radius ratio shown in Fig. 4, and also by the deviations from the Mollwo-Ivey relation in Fig. 5. The deviations from the line are plotted as a function of the same ionic-radius ratio in Fig. 6. This figure shows that for small values of the ratio R_H/R_A, the F-band transition energy is less than predicted. The variation of the pressure shifts in Fig. 4 shows that the transition energy actually decreases with decreasing lattice volume for the smallest value of R_H/R_A. Since the ratio R_H/R_A is a measure of the relative size of the vacancy in the lattice, these results suggest that when the relative vacancy size becomes small enough, the F-band transition energy decreases abruptly.

A qualitative consideration of a simple semicontinuum model of the F center suggests how this effect might arise. The model potential, shown schematically by the solid line in Fig. 7, is similar to that used by Simpson,[23] but differs in that it takes some account of the finite size of the alkali ions neighboring the vacancy. Its essential feature is a spherical-square-well core whose radius is limited to the radius of the vacancy $R-R_A$ (rather than the interionic distance R, as assumed by Simpson), and whose depth is taken to be the Madelung potential $-\alpha_M/R$. To this is joined a Coulombic part $-1/k_0r$, where k_0 is the high-frequency dielectric constant. We assume spherical symmetry for simplicity and ignore some polarization corrections. The potential is greatly oversimplified, as revealed by comparison with a recently computed pseudopotential[24] for the F center (shown by the dashed line in Fig. 7).

The crucial point of this model is that we let the size of the well depend on the size of the missing ion, while the depth of the well is determined by the interionic distance. The shape of the "wings" of the potential is not as important. This part serves mainly to allow both s and p states to be bound by the potential, so that there can be an F-band transition between bound states.

Rather than solve numerically for the eigenvalues of this schematic potential, we argue as follows. Since the square-well core is the dominant feature, we expect the eigenvalues to depend primarily on a single parameter, the "strength" of the potential, defined[25] as its depth times its radius squared, or $(\alpha_M/R)\ (R-R_A)^2$. For a finite square well, the binding energy of a given state is roughly proportional to the difference between the strength of the well and some threshold value of strength at which the state just becomes bound. When the square well is modified as in Fig. 7, the binding energy of the state will be somewhat greater for the same strength, and the threshold strength will be greatly reduced.

In Fig. 8, we have constructed some curves which suggest how the energies of the first two bound states of such a model might vary with the strength of the potential. The shapes of the two curves are only schematic and were chosen to resemble similar curves for a finite square-well potential. The strength of the model potential appropriate for a few of the alkali halides is indicated at the top of the figure.

The shape and spacing of these curves actually were adjusted to correspond approximately to the energies of the F-center states. The energy separation between the two dashed curves was chosen to match the experimental values for the F-band transition energy listed in Table I. (These energy separations are indicated by the pairs of circles in Fig. 8 for a few alkali halides.) If F- center binding energies were also known, the remaining arbitrariness could be removed. However, there are substantial discrepancies between different experimental and theoretical estimates for the binding energies. We have chosen to use a value for CsF based on the threshold energy for low-temperature photoconductivity[15] and values for NaF, KCl, and NaCl based on theoretical estimates[24] to adjust the shape of the curves. (These estimated ground-state binding energies are indicated by solid circles in Fig. 8.) The

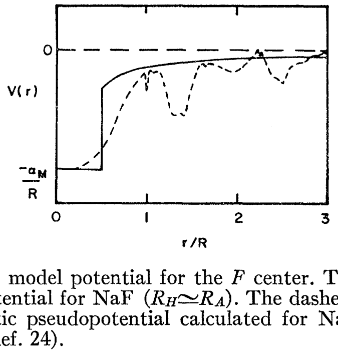

FIG. 7. The model potential for the F center. The solid curve shows the potential for NaF ($R_H \simeq R_A$). The dashed curve shows a more realistic pseudopotential calculated for NaF by Kübler and Friauf (Ref. 24).

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[23] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

[24] J. K. Kübler and R. J. Friauf, Phys. Rev. **140**, A1742 (1965).

[25] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), p. 76.

resultant curves suggest that a single-parameter fit based on this square-well strength is plausible, although a critical test will be to compare binding energies in more cases as these are measured.

There are two qualitative features of this model which provide a key to the explanation of the size effects mentioned earlier. One is the use of $R-R_A$ instead of R for the well radius. This gives nearly the same ordering of the alkali halides on the basis of potential-well strength as we found earlier on the basis of ionic-radius ratio R_H/R_A. The decrease in separation δ for small values of the strength parameter provides a natural explanation for the deviations from the Mollwo-Ivey relation noted in Fig. 6 for small values of R_H/R_A.

The second feature is the fact that δ is not a constant, as it would be for a deep or infinite square well. This has the following significance for the pressure behavior. The F-band transition energy E is related to the separation δ by

$$E=\delta/(R-R_A)^2 \tag{10}$$

and varies with nearest-neighbor distance as

$$\begin{aligned}-\left(\frac{\partial \ln E}{\partial \ln R}\right)_{T,R_A} &= +2\frac{\partial \ln(R-R_A)}{\partial \ln R} - \frac{\partial \ln\delta}{\partial \ln[(\alpha_M/R)(R-R_A)^2]}\,\frac{\partial \ln[(\alpha_M/R)(R-R_A)^2]}{\partial \ln R}\\ &= +2\left(\frac{R}{R-R_A}\right)-\frac{\partial \ln\delta}{\partial \ln[(\alpha_M/R)(R-R_A)^2]}\left[2\left(\frac{R}{R-R_A}\right)-1\right].\end{aligned} \tag{11}$$

For a deep or infinite square well with the conventional radius R (equivalent to $R_A=0$), the first term is $+2$ and the second term vanishes, yielding the Mollwo result $E\propto R^{-2}$. If δ is a constant, but $R_A>0$, then the shift is greater than 2. In this case, the factor $R/(R-R_A)$ arises because the alkali ions are assumed to be incompressible.

If δ is not a constant, then the second term contributes and partly cancels the first. The shifts determined from Eq. (11) and Fig. 8 are in qualitative agreement with those observed. For NaCl, the predicted shift is ~1.6, while for KF, RbF, and CsF, the shift decreases and becomes negative.

While this model is suggestive in considering the effects of finite ion size, it can only give a qualitative picture, as it ignores many features of the problem. Recently, there have been several attempts to include the effects of finite ion size in more realistic calculations of F-center energies.

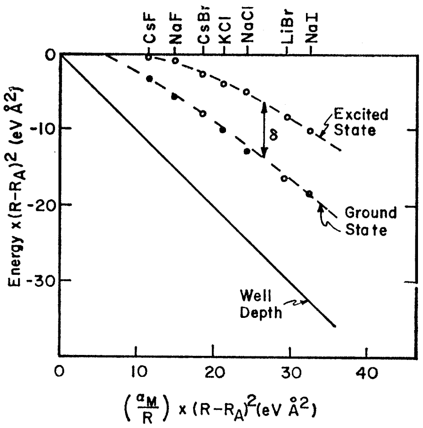

FIG. 8. F-center energies as a function of the strength of the model potential.

For instance, Wood[8] has recently investigated the dependence on interionic distance theoretically to compare with the Mollwo-Ivey relation. Using the point-ion model, he finds that the F-band transition energy can be expressed as

$$E=a/R+b/R^2, \tag{12}$$

where the coefficients give reasonable agreement with the Mollwo-Ivey line. He then includes effects due to the electronic structure of the neighboring ions, considering the penetration of the ion cores by the F electron and also exchange and overlap terms. He finds that these effects contribute several terms in higher inverse powers of R to Eq. (12). However, it is not possible to use his results to predict the dependence on R_H/R_A, because of some of the approximations made.

Gourary and Adrian[7] have calculated the effects of exchange and finite ion size on their point-ion–model F-center ground state in LiF, and found that the wave function avoids the region of the lithium ions and becomes more concentrated in the vacancy.

Kübler and Friauf[24] have also calculated F-center wave functions and energies, taking account of the structure of the ions neighboring the vacancy. They have used a localized pseudopotential of the form given by Austin and Heine.[26] Their most complete potential, using pseudopotentials based on 14 shells of neighbors for the F center in NaF, has the spherically symmetric part shown by the dashed line in Fig. 7. Since the pseudopotential for a positive ion has a partly repulsive core, it tends to exclude the F electron from these regions and reduces its binding energy from the point-ion estimate. In the three alkali halides which they studied, the pseudopotential corrections to the energy were nearly the same for both ground and excited state, and did not alter the transition energy.

These calculations support the view that the F electron is excluded from the region of the neighboring ion cores, as implied by the exaggerated potential of

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[26] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

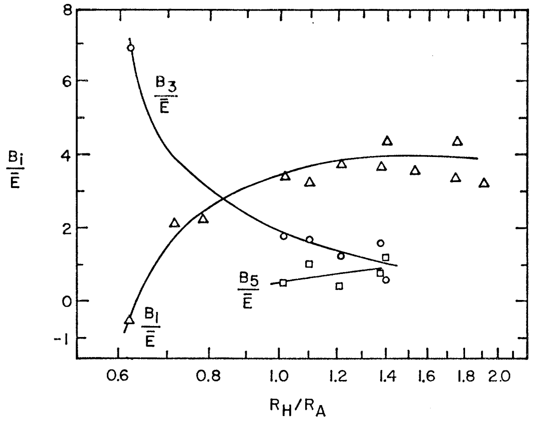

FIG. 9. Static-strain coefficients as a function of ionic-radius ratio. The values of $B_1/\bar{E}$ are taken from this work, the value of $B_3/\bar{E}$ for CsF from Ref. 15, and the remaining values of $B_3/\bar{E}$ and $B_5/\bar{E}$ from Ref. 19.

Fig. 7. It would be interesting to test the predictions of this simple model by extending the more realistic calculations to see what they predict in the regime of large alkali ion size, particularly for the alkali fluorides. The most convincing experimental check would be an ENDOR measurement of the hyperfine interaction at various shells of ions neighboring the F center in CsF, RbF, or KF. Attempts to observe the ESR signal of the F center in CsF were unsuccessful,[27] and there have been no attempts in RbF or KF, to our knowledge.

D. Comparison with Uniaxial Stress Behavior

In most recent F-center calculations, agreement with the observed F-band transition energy has been taken as an indication of validity of the model. However, Fowler and Dexter[28] point out that this is in fact a rather weak test which several overly simplified models can meet. Instead, it would seem appropriate to test future calculations also against the derivatives of the transition energy with respect to strain.

These are known experimentally, not only for cubic strains, but also for tetragonal and trigonal strains, from the work of Gebhardt and Maier[29] and of Schnatterly.[19] The energy shift per unit strain can be represented by a coupling coefficient B_1, B_3, or B_5, for a strain of Γ_1 (cubic), Γ_3 (tetragonal), or Γ_5 (trigonal) symmetry. The fractional shift with strain is actually more significant; for hydrostatic pressure, this is $B_1/\bar{E}$, which is just our shift $-(\partial \ln E/\partial \ln a)_T$.

The variation of these three coefficients for different alkali halides is shown in Fig. 9. Again, there seems to be a systematic variation with ion-size ratio, as first noted by Schnatterly. However, our conclusions differ from his because we have included our new pressure results and also a recent extreme value for B_3 in CsF.[15] The coupling to cubic strain falls off sharply for small values of R_H/R_A, whereas the sensitivity to tetragonal strain rises abruptly.

Schnatterly[19] considered how the p-like excited-state wave function of the F center might be affected by strains of different symmetries, because of electrostatic and overlap interactions with the first two shells of neighbor ions. Separating the coefficients to show each contribution explicitly, and using simple arguments to determine the sign of each term, he proposed that the strain coefficients could be written as

$$
\begin{aligned}
B_1 &= B_{11}{}^o + B_{12}{}^o - B_{11}{}^e + B_{12}{}^e,\\
B_3 &= B_{31}{}^o - B_{32}{}^o - B_{31}{}^e - B_{32}{}^e, \qquad (13)\\
B_5 &= -B_{51}{}^o + B_{52}{}^o + B_{51}{}^e + B_{52}{}^e
\end{aligned}
$$

(e = electrostatic, o = overlap).

He was then able to explain several of the features observed in Fig. 9. The fact that all the coefficients have the same sign (except for CsF) implies that these effects cannot be attributed to the electrostatic interaction alone and that the point-ion model is inadequate. The size of the overlap terms will be proportional to the size of the neighboring ions. Thus, as the first shell ions increase in size relative to the second shell ions, B_3 should increase and B_5 decrease, as observed. It would be interesting to measure B_5 for alkali halides with small R_H/R_A to see if it becomes negative as expected.

Schnatterly also proposed that B_1 is largest because both its overlap contributions have the same sign, and predicted that B_1 would become comparable to B_3 as the first shell ions become much larger than the second shell ions. His model does not explain the sharp decrease in B_1 for small values of R_H/R_A.

This is because his estimates are based only on the shifts and splitting of the excited state. This is sufficient for B_3 and B_5, which depend only on the splitting of this state, but not for B_1, which depends on the relative shift of the ground and excited state. Presumably, by including similar contributions to B_1 in Eq. (13) from ground and excited state, it would be possible to deduce the observed variation with ion size.

The large value of $B_3/\bar{E}$ for CsF is another consequence of the finite size of the alkali ions neighboring the vacancy. The splitting of the excited state under a [100] strain is enhanced for the relatively small vacancy by the factor $(R/R-R_A)$, while the energy $\bar{E}$ is excep- tionally small because of the weak potential in CsF.

E. Comparison with Dynamic-Strain Coupling

These static-strain coefficients can be compared with the contribution of cubic and noncubic vibrations to the

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[27] F. Hughes and H. Rabin, J. Phys. Chem. Solids **24**, 586 (1963).

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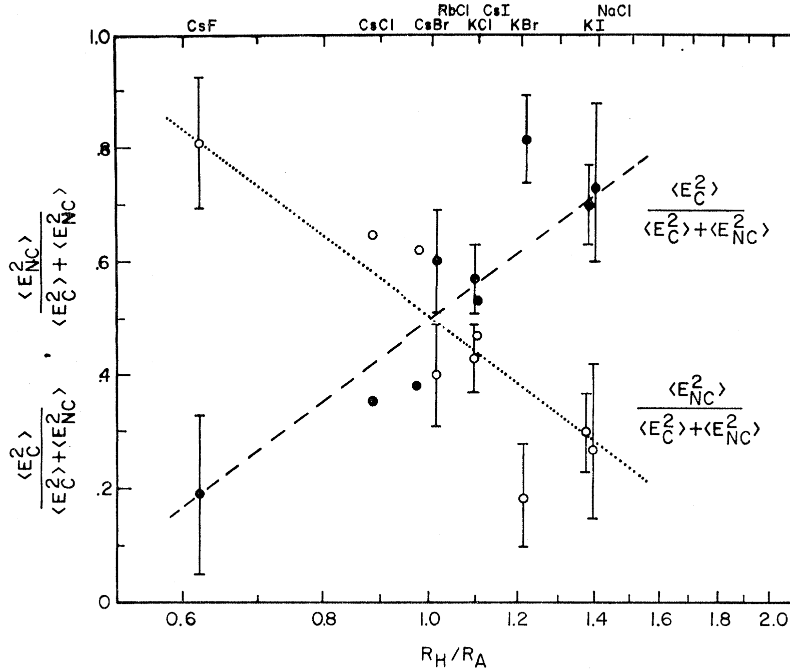

FIG. 10. Fractional contributions of cubic and noncubic vibrations to the second moment of the *F* band as a function of ionic-radius ratio.

broadening of the *F* band. These contributions are determined from moment analyses of the stress- and magnetic-field-induced dichroism of the *F* band. The relative contributions of cubic and noncubic strains are shown in Fig. 10, based on the stress measurements of Scatterly[19] for KCl, KBr, KI, NaCl, and RbCl, the line-shape analysis of Moran[18] for CsCl, CsBr, and CsI, and the magnetic measurements of Fulton[15] for CsF. The variation with ion-size ratio is qualitatively similar for static and dynamic strains.

The static-strain coefficients are a measure of the coupling of the *F*-band transition to long-wavelength acoustic phonons, whereas the second-moment contributions are due to both acoustic and optical phonons of both long and short wavelength. McCombie and Matthew[30] have calculated the contribution to the breadth of the *F* band of different lattice modes, taking account of the effect of the *F* center on these modes. They find that the mean-square amplitude of the low-frequency acoustic modes is greatly enhanced by the reduced force constants near the vacancy, while the amplitude of the optical modes is reduced. Supporting evidence comes from recent Raman spectra[31] which show that the *F* center does couple strongly to acoustic phonons. In fact, Benedek and Nardelli[21] have been able to calculate the Raman spectra with good results, using Schnatterly's static-strain-coupling coefficients. So it is not surprising that the static and dynamic coupling show a similar variation.

V. SUMMARY

The coupling of the *F*-band transition energy to cubic strain has been determined from hydrostatic-pressure measurements in several of the less common alkali halides. Whereas in most cases the *F*-band position shows a strong dependence on lattice volume, consistent with the Mollwo-Ivey relation, we have found an unexpected decrease in the shift for those alkali halides which have large alkali ions and small halogen ions. In the most extreme case, CsF, the shift has the opposite sign.

These results have been compared with other experimental and theoretical evidence for the volume dependence of the *F* center. An explanation for the dependence on relative ion size has been proposed, using a simple semicontinuum model which takes into account the finite size of the alkali ions neighboring the vacancy. This model also explains deviations from the Mollwo-Ivey relation and the large tetragonal strain coupling.

The variation of the cubic-strain-coupling coefficient has been compared with the variation of the coupling coefficients to static uniaxial strain and to lattice vibrations of various symmetries. The variation with ion-size ratio is qualitatively similar for static and dynamic strains.

ACKNOWLEDGMENTS

We wish to thank Dr. H. Rabin for the RbF sample, Dr. T. A. Fulton for advice on CsF, and Professor D. W. Lynch for communicating his pressure results. One of us (D.B.F.) would like to thank Professor D. Lazarus for sponsoring the initial studies of pressure techniques and *F*-band shifts.

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[31] J. M. Worlock and S. P. S. Porto, Phys. Rev. Letters **15**, 697 (1965).