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Band Shape and Phonon Broadening of *U* Bands in Alkali Halides*

S. S. MITRA AND R. S. SINGH†
Department of Electrical Engineering, The University of Rhode Island, Kingston, Rhode Island 02881

AND

Y. BRADA
Physics Department, The Hebrew University, Jerusalem, Israel

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The remarkable similarity of the *U* band originating from the first electronic transition of the H^- or D^- centers in an alkali halide to the *F* band in the corresponding alkali halide is pointed out. The band shape and phonon broadening of *U* bands in alkali halides of both NaCl and CsCl structures have been investigated by the method of moments employing a configurational coordinate model. It is found that the broadening is caused primarily by band-mode optic phonons. The interacting effective phonon frequencies for the H^- and D^- centers in a given alkali halide are thus given by $(\omega_e)_H \gtrsim (\omega_e)_D$. The Huang-Rhys factor is found to be two to three times larger than the corresponding quantity for the *F* band. The isotope shift upon deuteration can be explained by the present model without invoking the participation of localized vibrational modes. The positions of the *U* emission bands have also been predicted.

I. INTRODUCTION

THE study of the effect of point defects on the optical properties of solids has aroused renewed interest in recent years.[1] A solid with impurities may not only possess new features in the electronic spectrum but may also reveal modifications in its vibrational spectrum. The presence of the defects destroys the periodicity of the lattice, perturbs the phonon distribution of the host lattice, and, in some cases, gives rise to new modes of vibration known as localized modes and gap modes. Transitions of electrons associated with these defects are responsible for phenomena in the optical region. When the electronic transition is allowed and the defect is weakly coupled to the lattice, the spectrum consists of a sharp and relatively strong zero-phonon line and a well-separated vibronic structure. On the other hand, a very strongly coupled defect gives rise to a broad band whose peak positions in absorption and emission are different due to the so-called Stokes shift. The *F* center is an example of such a defect. Most defects fall in an intermediate category whose electronic spectra reveal both a broad band and an accompanying vibronic structure.

The simplest and the most widely studied system, both theoretically and experimentally, is the *F* center,[2] which is an electron trapped in a negative ion vacancy in an alkali halide. Recently, considerable interest has also been shown in the study of the *U* center. The *U* center is a H^- or D^- impurity substituting for an anion in an alkali halide. The *U* band arising from the first electronic transition of this center has been measured[3–5] in detail in a number of alkali halides of both NaCl and CsCl structures. Theoretical considerations of the electronic transition[6] and its interaction with the host lattice phonons[4,7] have also been put forward.

The purpose of this investigation is to point out the similarity between the *F* and the *U* bands and to analyze the available experimental data on the *U* band by the method of moments, under harmonic, adiabatic, and Condon approximations employing the configurational coordinate model, which had so successfully been used in the analysis of the *F* band.[8,9]

II. *F* AND *U* CENTERS

An inspection of *U*- and *F*-band shapes in an alkali halide dramatically points out their similarity. A plot of the *F*-band peak positions versus the *U*-band peak positions is shown in Fig. 1. The points fall on two straight lines, one for the NaCl structure and one for the CsCl structure. The ratio of the peak positions is around 2.5, which can be qualitatively understood in a very simple manner. It is well known that the *F* center can be represented by an electron in an octahedral box.[10] The *U* center similarly can be pictured as a single electron in the octahedron formed by the six nearest neighbors of alkali ions (cube of eight for the CsCl structure) in the

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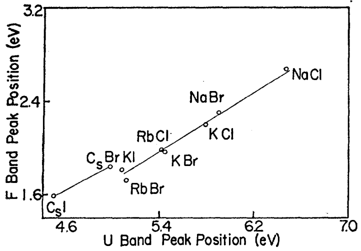

FIG. 1. *F*-band peak position versus the *U*-band peak position in different alkali halides. (Data from Refs. 2–5 and 32.)

center of which is a hydrogen atom. In terms of the *F*-centerlike eigenstates, the *U* center thus should have only eigenstates with even quantum numbers because of the necessity that the wave functions always vanish at the center as a result of the presence of the H atom. Thus, although for the *F* center the first electronic transition responsible for the *F* band corresponds to $\Delta n=1(1\rightarrow 2)$ transition, for the *U* band the corresponding transition must correspond to $\Delta n=2(2\rightarrow 4)$. This will predict that the *U*-band position should be between two to four times that of the *F* band. The *U*- to *F*-band position ratios should also be affected by other minor effects, e.g., (i) the energy levels may be slightly higher in the *U* center due to a smaller available volume; and (ii) the *F*- and *U*-band positions are not the pure (zero-phonon) electronic transition energies. The average of the absorption and the emission peak positions is sometimes taken as the zero-phonon transition energy for the *F* center, but so far no measurement of the *U* emission band has been reported. A more detailed quantum mechanical calculation[11] reveals these points in a more rigorous manner.

It has already been remarked that the *F* center is very strongly coupled to the lattice. That the *U* center is also strongly coupled is evident from the shape of the *U* band and also from the fact that although the first singlet transition of a free H^- ion only involves[12] an energy of about 0.5 eV, that of a H^- ion in the alkali halides range from 5 to 6 eV. The reason for this is that the second electron of a free H^- ion is very loosely bound to the hydrogenlike core, whereas the second electron of the *U* center, like the *F*-center electron, is very strongly bound to the lattice on account of net Coulomb attractive forces exerted by the alkali and halogen ions. The similarity of the electron-phonon interaction in the *U* and the *F* centers becomes readily apparent from a plot of the *U*-band half-width versus the *F*-band half-width in the same host lattice at various temperatures. Such plots are shown for KCl and RbCl in Fig. 2. As a result of Figs. 1 and 2 and the foregoing discussion, it becomes evident that an analysis of the *U*-band shape may be undertaken in a manner similar to that customarily used[2] for the *F* band.

It may be mentioned here that Baldini *et al.*[4] have recently used a rather complicated model to explain the *U* bands due to H^- and D^- centers in KCl, KBr, and RbCl. Although the model explains their data well, several criticisms can be made. These are as follows: (i) The effective band mode phonon frequency needed to fit the temperature dependence of the *U*-band peak position is significantly different from the effective phonon frequency needed to represent the temperature dependence of the half-width. (ii) Although it is well known that the local mode phonon frequency due to the *U* center follows the simple isotope rule $\omega_{\mathrm{loc}(H^-)}=\sqrt{2}\omega_{\mathrm{loc}(D^-)}$, Baldini *et al.* had to arbitrarily choose $\omega_{\mathrm{loc}(H^-)}=\omega_{\mathrm{loc}(D^-)}$ for the first excited singlet state. No reason is given for why an electronic transition will that drastically change a localized vibrational mode. (iii) Finally, far too many parameters are used in their model, thus reducing the effectivness of the so-called agreement between the observed and calculated properties of the *U* band.

The purpose of the present paper is to show that a simpler model, with fewer unknown parameters, may be used to analyze the *U*-band shape. In particular, we apply the "single-effective-frequency" model customarily used for analyzing the *F*-band shape, to our data on CsBr:H^- and to the data of Baldini *et al.*[4] on H^- and D^- centers in KCl, KBr, and RbCl. The temperature dependence of the half-widths and the peak positions are evaluated. Estimates of the Huang-Rhys factor *S* which represents the most probable number of phonons participating in an electronic transition are carried out assuming Gaussian or Poisson band shapes. Peak positions for the *U* emission bands in luminescence are also predicted.

III. *U* BAND IN CsBr

A preliminary study of the *U* band in CsBr has already been reported by us.[5] In this paper we use the data of Ref. 5 and some additional new data on the *U* center in CsBr for the purpose of a thorough analysis using the method of moments.

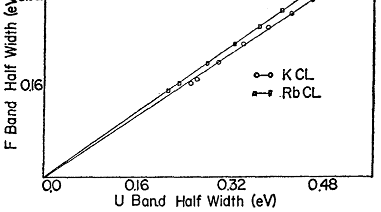

FIG. 2. Half-width of the *F* band versus the half-width of the *U* band in KCl and RbCl. Points correspond to a temperature range of 6–366°K at intervals of 40°K. (Data from Refs. 4, 8, and 9.)

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[11] See Ref. 6, especially Fig. 5.

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A. Shape of Absorption Band

The method of moments developed by Lax[13] and by O'Rourke[14] has been employed extensively in the analysis of the F absorption band shape.[8,9,15] The nth moment is defined by

$$M_n=\frac{1}{M_0}\int_{\text{band}}\alpha(\epsilon)\epsilon^n d\epsilon\,, \tag{1}$$

where ϵ is the photon energy and $\alpha(\epsilon)$ is the absorption coefficient at ϵ. M_0 represents the area under the absorption curve. The first moment gives the average value of the distribution, and the second moment defined about the mean $\bar{\epsilon}(\epsilon)$

$$m^2=\int_{\text{band}}\alpha(\epsilon)(\epsilon-\bar{\epsilon})^2 d\epsilon \tag{2}$$

gives the spread of the distribution. The higher moments, third, fourth, etc., yield the skewness of the distribution. We shall evaluate the zeroth, first, and second moments of the U band in CsBr at different temperatures.

The high-energy side of the U band lies close to the absorption edge of CsBr. This requires careful consideration in order to find out the true absorption-band shapes. Urbach[16] first pointed out that the absorption coefficient at the long-wavelength edge of the fundamental absorption in solids varies as

$$\alpha(\epsilon)=\alpha_0\exp[-\sigma_0(\epsilon_0-\epsilon)/kT]\,, \tag{3}$$

where α_0, σ_0, and ϵ_0 are three determinable constants. This rule has been found to hold good experimentally in a number of materials.[17,18] Klick, Patterson, and Knox[19] have examined critically the validity of this rule for absorption bands in KCl:F and KCl:Tl$^+$. Several theoretical studies have been made and a number of physical mechanisms were proposed[18,19] leading to the exponential tail of the absorption band.

The Urbach formula was fitted to the absorption curves on both sides of the U bands in regions away from the bands themselves. The background absorption due to the host lattice in the U-band absorption region was next obtained by an interpolation of the Urbach formula. The "true" U absorption band shapes were found by subtracting the respective background absorption from the total absorption spectra (see Fig. 3).

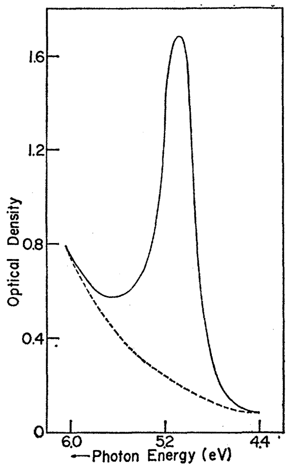

FIG. 3. U-band alsorption in CsBr at 85°K. Solid line: experimental data; dashed line: background calculated by Urbach's rule (see text).

TABLE I. Band parameters for the U band in CsBr (see text for notation).

T (°K)	ϵ_p (eV)	$H(T)$ (eV)	$Mo/\alpha_m H$	$\bar{\epsilon}$ (eV)	m (eV)	H/m
6	5.11	0.26	1.125	5.11	0.1247	2.089
85	5.08	0.32	1.127	5.10	0.1561	2.049
193	5.04	0.43	1.089	5.08	0.1972	2.181
297	4.98	0.54	1.109	5.04	0.2565	2.105
350	4.94	0.60	1.113	5.00	0.2799	2.143
361	4.95	0.61	1.109	5.00	0.2787	2.189

Average $H/m=2.110$

Once the U-band shapes were known at various temperatures, the zeroth moment (area under the curve), the first (corresponding to the peak position), and the second moment (corresponding to the half-width) were computed as functions of temperature. The results are shown in Table I. Here we note the following points:

(i) The zeroth moment M_0 is independent of temperature and is given by

$$\int_{\text{band}}\alpha(\epsilon)d\epsilon=a\alpha_m H\,, \tag{4}$$

where α_m is the maximum absorption coefficient, H is the half-width, and a is a constant, sometimes referred to as Smakula's constant.[20] Values of a are also listed in Table I.

(ii) The first moment $\bar{\epsilon}$ does not change appreciably over the temperature range considered. The variation in $\bar{\epsilon}$ with temperature shows[21] the change in force constant when the electron is in the excited state.

(iii) The ratio of the half-width to the square root of the second moment (i.e., H/m) is independent of temperature and its average value is 2.11.

In order to compare the U absorption band shape at different temperatures, the absorption curve was normalized with respect to maximum absorption coefficient and half-width, and the origin was shifted so that ϵ_r and ϵ_v coincide at each temperature, where ϵ_r and ϵ_v are, respectively, photon energies at low- and high-energy sides of the U band at half-height. The normalized

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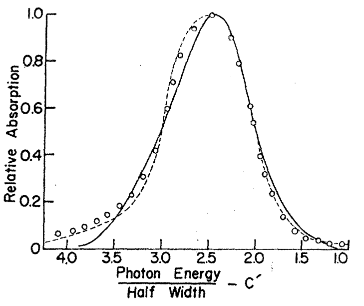

FIG. 4. Normalized U-band shapes in CsBr. Solid line: 361°K; circles: 85°K; dashed line: 6°K.

curves for 361, 85, and 6°K are compared in Fig. 4. The low-energy sides of the bands coincide well, but there are some deviations in the high-energy side. This deviation may be due to the uncertainty in selecting the appropriate points on the exponential-decay part of the absorption edge for evaluating the contribution from the absorption edge. The average of the curves, as given by the dashed curve of Fig. 5, is considered as the representative experimental curve, which is next compared with the theoretical absorption band shapes.

In the case of the F center, the single effective frequency model predicts[15] that the shape of the F band should be a Poisson distribution at low temperatures and a Gaussian distribution at high temperatures. The Poisson distribution is defined as

$$G(P)=S^Pe^{-P}/S!\,, \tag{5}$$

where P is the number of phonons created and S is the most probable number of phonons created after an electronic transition and is known as the Huang-Rhys factor. The average U band in CsBr is compared with the normalized Poisson distribution for $S=116$ in Fig. 5. The method for determining the Huang-Rhys factor S is discussed below. The agreement between the calculated and the experimental curves is fairly good in the low-energy side, while some deviation is apparent in the high-energy side, where the average experimental curve is not so reliable.

B. Temperature Dependence of Half-Width

The configurational coordinate model introduced by Von Hippel[22] and later used by Seitz[23] was applied to the understanding of the temperature dependence of the half-width of the KCl:Tl luminescence band by Williams and Hebb.[24] Markham and co-workers have used[2,8,9] this model on the half-width of F bands. In this case, the theory predicts[15] that the second moment varies with temperature as

$$m^2=\hbar^2\omega_e^2S\coth(\hbar\omega_e/2kT)\,, \tag{6}$$

where ω_e is an effective phonon frequency participating in the broadening process. Applying this model to the U band in CsBr, we notice from Table I that $H/m=2.11$ and is independent of temperature. Equation (6) may thus be rewritten as

$$H^2(T)=H^2(0)\coth(\hbar\omega_e/2kT)\,, \tag{7}$$

where

$$H(0)=2.11\hbar\omega_eS^{1/2}. \tag{8}$$

Assuming $H(0)\simeq H(6°\mathrm{K})$, a plot of $\coth^{-1}[H(T)/H(0)]^2$ versus $1/T$ is shown in Fig. 6. Here the plot is a straight line passing through the origin. Within the limits of experimental accuracy, this establishes the existence of a single effective phonon frequency $\hbar\omega_e=0.0114$ eV (91.7 cm^{-1}). In the framework of the present model, if there were more than one interacting phonon frequency, the line would not have passed through the origin.[25] Since at very low temperatures $H(T)\sim H(0)$ and $\coth^{-1}[H(T)/H(0)]^2\sim\infty$, a slight error in $H(T)$ will introduce a large error in $\coth^{-1}[H(T)/H(0)]^2$-versus-$1/T$ plot. Thus points corresponding to temperatures below 80°K were avoided. One may also represent the behavior of the half-width as a function of temperature by a H-versus-$T^{1/2}$ plot.[26] Here again, the high-temperature limit yields a straight line passing through the origin.

The phonon frequency corresponding to the long-wavelength TO and LO modes of oscillation in CsBr are 73 and 112 cm^{-1}, respectively.[27] The analysis of the U-band half-width data, as shown in Fig. 6, on the other hand, yields an effective phonon frequency of 92 cm^{-1}. The effective phonon frequency that interacts with the electronic transition is thus a band-mode frequency and does not correspond to the local mode frequency of 363 cm^{-1} which lies above the optic band continuum.[5]

The extrapolated value of $H(0)\simeq H(6°\mathrm{K})$ is 0.26 eV and the computed effective phonon energy $\hbar\omega_e$ is 0.0114 eV. One thus obtains from Eq. (8) a value of

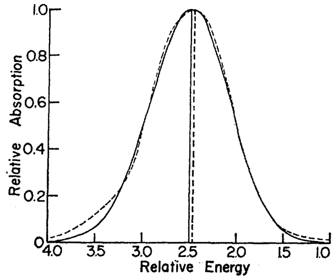

FIG. 5. Comparison of average experimental shape (dashed curve) of the U band in CsBr with one calculated from Eq. (5) with $S=116$ (solid curve).

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[27] E. Burstein, in *Phonons and Phonon Interactions*, edited by T. A. Bak (W. A. Benjamin, Inc., New York 1964), p. 296.

$S=116$ for the Huang-Rhys factor. Using this value of S, the Poisson distribution as given by Eq. (5) was calculated, and its normalized shape is compared with the experimentally determined absorption band in Fig. 5. If one assumes a Gaussian or a Poisson band shape *a priori*, then the ratio H/m is 2.36 instead of 2.11 as determined from experimental band shape and will give $S=92$. The normalized distributions for $S=92$ and $S=116$, however, are almost the same, except in the tail parts of the curves.

C. Temperature Dependence of Peak Position

Here we consider how the peak position of the U band in CsBr varies as the temperature changes. For the peak position of the F band, the single effective frequency model predicts[15] that

$$\epsilon_p(T)=\text{const}+\tfrac{1}{2}\hbar\Delta\omega\coth(\hbar\omega_e/2kT)\,, \qquad (9)$$

where $\Delta\omega$ is the difference between the sum of the angular frequency of all participating vibrational modes in the electronic ground state and the excited state. The data on CsBr:H$^-$ have been expressed by

$$\epsilon_p=C+D\coth(\hbar\omega_e/2kT) \qquad (9')$$

and are shown in Fig. 7. This yields $C=5.11$ eV and $D=-0.0367$ eV. Comparing Eqs. (9) and (9′), one obtains $\Delta\omega=-2\pi(1.773\times10^{13}\ \text{sec}^{-1})$ which corresponds to $-591\ \text{cm}^{-1}$. If only a single phonon mode were involved in the electron-phonon interaction, one should find $\Delta\omega\ll\omega_e$. Instead, one finds $\Delta\omega\gg\omega_e$, as has also been found for the F band in a number of alkali halides.[8,9] The reason for this is that ω_e is not a single phonon frequency, but rather a weighted mean phonon frequency of the host lattice. After an electronic transition, the individual phonon frequencies may change slightly, leaving the weighted mean ω_e virtually unchanged, but giving rise to a large difference in the sum of all phonon frequencies. In the case of the F band in KCl, the ratio $\Delta\omega/\omega_e$ was found[8] to be 4.40. This ratio for the U band in CsBr is 6.44.

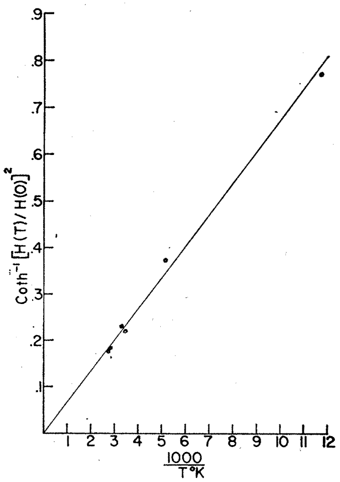

FIG. 6. Plot of $\coth^{-1}[H(T)/H(0)]^2$ of the U band in CsBr versus reciprocal of temperature.

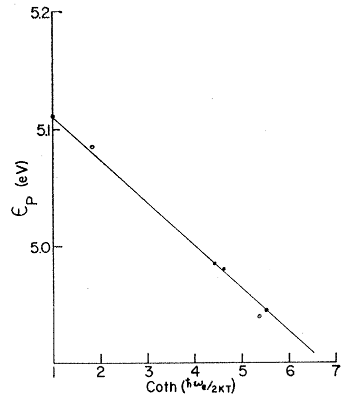

FIG. 7. Temperature dependence of the peak position of the U band in CsBr fitted to Eq. (9′).

Recently an electron-phonon interaction potential based on long-range Coulomb interactions has been proposed for the F center and has been successfully applied to calculate the half-width and effective lattice frequency for the F band in NaCl and KCl.[28] This method may also be applied to the U center. Thus, on the Ritter-Markham-Stettler model[28] one would expect that the effective frequency for the F center would approximately equal the one for the U center.[29]

IV. U BANDS IN ALKALI HALIDES WITH NaCl STRUCTURE

The temperature dependence of the first electronic transitions of H$^-$ and D$^-$ centers in KCl, KBr, and RbCl have been investigated in detail by Baldini *et al.*,[4] who covered the temperature range 4–400°K. Their data on the temperature dependence of the half-width and the peak positions of the U bands will be next analyzed by means of a single effective frequency model, salient results of which were described in Sec. III in connection with analysis of data on the U band in CsBr.

Baldini *et al.*[4] have reported their experimental data in the following functional forms:

$$H^2(T)=A^2\coth(\hbar\omega_2/2kT)+3\ln 2\hbar^2[(\omega_g^2-\omega_u^2)/\omega_g]^2 \times\coth^2(\hbar\omega_g/2kT) \qquad (10)$$

and

$$\epsilon_p(T)=E-B\coth(\hbar\omega_1/2kT)-\tfrac{3}{4}\hbar[(\omega_g^2-\omega_u^2)/\omega_g] \times\coth(\hbar\omega_g/2kT)\,, \qquad (11)$$

where A, E, B, ω_1, ω_2, ω_g, and ω_u are fitting parameters determined for the best fit of the experimental data. For our purpose, with the help of these constants, inter-

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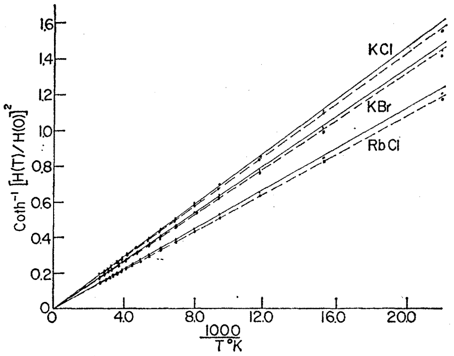

FIG. 8. Data on KCl:H$^-$, KCl:D$^-$, KBr:H$^-$, KBr:D$^-$, RbCl:H$^-$, and RbCl:D$^-$ fitted to Eq. (7). Solid lines: H$^-$ centers; dashed lines: D$^-$ centers.

polated values of $H(T)$ and $\epsilon(T)$ have been obtained in the temperature range 6–386°K at intervals of 20°K. These interpolated values as such have been treated as experimental data in our analysis.

Assuming $H(6°\mathrm{K})\sim H(0)$, $\coth^{-1}[H(T)/H(0)]^2$ versus $1/T$ is shown in Fig. 8 for KCl:H$^-$, KCl:D$^-$, KBr:H$^-$, KBr:D$^-$, RbCl:H$^-$ and RbCl:D$^-$. For the reasons given above, this plot was limited to the temperature range 66–386°K. A family of straight lines passing through the origin are obtained (Fig. 8). As indicated by Eq. (7), slopes of these lines give the effective frequency of the interacting phonons. These are listed in Table II. For comparison, the corresponding effective phonon frequencies for the F band are also included in Table II. The following significant points may be noted. (i) In each case considered, a single effective phonon frequency expresses the temperature dependence of the half-width well. (ii) The phonons interacting with the optic electron responsible for the U absorption band are band phonons. In the framework of the present model, it is not necessary to invoke the participation of a localized mode. (iii) The effective phonon frequencies for the H$^-$ and D$^-$ centers in any given alkali halide are, within the limits of experimental accuracy, equal. If any significance at all is to be attached to the slight difference between $\omega_e(\mathrm{H}^-)$ and $\omega_e(\mathrm{D}^-)$, it may be noted that in every case $\omega_e(\mathrm{H}^-)\geqslant\omega_e(\mathrm{D}^-)$, as it should be for a very slight perturbation of band phonons by impurities of different masses. (iv) The effective phonon frequencies responsible for the broadening of F and U bands are nearly equal, confirming our original contention that the nature of the electron-phonon interaction in the F and U centers are very similar. The model normally used for the understanding of the temperature dependence of the F-band shape should thus also be applicable to the understanding of the U-band shape. It is therefore not essential to introduce a more complicated model for the U center utilizing a large number of arbitrary parameters.

For Gaussian or Poisson band shape, the ratio $H(0)/m$ is 2.36. Employing the relation $H(6°\mathrm{K})=2.36\hbar\omega_e S^{1/2}$, the Huang-Rhys factor has been evaluated for each system considered. Values of S thus obtained are also listed in Table II. It may be noticed that S for H$^-$ and D$^-$ centers in any given alkali halide is the same and is two to three times larger than the S for the F center.

TABLE II. Effective phonon frequency and Huang-Rhys factor for H$^-$, D$^-$, and F centers in alkali halides of NaCl structure.

Crystal	Center	$\hbar\omega_e$ (cm^{-1})	S
	H$^-$	101.2	68
KCl	D$^-$	100.1	68
	F^{a}	98.6	28
KBr	H$^-$	93.6	79
	D$^-$	92.4	80
	H$^-$	78.2	83
RbCl	D$^-$	76.6	84
	F^{b}	81	31

[a] Data from Ref. 8.
[b] Data from Ref. 9.

The peak positions of the H$^-$ and D$^-$ bands are next fitted to the relation (9′). Plots of ϵ_p versus $\coth(\hbar\omega_e/2kT)$ are shown in Fig. 9 for KCl:H$^-$ and KCl:D$^-$. The ω_e's used in these plots are the same ω_e's determined from the data on half-widths as listed in Table II. The plots, as expected, are straight lines except at very low temperatures, where the value of $\coth(\hbar\omega_e/2kT)$ approaches unity. Similar curves were drawn for KBr and RbCl also. In Table III are listed the constants C and D of Eq. (9′) and also $\Delta\omega/\omega_e$ as defined earlier. $\Delta\omega/\omega_e$ is nearly 6 in all cases and agrees fairly well with the value for the F center.[8]

V. ISOTOPE SHIFT

When the H$^-$ center is replaced by the D$^-$ center in an alkali halide, the measured U absorption band position shifts by 0.02 eV towards the high-energy side.[4] Baldini *et al.*[4] have accounted for this isotope shift in terms of an infrared-active local mode. Recently, Mathew and Hart-Davis[30] have developed a model which also utilizes an electron-local mode coupling. However, both these models are *ad hoc* in the sense that they do not present an independent confirmation of an interaction involving a localized vibrational mode. In particular, we have already pointed out several inconsistencies of the model used by Baldini *et al.* Furthermore, the body of evidence presented in this paper, specifically the remarkable similarity between the U and F centers, makes the role of local modes in the U-band absorption process extremely doubtful.

We have a simple explanation for the isotope shift in terms of our model. We believe that the isotope shift consists of two parts—a blue shift arising from a change of volume of the octahedron surrounding a U center

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[30] J. A. D. Matthew and A. Hart-Davis, Phys. Rev. 168, 936 (1968).

TABLE III. Fitting parameters for Eq. (9′).

Center	C (eV)	$-D$ (eV)	$(\Delta\omega)/\omega_e$
KCl:H^-	5.911	0.0394	6.25
KCl:D^-	5.927	0.0371	5.99
KBr:H^-	5.544	0.0360	6.15
KBr:D^-	5.557	0.0328	5.70
RbCl:H^-	5.529	0.0304	6.20
RbCl:D^-	5.545	0.0284	6.05
CsBr:H^-	5.110	0.0367	6.44

when the H^- ion is replaced by a D^- ion, and a smaller red shift due to the very small difference in the effective phonon frequencies involved.

It is not possible to determine the actual change in volume. However, it is certain that a decrease in volume takes place around the center when a D^- ion replaces an H^- ion. An approximate estimate of this change is possible. For example, the lattice constant[31] of LiD is 4.065 Å compared with a value of 4.085 Å in LiH. Both LiH and LiD crystallize in the NaCl structure. Similar change in the lattice constant upon deuteration is likely in other alkali hydrides as well. Finally, it may be assumed that the linear dimensions of the octahedron surrounding a *U* center in an alkali halide also undergo changes of this order when the H^- ion is replaced by a D^- ion.

Using a point-ion model, Spector *et al.*[6] have shown that the *U*-band peak positions follow an Ivey relation

$$\epsilon_P = \text{const}/a^n, \tag{12}$$

where a is the lattice constant. The theoretical value of n was found to be 1.14, which compares very well with a value of 1.10 found experimentally.[32] The blue shift due to the change in volume upon deuteration then is given by $\delta\epsilon_P/\epsilon_p = n\delta a/a = 5.58\times10^{-3}$, where we have used the theoretical value of n and $\delta a/a$ from the LiH, LiD lattice-constant data cited earlier.

In addition to this a small red shift is expected due to the slightly different Stokes shift arising from a small difference in the effective band mode phonon frequency of the lattice for the H^- and D^- impurities. From Table III it may be noted that on the average $(\omega_e)_{H^-} - (\omega_e)_{D^-} = 1.3$ cm^{-1}. The average Huang-Rhys factor S for the *U* center in the NaCl-type crystals is about 77. Thus the red shift arising from the different Stokes shift of H^- and D^- ions is approximately given by $\delta\epsilon_P/\epsilon_P = -2.19\times10^{-3}$.

TABLE IV. Experimental and theoretical values of the *U*-band energy in eV (at 300°K).

Host lattice	Theory (without Stokes-shift correction)[a]	Values corrected for Stokes shift	Expt.
KCl	4.84	5.70	5.79[b]
KBr	4.60	5.52	5.43[b]
RbCl	4.60	5.41	5.41[b]
CsBr	4.16	5.21	4.99[c]

[a] From Ref. 6.
[b] From Ref. 4.
[c] From Ref. 5.

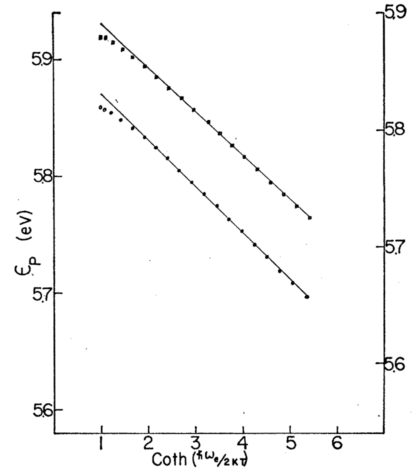

FIG. 9. Peak positions of the *U* bands due to H^- and D^- centers in KCl as functions of temperature fitted to Eq. (9′). lower curve: H^-; upper curve: D^-. The right-hand ordinate is for the data on D^-.

The total expected relative isotope shift upon deuteration is thus about 3.39×10^{-3} in the dimensionless unit considered so far. In comparison, the experimental values[4] are 3.41×10^{-3} for KCl, 3.45×10^{-3} for KBr, and 3.64×10^{-3} for RbCl. Considering the various approximate estimates involved in the calculated isotope shift, the agreement is almost fortuitously good.

VI. STOKES SHIFT AND PREDICTED POSITIONS OF *U* EMISSION BANDS

The *U* absorption band positions in alkali halides of both NaCl and CsCl structures were predicted by Spector *et al.*[6] using a point-ion model. The predicted values were consistently lower than the experimental values by about 16%. One of the reasons for this discrepancy may be due to the fact that the electron-phonon interaction was not explicitly taken into consideration. With the knowledge of the Huang-Rhys factor and the effective phonon frequencies these values can now be approximately corrected for the expected Stokes shift. The corrected values are given in Table IV. The agreement is good, but may only be regarded fortuitous, because it is not certain what the point-ion model really calculates.[33] Specifically, it is not readily apparent if the phonon contribution is truly implied in a point-ion model or not. The values given by the point-ion model are usually too low and any correction of an electron volt or so helps.

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TABLE V. Predicted U luminescence band peak positions.

Crystal	ϵ_p (eV)
KCl	4.07
KBr	3.58
RbCl	3.79
CsBr	2.89

It is possible to predict the peak positions of the U-center luminescence band from the consideration of the Stokes shift. To date, however, no emission study of the U center has been made, presumably because of the relative unstability of the U center when irradiated by ultraviolet light. In the case of the F center, the Huang-Rhys factor for absorption and emission does not differ. If we assume that the same is true in the case of the U center, the Stokes shift between the emission and absorption bands will be given by $2\hbar\omega_e S$. The estimated U emission band positions are given in Table V. Some of the problems involving the study of luminescence spectrum of the U center have been discussed elsewhere[6] and will not be elaborated here.

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Defect Cluster Centers in MgO[†]

Y. CHEN, R. T. WILLIAMS,[*] AND W. A. SIBLEY

Solid State Division, Oak Ridge Hational Laboratory, operated by Union Carbide Corporation for the U. S. Atomic Energy Commission, Oak Ridge, Tenenssee 37830

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A study of the production and annealing of defect cluster centers in MgO single crystals has been undertaken. A comparison of the annealing of single negative-ion vacancies in neutron-irradiated, electron-irradiated, and Mg-additively colored samples is made. The results indicate that isolated negative-ion vacancies are not mobile below 900°C, and the annealing of these defects at lower temperatures in irradiated crystals is due to interstitial migration. The broad absorption bands at 352, 573, and 975 nm and the zero-phonon lines observed in neutron-irradiated crystals, previously proposed as due to F-aggregate centers, are not observed in electron-irradiated and additively colored samples even after annealing. Therefore, there is some uncertainity whether these lines and/or bands are due to F-aggregate centers.

INTRODUCTION

COLOR centers in MgO have been studied extensively the past few years.[1–13] The most intense optical absorption band in these crystals whether neutron-irradiated, electron-irradiated, or additively colored occurs at 250 nm. There is little doubt that this band is due to F-type (oxygen vacancy) centers. In fact, it may be due to both positively charged F^+ centers (negative-ion vacancies each possessing one electron)[14] and neutral F centers (negative-ion vacancies each with two electrons), absorbing light at about the same wavelength.[15]

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[*] Oak Ridge Associated Universities Undergraduate Research Participant from Wake Forest University, now at Princeton University, Princeton, N. J.

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