[14] L. Bohlin and T. Högberg, J. Phys. Chem. Solids 29, 1805 (1968).

[15] A. A. Maradudin, A. E. Fein, and G. H. Vineyard, Phys. Status Solidi 2, 1479 (1962).

[16] V. V. Goldman, G. K. Horton, T. Keil, and M. L. Klein, J. Phys. C 3, 133 (1970).

[17] G. K. Horton, V. V. Goldman, and M. L. Klein, J. Appl. Phys. 41, 5139 (1970).

[18] N. S. Gillis, N. R. Werthamer, and T. R. Koehler, Phys. Rev. 165, 951 (1968).

[19] H. Egger, M. Gsänger, and E. Lüscher, Phys. Letters 28A, 433 (1968).

[20] B. Dorner and H. Egger. Phys. Status Solidi 43, 611 (1971).

[21] R. H. Beamont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. (London) 78, 1462 (1961).

[22] V. V. Goldman, G. K. Horton, and M. L. Klein, Phys. Rev. Letters 24, 1424 (1970).

[23] T. R. Koehler, Phys. Rev. Letters 22, 777 (1969).

[24] H. Meixner, G. Winterling, W. Heinicke, and M. Gsänger, Phys. Letters 31A, 295 (1970).

[25] W. S. Gornall and B. P. Stoicheff, Solid State Commun. 8, 1529 (1970).

[26] M. B. Doran and I. J. Zucker, J. Phys. C 4, 307 (1971).

[27] A. Hüller (unpublished).

[28] C. E. Swenberg, Phys. Letters 24A, 163 (1967).

PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

Infrared Absorption of *U* Centers in CsBr and CsI[†]

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(Received 30 April 1971)

Measurements were made of the absorption of the infrared-active local mode of H^- and D^- substitutional impurities in CsBr and CsI from 5 to about 100 K. In CsBr, the T^2 dependence of the half-width above about 30 K indicates the local mode is broadened by the Raman or scattering mechanism, while the constant low-temperature half-widths are characteristic of the decay of the local mode into three (D^-) or four (H^-) lattice phonons. The sidebands are weak, and are described well by the model of Bilz, Fritz, and Strauch, in which the polarizability of the impurity is important. The resultant lattice density of states for CsBr is in good agreement with that calculated by Karo and Hardy using a model with the deformation dipoles on anions only. The main absorption peak in CsI was not Lorentzian, but no origin for the unresolved structure was found. The phonon density of states deduced from the sidebands in CsI agrees reasonably well with Karo and Hardy's calculated curve.

INTRODUCTION

A *U* center is a hydrogen or deuterium negative ion at a normal cation site in an alkali or alkaline-earth halide. The very light mass of this ion results in a threefold degenerate vibrational mode which cannot propagate through the lattice, a mode which is confined to the immediate vicinity of the defect. The excitation of this localized mode gives rise to a narrow temperature-dependent infrared absorption peak.[1] In addition, the defect destroys the translational invariance of the crystal, removing the wave-vector selection rule for optical processes. The result is the occurrence of sidebands on the main local-mode absorption peak, corresponding to the excitation of the local mode plus the creation or absorption of a lattice phonon.

Measurements of the peak position of the local-mode absorption and its dependence on the mass of the defect (isotope effect) give information on the force-constant changes which occur when the defect is introduced. Measurements of the half-width of the local-mode peak as a function of temperature, and its isotope effect, yield information on the anharmonic coupling of the local mode to the lattice, and on the decay mechanism of the excited local mode. The observed sidebands can be compared with the density of states for the phonons in the perfect crystal or, if necessary, in the crystal with defects. The temperature dependence of the peak position can be observed, but its interpretation is not clear.

Studies of the *U* center local mode have been carried out for most alkali halides of the NaCl structure,[1–5] and a very complete study[6] was made for alkaline-earth fluorides. Very little work has been reported for *U* centers in the CsCl lattice, the only work[7–10] being at temperatures above 20 K. The isotope effect was not studied completely, nor was the low-temperature limit of the width of the main peak. Sidebands were found on the CsCl and CsBr local-mode peak,[10] but not CsI, and the resolution was limited. The sidebands are important because the phonon spectrum for the cesium halides has never been measured by inelastic neutron scattering. Our sideband measurements on CsBr strongly favor one of four calculated spectra based on different force-constant models. We also are able to analyze the shape of the main peak in CsBr. Our data on CsI are difficult to interpret, but suggest at least that U center local modes do occur in CsI and that one of the calculated phonon density of states is more suitable than others.

THEORY

In the past ten years local modes have received a great deal of attention. In general a simple mass-defect model produces a sizable error in predicting the local-mode frequency.[11,12] Two approaches have been very successful for U centers in crystals with the NaCl structure. In studying KBr sidebands, Timusk and Klein[13-15] assumed the primary effect of the defect was to change the short-range force constant between the hydride ion and the nearest neighbor. The force-constant change was found by forcing a fit to the local-mode frequency and this parameter was used to calculate a perturbed one-phonon density of states which was then compared to the sideband structure. This model has been used by others to calculate sideband structure[16,17] and the temperature dependence of the half-width of the main peak.[18-20] In an alternate model, Bilz, Fritz, and Strauch[21] assumed the most significant correction to the mass-defect model was the consideration of the hydride polarizability (i.e., a change in a fairly long-range force constant). This model resulted in an isotope shift of the local-mode frequency very nearly $\sqrt{2}$ and only a slight perturbation of the lattice modes. (The isotope shift here is the ratio of position in energy of the main peak for H^- to that for D^-.)

Many of the features of the main peak absorption may be explained without recourse to a detailed model of the defect. Hanamura and Inui[22] have derived an expression for the temperature dependence and isotope dependence of the half-width of the main peak in terms of the anharmonic potential coefficients.

The Hamiltonian of the lattice is

$$H = H_0 + H' ,$$

where H_0 is the harmonic part and H' is the anharmonic part which may be expanded as

$$H' = V^{(3)} + V^{(4)} + V^{(5)} + \cdots .$$

We need only the third-, fourth-, and fifth-order terms. Using creation and annihilation operators for the ith normal mode, we have

$$H_0 = \tfrac{1}{2} \sum_i \hbar\omega_i (b_i^\dagger b_i + b_i b_i^\dagger)$$

and

$$\begin{aligned} H' = {} & \frac{1}{3!} \sum_i \sum_j \sum_k C^{(3)}_{ijk} (b_i + b_i^\dagger)(b_j + b_j^\dagger)(b_k + b_k^\dagger) \\ & + \frac{1}{4!} \sum_i \sum_j \sum_k \sum_l C^{(4)}_{ijkl} (b_i + b_i^\dagger)(b_j + b_j^\dagger) \\ & \times (b_k + b_k^\dagger)(b_l + b_l^\dagger) + \cdots . \end{aligned} \tag{1}$$

The coefficients $C^{(n)}$ are of the form

$$C^{(3)}_{ijk} = \left(\frac{\hbar}{2}\right)^{3/2} \frac{1}{(\omega_i \omega_j \omega_k)^{1/2}} \sum_a \sum_b \sum_c A^{(3)} \frac{v_a v_b v_c}{(m_a m_b m_c)^{1/2}} . \tag{2}$$

$A^{(n)}$ is the nth derivative of the potential evaluated at equilibrium and the v_a are eigenvectors of the harmonic portion of the Hamiltonian. Hanamura and Inui showed that the width of the absorption curve at half-maximum could be expressed as

$$\Gamma_\alpha = \frac{2\pi}{\hbar^2} \frac{\langle \{ [[a_\alpha^\dagger, H'(0)], H'(0)] a_\alpha \} \rangle}{2\bar{n}_\alpha + 1} . \tag{3}$$

$H'(0)$ is the $\omega = 0$ Fourier coefficient of the anharmonic parts of the Hamiltonian and $\bar{n}_\alpha$ is the average phonon number for the local mode. The curly brackets mean symmetrize. In the above equation and the following discussion, a and $a^\dagger$ will be used for operators which are restricted to local modes. The operators b and $b^\dagger$ refer only to lattice modes. Similarly ω_α is a local-mode frequency and m_α is the U center mass where the subscript α may refer either to hydrogen or deuterium.

Each of the terms of the anharmonic portion of the Hamiltonian may be expanded and many of the cross terms identified with physical processes. The terms to be discussed are listed in Table I.

Half-Width of Main Peak

The restriction from Eq. (3) that terms leading to broadening have no net frequency change restricts broadening mechanisms. Broadening mechanisms are identified in Table I by the δ function. We now discuss these terms. The decay of the local mode into two lattice modes is energetically not possible for any of our samples. All local-mode frequencies are higher than twice the highest lattice-mode frequency, which is that of the long-wavelength longitudinal optical mode. Decay into three lattice modes is energetically allowed in CsBr : D^- and CsI : D^- but not for hydride U centers in these salts. From Eq. (3) this process leads to a half-width varying as T^2 at high T and to a constant finite width at low temperature.[18,21,22] The low-temperature half-width is determined by $C^{(4)}$ which depends on $A^{(4)}$, the defect mass, and the local-mode frequency. The "scattering" term $a a^\dagger b_i b_j^\dagger \delta(\omega_i - \omega_j)$, also called the Raman or modulation term,[6,18,19,21] is allowed for all U centers. A lattice mode is scattered into another mode of different wave vector, but the same frequency. This "interrupts" the local-mode vibration and gives a lifetime broadening. The half-width varies as T^2 at high T and goes to zero at low T. Decay of a local mode into four lattice modes is possible for all the *U* centers we have studied, and is the simplest decay mechanism available for our hydride *U* centers. It comes from $V^{(5)}$. The half-width varies as T^3 at high T and goes to a constant at low T. Broadening through interaction of two local modes should be negligible since the modes are well localized and the *U* center concentration is low.

Harmonics

The double excitation of a local mode is symmetry forbidden for impurities on sites of O_h symmetry, but the triple excitation ($\Delta n = 3$) is allowed.[6] It should give rise to absorption at three times the energy of the main peak. Other high-order terms in Eq. (1) play no role in the discussion.

Sidebands

The third-order anharmonic term may produce sidebands. Some of the most important features are independent of the detailed model used. If the frequency dependence of the eigenvectors is neglected, Eq. 2 shows the frequency dependence of $V^{(3)}$ to be $1/\omega_a \sqrt{\omega_i}$. This leads to the functional form of $(\omega_i^\pm)^2 \rho\,(\omega_i^\pm)$ for the sideband absorption coefficient due to the third-order anharmonic potential, where $\omega_i^\pm$ is the frequency with respect to the local mode, $|\omega_i - \omega_\alpha|$. There are several important qualifications. The above frequency dependence is not correct for low-frequency lattice phonons. In this range the sidebands are proportional to $\omega_i^\pm \rho\,(\omega_i^\pm)$.[21] $\rho(\omega_i^\pm)$ is the perturbed one-phonon density of states, but including only those phonons that couple to the *U* center. It is not possible to couple to all lattice phonons due to parity considerations. This will be discussed in detail later. The coupling mechanism determines the degree of perturbation of the perfect lattice density of states. A model employing a large change in force constant[11–13,15,16] will result in a significant perturbation of the phonon spectra with the possibility of introducing gap modes in crystals which have a gap in their phonon spectrum. On the other hand the model of Biltz, Fritz, and Strauch[21] results in a very slight perturbation since the force constant is not changed. Sidebands can also result from a deformation dipole mechanism,[23] but most authors find this does not fit experiment. Page and Dick[17] show that it can give sidebands in reasonable agreement with experiment. We fit our results to theory without their use.

There has been some controversy about whether the integrated area of the absorption peak should be temperature independent when the anharmonic terms are considered. It now appears that the area of the main peak plus the area under all sidebands should be a constant as long as deformation dipoles are unimportant. The early experimental results were not in agreement on the temperature dependence of the area.

EXPERIMENTAL

U centers were produced by additively coloring crystals with potassium and then heating the crystals to 425 °C in a hydrogen (1400 psi) or deuterium (600 psi) atmosphere. Concentration adjustments were made by varying the *F* center concentration. Relative concentrations were monitored by measuring the ultraviolet *U* band due to electronic excitation of the *U* center electron.[9]

Since CsBr and CsI do not cleave, it is difficult to measure the absorption coefficient in the peak of the ultraviolet *U* band for large concentrations of *U* centers. Moreover, the *U* center distribution was far from uniform. The *U* center concentration was higher near the faces of the crystals. A slice from the surface of one sample was thinned

TABLE I. Some terms in the anharmonic Hamiltonian. Those terms with a δ function are possible broadening mechanisms. The δ function is not part of H' but was added as a label. It is needed in Eq. (3).

Order	Term	Process
3	$a^\dagger b_i b_j \delta(\omega_\alpha - \omega_i - \omega_j)$	Two-phonon decay
	$a a^\dagger b_i$	High-frequency sideband
	$a a^\dagger b_i^\dagger$	Low-frequency sideband
	$a a^\dagger a$	Second harmonic
4	$a^\dagger b_i b_j b_k \delta(\omega_\alpha - w_i - \omega_k)$	Three-phonon decay
	$a a^\dagger b_i b_j{}^\dagger \delta(\omega_i - \omega_j)$	Raman, modulation, or scattering process
	$a a^\dagger b_i b_j$	Two-phonon high-frequency sideband
	$a a^\dagger b_i b_j{}^\dagger$	Two-phonon difference sideband
	$a a^\dagger b_i{}^\dagger b_j{}^\dagger$	Two-phonon low-frequency sideband
	$a a^\dagger a a$	Third harmonic
	$a_i a_j{}^\dagger a_j a_j{}^\dagger$	Broadening by interaction between two local modes
5	$a^\dagger b_i b_j b_k b_l \delta(\omega_\alpha - \omega_i - \omega_j - \omega_k - \omega_l)$	Four-phonon decay
	$a^\dagger b_i{}^\dagger b_j b_k b_l \delta(\omega_\alpha + \omega_i - \omega_j - \omega_k - \omega_l)$	Decay process energetically allowed for D⁻ centers

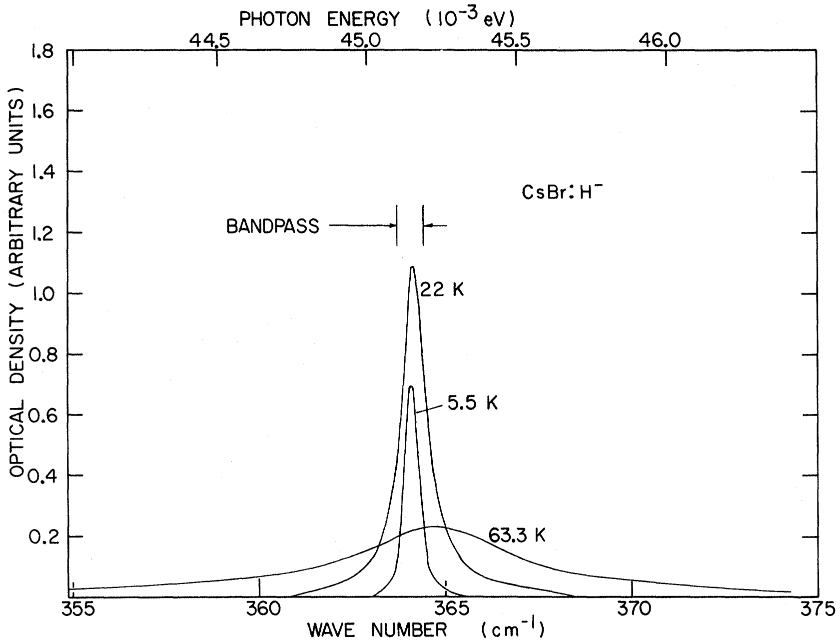

FIG. 1. Absorption spectrum of CsBr: H⁻ at several temperatures.

to 0.2 mm. It had an optical density of 5–7 at the *U* band peak, corresponding to about 10^{18} (*U* centers)/cm^3 if the oscillator strength is 1. Comparing the infrared absorption peaks of all our samples with this one leads us to estimate a range 10^{17}–5×10^{18} (*U* centers)/cm^3 in the various samples we measured. The hydrogen concentrations of several moderately densely colored samples were measured by the pH change upon solution. They were about 10^{18} (*U* centers)/cm^3 for an average over the volume of the samples.

Transmission measurements were made using a conventional optical cryostat with liquid-helium temperature polyethylene exchange gas windows. Samples for main peak measurements were mounted in poor thermal contact to the sample holder. Adjustments in the exchange gas pressure resulted in sample temperatures between 5 and 37 K as measured with a Au–0.02% Fe | Cu thermocouple imbedded in the sample. Measurements at higher temperatures were made as the sample warmed after the helium evaporated. With a good vacuum in the exchange gas space, temperature drift during a scan was no problem.

Two different spectrometers were used. In measuring the main peak absorption the primary considerations were high resolution and wavelength stability. The monochromator used was a single-pass Perkin-Elmer 98G grating monochromator. A Ge : Zn detector was used for all measurements except for the CsI : D^- peak at 50 μm, where a thermocouple was used. Order-sorting was done with bandpass filters, plus reststrahl filters, where necessary. Normally, stray light was not a problem since the doped detector sensitively was lower for higher-order light. Measurements of very dense samples showed a negligible amount of stray light at the *U* center peak. The exception to this was CsI : D^- where appropriate corrections were made.

The absorption due to *U* centers was measured by alternately scanning a sample and a blank of the same material and equal thickness. Over most of the temperature range studied, the apparent shape of the main peak absorption was influenced by the bandpass of the spectrometer (typically 0.6–0.7 cm^{-1}). Whenever possible the correction tables compiled by Ramsay[24] were used.

The sideband spectra were measured on a double-pass prism monochromator (Perkin-Elmer model 99) with a thermocouple detector. The absorption was measured point by point, again using a blank to eliminate the effect of reflection losses and host lattice absorption. Because of nonuniformity in the samples, the absorption was measured at constant slit width which resulted in rather poor wavelength resolution in some regions.

DISCUSSION

U centers in CsBr and CsI have somewhat different properties and will be discussed separately. Representative absorption curves for the CsBr : H^- and CsBr : D^- local modes are given in Figs. 1 and 2. They are generally symmetric, have a pronounced temperature-dependent width, and have a slight shift of peak energy with temperature. The apparent large change in integrated absorption as a function of temperature is a manifestation of

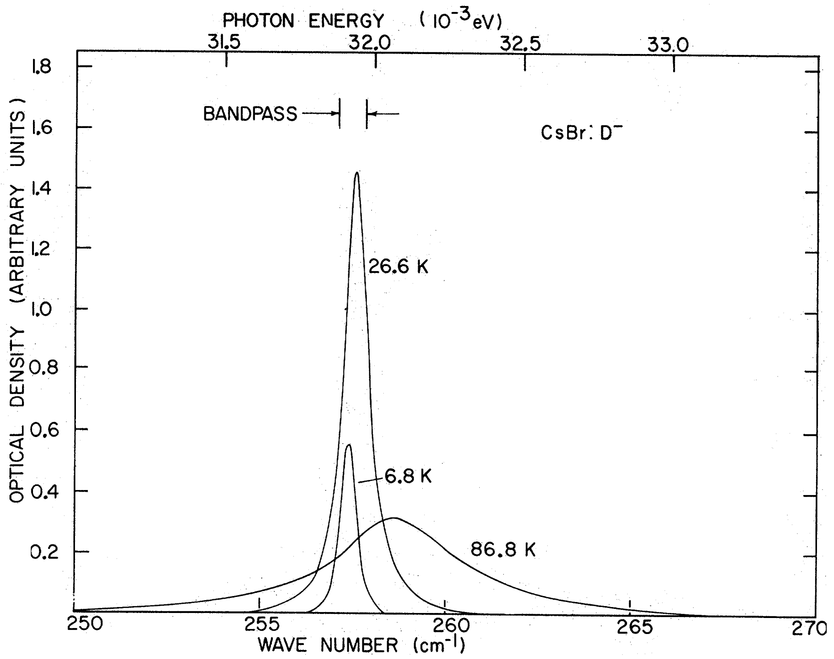

FIG. 2. Absorption spectrum of CsBr : D$^-$ at several temperatures.

finite bandpass. As the width of a true absorption band becomes very narrow with respect to the bandpass of the monochromator, the apparent absorption will decrease in strength.[25] The corrections at very low temperature would be so large that they cannot be made accurately. However, an absorption strength independent of temperature would be within the probable range of our corrected measurements.

Most features of the CsBr *U* center local-mode absorption can be explained in terms of the models mentioned. Figure 3 shows the half-width of CsBr : H$^-$ as a function of T^2. In the range where it was possible the half-width has been corrected using the tables compiled by Ramsay.[26] The corrections cannot be applied below 25 K as the measured width is too narrow. To examine this region, the inset shows the half-width of the measured transmission plotted as a function of T^2. The absorption becomes extremely narrow but finite and apparently constant by 8 K.

Figure 4 is a similar plot for CsBr : D$^-$. In general this peak is narrower and bandpass corrections cannot be applied below 40 K. The temperature dependence of the half-width is T^2 from 40 to 95 K, where it becomes somewhat less. At low temperatures the transmission half-width approaches a constant value. Dötsch and Mitra[10] found a half-width varying between T^1 and T^2 for $T > 100$ K, while the behavior below this temperature was obscured by finite bandpass effects.

The highest lattice-mode frequency $\omega_{LO} = 118$ cm^{-1} is known for CsBr at 4 K from recent data.[27,28] The decay of the CsBr : H$^-$ local mode into lattice modes requires four lattice phonons leading to a T^3 dependence at high temperature and going to a constant value at $T = 0$, determined in part by the magnitude of the fifth-order anharmonic term. The CsBr : D$^-$ local mode could decay into three lattice phonons through the fourth-order term. The temperature dependence for this would be T^2, again going to a constant at $T = 0$. The actual mechanism appears to be the scattering or modulation term which goes as T^2 for both centers. The isotope effect in the half-width comes from the isotope mass and local-mode frequency. [Eq. (2)]. Theory for the scattering process gives a ratio of half-widths of 2, in agreement with our data above 40 K. At low temperatures the modulation term goes to zero and the relatively weak decomposition terms predominate. That the CsBr : D$^-$ width is greater in this limit is an indication that the fourth-order anharmonic term is larger than the fifth-order term and/or that the one-phonon density of states is larger at $\frac{1}{3}\omega_D$ than at $\frac{1}{4}\omega_H$. Ivanov *et al.*[18] have shown that a slight admixture of the two mechanisms can maintain a T^2 dependence to quite low temperatures.

Fig. 5 shows the peak energy for both isotopes as a function of temperature. Each approaches a constant value at low temperature: 364.08 cm^{-1} eV for CsBr : D$^-$ and 257.40 cm^{-1} eV for CsBr : H$^-$.[29] The ratio of peak energies is 1.414, the square root of 2 within the limits of wavelength calibration. This supports an essentially static lattice model, or a model such as that of Bilz *et al.*[21]

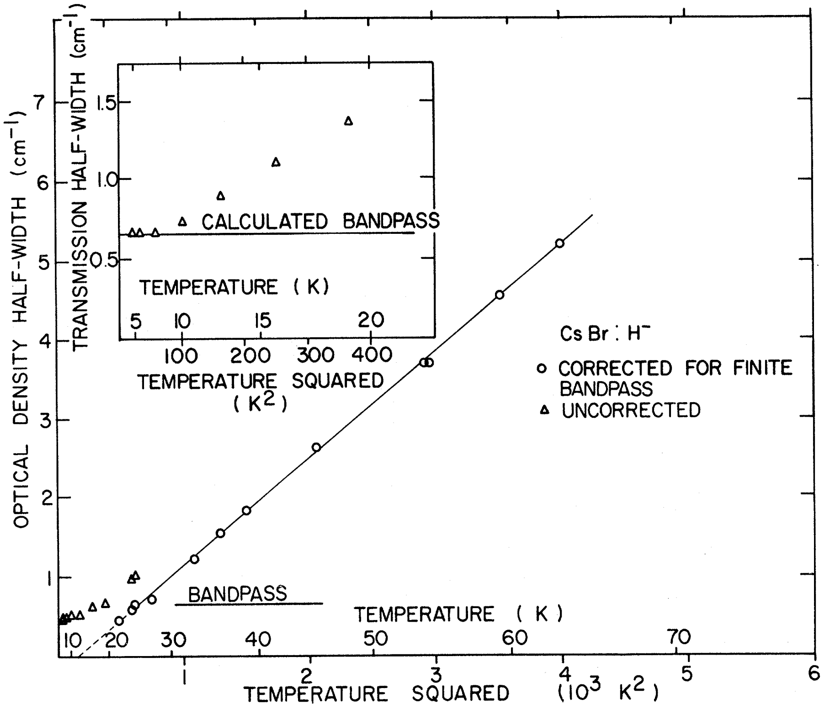

FIG. 3. Half-width of the CsBr:H⁻ local-mode absorption vs the square of the temperature, with and without corrections for finite bandpass of the monochromator. The inset shows the "limiting" behavior at low temperature.

in which the H⁻ polarizability rather than a short-range force-constant change is the main feature. The energies of the peaks at 100 K are in good agreement with those of Ref. 10.

Both *U* centers show a positive energy shift which is linear with temperature. Again neglecting the high-temperature data for CsBr:D⁻, we obtain

$$\hbar\left(\frac{\partial\omega_H}{\partial T}\right)_p = 1.79\times10^{-6}\ \mathrm{eV/K}\,,$$

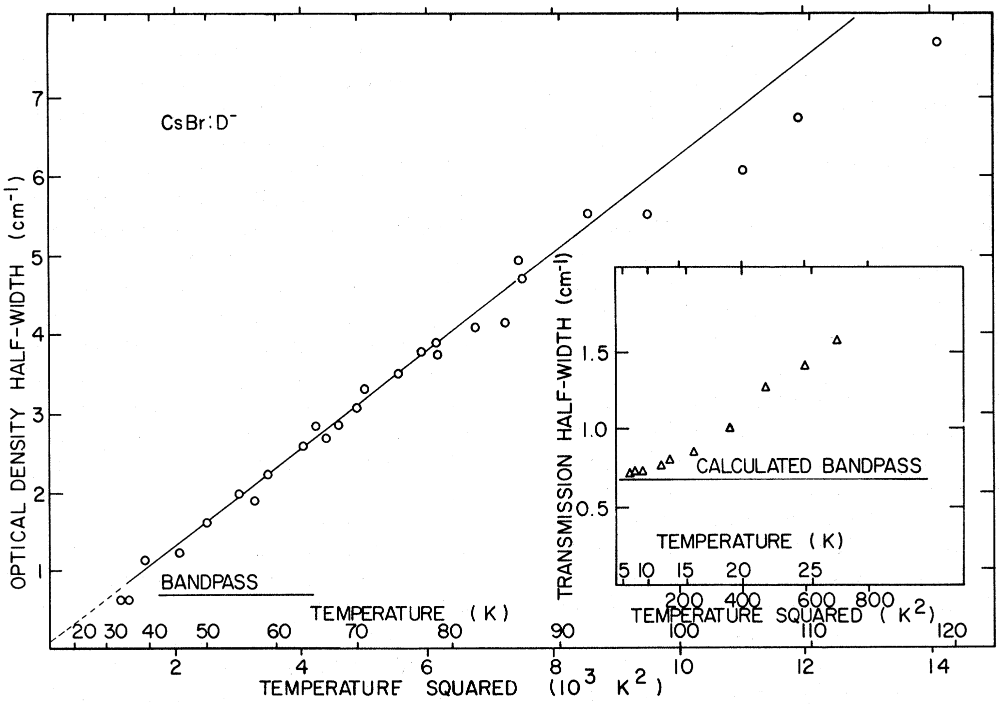

FIG. 4. Half-width of the CsBr: D⁻ local-mode absorption. See caption to Fig. 3.

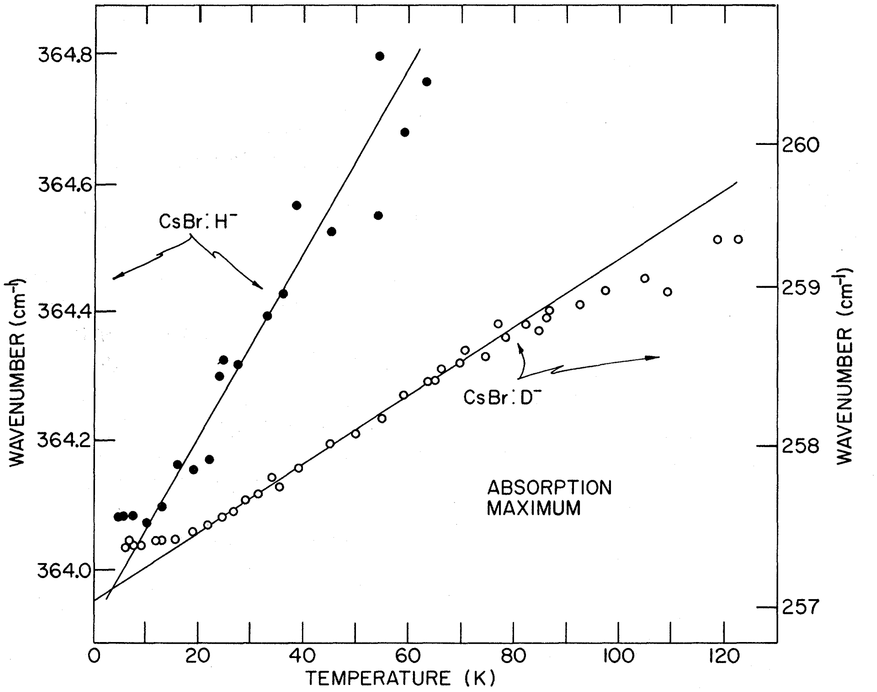

FIG. 5. Peak positions of the CsBr : H⁻ and CsBr : D⁻ local modes vs temperature.

$$\hbar\left(\frac{\partial\omega_p}{\partial T}\right)_p = 2.64\times10^{-6}\ \mathrm{eV/K}\ .$$

The ratio is 1.48. It is expected that third-order terms (or fourth-order terms taken in first-order perturbation theory) would lead to a linear temperature dependence. The role of thermal expansion in $(\partial\omega/\partial T)_p$ is not known. The magnitude, sign, and isotope dependence of the temperature shift cannot be predicted without further calculations involving the actual phonon spectrum.

The temperature dependence of both the half-width and the peak shift of CsBr : D⁻ begin to deviate from a straight line at higher temperatures, about 90 K (see also Ref. 10). The dominant term in the half-width is $V^{(4)}$ while the peak shift is due, at least in part, to $V^{(3)}$ or $V^{(4)}$. The deviations could be explained consistently by a weakening of the fourth-order anharmonic potential at higher temperatures. Lowndes[28] has resolved the temperature and pressure shift of the long-wavelength longitudinal-optical frequency (ω_{LO}) of CsBr into two temperature-dependent terms—that due to thermal expansion and that due to a change in the phonon self-energy term. These changes are a function of the host lattice anharmonicity, however, not the anharmonicity of the defect potential. His results suggest that the source of the relative decrease in the shift function is thermal expansion of the lattice.

The sideband spectra of the CsBr *U* centers are given in Fig. 6. In comparison to most NaCl structure *U* centers, the sidebands are extremely weak. Two-phonon sidebands are thus too weak to appear in Fig. 6. This is consistent with weak coupling to the lattice and a $\sqrt{2}$ isotope shift of the local mode. One interesting feature is that the high-

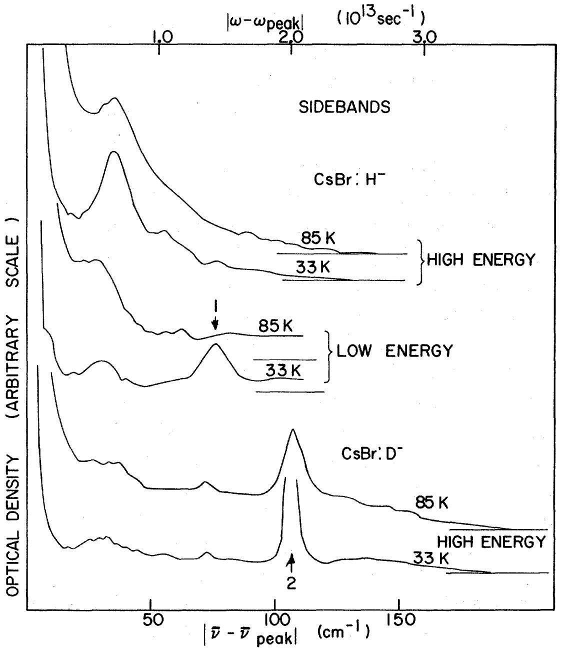

FIG. 6. *U* center local-mode sidebands in CsBr : H⁻ and CsBr : D⁻. The structures marked 1 and 2 are spurious as discussed in the text.

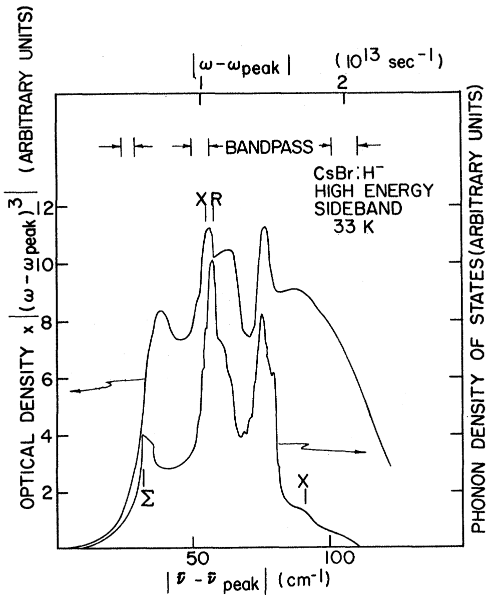

FIG. 7. Comparison of the CsBr : H^- sideband absorption weighted by a factor of $(\omega-\omega_{peak})^3$ with the calculated phonon density of states (Ref. 31). Critical points in the calculated density of states are marked.

and low-energy sidebands are not exactly symmetric about the local mode. This is the effect of a shift function with a non-negligible frequency dependence.[21] No third harmonic absorption was found in any of the CsBr or CsI samples.

There is an extra peak, labeled 1 in Fig. 6, in the low-energy sideband at $\omega_i^- = 1.42\times10^{13}$ sec^{-1} (75.4 cm^{-1}). The absorption is weak, but it appears in all samples with a sufficiently high concentration of *U* centers. The shape and width of the measured peak at 33 K are almost entirely that of the bandpass function. Corrected, it shows typical local-mode behavior—very narrow and very temperature dependent. The peak position is consistent with that expected for a *U* center having a light impurity on an adjacent Cs site. This would perturb all three modes equally since the impurity is in a (111) direction and the H^- vibrations are in the (100) directions. The degeneracy would be maintained. A smaller ion such as rubidium or potassium would provide a weaker-coupling and hence lower-frequency vibration. Either impurity is possible since rubidium is a common impurity in cesium and the crystals were additively colored with potassium. The mode is not consistent with an adjacent halogen impurity such as a second H^- ion. This would split the local mode into a singlet and doublet. A second mode in the sideband spectrum is not seen below 40 μm. The other possibility is an interstitial. This, however, would produce a shift to high energy. The extra peak in the CsBr : D^- sideband, labeled 2 in Fig. 6, is due to hydrogen impurity in the deuterium.

Figure 7 shows the high-energy low-temperature CsBr : H^- sideband with a weighting factor of $(\omega_i^+)^3$. This should be proportional to the perturbed one-phonon density of states. The perturbation arises not only from a possible change of force constant, but from the fact that symmetry considerations prevent coupling to some of the lattice modes.

The introduction of the defect reduces the symmetry of the lattice. The representations of the lattice modes may be expanded in terms of the representations of the point group of the defect. Then with a knowledge of the symmetry of the defect and the electric dipole operator, the selection rules for the lattice modes may be determined. Loudon[30] has considered the case of the NaCl and CaF_2 *U* centers in detail. Extension to the CsCl structure *U* centers is rather straightforward. The significant modes which may not appear in the sidebands are all phonons at *M*, the acoustic phonons at *X*, and the optic branch at *R*.

Karo and Hardy[31] have calculated the phonon spectra and density of states for CsCl, CsBr, and CsI using three force-constant models: rigid ions, "polarization dipole," and "deformation dipole." Two variations of the latter were used, one in which the deformation dipole moment was localized on the cation, the DD(+) model, and one with it on the anion, the DD(−) model. Our sideband data for CsBr were compared with all four of the calculated phonon density of states curves. Agreement with all but the DD(−) model was fairly poor, while the agreement with the DD(−) results was excellent. We henceforth refer to the results of the DD(−) model calculations as the calculated results. Figure 7 shows Karo and Hardy's calculated density of states with the most significant permitted phonons labeled. It can be seen that, while selection rules will modify the one-phonon density of states, none of the structure is removed, and the general shape is preserved. The agreement is remarkably good. The proper weighting factor at low frequency is ω_i^+, not $(\omega_i^+)^3$. This will have the effect of moving the lowest measured peak to lower frequency, improving agreement with the calculated curve. The fact that it is still at too high a frequency may be an indication that there is some perturbation of the lattice phonons.

The CsI *U* center has some features which are not as readily explained. Figures 8 and 9 show the local-mode absorptions of CsI : H^- and CsI : D^-. The positions are not close to those predicted on a simple mass-defect model.[32] They are in accord with those of Ref. 10, except for temperature differences. The significant difference from the CsBr centers is the rapid increase of a high-energy shoulder with temperature. This asymmetry

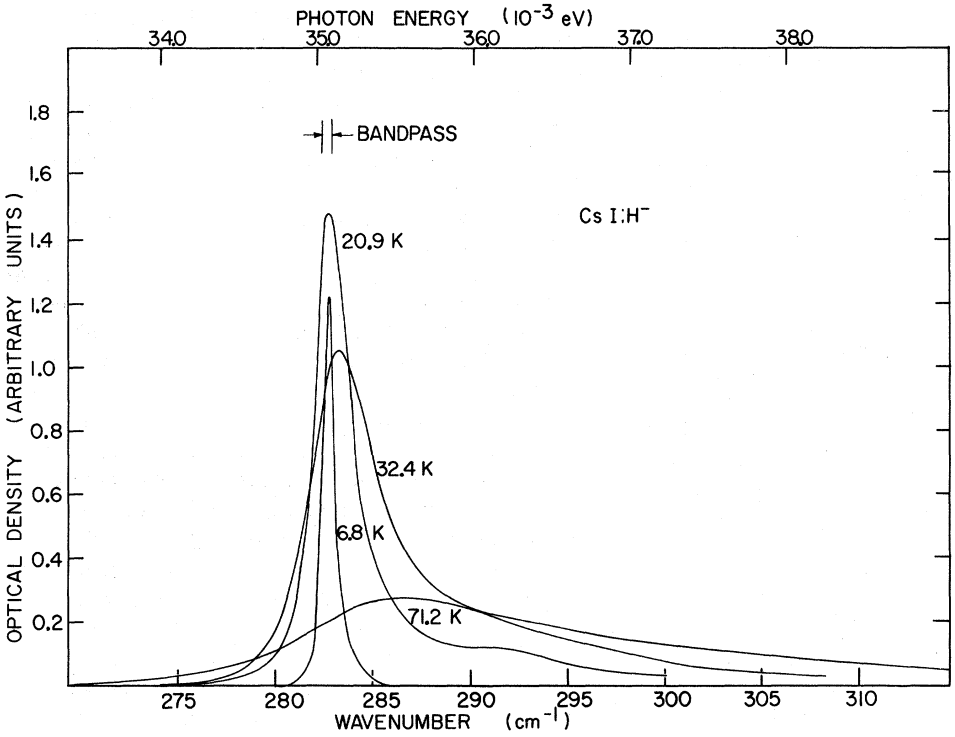

FIG. 8. Absorption spectrum of CsI: H$^-$ at several temperatures.

appears to be characteristic of CsI. It appears in all samples measured and the relative magnitude is the same at all concentrations within the relatively small range used. It appears in CsI purchased at widely different times and with all monochromator-detector combinations. It does not change with repeated cooling and warming cycles nor with annealing near the melting point and

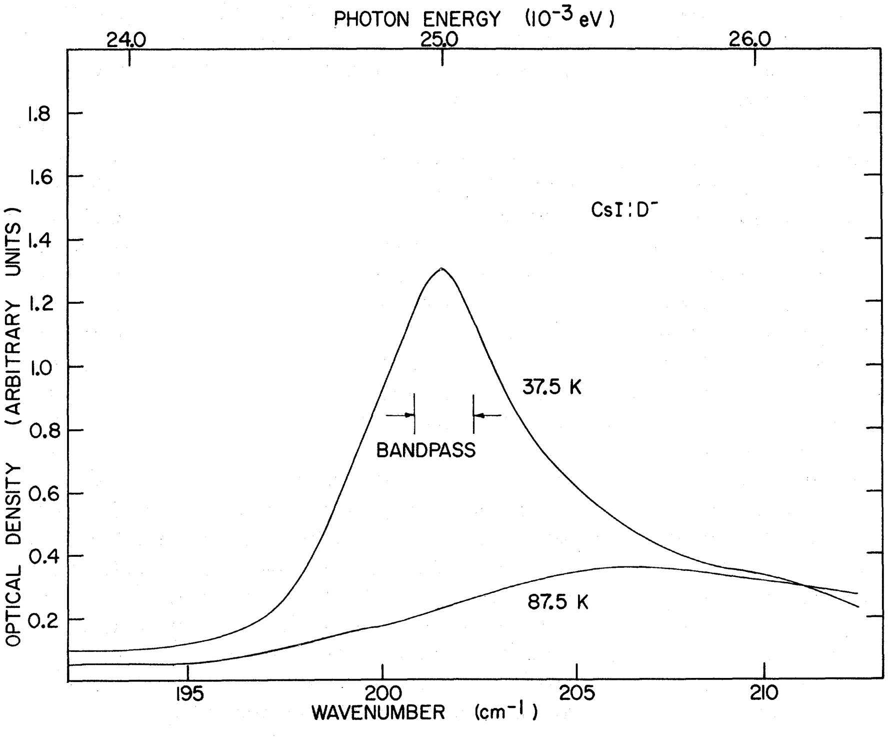

FIG. 9. Absorption spectrum of CsI: D$^-$ at two temperatures.

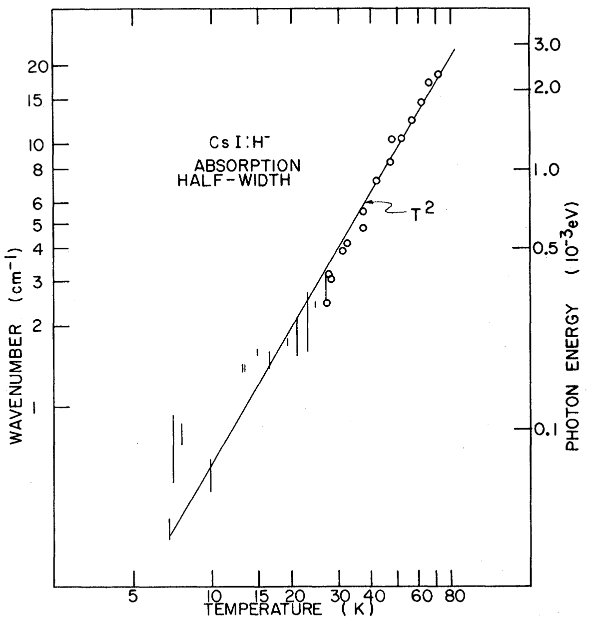

FIG. 10. Half-width of the CsI:H^- local-mode absorption vs temperature, subject to the uncertainty in definition of the half-width in CsI discussed in the text.

quenching. The only published data on CsI U centers[10] are for higher temperatures, but they also show the asymmetry.

The temperature dependence of the half-width is given in Fig. 10. The choice of a significant half-width is not apparent. The asymmetry persists to very low temperatures. In addition, the measured curve is neither Lorentzian nor Gaussian on either side. For these reasons, correction tables are not strictly applicable. An approximation of the half-width, corrected for bandpass, was obtained by fitting a symmetric band to each side. The vertical lines in Fig. 10 indicate a reasonable range of corrected widths obtained this way. At higher temperatures the absorption becomes so wide that no corrections are required. In these cases, the over-all width of the asymmetric band is plotted, even though this may not be the physically significant width. The measured widths may be fit reasonably well by a T^2 temperature dependence. Since the highest lattice-mode frequency ω_{LO} is 91 cm^{-1},[27,28] the CsI:D^- local mode could just barely decay into three lattice modes, but the CsI:H^- mode requires four lattice modes for decay.

The absorption of the CsI:D^- center was measured only at two temperatures. The degree of asymmetry appears to be the same as for the CsI:H^- center. In fact, the half-width of the absorption at 37 K is the same for the two isotopes to well within the uncertainty of the measurement. Until the origin of the asymmetry or unresolved structure of this peak is known, no interpretation should be placed on the lack of isotope effect in the half-width of the main peak.

A similar ambiguity arises in deciding how to represent the temperature dependence of the peak energy. The energies plotted in Fig. 11 are those of the entire curve. Over most of the range the shift has a T^2 dependence and the net shift is more than five times that of CsBr. The ratios of the peak energies at 37 K give an isotope shift of 1.41.

The high-energy sideband is weak and is generally obscured by the tail of the high-energy shoulder. The low-energy sideband occurs in a region where sufficiently accurate measurements could not be made. The absorption on the high-energy side of the local mode is given in Fig. 12. Consistently measurable absorption occurs out to an energy three times that of the maximum lattice phonon energy. In Fig. 13 the low-temperature sideband is given with an $(\omega_i^+)^3$ weighting factor. It is meaningless to attach physical significance to this curve for two reasons. First, until the origin of the high-energy asymmetry is known, the appropriate origin for this weighting factor is unknown. The measurement might represent a large series of sidebands. Secondly, determining the perturbed one-phonon density of states for a given model requires knowledge of the symmetry of the defect mode. In spite of these unknowns, the Karo and Hardy DD(−) density of states is given in Fig. 13. Some of the permitted modes are marked, assuming cubic (Γ_{15}^-) symmetry for the defect local mode. The calculated density of states for the other models do not give better agreement. Eldridge[33] has shown that the DD(−) model is superior to the DD(+) model in fitting phonon spectra determined by thermal diffuse x-ray scattering in CsI.

An explanation of the shape of the CsI U center peak is not available at this time. If a plot is made of U center infrared absorption peak frequency vs the interatomic spacing[1] the CsI absorption occurs at the expected frequency, so we are quite certain we are dealing with U centers in CsI. Possible sources of this strange shape are (i) unresolved structure due to strains,[34] to impurities near the H^- ion, to some interstitial H^- ions (U_1 centers), or to two H^- ions in proximity; (ii) a large component in the sideband structure due to strong coupling to a low-frequency mode or to difference sidebands; and (iii) a change in the site of the H^- ion. Interstitial H^- ions[35–37] and U center pairs[38] have been observed before, and they produce peaks further from that of the substitutional H^- ion than is needed here. Moreover, at room temperature no U_1 band was seen in the ultraviolet. (In several alkali halides with the NaCl structure, this is a band at lower energy than the U band due to electronic excitation of interstitial H^- ions.[39])

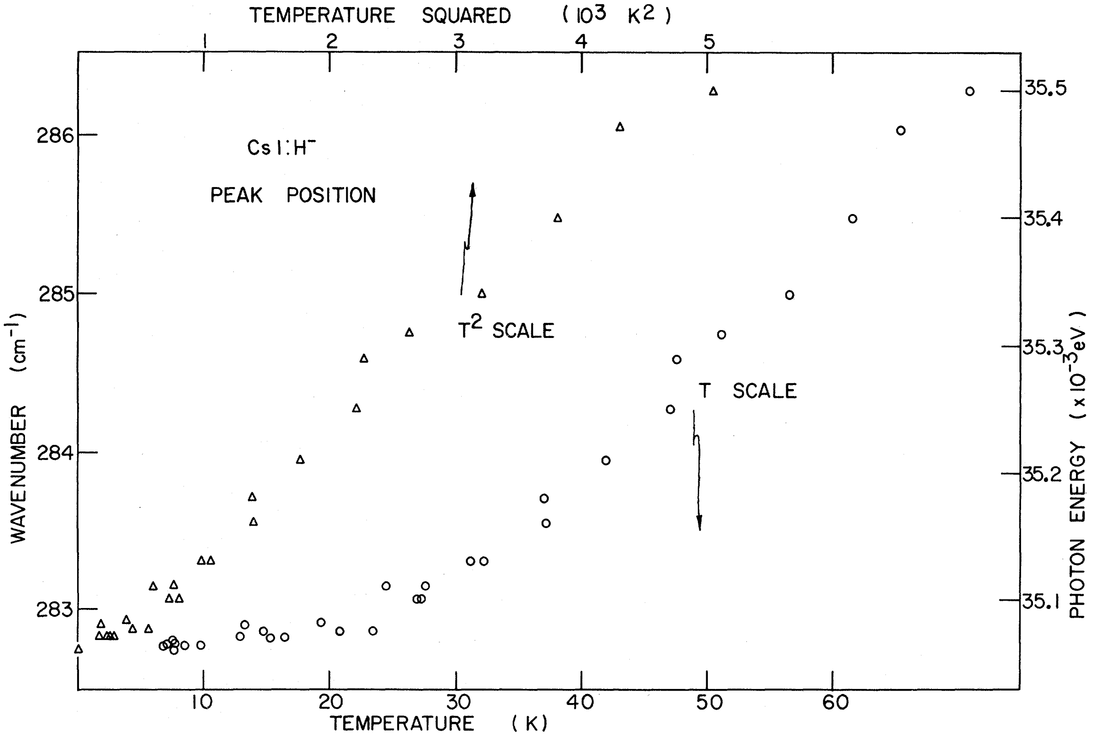

FIG. 11. Peak position of the CsI : H$^-$ local-mode absorption vs temperature.

The fact that the main peak in CsI : H$^-$ becomes very narrow at low temperatures seems to rule out any unresolved structure as the origin of the line shape. The temperature dependence of the strength of a high-frequency sideband is expected to be $(e^{\hbar\omega_i^{\dagger}/kT}-1)^{-1}$. The temperature dependence of a sideband peak some 5–10 cm^{-1} from the main peak is inconsistent with that observed in the high-energy "component" of the CsI : H$^-$ peak. Two phonon difference sidebands should vanish at $T=0$,

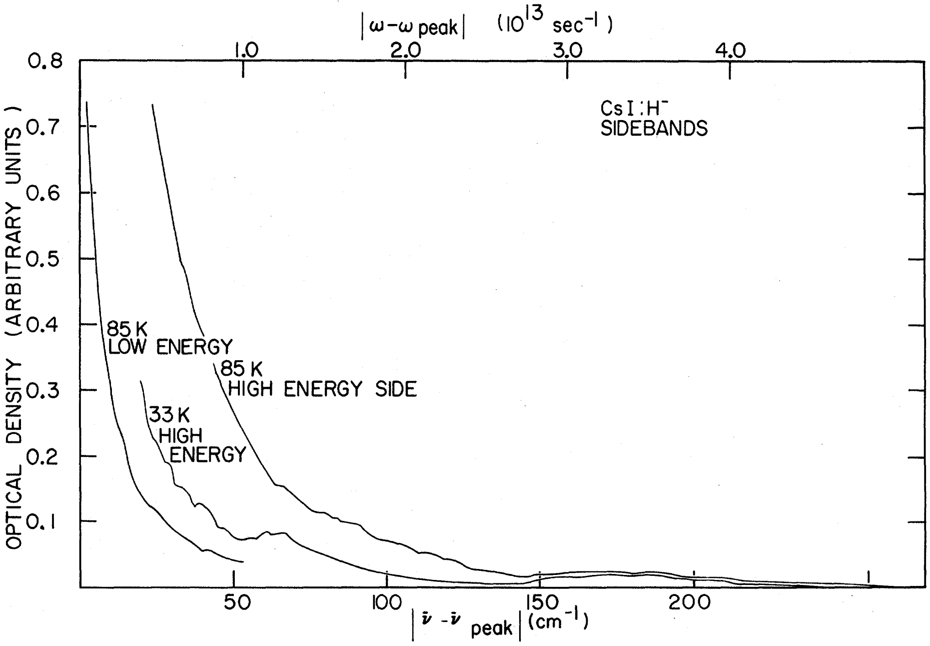

FIG. 12. *U* center local-mode sidebands in CsI : H$^-$.

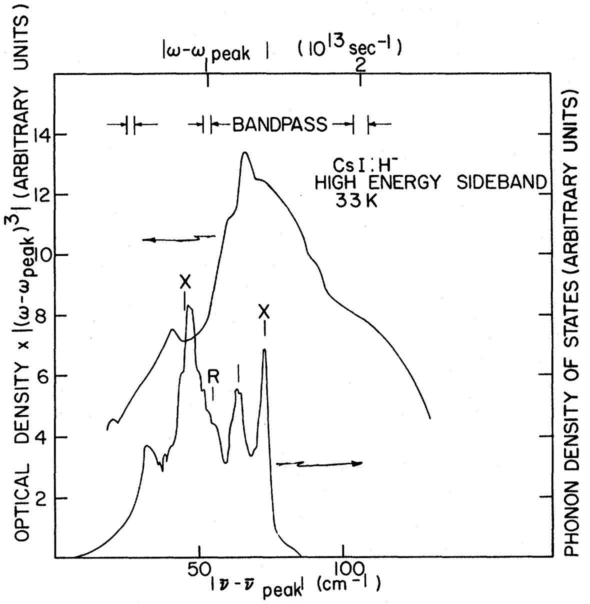

FIG. 13. Comparison of the CsI:H⁻ sideband absorption, weighted by a factor of $(\omega-\omega_{\text{peak}})^3$ with the calculated phonon density of states (Ref. 31). Critical points in the calculated density of states are marked.

since a thermally excited lattice mode is required, then increase with increasing *T*. However, they should be weaker than the one-phonon sidebands and should occur on both sides of the main peak. They, too, seem to be unlikely explanations of the shape. If the crystal warms from 0 K, and the lattice expands, the H⁻ ion may move off its lattice site into an off-center equilibrium site. (The usual occurrence[40] would be for the impurity to be in the off-center site at $T=0$, then be "thermally excited" into equivalent off-center sites at larger *T*, finally reaching full cubic symmetry when enough sites are sampled during a characteristic time for a measurement.) The off-center H⁻ ions would vibrate at more than one frequency, the three fold degeneracy of the low-frequency mode being partly lifted. Such a displacement of equilibrium is capable of being tested, however, for CsI:H⁻ should then have unusual low-temperature dielectric properties. It should be pointed out that both CsI:H⁻ and CsI:D⁻ display this odd shape and have qualitatively the same temperature-dependence for the shape. It is anticipated that there should be some mass-dependence in the hypothetical motion off-axis, especially in the tunneling to restore effective cubic symmetry. In short, there is no real explanation of the line shape of the CsI:H⁻ local-mode absorption peak.

SUMMARY

The infrared absorption due to H⁻ or D⁻ substitutional impurities has been measured in CsBr and CsI. In CsBr it is described very well by the model of Bilz *et al.* The coupling to the lattice is weak, since the sidebands are weak. The density of states obtained from the sidebands, assuming a simple model for the coupling, is in good agreement with that calculated by Hardy and Karo with a deformation-dipole model, placing these dipoles on anion sites. The half-width of the main peak at high temperatures is due to Raman or scattering processes brought about by anharmonic terms in the Hamiltonian, while at low temperatures the half-width is due to possible residual strains and decay of the local mode into three lattice modes (CsBr:D⁻) or four lattice modes (CsBr:H⁻). The absorption in CsI seems to be due to H⁻ and D⁻, but its shape is unusual and most features of this absorption have not been interpreted.

ACKNOWLEDGMENTS

The authors are indebted to Dr. A. D. Brothers for experimental assistance and to J. V. Bauer who initiated this study.

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†Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission, Contribution No. 2979.

[1] G. Schaefer, J. Phys. Chem. Solids 12, 233 (1960).

[2] B. Fritz, V. Gross, and D. Bäuerle, Phys. Status Solidi 11, 231 (1965).

[3] H. Dötsch, W. Gebhardt, and C. Martius, Solid State Commun. 3, 297 (1965).

[4] D. Bäuerle and B. Fritz, Phys. Status Solidi 24, 207 (1967).

[5] D. N. Mirlin and I. I. Reshina, Fiz. Tverd. Tela 6, 3945 (1964) [Sov. Phys. Solid State 6, 728 2454 (1964)].

[6] R. J. Elliott, W. Hayes, G. D. Jones, H. F. MacDonald, and C. T. Sennett, Proc. Roy. Soc. (London) A289, 1 (1965).

[7] G. R. Wilkinson (unpublished).

[8] J. V. Bauer, M. S. thesis (Iowa State University, 1966) (unpublished).

[9] S. S. Mitra and Y. Brada, Phys. Rev. 143, 626 (1966).

[10] H. Dötsch and S. S. Mitra, Phys. Rev. 178, 1492 (1969).

[11] S. S. Jaswal and D. J. Montgomery, Phys. Rev. 135, A1257 (1964).

[12] R. Fieschi, G. F. Nardelli, and N. Terzi, Phys. Rev. 138, A203 (1965).

[13] T. Timusk and M. V. Klein, Phys. Rev. 141, 664 (1966).

[14] M. V. Klein, in *Physics of Color Centers*, edited by W. Beall Fowler (Academic, New York, 1968), p. 429.

[15] T. Gethins, T. Timusk, and E. J. Woll, Phys. Rev. 157, 744 (1967).

[16] N. X. Xinh, Phys. Rev. 163, 896 (1967).

[17] J. B. Page and B. G. Dick, Phys. Rev. 163, 910 (1967).

[18] M. A. Ivanov, M. A. Krivoglaz, D. N. Mirlin, and I. I. Reshina, Fiz. Tverd. Tela 8, 192 (1966) [Sov. Phys. Solid State 8, 150 (1966)].

[19] M. A. Ivanov, L. B. Kvashnina, and M. A. Krivoglaz, Fiz. Tverd. Tela 7, 2047 (1965) [Sov. Phys. Solid State 7, 1652 (1966)].

[20] T. Gethins, Can. J. Phys. 48, 580 (1970).

[21] H. Bilz, B. Fritz, and D. Strauch, J. Phys. (Paris) Suppl. 27, C2-3 (1966).

[22] E. Hanamura and T. Inui, J. Phys. Soc. Japan 18, 690 (1963).

[23] M. Lax and E. Burstein, Phys. Rev. 97, 39 (1955).

[24] D. A. Ramsay, J. Am. Chem. Soc. 74, 72 (1954).

[25] P. A. Jansson, J. Opt. Soc. Am. 60, 184 (1970).

[26] Ramsay's tables (Ref. 24) pertain to Lorentzian absorption bands and triangular bandpass functions. The convolution of these gives an observed absorption band which is nearly Lorentzian—that is, a function which may be fit by a single Lorentzian either in the main peak or the wings but not both. The measured absorption was of this nature.

[27] P. Vergnat, J. Claudel, A. Hadni, P. Strimer, and F. Vermillard, J. Phys. (Paris) 30, 723 (1969).

[28] R. P. Lowndes, Phys. Rev. B 1, 2754 (1970).

[29] The uncertainty in these positions is roughly 0.02–0.04 cm^{-1} despite the large bandpass. Well-known water-vapor absorption bands near these peaks, observed in our single-beam system, made this accuracy possible.

[30] R. Loudon, Proc. Phys. Soc. (London) 84, 379 (1964).

[31] A. M. Karo and J. R. Hardy, J. Chem. Phys. 48, 3173 (1968).

[32] N. Krishnamurty and T. M. Haridasan, Proc. Phys. Soc. (London) 87, 869 (1966).

[33] J. E. Eldridge, J. Phys. C 3, 1527 (1970).

[34] B. Fritz, J. Gerlach, and V. Gross, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 504.

[35] B. Fritz, J. Chem. Phys. Solids 23, 375 (1962).

[36] D. Bäuerle and B. Fritz, Phys. Status Solidi 29, 639 (1968).

[37] U. Dürr and D. Bäuerle, Z. Physik 233, 94 (1970).

[38] M. deSouza, A. D. Gongora, M. Aegerter, and F. Lüty, Phys. Rev. Letters 25, 1426 (1970).

[39] C. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. 104, 599 (1956).

[40] V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. 42, 201 (1970) and references therein.

PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

Ultraviolet Absorption Spectra of Photochromic Centers in CaF_2 Crystals

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(Received 14 December 1970)

Photochromic color centers are known to exist in additively colored CaF_2 doped with La, Ce, Gd, Tb, Lu, or Y. It is also known that these centers consist of one or two electrons bound at the fluorine vacancy adjacent to the trivalent impurity cation. The ultraviolet (uv) absorption spectra of photochromic centers (PC) in CaF_2 were measured from 35 000 to 80 000 cm^{-1}, the band edge of the host crystal, at both room and liquid-nitrogen temperatures. The spectra show two regions of absorption. The low-energy region, up to 57 000 cm^{-1}, has bands at 44 000 and 52 000 cm^{-1}, which are conjectured to be analogous to the L bands of F_A centers in alkali halides. The high-energy region, from 57 000 cm^{-1} on, is characterized by a band at 62 000 cm^{-1}, which is interpreted as charge transfer from PC to nearby impurities. At the band edge, an extra absorption appears in the uv-switched CaF_2: 0.1-at.%-Gd sample, and it is speculated that it is the $4f^7 \rightarrow 4f^6 5d$ transition of Gd^{3+}. This interconfigurational transition is "red shifted" due to the screening effect of electrons, which have been released from the ionized PC and trapped in the vicinity of Gd^{3+}.

I. INTRODUCTION

The photochromic centers (PC) in CaF_2 have aroused much interest[1] in recent years. These centers are produced[2–4] either by x irradiation or by additive coloration of CaF_2 crystals doped with certain rare earths (RE) (La, Ce, Gd, Tb, and Lu) or yttrium. The PC produced by additive coloration can be photoswitched[2–4] reversibly between two states, the thermally stable original state and the ultraviolet (uv)-switched or the ionized state. We shall restrict our discussion to the PC produced by additive coloration[2–4] only.

The absorption spectra of PC below 50 000 cm^{-1} have been extensively studied.[2,3,5] Three absorption bands around 25 000 cm^{-1} have been identified as π, σ, and π transitions from the A_1 ground state.[2,3,5] From the optical[2,3] and EPR studies[6] the PC has been described[3–5] as a complex consisting of a fluorine vacancy with one of the above-mentioned dopants as a nearest neighbor. In the thermally stable state the PC has two electrons and is electrically neutral.[3–5] The uv switching light ionizes[3–5] the PC by releasing one electron, which in