

TABLE II. Values of the different parameters used in the analysis of the phonon conductivity of the $\text{KBr}:\text{NO}_2^-$ ion system.

Sample	Concentration (cm^{-3})	Kwok's ω^2 dependence (Green's function) $H_1(10^{-8} \text{ sec}^{-1} \text{ cm}^2 \text{ }^\circ\text{K}^2)$	ω^4 dependence $H(10^{-12} \text{ sec}^3 \text{ cm}^{-1} \text{ g}^{-2})$	Kwok's dependence (including inelastic scattering) $H(10^{-13} \text{ sec}^3 \text{ cm}^{-1} \text{ g}^{-2})$	Kwok's dependence (excluding inelastic scattering) $H(10^{-12} \text{ sec}^3 \text{ cm}^{-1} \text{ g}^{-2})$
A	3.5×10^{17}	0.1	12.4350	12.4350	12.435
B	5.3×10^{18}	1.0	8.2119	8.2119	8.2119
C	5.7×10^{19}	5.0	7.6356	7.6356	7.6356

on the basis of a Green's function. It may be seen from Figs. 5-7 that the agreement between the theoretical and experimental values is in general poor. However, the ω^2 dependence of τ_r^{-1} gives better agreement between theoretical and experimental values of phonon conductivity.

IV. CONCLUSION

The phonon-conductivity resonant dips in $\text{KCl}:\text{NO}_2^-$ and $\text{KBr}:\text{NO}_2^-$ systems cannot be explained by an ω^4 dependence of the resonant-scattering relaxation rate of phonons. Much better agreement between theoretical

and experimental values of the phonon conductivity of the $\text{KCl}:\text{NO}_2^-$ system is achieved with the formula $\tau_r^{-1} \propto \omega^2 / (\omega^2 - \omega_0^2)^2$, which is obtained on the basis of Green's functions. The agreement for $\text{KBr}:\text{NO}_2^-$ is not so good.

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Infrared Absorption by U Centers in CsCl , CsBr , and CsI^\dagger

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The infrared absorption by the localized vibrational modes of H^- and D^- centers in CsCl , CsBr , and CsI has been measured in the temperature range 20 to 300°K. Above 100°K, the temperature dependence of the half-widths of the local-mode absorption bands in CsBr and CsI follows a T^n dependence, where $2 > n > 1$ (instead of $n \cong 2$, as is usually the case with the other alkali halides). Side-band structures are observed in CsCl and CsBr . These can be explained as arising from the coupling of the local-mode phonon with band phonons through anharmonic interactions. In the case of CsI , no such side-band structure is noted in the temperature range studied, except for a weak shoulder occurring very close to the main local-mode band.

INTRODUCTION

IN alkali halides, U centers are H^- or D^- ions replacing anions. They give rise to localized vibrations with frequencies two to four times higher than the maximum frequency of the host lattice. These vibrations are infrared active and show strongly temperature-dependent absorption spectra which were experi-

mentally¹⁻³ and theoretically⁴⁻⁶ investigated in most of the alkali halides with NaCl structure. So far only a few data were available for the alkali halides with CsCl structure.^{7,8} In this paper we present the results of a

¹ G. Schäfer, *J. Phys. Chem. Solids* **12**, 233 (1960).

² A. Mitsubishi and H. Yoshinaga, *Progr. Theoret. Phys. (Kyoto)*, Suppl. **23**, 251 (1962).

³ B. Fritz, U. Gross, and D. Bauerle, *Phys. Status. Solidi* **11**, 231 (1965).

⁴ H. Bilz, D. Strauch, and B. Fritz, *J. Phys. Suppl.* **27**, C2 (1966).

⁵ S. S. Mitra and R. S. Singh, *Phys. Rev. Letters* **16**, 694 (1966).

⁶ M. V. Klein, in *Physics of Color Centers*, edited by W. B. Fowler (Academic Press Inc., New York, 1968), Chap. 7.

⁷ S. S. Mitra and Y. Brada, *Phys. Rev.* **145**, 626 (1966).

⁸ G. R. Wilkinson (unpublished) has measured the U -center local-mode frequencies in CsCl and CsBr , quoted in A. A. Maradudin, *Solid State Phys.* **19**, 1 (1966).

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systematic investigation of the infrared spectra of H^- and D^- centers in CsCl, CsBr, and CsI.

EXPERIMENTAL

Single crystals of CsBr and CsI were used. For CsCl, only small polycrystalline pieces were available. All crystals were obtained from the Harshaw Chemical Company. U centers were produced by heating these crystals in a nickel tube in an atmosphere of hydrogen or deuterium at about 3 atm pressure, together with potassium metal. In the case of CsI, the U centers were distributed homogeneously over the whole crystal, whereas in CsBr and especially in CsCl, the U -center concentration decreased going from the surface to the interior of the crystals. Average U -center concentrations up to 10^{19} cm^{-3} were obtained. The optical measurements were performed with a Perkin-Elmer model 301 far-infrared spectrophotometer. With our cryostat, we could cover the range from 20°K up to the room temperature.

RESULTS

Figures 1–3 show the temperature dependence of the frequencies of the main local-mode bands. Figures 4 and 5 show the temperature dependence of the half-widths of the main local-mode bands in CsBr and CsI. According to our finite spectral-slit width of about 1.5 cm^{-1} , the measured half-widths had to be corrected. As at low temperatures and low concentrations the band shape

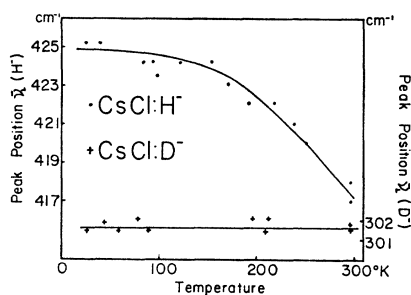


FIG. 1. Frequencies of the main local-mode bands in CsCl: H^- , D^- versus temperature.

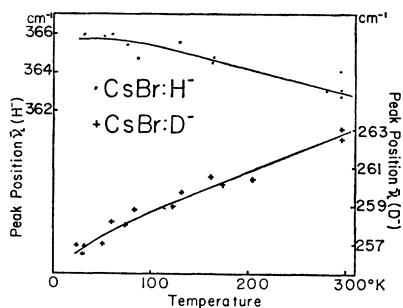


FIG. 2. Frequencies of the main local-mode bands in CsBr: H^- , D^- versus temperature.

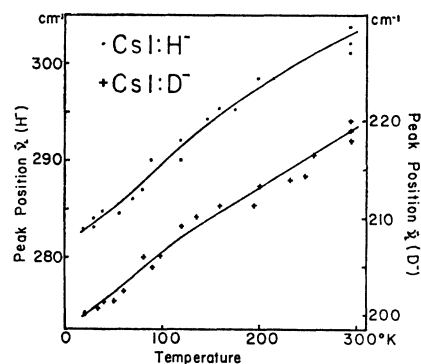


FIG. 3. Frequencies of the main local-mode bands in CsI: H^- , D^- versus temperature.

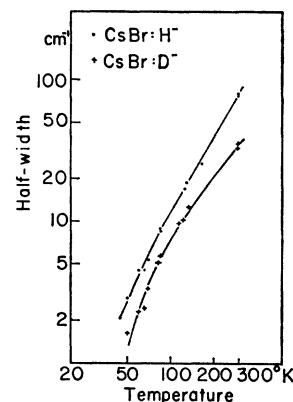


FIG. 4. Temperature dependence of the half-widths of the main local-mode bands in CsBr: H^- and CsBr: D^- .

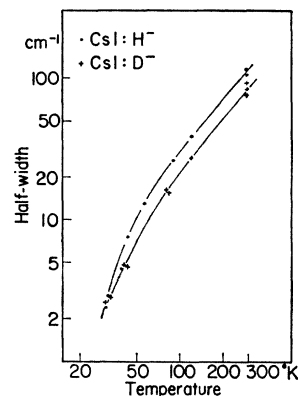


FIG. 5. Temperature dependence of the half-widths of the main local-mode bands in CsI: H^- and CsI: D^- .

is nearly Lorentzian, we used the correction tables of Ramsay.⁹

Figures 6 and 7 show the side bands of CsCl: H^- and CsBr: H^- which are due to the coupling of the local-mode phonon to band phonons. However, on the low-frequency side the anti-Stokes side bands are masked by some shifted local-mode bands. In each case there appears a pair of shifted bands in the immediate neighborhood of the main local-mode band. This is

⁹ D. A. Ramsay, J. Am. Chem. Soc. 74, 72 (1952).

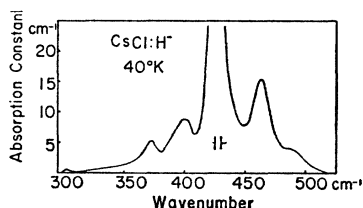


Fig. 6. Side-band spectrum of CsCl:H⁻ at 40°K.

probably caused by an interaction among the local-mode phonons due to a high-local concentration of the U centers near the crystal surface. The other shifted modes at 290 and 304 cm⁻¹ in CsBr and at 303 cm⁻¹ in CsCl may be due to some other impurities. In Fig. 8 the spectrum of CsI:H⁻ is shown at different temperatures. The main local-mode band is very asymmetric, but there is no side-band structure (a very weak indication of a side band at 355 cm⁻¹ lies within the limits of error). However, the main local-mode band shows a shoulder

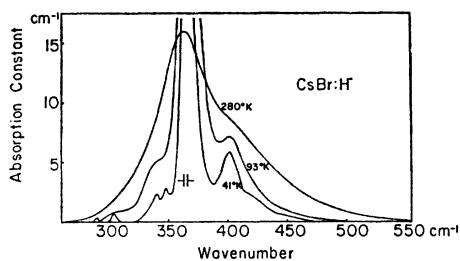


Fig. 7. Side-band spectra of CsBr:H⁻ at different temperatures.

which is shown on a larger scale at the top right of Fig. 8. A similar shoulder occurs also in CsI:D⁻. The H⁻ and D⁻ local-mode peak positions at 100°K in CsCl, CsBr, and CsI are listed in Table I.

DISCUSSION

Local-Mode Frequency

In Fig. 9 we have plotted the Ivey relation for the local-mode frequencies in CsCl, CsBr, and CsI. The

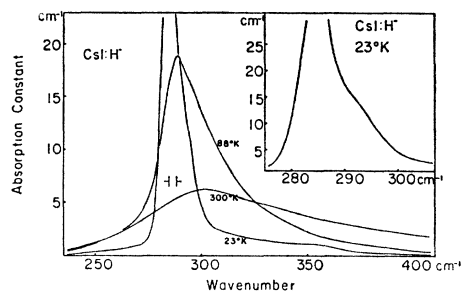


Fig. 8. Absorption spectra of CsI:H⁻ at different temperatures.

TABLE I. U -center local-mode phonon frequencies (in cm⁻¹) at 100°K.

Impurity	Host lattice		
	CsCl	CsBr	CsI
H ⁻	424	365	290
D ⁻	302	259	207

slope of the curve is 4.0 if the 50°K values of the frequencies are chosen (the room-temperature values give a slope of 3.2). For the other alkali halides with NaCl structure, one gets slopes between 2.0 and 2.5.¹ The higher slope for the CsCl structure indicates that the U centers are more tightly bound in this structure than in the NaCl structure. This is due to the fact that in the CsCl structure the U center has eight instead of six next neighbors and that the second next neighbors are relatively closer than in the NaCl structure.

The temperature shift of the frequencies consists of two parts. First, a quasiharmonic shift which is due to the change in lattice constant and shifts only to higher frequencies with decreasing temperature. Second, an anharmonic shift which is due to the anharmonic interaction of the local-mode phonon with the band phonons. According to Bilz *et al.*,⁴ there are several phonon processes with temperature-dependent positive and negative contributions to the anharmonic shift.

Half-Width of the Local Mode

For the damping of the local mode there are usually two processes considered. First, a scattering process where a band phonon is scattered by the local-mode phonon. This process gives rise to a T^2 dependence of the half-width at high temperatures and to a T^7 dependence at low temperatures.⁵ Second, a decay process where the local-mode phonon decays into several band phonons. Considering the frequencies of the long-wavelength optical phonons of the cesium halides,¹⁰ it becomes evident that the local-mode phonon must

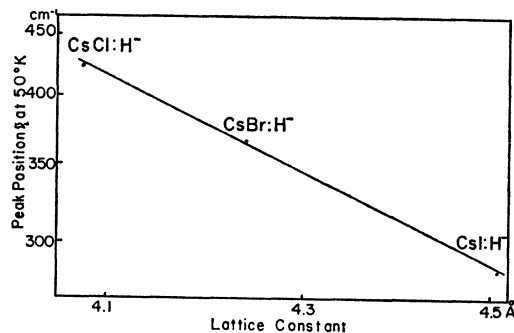


Fig. 9. Ivey plot for the frequencies of the U -center local modes in CsCl, CsBr, and CsI.

¹⁰ G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) A261, 10 (1961).

decay at least into two phonons in CsCl:D^- , into three phonons in CsCl:H^- , CsBr:D^- , and CsI:D^- , and into four phonons in CsBr:H^- and CsI:H^- . At low temperatures all decay processes cause a constant half-width while at high temperatures they give rise to a T , T^2 , and T^3 dependence for the two-, three-, and four-phonon decay.

However, one observes in CsBr and CsI at high temperatures a dependence which lies between T and T^2 . As in this region the half-widths are very large, one can have a contribution by a two-phonon decay where one of the two phonons is the local-mode phonon itself. This decay process usually gives rise to the side bands, but in this case now it causes a linear temperature dependence of the half-width. A superposition of this process with the scattering process could then explain the measurements.

Below 100°K the half-widths become so small that the contribution from the "side-band process" vanishes while the contribution from the scattering process remains. At very low temperatures, however, one should see a constant half-width according to the allowed decay processes.

Side Bands

According to Bilz *et al.*,⁴ the imaginary part of the dielectric constant for the side-band spectra at 0°K may be written, in the density approximation, as

$$\epsilon''(\omega) = \frac{n(\omega)c}{\omega} K(\omega) = 16\pi^2 \times \left[\frac{3M_1V_3}{\omega_L\omega_i(1+\omega_i/2\omega_L)} + M_2 \right]^2 \frac{\rho(\omega_i)}{\omega_i\omega_L}, \quad (1)$$

where $n(\omega)$ is the refractive index which is set constant for the side-band region and $K(\omega)$ is the absorption

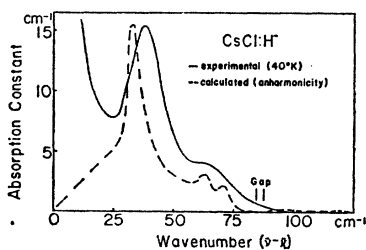


FIG. 10. Calculated (anharmonicity only) and experimental side bands in CsCl:H^- .

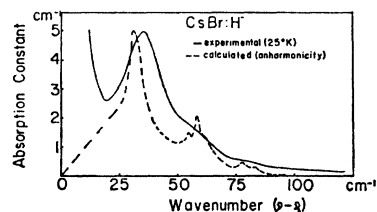


FIG. 11. Calculated (anharmonicity only) and experimental side bands in CsBr:H^- .

constant; i indicates band phonons, L is the local-mode phonon, and $\rho(\omega_i)$ is the density of states for the pure crystal. M_j and V_j are expansion coefficients of the dipole moment M and the potential V in the j th order; for high frequencies they are set constant while for low frequencies they are proportional to ω_i . To take into account the different coupling of the local-mode phonon to acoustic and optical phonons, the density $\rho(\omega_i)$ is multiplied in the optical region by the factor $Q = X^2$ (optical branch, cation)/ X^2 (acoustic branch, cation), where X is the polarization vector of those phonons. According to Bilz *et al.*,⁴

$$Q \geq m_{\text{anion}}/m_{\text{cation}}. \quad (2)$$

Using the calculated density of states by Karo and Hardy¹¹ (Fig. 8 of their paper) in Eq. (1), one gets with $M_2=0$ (only anharmonicity) the calculated curves in Figs. 10 and 11. In comparison with the experimental curves, they are fitted to the maximum of the measured side bands. With $V_3=0$ in Eq. (1) (only nonlinear dipole moments) the agreement is much worse.

According to Eq. (1) and Karo and Hardy's density of states,¹¹ a similar side-band structure should also appear for CsI:H^- , which, however, is not the case as may be seen from the experimental results (Fig. 8). The separation of the weak shoulder from the main local-mode band is too small to be identified with a phonon side band. Measurements with higher concentrations and at lower temperatures are desirable in this case.

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¹¹ A. M. Karo and J. R. Hardy, *J. Chem. Phys.* **48**, 3173 (1968).