tal value[18] is 4.639 Å. While our results show a marked improvement over the older values, there are still significant discrepancies with experiment, and revisions of our table may prove desirable after more data is obtained on $A^{II}B^{IV}C^{V}_2$ compounds. It is worth noting that the cases $Q = \pm 1$ correspond to donor or acceptor impurities, so that further study of this question may supply valuable insight into the strain fields surrounding electrically active impurities in semiconductors.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Lattice Dynamics, Mode Grüneisen Parameters, and Coefficient of Thermal Expansion of CsCl, CsBr, and CsI†

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(Received 29 December 1969)

The phonon dispersion curves for CsCl, CsBr, and CsI have been obtained using a rigid-ion model with an appropriate effective ionic charge. The five model parameters for each crystal are obtained from three elastic constants and the two long-wavelength optic-mode frequencies, reliable data for which exist for all three crystals. Our results are in agreement with those of more elaborate models. The phonon density of states and the Debye characteristic temperatures are also calculated. A Born-Mayer-type potential is used to calculate long-wavelength LO and TO mode frequencies as functions of pressure from pressure dependence of bulk modulus. The result for TO of CsBr agrees well with a recent experimental determination. Next, using the values of the elastic constants and LO and TO frequencies at various pressures, ω-versus-$\vec{k}$ curves in selected directions are generated as functions of pressure. Mode Grüneisen parameters are then calculated as functions of $\vec{k}$. Finally, the Grüneisen constant and the volume coefficient of thermal expansion are obtained as functions of temperature. They agree very well with available experimental data.

I. INTRODUCTION

The lattice dynamics of crystals having the CsCl structure was first worked out by Ganesan and Srinivasan.[1] They used the results from the lattice dynamics to predict the temperature variation of the Grüneisen constant. Their calculations were based on a Born-Mayer-type potential incorporating an r^{-n}-type repulsive term and a formal ionic charge of unity. This treatment is thus essentially similar to the one first introduced by Kellermann[2] for crystals having the NaCl structure. To obtain a reasonable value of the Grüneisen constant, Ganesan and Srinivasan varied n as a parameter. They did not attempt to obtain phonon dispersion curves or frequency distribution functions. Subsequently, a rigid-ion model was used by Krishnamurthy[3,4] to obtain the phonon density of states for CsI and CsBr. Karo and Hardy[5] studied the lattice dynamics of CsCl, CsBr, and CsI utilizing three different models, a rigid-ion model of the Kellermann type, the polarizable-dipole model, and the deformation-dipole model. They concluded, on the basis of experimental data for specific heat, that the deformation-dipole model produced the most favorable comparison. This work was closely followed by two shell-model calculations[6,7] on CsCl, CsBr, and CsI. To date no neutron scattering measurements have been done on either CsCl, CsBr, or CsI, thus it is not possible to evaluate the relative merits of the various lattice dynamical calculations on a direct comparison basis. Recently, Dötsch and Mitra[8] have studied the spectra of U centers (H^- and D^- substitutional impurities) in CsCl, CsBr, and CsI. The structure of the sidebands associated with the local mode spectra of U centers in CsCl and CsBr agree fairly well with the calculated phonon density of states obtained by the deformation-dipole model.[5]

The purpose of the present paper is to develop a reasonably realistic lattice dynamical model which can be readily adapted to the determination of the pressure dependence of lattice dynamics, or in particular, which will permit one to obtain the mode Grüneisen parameters $\gamma_i(\vec{k}) = -d\ln\omega_i(\vec{k})/d\ln V$ for all i's and k's, where the former denotes the branch number and the latter the phonon wave vector. ω and V stand for phonon frequency and the crystal volume. This restricts us to models for which all the parameters are or can be available as functions of volume. Thus some lattice dynamical models, including the shell model, have to be excluded.

In the past the mode Grüneisen parameters and the thermal-expansion coefficient of certain crystals have been obtained using more elaborate lattice dynamical models.[9,10] But usually the parameters used have been obtained by curve-fitting techniques, using not only extensive phonon data measured by neutron scattering, but also thermal-expansion data which the models purport to predict. We use essentially a rigid-ion model with an appropriate effective ionic charge, ensuring a proper LO-TO splitting. This model has been fairly successfully used for certain zinc-blende-type crystals.[11] The criteria governing their applicability have also been discussed.[12] The model may, however, be somewhat approximate for certain crystals as far as phonon dispersion is concerned.[12,13] Nevertheless, for CsCl, CsBr, and CsI such considerations are only academic since no neutron scattering data exist.

The present lattice dynamical model utilizes the two long-wavelength optic-mode phonon frequencies and the three elastic constants as input data for the determination of the five model parameters. The phonon dispersion, phonon density of states, and the specific heat of CsCl, CsBr, and CsI are calculated using this model. Next the pressure dependence of the model parameters is obtained from pressure derivatives of the five input data. Of these, the pressure dependence of the elastic constants of all the three crystals is known experimentally, whereas the pressure dependence of the Brillouin-zone-center optic-phonon frequencies is determined from the values of the corresponding mode Grüneisen parameters obtained from a Born-Mayer-type potential. Next, the lattice dynamical calculations are performed at a higher pressure which gives for each crystal the mode Grüneisen parameters for the six phonon branches as functions of the wave vector. Finally, the Grüneisen constant and the coefficient of thermal expansion are evaluated as functions of temperature. The latter will be shown to agree well with available experimental data.

II. LATTICE DYNAMICS

Under the harmonic approximation the system of equations of motion for the rigid-ion model are expressible as

$$\underline{M}\,\omega^2\underline{u} = (\underline{R} + \underline{Z}\,\underline{C}\,\underline{Z})\,\underline{u} \quad . \qquad (1)$$

The matrices $\underline{R}$ and $\underline{C}$ represent the short-range and Coulomb interactions, respectively, $\underline{M}$ and $\underline{Z}$ are diagonal matrices representing the particle masses and the charge number, and $\underline{u}$ is a column matrix representing the particle displacements. The normal-mode frequency is designated by ω.

The condition for a nontrivial set of solutions for the displacements $\underline{u}$ reduces to the following secular equation for the normal-mode frequencies:

$$|\underline{M}\,\omega^2 - \underline{R} - \underline{Z}\,\underline{C}\,\underline{Z}| = 0 \quad . \qquad (2)$$

For the short-range interactions the application of the symmetry properties of the cesium chloride structure considerably simplifies the number of independent force constants. There are two independent force constants α and β for the first-neighbor cation-anion interactions. In order to completely describe the second-neighbor anion-anion and cation-cation interactions there are a total of four force constants.

For second-nearest neighbors the anion-anion and cation-cation interactions are assumed to be equal, reducing the number of second-neighbor force constants to two, δ and η. Interactions between third and higher neighbors are neglected in this work. Following standard techniques[14] the following expression for the short-range interaction terms in the R matrix are obtained:

$$R_{xx}(KK) = -2\eta\cos 2\pi q_x - 2\delta(\cos 2\pi q_y + \cos 2\pi q_z) + 8\alpha + 2\eta + 4\delta\,,$$

$$R_{xy}(KK) = 0\,,$$

$$R_{xx}(KK') = -8\alpha\cos\pi q_x\cos\pi q_y\cos\pi q_z\,, \tag{3}$$

and

$$R_{xy}(KK') = 8\beta\sin\pi q_x\sin\pi q_y\cos\pi q_z\,,$$

where

$$\vec{q} = a\vec{k}$$

and a represents the lattice constant. The remaining short-range interaction terms in the $\underline{R}$ matrix are generated by a cyclic permutation of the coordinate indices in Eq. (3) along with the Hermitian property of the $\underline{R}$ matrix.

The expressions for the Coulomb coupling coefficients for $\vec{k} \neq 0$ can be generated following the technique of Kellermann[2] and in particular have been given for the cesium chloride structure by Ganesan and Srinivasan.[1] For the special case of $k = 0$, the only nonzero Coulomb coupling coefficients are

$$C_{xx}(KK') = (8\pi/3)(e_K\,e_{K'}/v_a)$$

and

$$C_{yy}(KK') = C_{zz}(KK') = (-4\pi/3)(e_K e_{K'}/v_a), \tag{4}$$

where v_a is the volume of the unit cell and $e_K = ze$ and $e_{K'} = -ze$ are the effective ionic charge on the ions.

Taking account of the contribution to the elastic constants C_{11}, C_{12}, and C_{44} due to the Coulomb coupling coefficients evaluated by Ganesan and Srinivasan,[1] it can be shown that the following expressions result for the elastic constants:

$$C_{11} = (1/a)(2\alpha + 2\eta + 5.62\,e^2z^2/av_a)\,,$$

$$C_{12} = (1/a)(4\beta - 2\delta - 2\alpha - 5.5\,e^2z^2/av_a)\,, \tag{5}$$

and

$$C_{44} = (1/a)(2\alpha + 2\delta - 2.83\,e^2z^2/av_a)\,.$$

The equations relating the LO and TO mode frequencies at the zone center to the force-constant parameters are obtained by solving the secular equation at $k = 0$ and are given as

$$\omega_{\mathrm{TO}}^2 = (1/\mu)[8\alpha - 4\pi e^2z^2/3v_a]$$

and

$$\omega_{\mathrm{LO}}^2 = (1/\mu)[8\alpha + 8\pi e^2z^2/3v_a]\,, \tag{6}$$

where μ is the reduced mass.

The simultaneous solution of the three elastic constant equations and the two zone-center equations enables us to obtain explicit expressions for α, β, η, δ, and z. This also guarantees an exact agreement at $\vec{k} \simeq 0$ for the LO and TO branches. The experimental values of the elastic constants of CsCl, CsBr, and CsI were determined by Chang, Barsch, and Miller.[15] The zone-center frequencies utilized were determined by Jones *et al.*[16] The values of the zone-center frequencies and the elastic constants are summarized in Table I. The values of the force constants and the charge numbers obtained from the solution of Eqs. (5) and (6) are presented in Table II. It may be noted that the z values obtained by this model compare well with the Szigeti effective charge of $0.85e$, $0.78e$, and $0.67e$ for CsCl, CsBr, and CsI, respectively.

The phonon dispersion is calculated in various symmetry directions for CsCl, CsBr, and CsI, and is presented in Fig. 1. Our calculated phonon dispersion with a five-force-parameter model agrees qualitatively with Karo and Hardy's deformation-dipole model[5] calculation and the shell-model calculation of Srivastava and Dayal.[6] It may be mentioned here that Karo and Hardy's rigid-ion model and deformation-dipole model do not give the correct splitting of LO and TO modes at $\vec{k} \simeq 0$.

The frequency distribution function $g(\omega)$ was calculated for a mesh of 1000 points in the first Brillouin zone. Due to the symmetry properties of the Brillouin zone, one need only consider the determination of the eigenfrequencies at 56 nonequivalent points in the $\vec{k}$ space defined as

$$\vec{q} = (q_x,\ q_y,\ q_z)\,,$$

where

$$0.5 \geq q_x \geq q_y \geq q_z \geq 0\,. \tag{7}$$

This type of sampling gave a total of 6000 frequencies from which histograms of $g(\omega)$ for CsCl, CsBr, and CsI were plotted. The resulting histograms with frequency sampling widths of $\Delta\omega = 0.1\times10^{13}\ \mathrm{sec}^{-1}$ are presented in Fig. 2. The calculated frequency distribution qualitatively agrees with previous calculated results.[5,7]

In the case of CsCl the frequency distribution function was also calculated for a mesh of 8000 points in the first Brillouin zone. This type of sampling gave a total of 48 000 frequencies from which a resulting curve was plotted as shown in Fig. 3. In the case of CsCl the possibility of a narrow gap around 83 cm^{-1} is thus suggested by our model. A gap mode due to Na as a substitutional impurity in CsCl has indeed been observed[17] at about 83 cm^{-1}.

TABLE I. Elastic constants[a] and the Brillouin-zone-center optic-mode frequencies[b] of CsCl, CsBr, and CsI.

Compound	Pressure	C_{11} 10^{11} dyn/cm^2	C_{12} 10^{11} dyn/cm^2	C_{44} 10^{11} dyn/cm^2	ω_{LO} (cm^{-1})	ω_{TO} (cm^{-1})
CsCl	STP	3.683	0.893	0.817	165	99
	4.5 kbar	3.963	1.107	0.962	171.9	108.2
CsBr	STP	3.077	0.827	0.760	112	73
	9 kbar	3.607	1.236	1.061	122.5	86.1
CsI	STP	2.462	0.659	0.644	85	62
	9 kbar	3.015	1.076	0.950	93	71

[a] From Ref. 15.

[b] STP values are from Ref. 16; values at higher pressures are calculated by the method outlined in this paper.

The calculated Debye characteristic temperatures as a function of temperature are shown in Fig. 4 and compared to available experimental values.[18,19] Considering the simplicity of the present lattice dynamical model, the agreement may be regarded surprisingly good. It may also be pointed out that in this comparison no anharmonic corrections were made which become operative at higher temperatures.

III. LATTICE DYNAMICS AT DIFFERENT PRESSURES

The calculation of the lattice dynamics at different pressures is rather straightforward if the pressure dependence of both the elastic constants and the zone-center frequencies are known. In the case of the cesium halides, only data on the pressure dependence of the elastic constants are known.[15] To date, data on the pressure dependence of the zone-center mode frequencies exist only for the traverse optic mode of CsBr.[20] These are therefore obtained using a Born-Mayer-type potential, which is known to predict[21,22] the zone-center optic-mode Grüneisen parameters of alkali halides rather well. It is realized, however, that the use of a central potential for this purpose is certainly a lower approximation compared with the lattice dynamical model used here. But for the zone-center modes of alkali halides at least, such an approximation has in the past been demonstrated[21–24] to work well.

Adapting to the CsCl structure the relations given by Mitra[23] for the NaCl structure, one may write for ω_{TO} and ω_{LO}

$$\omega_{\mathrm{TO}}^2 = \frac{\alpha_M(r_0/\rho - 2)\, e^2 z^2}{3 r_0^3\, \mu} - \frac{\sqrt{3}\pi e^2 z^2}{2 r_0^3\, \mu}$$

and (8)

$$\omega_{\mathrm{LO}}^2 = \frac{\alpha_M(r_0/\rho - 2) e^2 z^2}{3 r_0^3\, \mu} + \frac{\sqrt{3}\pi e^2 z^2}{r_0^3\, \mu} \quad ,$$

where α_M is the Madelung constant, r_0 is the near-neighbor distance, and ρ is a Born-Mayer potential constant. Since for the CsCl structure the bulk modulus B and ρ are related in the following manner[24]:

$$B = \frac{\alpha_M(r_0/\rho - 2) e^2 z^2}{8\sqrt{3}\, r_0^4} \quad , \tag{9}$$

one may rewrite Eq. (8) as

$$\omega_{\mathrm{TO}}^2 = 8 B r_0/\sqrt{3}\, \mu - \sqrt{3}\pi e^2 z^2/2 r_0^3\, \mu$$

and (10)

$$\omega_{\mathrm{LO}}^2 = 8 B r_0/\sqrt{3}\, \mu + \sqrt{3}\pi e^2 z^2/r_0^3\, \mu \quad .$$

For not too large values of pressure the $\vec{k} \sim 0$ LO and TO mode frequencies may now be obtained as functions of pressure according to

$$\omega_{\mathrm{TO}(P)} = \omega_{\mathrm{TO}(0)} + P \frac{d\omega_{\mathrm{TO}}}{dP}$$

and (11)

$$\omega_{\mathrm{LO}(P)} = \omega_{\mathrm{LO}(0)} + P \frac{d\omega_{\mathrm{LO}}}{dP} \quad ,$$

where $\omega_{\mathrm{TO}(P)}$ and $\omega_{\mathrm{LO}(P)}$ represent the quantities at a pressure P and $\omega_{\mathrm{TO}(0)}$ and $\omega_{\mathrm{LO}(0)}$ the same quantities at the ambient pressure. Since both B

TABLE II. Rigid-ion-model force constants and the effective ionic charge for CsCl, CsBr, and CsI.

Compound	Pressure	α 10^3 dyn/cm	β 10^3 dyn/cm	δ 10^3 dyn/cm	η 10^3 dyn/cm	z
CsCl	STP	3.223	4.142	0.153	2.555	0.830
	4.5 kbar	3.646	4.551	−0.050	2.281	
CsBr	STP	2.850	3.463	−0.047	2.740	0.760
	9 kbar	3.664	4.274	−0.337	2.878	
CsI	STP	2.383	2.560	−0.369	3.566	0.651
	9 kbar	2.991	3.406	−0.184	4.410	

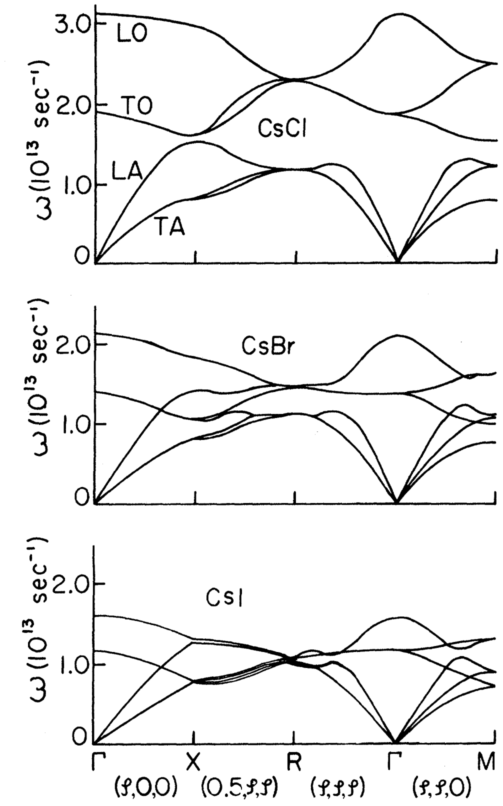

FIG. 1. Phonon dispersion relations for CsCl, CsBr, and CsI in selected symmetry directions in the first Brillouin zone. ζ is the reduced wave-vector coordinate defined as *ak*. The critical points are defined as $\Gamma \equiv (0,0,0)$, $X \equiv (0.5,0,0)$, $R \equiv (0.5,0.5,0.5)$, and $M \equiv (0.5,0.5,0)$.

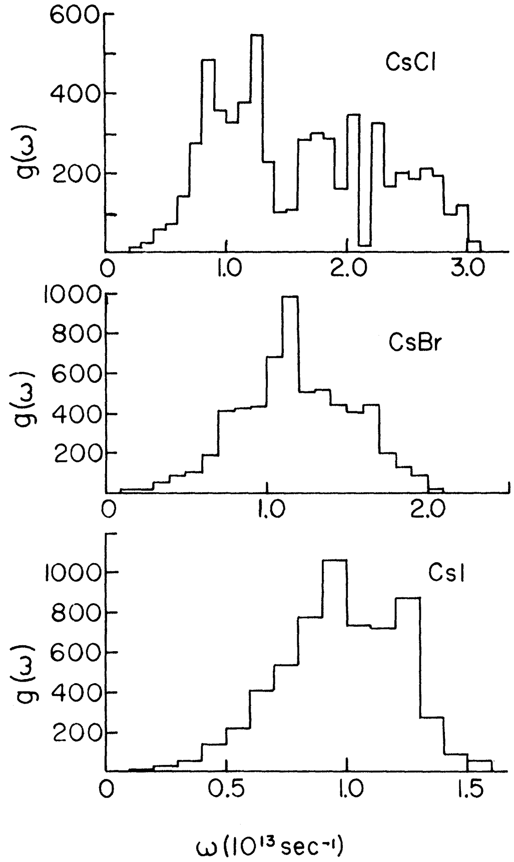

FIG. 2. Calculated phonon density of states $g(\omega)$ of CsCl, CsBr, and CsI as functions of frequency. Histograms are calculated for a frequency interval of 0.1×10^{13} sec^{-1}.

and r_0 are known as functions of pressure,[15] $d\omega_{\mathrm{TO}}/dP$ and $d\omega_{\mathrm{LO}}/dP$ can be obtained readily from Eq. (10) provided it is assumed that the charge number z remains constant with pressure for the pressure range considered. The latter assumption was also made in the calculations on the NaCl structure[21–23] and also appears to be experimentally evident.[25,26]

The calculated values of the zone-center frequencies at a higher pressure along with the values of elastic constants are presented in Table I. It is to be noted that agreement between the calculated long-wavelength TO mode frequency for CsBr and the experimentally measured value is quite good. The predicted shift for a pressure of 9 kbar is 13 cm^{-1} while the experimental value[20] is 11 ± 2 cm^{-1}. Furthermore, the experimental data on CsBr show a linear variation of ω_{TO} with P up to a pressure range of 30 kbar in accordance with the assumed linear dependence in Eq. (11).

The results derived from Eq. (10) are valid for the Born-Mayer potential assumed for the long-

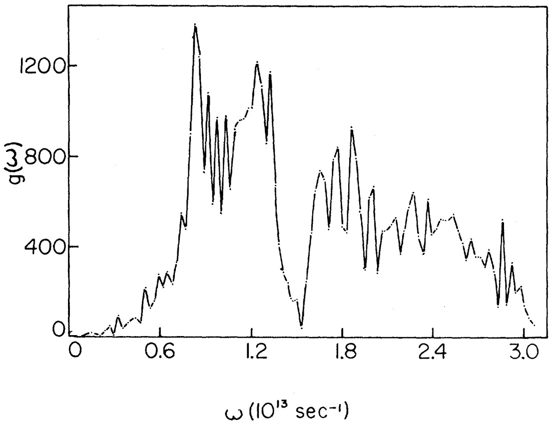

FIG. 3. Phonon density of states for CsCl calculated with a frequency interval of 0.03×10^{13} sec^{-1}.

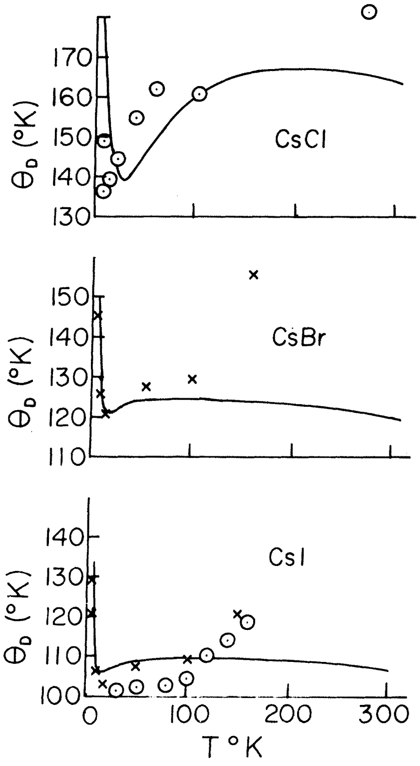

FIG. 4. Debye characteristic temperature of CsCl, CsBr, and CsI as functions of temperature. Sources of experimental points are as follows: Circles (Ref. 18); crosses (Ref. 19).

wavelength optic modes and need not be confused with the results of Eq. (6) which are for a more elaborate model that assumes noncentral forces and are used here for the calculation of lattice dynamics. It may be emphasized that the use of Eqs. (8) or (10) for the calculation of the volume dependence of the long-wavelength LO and TO mode frequencies are justified to the extent that such a treatment was found quite satisfactory for LiF, NaF, KCl, and KBr for which data exist[21,22] and also for ω_{TO} of CsBr as indicated above.

With the use of the high-pressure data for the elastic constants and zone-center frequencies the calculation of the phonon dispersion at a higher pressure is performed in a manner analogous to the treatment at standard pressure. Table II presents the values of the force constants at a higher pressure.

IV. MODE GRÜNEISEN PARAMETERS, GRÜNEISEN CONSTANT, AND LINEAR THERMAL-EXPANSION COEFFICIENT FOR CsCl, CsBr, AND CsI

The Grüneisen parameter for the phonon frequency of the ith branch at a point $\vec{k}$ in the Brillouin zone is given by

$$\gamma_i(\vec{k}) = -\frac{d\ln\omega_i(\vec{k})}{d\ln V} \quad . \tag{12}$$

In terms of the bulk modulus and the pressure dependence of the phonon frequencies, the Grüneisen parameter can be expressed as

$$\gamma_i = (B/\omega)(\Delta\omega/\Delta p)_T \quad . \tag{13}$$

It is then possible to obtain the variation of the Grüneisen parameter as a function of wave vector $\vec{k}$. Figure 5 presents the wave-vector dependence of γ_i in the $(\zeta 00)$ and $(\zeta\zeta\zeta)$ directions for CsCl, CsBr, and CsI, respectively, where ζ is the reduced wave-vector coordinate. The crosses and circles in the figures represent the long-wavelength limit of the mode Grüneisen parameter for the LA and TA modes calculated from the contin-

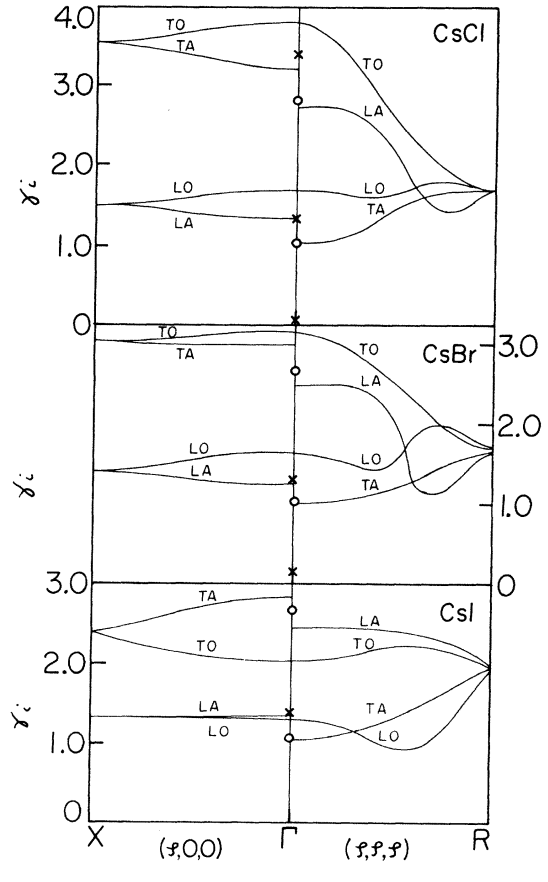

FIG. 5. Mode Grüneisen parameters for CsCl, CsBr, and CsI as functions of reduced wave vector in $[\zeta 00]$ and $[\zeta\zeta\zeta]$ directions. Long-wavelength values of γ_{TA} and γ_{LA} calculated for the continuum model are indicated by crosses (coming from $[\zeta 00]$ direction) and circles (coming from $[\zeta\zeta\zeta]$ direction).

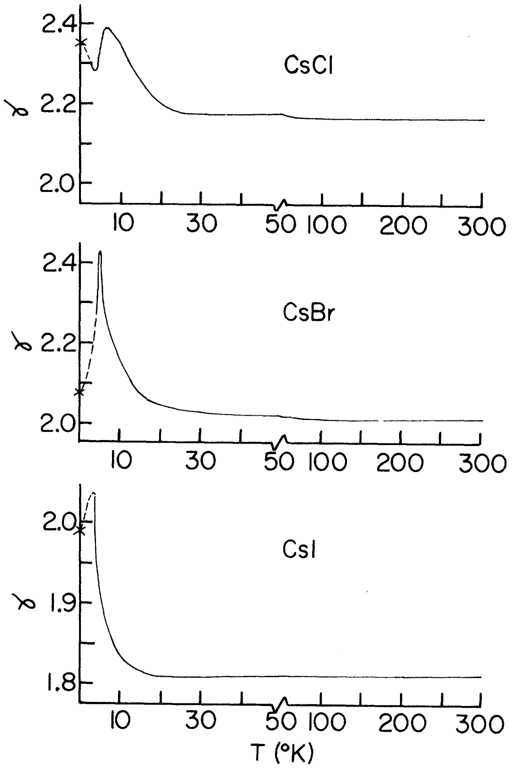

FIG. 6. Grüneisen constant of CsCl, CsBr, and CsI as functions of temperature. Crosses indicate low-temperature limits calculated by the method of Ref. 27.

uum case.

The Grüneisen constant defined as $\gamma \equiv \sum_i \gamma_i C_i / \sum_i C_i$ was calculated using the calculated frequency distribution functions for CsCl, CsBr, and CsI. It is expressible as

$$\gamma(T) = \sum_{i=1}^{P} \sum_{j=1}^{J} \gamma_{ji} C_i \tfrac{1}{2}(a_i - a_{i-1}) \Big/ \sum_{i=1}^{P} h_i C_i \tfrac{1}{2}(a_i - a_{i-1}) , \qquad (14)$$

where $a_i = \hbar\omega_i/kT$ and C_i is the Einstein specific-heat function. h_i is the height of the distribution function between ω_{i-1} and ω_i. γ_{ji} is the individual mode Grüneisen parameter of the jth frequency in the ith interval, J is the number of frequencies in the ith interval, and P is the number of frequency intervals.

The variation of the Grüneisen constant with temperature is presented in Fig. 6 for CsCl, CsBr, and CsI. The crosses in the figure indicate the low-temperature limit of the Grüneisen constant from a relationship given by Daniels.[27]

A formal calculation of the Grüneisen constant as a function of temperature using results of lattice dynamics was first attempted by Barron,[28] who showed that γ, even in some simple crystals may be expected to exhibit considerable temperature dependence at low temperatures ($T < \theta_D$). Although the individual mode Grüneisen parameters varied widely in their values, γ of the CsCl-type crystals appears to be almost independent of temperature except for a small bump at very low temperatures. Thus the three crystals considered here appear to constitute a type of nearly perfect "Grüneisen solids," the condition for the existence of which was given by Blackman.[29] Ganesan and Srinivasan[1] also recognized that γ may be independent of T for the CsCl structure when a certain value of the exponent n was chosen for the repulsive term in the Born-Mayer-type potential they used.

Once γ is known, the linear thermal-expansion coefficient is obtained by the relation

$$\alpha(T) = \gamma(T) C_v(T) / 3Bv_a \quad , \qquad (15)$$

where C_v is the specific heat at constant volume. The variation of the linear thermal-expansion coefficient with temperature was calculated from Eq. (15) using calculated values of γ and C_v as obtained from the present lattice dynamical calculation. In particular, the specific heat was obtained using the relation developed by Vetelino and Mitra.[11] The results are presented in Figs. 7–9, and are compared with available experimental data.[30–32] It may be remembered that the calculated values are obtained using only elastic constants, their pressure derivatives and the long-wavelength optic-mode frequencies. The calculated curves not only give the right trends of temperature dependence, even

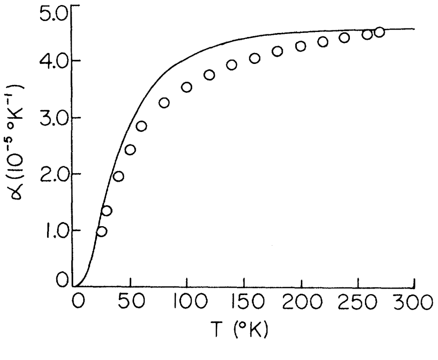

FIG. 7. Linear thermal-expansion coefficient of CsCl as a function of temperature. Experimental data from Bailey and Yates (Ref. 30) are indicated by circles.

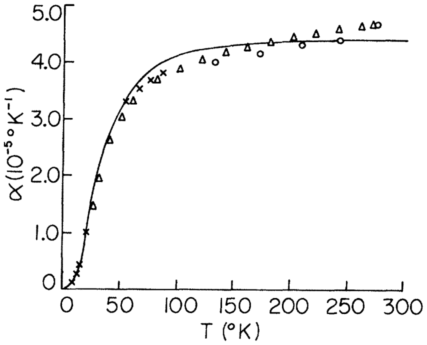

FIG. 8. Linear thermal-expansion coefficient of CsBr as a function of temperature. Experimental data are from X – White (Ref. 31); ○ – Krishman and Srinivasan (Ref. 31); Δ – Bailey and Yates (Ref. 30).

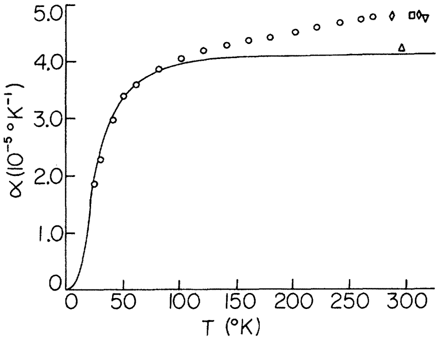

FIG. 9. Linear thermal-expansion coefficient of CsI as a function of temperature. Experimental data are from Ref. 32. ○ – James and Yates; □ – Rymer and Hambling; Δ – Johnson, Agron, and Bredig; ∇ – Pathak and Pandya; ◇ – Baxter and Wallace.

the absolute values of the coefficient of thermal expansion agree remarkably well. This is particularly so for CsBr.

Note added in proof. Recently, R. P. Lowndes [Phys. Rev. B 1, 2754 (1970)] has experimentally determined the long wavelength γ_{LO} for CsBr and CsI. His values are 0.63 and 0.68, respectively. These are somewhat smaller than the values calculated from dB/dP in this paper (see Fig. 5). Instead of using dB/dP, if one used directly the Born Mayer potential constant r_0/ρ (Ref. 24, p. 26), one obtains $\gamma_{TO} = 3.2$ and $\gamma_{LO} = 1.2$ for both CsBr and CsI. This γ_{TO} is in excellent agreement with the experimental value for CsBr as given in Ref. 20. But γ_{LO} is still somewhat higher than that obtained by Lowndes. However, it is worth mentioning here that the over-all agreement of $\underset{\sim}{\alpha}$ versus T is not very sensitive to the choice of $\vec{k} \simeq 0$, γ_{TO}, and γ_{LO}.

ACKNOWLEDGMENTS

We are indebted to Dr. J. N. Plendl and L. C. Mansur for their keen and continued interest in these investigations. All computation was done with an IBM 360 computer at the University of Rhode Island Computer Laboratory, which is supported by Grant No. GP 6037 from the National Science Foundation.

[†] Work supported in part by the U. S. Air Force In-House Laboratory Independent Research Fund under Contract No. AF19(628)6042.

[*] Paper forms part of a thesis submitted in partial fulfillment of the requirements for the Ph. D. degree at the University of Rhode Island, Kingston, R. I. 02281.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Excitonic Processes and Thermoluminescence

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(Received 26 January 1970)

Processes of defect creation by nonionizing radiation were studied by applying thermoluminescence methods. KBr crystals were irradiated at 80 K by monochromatic uv light in the region of 1800–2300 Å. Shapes of glow curves were found to differ from those obtained after *x* coloration. Excitation spectra of the various glow peaks as well as dose dependence of their intensities were investigated. The excitation spectrum showed maxima at the α band and on the long-wavelength tail of the fundamental absorption. Most of the glow peaks showed a linear dose dependence. The mechanism proposed by Pooley and by Hersh is extended to the case of defect creation by irradiation into a perturbed exciton state and excitation of thermoluminescence. An expression for the number of the defects created by the uv irradiation is derived as a function of the radiation dose. This expression takes into account the absorption coefficient of the crystal and, therefore, the penetration depth of the exciting monochromatic light. Experimental results were found to be in good agreement with those predicted by the model.

I. INTRODUCTION

Color-center formation in alkali halide crystals by uv radiation has been investigated by various authors.[1] Several models have been suggested to explain defect generation by ionizing and nonionizing radiation; an excitonic mechanism for the creation of *F* centers in alkali halides has been proposed independently by Hersh and by Pooley.[2] This mechanism is now extended in order to take in account creation of defects by irradiation into a perturbed exciton state, and to explain excitation of thermoluminescence (TL) by uv irradiation.

In most previous experimental investigations, crystals were irradiated with polychromatic uv light, since the low intensities of the uv light sources and the relatively low sensitivity of absorption methods did not permit the use of monochromatic uv light. The use of monochromatic light appears to be of advantage in the study of the energies connected with the creation of defects and the processes involved.

In the present work, TL methods have been applied to study the processes of defect formation by nonionizing radiation. The relatively high sensitivity of TL compared with optical-absorption measurements enabled us to use monochromatic uv light for excitation. The excitation spectra of the main glow peaks revealed information concerning defects which were undetectable by other means under similar excitation conditions.

II. THEORETICAL MODEL

We start from the model which has been given by Pooley and by Hersh[2] for the creation of defects in alkali halides by irradiation into the fundamental absorption bands. We consider defect generation by uv light in the case of irradiation into the edge of the fundamental absorption as well as into the α band. We take into account the penetration depth of the exciting uv light depending on the absorption coefficient of the crystal.