

Low Lying Resonant Band Modes in CsBr and CsI Crystals Doped with In^+ and Tl^+

By

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Measurements of the far infrared absorption due to In^+ and Tl^+ impurities in CsBr and CsI single crystals yielded low frequency resonances with narrow linewidths at 11.0 cm^{-1} in CsBr: In^+ , 12.0 cm^{-1} in CsI: In^+ , 14.1 cm^{-1} in CsI: Tl^+ , and 16.95 cm^{-1} in CsBr: Tl^+ . The frequencies of the resonant band modes in the Tl^+ doped crystals shift to higher values with increasing temperature. Using a model of the perturbed crystal which involves the mass defect and the change of the central force constants between the defect and its eight nearest neighbours, the force constant change is fitted to the various resonance frequencies. The resulting linewidths are compared with the experimentally determined values.

Messungen der Fern-Infrarot-Absorption von In^+ und Tl^+ Defekten in CsBr- und CsI-Einkristallen ergaben niederfrequente und schmalbandige Resonanzen bei $11,0\text{ cm}^{-1}$ in CsBr: In^+ , $12,0\text{ cm}^{-1}$ in CsI: In^+ , $14,1\text{ cm}^{-1}$ in CsI: Tl^+ und $16,95\text{ cm}^{-1}$ in CsBr: Tl^+ . Die Frequenzen der resonanten Bandschwingungen in den Tl^+ -dotierten Kristallen verschieben sich mit zunehmender Temperatur zu höheren Werten. Mit Hilfe eines Modells des gestörten Kristalls, welches den Massendefekt und die Änderung der zentralen Kraftkonstanten zwischen dem Defekt und seinen acht nächsten Nachbarn berücksichtigt, wurde die Kraftkonstantenänderung an die verschiedenen Resonanzfrequenzen angepaßt. Die hieraus resultierenden Linienbreiten wurden mit den experimentell ermittelten Werten verglichen.

1. Introduction

Various investigations concerning the lattice dynamics of defect crystals have shown that particular atomic impurities in alkali halide crystals exhibit resonances whose frequencies lie in the continuum of the long wavelength acoustic phonons. Resonant lattice modes in which an impurity vibrates with a different amplitude than does the replaced ion are associated with an electric dipole moment and can be directly observed as narrow absorption lines in the far infrared. Such defect modes result from either a heavy impurity or, which is more reasonable in most cases, from a weak coupling between the defect ion and the lattice. The linewidth of a resonant mode is finite even at zero temperature due to scattering of phonons of the unperturbed lattice by the impurity. Therefore the relative linewidth of a resonant mode is proportional to the phonon density of states. In [1] to [6] full details of the properties of low frequency resonant modes are given.

So far much work has been done on the far infrared absorption of doped alkali halides with sodium chloride structure. In this paper we present results concerning In^+ and Tl^+ impurities in cesium bromide and cesium iodide host lattices both of which crystallize with the cesium chloride structure. Preliminary measurements of the impurity induced absorption of CsI: Tl^+ have already been published elsewhere [7].

2. Experimental

2.1 Technique

The absorption measurements were made using a commercial RIIC Michelson interferometer, FS 720, and a Fourier transform computer, FTC 100. The Tl^+ doped single crystals were grown from u.p. material by the Czochralski technique in air. The Tl^+ concentrations of these samples were determined by colorimetric chemical analysis [8]. The In^+ doped samples were grown with the vacuum Bridgman method.¹⁾ Their impurity concentrations are only approximately known. The samples were mounted in a cryostat and were cooled by helium exchange gas in thermal contact with liquid helium or nitrogen. The temperature was adjusted by electrical heating of the exchange gas chamber and was measured using a calibrated Allen Bradley carbon resistor of 100 Ω nominal resistance. The coefficient of additional absorption was determined by the usual manner of comparing the transmission spectra of a doped and an undoped sample of equal thicknesses.

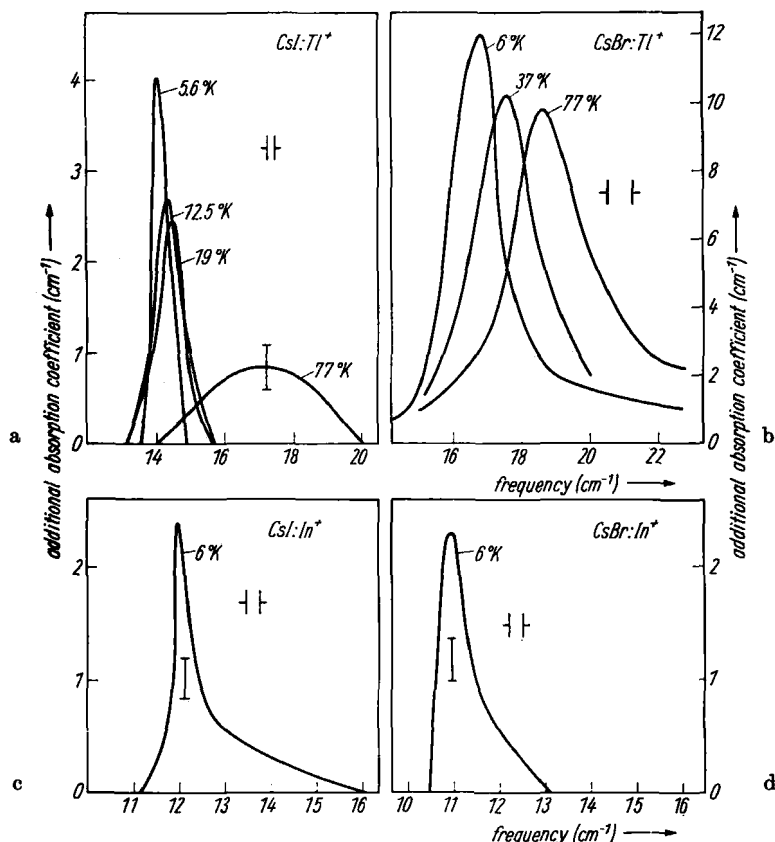


Fig. 1. Resonant band mode absorption. Impurity concentrations: CsI:Tl^+ 1.5×10^{-2} mol%, CsBr:Tl^+ 6.4×10^{-2} mol%, CsI:In^+ and CsBr:In^+ $\approx 10^{-3}$ mol% [16]

¹⁾ These crystals were grown by Dr. K. MAIER at the University of Frankfurt and placed at our disposal.

2.2 Results and discussion

The experimental results are shown in Fig. 1 where the curves of the additional absorption due to the impurities are given. In all four systems resonant band modes were found whose frequencies lie close together between 11.0 and 16.95 cm^{-1} . The resonance frequencies and the linewidths (full width at half maximum absorption) at about 6 °K are listed in Table 1 column (a) and (b), respectively. The given values of the linewidths are corrected to eliminate the instrumental resolution according to Kirby et al. [6]. All absorption curves are more or less asymmetric. The asymmetry of the TI^+ modes is largely due to the increasing phonon density of states. It becomes nearly symmetrical upon dividing by the density of states calculated from the breathing shell model [9, 10]. The origin of the asymmetry of the In^+ resonances is not quite clear. Though natural mixtures of isotopes have been used for doping, a hidden isotope splitting is not to be expected, because the abundance of the lighter In isotope amounts to only 4.23%. Also a ground state splitting caused by off-centre equilibrium positions of the In^+ ion cannot be concluded from the absorption curves because the temperature during the measurement was too high. Tentatively the asymmetry might be assigned to dislocations interacting with the volume defect In^+ . The small sized impurity has its stable equilibrium position in the compressional part of a dislocation, hence the frequency of impurities on such sites would be increased thus causing the high frequency shoulder of the line. A side band of the resonant mode in $\text{NaCl}:\text{Cu}^+$ could be explained with similar arguments [11].

The weak coupling of the defect ions might be qualitatively explained by the following arguments:

(i) The ionic radii of In^+ and TI^+ are, respectively, about 22 and 17% smaller than that of the substituted Cs^+ ion [12]. Moreover the polarizability of TI^+ is larger than that of Cs^+ [13].

(ii) The Br^- and I^- have ionic radii approximately 6 and 8%, respectively, less than one half of the lattice constant of the corresponding cesium halide. Thus, no substantial inward relaxation of the neighbouring ions of the impurities is to be expected. The eight nearest neighbours located on the corners of a cube form an ample cage around one impurity.

Table 1

(a) Resonance frequencies, (b) experimental determined linewidths, (c) theoretical linewidths, (d) fractional change of the nearest neighbour force constants. All frequencies given in wavenumbers (cm^{-1})

host lattice	defect	(a) ω_r	(b) $\Delta\omega_{\text{exp.}}$	(c) $\Delta\omega_{\text{th.}}$	(d) $\Delta f/f$
CsBr	In^+	11.0	0.64	0.15	-0.976
	TI^+	16.95	1.5	0.76	-0.921
CsI	In^+	12.0	0.26	0.3	-0.956
	TI^+	14.1	0.5	0.6	-0.925

(iii) The uv absorption spectrum of the Tl^+ centre in CsI caused by electronic transitions is known to display some anomalies compared with the spectrum of Tl^+ in other alkali halides [14]. There are more absorption bands partly with different temperature dependence than expected for an $(ns)^2$ -ion in a crystal field of O_h symmetry. Recently Maier observed that the uv absorption of CsBr:Tl^+ and also that of the isoelectronic ion In^+ in CsI and CsBr reveals a similar behaviour as CsI:Tl^+ [15, 16]. Moreover he clarified these anomalies assuming LCAO-molecular orbitals constructed from the electronic wave functions of the impurity and its neighbouring lattice ions instead of treating the problem with simple crystal field theory. This result indicates that the chemical bonding is rather similar for both impurities in both host lattices. This covalent bond might increase the negative charge density between the impurity and its neighbours and hence shield the Coulomb interaction.

The absorption curves of the Tl^+ resonances have been measured at different temperatures (see Fig. 1a and b). The linewidths show the usual temperature dependent broadening of low frequency resonant modes which results from the anharmonicity. For both systems the integral absorption is nearly independent of temperature within the accuracy of the measurements. A remarkable effect is the shift of the Tl^+ resonances to higher frequencies with increasing temperature. Between 5.6 and 77 °K this shift runs up to 20% for CsI:Tl^+ and 9% for CsBr:Tl^+ . This behaviour may be qualitatively understood by assuming that there is a positive self energy due to anharmonic processes, which increases with temperature and overcompensates the lowering of the frequency arising from the thermal expansion of the crystal [5, 17].

Earlier measurements of the resonant mode in CsI:Tl^+ under applied uniaxial stress did not show a splitting of the line. Therefore, in a previous paper [7] we concluded that thermal expansion does not influence this frequency. Recently improved measurements were performed with CsI crystals hardened by additional doping of about 10^{-3} mol% Ca^{2+} ions [18]. Thus uniaxial stress could be applied up to 21.6 Nmm^{-2} which is about three times larger than the elasticity limit of pure or Tl^+ doped CsI crystals. Then a splitting of the mode could be observed. The same experiment was done with CsBr:Tl^+ crystals. The temperatures of the samples were in both cases 6 °K. From these measurements it was found

$$s(I_1^+) A(I_1^+) = (1.0 \pm 0.4) \times 10^{-3} \text{ cm}^{-1}/\text{bar for CsI:Tl}^+ \text{ and}$$

$$s(I_1^+) A(I_1^+) = (1.7 \pm 0.3) \times 10^{-3} \text{ cm}^{-1}/\text{bar for CsBr:Tl}^+.$$

Here $A(I_1^+)$ is the linear anharmonic coupling coefficient, which describes the coupling of the resonant mode to a hydrostatic deformation [2, 19] and which is responsible for the shift of the frequency caused by thermal expansion, and $s(I_1^+) = s_{11} + 2 s_{12}$ is the corresponding compliance of the crystal. To evaluate $A(I_1^+)$ local compliances of the defect system should be used. However, such compliances are not yet known. Nevertheless, this result shows that at least the Tl^+ resonances will be affected by thermal expansion, hence, the self energy of the anharmonic processes must be still larger than the directly observed frequency shift.

3. Theory

3.1 Defect model

The purpose of the following model calculation is to demonstrate the decoupling of the In^+ and Tl^+ impurities from the host lattices. We consider one substitutional impurity at a Cs^+ site in a lattice of CsCl type neglecting any interaction between the defects. Such an approximation is reasonable because of the low defect concentrations in the studied samples. A harmonic model is used involving the mass change and the change of the central force constants between the impurity and its eight nearest neighbours. The force constant change will be fitted to the resonance frequency. The theoretical concept of our calculation is reviewed in several articles [3, 20, 21]. Hence, only the basic equations will be stated whereas the results relevant for the CsCl structure will be given in more detail.

The frequencies of resonant modes are given by the solutions of the equation

$$\text{Re } D(\omega^2) = 0, \quad (1)$$

where

$$D(\omega^2) = \det |I + G A| \quad (2)$$

is the denominator of the T -matrix (in matrix notation)

$$T = A (I + G A)^{-1}. \quad (3)$$

In this expression I is the unit matrix, G refers to the Green's function of the pure crystal, and A is the local perturbation matrix containing the mass defect and the force constant change. The linewidth of a narrow resonance is given by

$$\Delta\omega = \text{Im } D(\omega_r^2) \left\{ \omega_r \frac{d}{d\omega^2} \text{Re } D(\omega_r^2) \right\}^{-1}, \quad (4)$$

where ω_r is the resonance frequency.

Considering only a change of the nearest neighbour interaction, A becomes a 27×27 matrix with non-vanishing matrix elements corresponding to the subspace of the lattice affected by the impurity. The displacement vectors of the ions in this defect space form a reducible basis of the site symmetry of the impurity — in the present case the point group O_h — which can be reduced to symmetry coordinates transforming according to the irreducible representations of the point group. The reduction is performed according to the same technique used to get the normal coordinates of a molecule. Then it is found that the irreducible representation Γ of the group O_h appears in the defect space $n(\Gamma)$ times where

$$\left. \begin{aligned} n(\Gamma_1^+) &= 1, & n(\Gamma_3^+) &= 1, & n(\Gamma_4^+) &= 1, & n(\Gamma_5^+) &= 2, \\ n(\Gamma_2^-) &= 1, & n(\Gamma_3^-) &= 1, & n(\Gamma_4^-) &= 3, & n(\Gamma_5^-) &= 1. \end{aligned} \right\} \quad (5)$$

The irreducible representations Γ_2^+ and Γ_1^- do not enter the defect space [22]. The symmetry coordinates for the present impurity system are explicitly given in [23] and are used to determine the matrix elements of the defect matrix in

the representation of these coordinates denoted by A^r :

$$A^{r\pm} = \frac{\Delta f}{M_-}; \quad A^{r\pm} = A^{r\pm} = A^{r\pm} = A^{r\pm} = \frac{\Delta g}{M_-} \quad (6)$$

$$A_{jj'}^{r\pm} = \begin{pmatrix} \frac{8(\Delta f + 2\Delta g)}{3M_+} - \frac{\Delta M_+}{M_+} \omega^2 & -\frac{8\Delta f}{(24M_+M_-)^{1/2}} & -\frac{8\Delta g}{(12M_+M_-)^{1/2}} \\ -\frac{8\Delta f}{(24M_+M_-)^{1/2}} & \frac{\Delta f}{M_-} & 0 \\ -\frac{8\Delta g}{(12M_+M_-)^{1/2}} & 0 & \frac{\Delta g}{M_-} \end{pmatrix},$$

$$A_{jj'}^{r\pm} = \begin{pmatrix} \frac{\Delta f + 2\Delta g}{3M_-} & \frac{\sqrt{2}(\Delta f + 2\Delta g)}{3M_-} \\ \frac{\sqrt{2}(\Delta f + 2\Delta g)}{3M_-} & \frac{2\Delta f + \Delta g}{3M_-} \end{pmatrix}.$$

Here M_+ and M_- are the masses of the positive and negative ions of the host crystal respectively, $\Delta M_+ = M'_+ - M_+$ is the mass defect and $\Delta f = f' - f$, and $\Delta g = g' - g$ are the changes of the nearest neighbour central and noncentral force constants. Primed letters refer to the defect crystal. f and g are related to the elements of the force constant matrices in the notation of Leibfried [24] as follows: $f = \alpha'' + 2\gamma''$ and $g = \alpha'' - \gamma''$. For the further discussion we only need $A_{jj'}^{r\pm}$, because only modes transforming according to the irreducible polar vector representation Γ_4^- interact with the radiation field by electric dipole absorption.

The Green's function of the pure crystal is evaluated using the Debye approximation with one Debye frequency given by Timmesfeld [25]. This approximation is reasonable because the resonant modes are lying in the very low frequency region of the phonon spectrum. According to Timmesfeld the Green's function of the unperturbed lattice has the form

$$G_{\alpha\alpha'} \left(\begin{matrix} l l' \\ K K' \end{matrix} \middle| \omega \right) = \delta_{\alpha\alpha'} \frac{3(M_K M_{K'})^{1/2}}{(M_+ + M_-)\omega_D^2} g(d, \omega), \quad (7)$$

where

$$g(0, \omega) = 1 + \frac{\omega}{2\omega_D} \ln \left| \frac{1 - \omega/\omega_D}{1 + \omega/\omega_D} \right| + i \frac{\pi}{2} \frac{\omega}{\omega_D} \quad (8)$$

and

$$\text{Im } g(d, \omega) = \frac{\pi}{2} \frac{\sin(q_D d \omega/\omega_D)}{q_D d} \quad \text{for } d \neq 0. \quad (9)$$

Here l and $K = \pm$ label a unit cell and an ion in it respectively, $d = \left| \mathbf{R} \left(\begin{matrix} l \\ K \end{matrix} \right) - \mathbf{R} \left(\begin{matrix} l' \\ K' \end{matrix} \right) \right|$ is the equilibrium distance between two ions, q_D is the radius of a sphere in the reciprocal lattice having the same volume as the first Brillouin zone, ω is the frequency, and ω_D the Debye frequency. The real part of $g(d, \omega)$

can be calculated by the Kramers-Kronig relation from $\text{Im } g(d, \omega)$. With these expressions the Green's function in the representation of the Γ_4^- symmetry coordinates is found to have the following matrix elements:

$$\begin{aligned}
 G_{11} &= \frac{3 M_+}{f_D} g(0, \omega) ; \\
 G_{12} &= \frac{(24 M_+ M_-)^{1/2}}{f_D} g\left(\frac{\sqrt{3}}{2} a, \omega\right) ; \\
 G_{13} &= \frac{(6 M_+ M_-)^{1/2}}{f_D} g\left(\frac{\sqrt{3}}{2} a, \omega\right) ; \\
 G_{22} &= \frac{M_-}{f_D} \{3 g(0, \omega) + g(a, \omega) + g(\sqrt{2} a, \omega) + 3 g(\sqrt{3} a, \omega)\} ; \\
 G_{23} &= \frac{4 \sqrt{2} M_-}{f_D} \{g(a, \omega) + g(\sqrt{2} a, \omega)\} ; \\
 G_{33} &= \frac{M_-}{f_D} \{3 g(0, \omega) + 5 g(a, \omega) + 5 g(\sqrt{2} a, \omega) + 3 g(\sqrt{3} a, \omega)\} ,
 \end{aligned} \tag{10}$$

where $f_D = (M_+ + M_-) \omega_D^2$ and a is the lattice constant.

When the matrices $A_{jj'}^{\Gamma_4^-}$ and $G_{jj'}$ are substituted into equation (2) the denominator $D^{\Gamma_4^-}(\omega^2)$ corresponding to the Γ_4^- irreducible representation of the T -matrix turns out to be

$$\begin{aligned}
 D^{\Gamma_4^-}(\omega^2) &= 1 + \Delta f \left\{ \frac{3}{8} \frac{1}{M_+} G_{11} - \frac{16}{(24 M_+ M_-)^{1/2}} G_{12} + \frac{1}{M_+} G_{22} \right\} - \frac{\Delta M_+}{M_+} \omega^2 G_{11} - \\
 &\quad - \frac{\Delta f}{M_-} \frac{\Delta M_+}{M_+} \omega^2 \det |G_{jj'}| .
 \end{aligned} \tag{11}$$

Evaluating this expression, the non-central part of the coupling Δg has been neglected. Thus $A_{jj'}^{\Gamma_4^-}$ was reduced to a 2×2 matrix as can be seen from equation (6). This was obtained by choosing an appropriate orthonormal basis in the Γ_4^- subspace of which the mode labelled by $j = 3$ affects only the non-central part of the coupling.

3.2 Numerical results

Now the resonance condition for optically active resonances $\text{Re } D^{\Gamma_4^-}(\omega^2) = 0$ was solved to get the change of the force constant $\Delta f(\omega)$ as a function of the frequency. Using this relation Δf can be fitted to the observed resonance frequency. An effective low frequency nearest neighbour force constant f of the unperturbed lattice is given by the solution of the resonance condition at zero frequency putting $\Delta f(\omega = 0) = -f$ [20]. For the present Debye model it turns out to be $f = 0.276 f_D$. Thus, the fractional change of the force constant $\Delta f/f$ can be calculated. The result is plotted in Fig. 2 versus the squared frequency ω^2 within a frequency range reasonable for the Debye approximation.

The Debye frequencies determined by specific heat measurements are $\omega_D = 97 \text{ cm}^{-1}$ for CsBr at 6 °K and $\omega_D = 81 \text{ cm}^{-1}$ for CsI at 5.6 °K [26]. These values were used to find the appropriate $\Delta f/f$ from Fig. 2 for the four defect

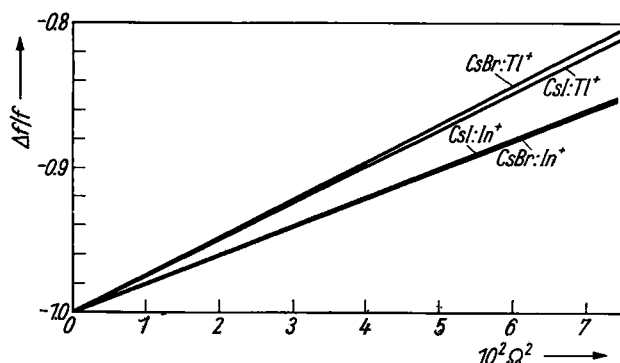


Fig. 2. Fractional change of the nearest neighbour central force constant $\Delta f/f$ versus normalized squared frequency $\Omega^2 = (\omega/\omega_D)^2$

systems. Knowing Δf the imaginary part of $D^{T_4}(\omega^2)$ (equation (11)) and the linewidth (equation (4)) can be evaluated. The resulting values of the force constant changes and the linewidths are given in Table 1 (c) and (d). The most weakly coupled defect is In^+ in CsBr whose force constant f' is only 2.4% of the original one. The ratio f'/f is nearly the same for both Tl^+ resonances: 7.9% for CsBr and 7.5% for CsI . In $\text{CsI}:\text{In}^+$ f'/f equals 4.4%. The agreement between the experimental and theoretical linewidths is rather good for the resonances occurring in CsI but is bad for the resonant modes in CsBr . In this case the calculated linewidths are too narrow. This might be due to the shortcomings of the applied simple defect model especially due to the disregarding of the non-central forces. Calculations using the breathing shell model [10] for the host lattice phonons are performed by Martin and will be published later [27].

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