IMPURITY INDUCED FAR INFRARED ABSORPTION OF CsI CRYSTALS

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The impurity induced band mode absorption of CsI:Li^+, Na^+, K^+, Rb^+, Tl^+ has been studied in the far infrared and compared with the calculated density of phonon states of CsI. CsI:Tl^+ yields a resonant mode at 14.1 cm^{-1} (5.6°K), the temperature dependence of which has been studied.

In perfect alkali halide crystals only the transverse optic phonons of zero wave vector absorb far infrared radiation in first order. The introduction of impurities in the lattice removes the translational invariance and almost all phonons become optically active. In addition to the absorption at the reststrahlen frequency, impurity induced absorption appears in the phonon band region and sometimes outside the bands as localized or gap modes [1]. In frequency regions with high density of states the coefficient of the impurity induced absorption is correlated to the density of phonon states in the perturbed crystal, which for low defect concentrations is nearly that of the host lattice. Thus this additional absorption gives information about the density of phonon states [2]. Besides this, weakly bound impurities can cause resonant band mode absorption in the low density region of the acoustic bands [3].

This paper deals with the far infrared absorption in the phonon bands of CsI doped with Li^+, Na^+, K^+, Rb^+ and Tl^+. The single crystals were grown from u.p. material by the Czochralski-technique in air. The impurity concentration of the Tl^+ doped crystals was determined by colorimetric chemical analysis [4]. In the other cases only the contents of impurities in the melt are quantitatively known. Their presence in the crystals was established by flame spectroscopy. The crystals were mounted in a cryostat and cooled by a cold finger or by helium exchange gas, which was in thermal contact with liquid helium or nitrogen. The temperature was measured with an Allen Bradley carbon resistor. The additional absorption was determined by comparison of the transmission of a doped and an undoped sample of equal thickness. The transmission measurements were performed by a commercial RIIC Michelson Interferometer, FS 720, and a Fourier transform computer, FTC 100. The spectra below 20 cm^{-1} were checked with a self-constructed Michelson Interferometer [5] employing a Texas Instruments Germanium bolometer which afforded a higher signal to noise ratio.

The impurity induced absorption of the doped CsI crystals is plotted in fig. 1. All dopings show a broad absorption in the region between about 35 cm^{-1} and the reststrahlen frequency at 66 cm^{-1}, which is nearly independent of temperature between 11°K and 77°K. The absorption coefficients of CsI:K^+ and CsI:Rb^+ exhibit a distinct maximum at 41 and 42 cm^{-1} respectively. The same structure also occurs, but to a lesser extent, in CsI:Na^+ and CsI:Tl^+ and could not be found in CsI:Li^+. Moreover in the system CsI:Tl^+ a resonant mode at 14.1 cm^{-1} was observed, which will be discussed later. In all other CsI crystals doped with alkali ions no resonant absorption has been found above 10 cm^{-1}, the lower frequency limit of this investigation.

CsI crystallizes with CsCl structure of space group O_h^1. The phonon dispersion curves have been calculated for 4.2°K by Mahler [6] using Schröder's breathing shell model [7]. The resulting density of states in the region of interest and the phonon frequencies at critical points are shown at the bottom of fig. 1. Below the reststrahlen frequency the phonon density possesses two maxima. One maximum arises from the phonons M_5' (TA), M_4' and X_5' (TA) and the other from the phonons M_2' (LO) and X_5 [8]. The site symmetry of a substitutional defect ion in the CsI lattice is O_h. It follows from the reduction of the O_h^1 symmetry to O_h, that only the representations M_5' (TA), M_4', X_5' (TA) contain the vector representation of the O_h point group.

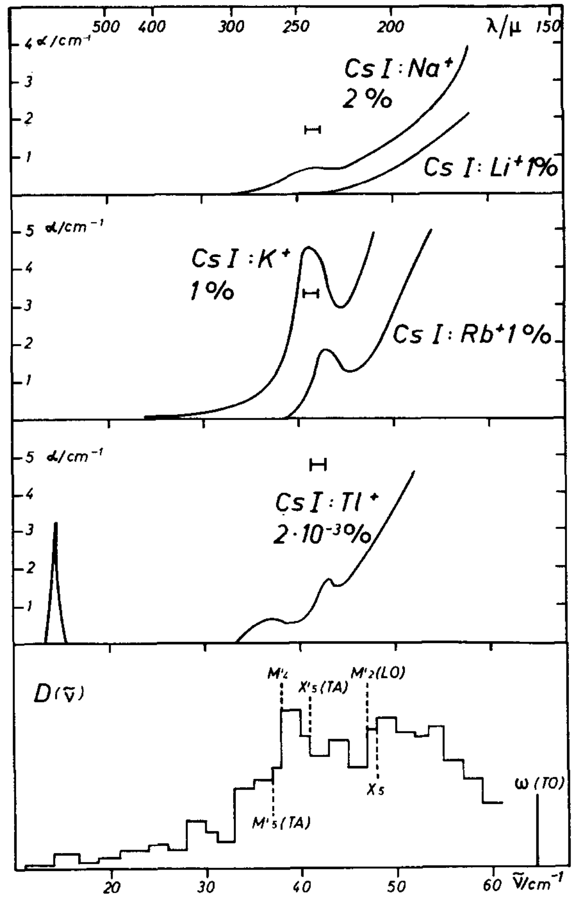

Fig. 1. Measured impurity induced absorption in CsI at 11°K and calculated density of phonons D(ν) at 4.2°K according to Mahler [6]. The concentrations are given in mol %. The Tl^+ concentration was determined colorimetrically, the others are the concentrations in the melt.

Thus the phonons of these symmetries become optically active whereas the phonons M_2' (LO) and X_5 remain inactive. A comparison between the calculated phonon density and the measured absorption of the doped crystals reveals that the absorption maxima between 41 and 42 cm^{-1} are caused by the phonons M_4' and X_5' (TA). For this conclusion to be true, the impurity ions must be assumed to occupy a Cs^+ lattice site.

The absorption coefficient of the resonant mode of $CsI:Tl^+$ was determined at different temperatures and is shown in fig. 2. The resonance frequency is 14.1 cm^{-1} at 5.6°K and increases with temperature to 17 cm^{-1} at 77°K. A similar temperature dependence was found for the U-center frequency in CsI [9]. Preliminary measurements of the behaviour of this resonant mode under applied uniaxial stress were made at 4.3°K * with an experimental device as described in ref. [11]. This gave a qualitative insight as to why the frequency increased with temperature. It was found that the anharmonic linear coupling coefficients A, B and C [12] vanish within the experimental error. Hence it follows that there is no linear coupling between the resonant mode and the lattice. Thus the thermal expansion of the lattice, which always lowers the frequency, has no influence on the impurity mode in first order and only third order anharmonic terms, quadratic in the lattice coordinates and higher order terms exist. The anharmonic processes resulting from these terms may shift the resonance to higher frequency [13].

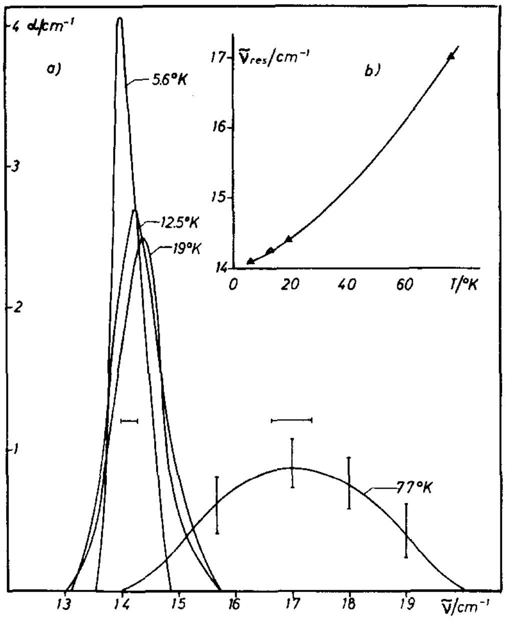

Fig. 2. a. Resonant mode in $CsI:Tl^+$ at different temperatures, Tl^+ concentration 2.10^{-3} mol %.
b. Temperature dependence of the resonance frequency

The line width of the resonant absorption is 0.5 cm^{-1} ay 5.6°K and increases to 3.7 cm^{-1} at 77°K. The integral absorption remains nearly constant in the whole temperature range.

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