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EVIDENCE FOR A QUASI-PHONON GAP IN CsCl*

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The observed impurity induced far-infrared absorption in CsCl : Rb^+ and CsCl : K^+ is compared with a calculated density of acoustic phonon states in CsCl. The absorption due to CsCl : Rb^+ displays a minimum between the acoustic and optic phonon bands. A narrow line is observed in CsCl : K^+ at 85.8 cm^{-1} which falls in this quasi-phonon gap.

A GAP BETWEEN the acoustic and optic phonon bands in CsCl has been predicted by Mahler [1] utilizing Schröder's 'breathing shell' model. [2] The present far-infrared measurements are an attempt to show if such a gap exists or not. More recently, an extension of Mahler's calculation by Jex [3] to over 1.7×10^5 points in the Brillouin zone, predicts a small, but nevertheless finite, density of phonon states between the acoustic and optic branches.

As has been known for some time, CsCl undergoes a phase transition [4][CsCl (b.c.c.) CsCl (f.c.c.)] at 469°C which makes it difficult to grow single crystals of CsCl. However, by using platinum as a seed crystal and slowly cooling the resultant crystals, single crystals of CsCl were grown from the melt in an argon atmosphere using the Kyropoulos method. In addition, one crystal was grown in air. The concentration of K^+ in the doped crystals was determined by flame spectroscopy [5] whereas a similar determination of Rb^+ was not possible due to the close proximity of Rb^+ and Cs^+ lines. The far infrared measurements were made on crystals at 4.9–5.1°K using a RIIC Fourier spectrometer employing a Golay cell as a detector.

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Mahler's gap and Jex's minimum occur at approximately 87–97 cm^{-1} and 79–98 cm^{-1} at 4.2°K respectively. Experimentally, a minimum in the additional absorption induced by Rb^+ was observed at the somewhat lower frequency range of 76–88 cm^{-1} as shown in Fig. 1. However, at

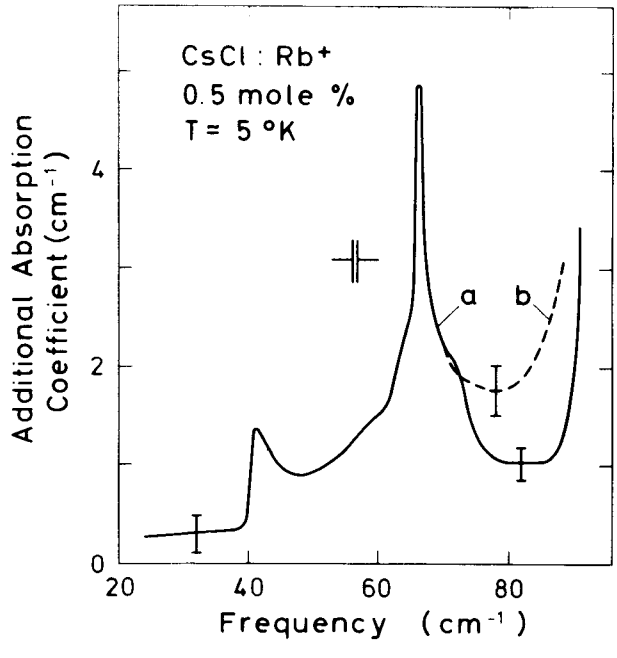

FIG. 1. Impurity induced absorption in CsCl : Rb^+; (a) grown in an argon atmosphere and (b) grown in air. The given mole per cent of Rb^+ is the concentration in the melt.

frequencies approaching 88 cm^{-1} a good assignment was not possible due to the strong absorption of the hot crystal itself. Hence, 88 cm^{-1} is merely a lower limit for the high frequency edge. This minimum, with respect to other features in the spectrum, was found to be shallower for a similarly doped crystal which was grown in air instead of argon and which therefore contains, among other things, large quantities of OH^-. This may be explained by a preferential increase in activation of one-phonon processes which results from the translational symmetry perturbation of the additional impurities.

A narrow line in $CsCl:K^+$ was observed at 85.8 cm^{-1} which falls within the minimum mentioned above; see Fig. 2. This line has a

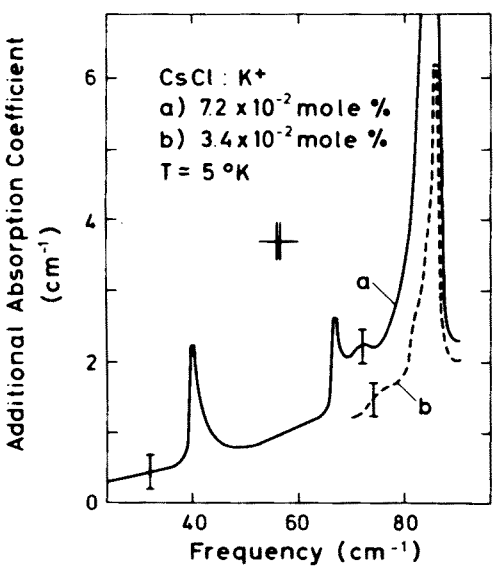

FIG. 2. Impurity induced absorption in $CsCl:K^+$. The K^+ concentrations were determined photometrically.

width at half-maximum of about 1 cm^{-1} which would be smaller if it were not for a low frequency shoulder due, in all probability, to a heavier isotope, ^{41}K, whose natural abundance is 6.91 per cent. The narrowness of this line is a good argument for a small, if not zero, density of phonon states within this minimum. Thus, subject to future slow neutron scattering experiments, we tentatively assign the absorption in this minimum to one-phonon processes and the minimum itself to a quasi-phonon gap.

Two maxima occur at 41.1 and 66.2 cm^{-1} in $CsCl:Rb^+$. The latter is relatively narrow with a width at half-maximum of $\leqslant 2$ cm^{-1}, while the former is somewhat broader due to a shoulder on the high frequency side. Moreover, two similar maxima occur in $CsCl:K^+$ at 40.1 and 67.0 cm^{-1}. In this case the former is more symmetrical and therefore narrower. It seems reasonable that the two maxima in both $CsCl:Rb^+$ and $CsCl:K^+$ are due to the same two critical points in the Brillouin zone because the differences in frequency are smaller than those which may accompany the activation of phonons.[6] Furthermore, using the assumption that the impurity ions occupy a Cs^+ lattice site, these two critical points are assigned to X_5' and R_{15} by means of Mahler's calculation shown schematically in Fig. 3.

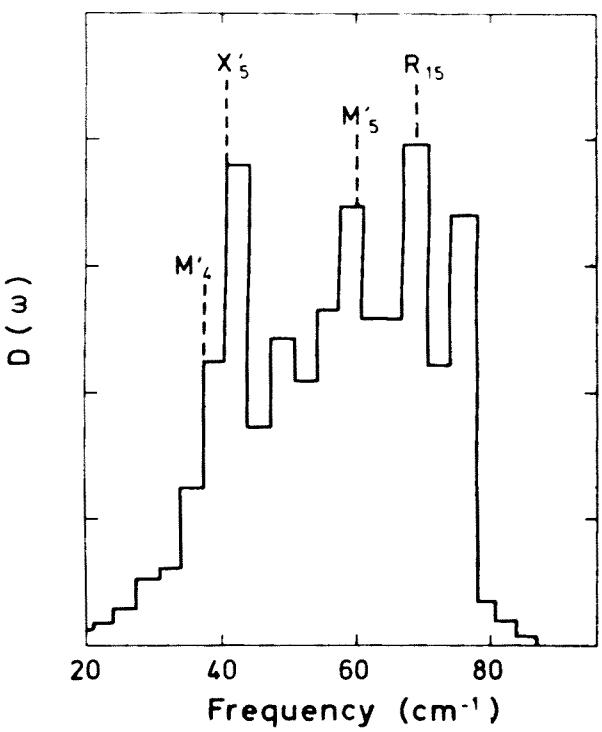

FIG. 3. The calculated density of phonon states, $D(\omega)$, at 4.2°K according to Mahler.

An observed minimum in the additional absorption of $CsCl:Rb^+$ has been tentatively

assigned to a quasi-phonon gap. Within this quasi-phonon gap, $CsCl:K^+$ produced a narrow line at 85.8 cm^{-1} reminiscent of a localized gap mode.* Two maxima in the spectra have been assigned to two critical points, X_5' and R_{15}, in the Brillouin zone.

* If the density of phonon states is not zero, this is really a resonant mode.

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Defektinduzierte Fern-Infrarot Absorption in $CsCl:Rb^+$ und $CsCl:K^+$ wird mit einer berechneten Zustandsdichte der akustischen Phononen verglichen. Die Absorption von $CsCl:Rb^+$ zeigt ein Minimum zwischen den akustischen und optischen Phononenzweigen. In $CsCl:K^+$ wird eine schmale Linie bei 85,8 cm^{-1} beobachtet, die in das quasi-phonon-gap fällt.