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IMPURITY–INDUCED ABSORPTION IN OR NEAR THE PHONON GAP OF KI

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In or near the phonon gap of KI a single weak line due to OH^- (OD^-) at 69.7 (69.3) cm^{-1} has been observed. A second and much stronger line at 94.1 cm^{-1} was shown not to be related to OH^-, but instead is thought to be due to $CO_3^=$.

A GAP between the acoustic and optical phonon bands of KI has been experimentally observed by slow neutron scattering by Dolling *et al.*[1] Within or near this gap, several far-infrared absorption bands have been observed in KI doped with OH^- by Renk[2,3] and Grisar *et al.*[4] These lines were subsequently assigned by the above investigators to localized librational and translational modes of OH^-. The present measurements were undertaken because some uncertainity as to the origin of these lines existed and because crystals grown under more closely controlled conditions became available.

The far-infrared measurements were made on crystals at 5.5–6.0°K using a Michelson interferometer* with a germanium bolometer as a detector. The samples were from single crystals grown under an inert atmosphere with the exception of one crystal grown in air.† This series of crystals was doped in such a way as to make the lines due to these three impurities distinguishable. In addition, a KI:Tl^+ crystal was supplied by the Harshaw Chemical Company.

The gap between the acoustic and optical phonon bands extends from 69.7 to 95.5 cm^{-1} at 90 K according to Dolling *et al.* Their calculated density of states for the acoustic band is similar to the additional absorption induced by Tl^+ which was originally reported by Sievers[5] and was repeated in the present investigation; see Fig. 1. The two maxima occur at approximately 52 and 62 cm^{-1} for Dolling *et al.*, at 55 and 64.5 cm^{-1} according to Sievers and at 54 and 62.5 cm^{-1} for the present investigation. Furthermore, recent Raman scattering measurements by Harley *et al.*[6] on KI:Tl^+ give similar results with two lines falling at 51 and 62 cm^{-1}.

Unlike Tl^+, OH^- does not systematically activate the acoustic phonons as can be seen in Fig. 2. Instead, a weak line is observed at 69.7 cm^{-1} which shifts to 69.3 cm^{-1} for OD^-. A weak line at 69.5 cm^{-1} was also observed by Renk and Grisar *et al.* in hydroxide doped KI, and recently Klein *et al.*[7] reported a line at 70 cm^{-1}. As an additional proof that this line is due to hydroxide, the integrated intensities were shown to be proportional to the hydroxide concentrations which were determined both by near infrared and u.v. (230 mμ) measurements. Both the isotope shift and concentration effect are shown in Fig. 3. The magnitude of this isotope shift is much smaller than the theoretical shift of an harmonic oscillator with a mass of OH (2.2 cm^{-1}). This is equivalent to saying that the neighboring atoms also take

* This Michelson interferometer was built here in Freiburg im Br. and is described in the Diplom Arbeit of C. Irslinger.

† These crystals were grown by Prof. Dr. Lüty at the University of Utah.

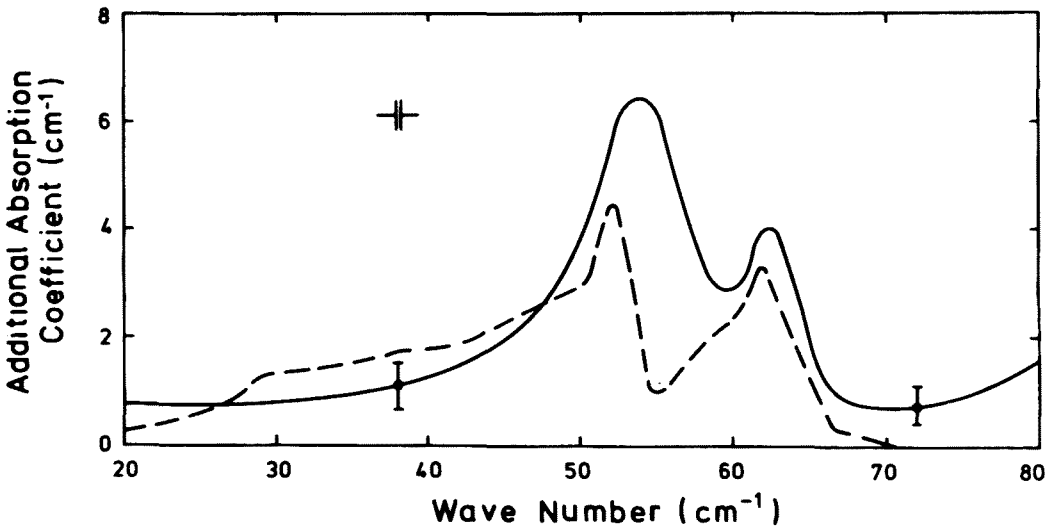

FIG. 1. Impurity induced absorption (arbitrary units) in KI:Tl^+. The dashed line represents the density of phonon states as calculated by Dolling *et al.*[1]

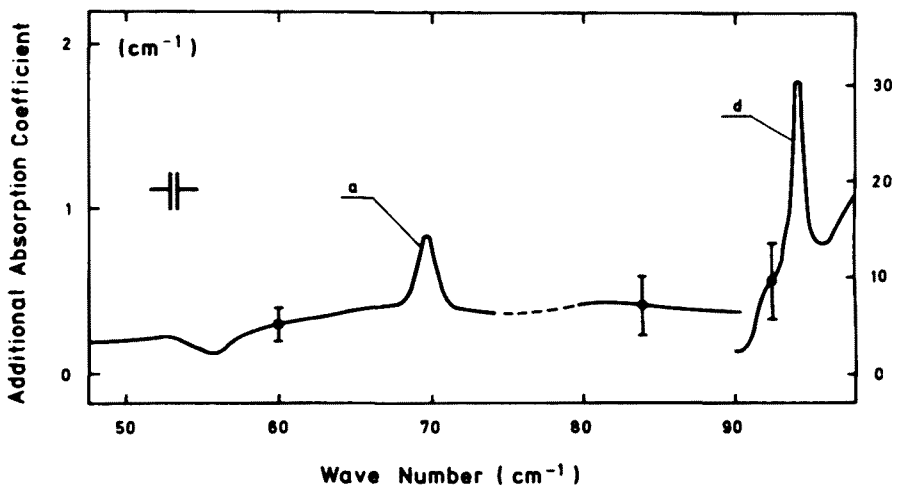

FIG. 2. Impurity induced absorption (arbitrary units) in the following systems; (a) KI:110ppm KOH and (b) KI:15ppm CO_3. The dashed line indicates a region where the absorption coefficient is not well known due to the presence of CI^-, see reference 8.

part in the motion. Sievers and his colleagues[8] have observed a similar frequency shift (76.7–77.10 cm^{-1}) for ^{37}Cl and ^{35}Cl in Ki with a discrepancy between the experimental and theoretical shifts of approximately the same size. The similarities end here, because the hydroxide line, which has a width at half-maximum of at least 1.5 cm^{-1}, is much broader than the Cl^- line. This is to be expected, because the hydroxide frequency lies just inside the acoustic phonon band where the density of states is small but nevertheless not zero according to Dolling *et al.*

Thus this line at 69.7 (69.3) cm^{-1} is assigned to a translational motion of OH^- and the neighbori

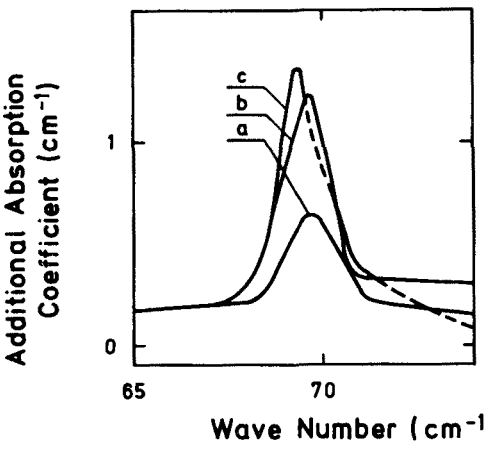

FIG. 3. Impurity induced absorption (arbitrary units) in the following systems; (a) KI:110ppm KOH, (b) KI: 200ppm KOH and (c) KI: 260ppm KOD.

atoms. Although it is impossible to say how many neighboring atoms are involved or to what extent the mode is localized, suffice it to say that it is, in all probability, best described as something between a localized and resonant mode.

A very strong line was observed at about 94 cm^{-1} by Grisar *et al.* and was assigned to a localized translational mode of OH^-. In the present investigation a strong line of 94.1 ± 0.1 cm^{-1} was also observed but only in crystals containing appreciable amounts of $CO_3^=$. Hence we may say that this line is definately not due to OH^-. This line lies very close to the optical band edge where the intensity of the transmitted light is very small. Hence a concentration effect is difficult to demonstrate and therefore subject to criticism. Consequently without further proof this line is tentatively assigned to a localised translational mode of $CO_3^=$.

In conclusion, only a single weak line due to OH^- (OD^-) at 69.7 (69.3) cm^{-1} was observed in whereas this line, several other weaker lines, and a very strong line at 94 cm^{-1} have been attributed to OH^- by Renk and Grisar *et al.* A strong line at 94.1 cm^{-1} was also observed in the present investigation but it was shown not to be due to OH^-. This strong line is thought to be due to $CO_3^=$.

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Innerhalb oder in der Nähe des Phonons Gaps von KI befindet sich eine einzige schwache Linie bei 69.7 (69.3) cm^{-1}, die auf OH^- (bzw. OD^-) zurückzuführen ist. Es wurde gezeigt, daß eine zweite erheblich intensivere Linie bei 94.1 cm^{-1} nich auf OH^-, sondern wahrscheinlich durch $CO_3^=$ bedingt ist.