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ABSTRACT

High-resolution measurements of the far-infrared lattice gap mode of Cl^- in KI at 1.2°K reveal the presence of three absorption lines at 76.46 ± 0.05 , 76.75 ± 0.02 and $77.08 \pm 0.02 \text{ cm}^{-1}$. These lines are explained in a model which includes the isotope splitting resulting from both the Cl^- impurity and its K^+ nearest neighbors. In addition, the full linewidth of the 77.08 cm^{-1} line is determined to be $0.06 \pm 0.02 \text{ cm}^{-1}$ and is ascribed to strain broadening.

Early theoretical calculations predicted the existence of localized modes in the gap between the acoustic- and optic-phonon branches of a diatomic linear chain.¹ The Cl^- impurity-induced absorption in KI constituted one of the first experimental observations of gap modes.² These measurements were performed with a resolution of 1 cm^{-1} and a single gap mode was found at 77 cm^{-1} . Later, with five times higher resolution, Nolt, et al. demonstrated that the Cl^- gap mode was a doublet with a splitting of 0.31 cm^{-1} attributed to the Cl^{35} and Cl^{37} isotopes.³ More recent experimental studies of highly-doped $\text{KI}:\text{Cl}^-$ have revealed pair modes which also occur in the gap.⁴

The isotope shift of the Cl^- gap mode has been the subject of numerous theoretical calculations. Three-dimensional point-defect models which included impurity mass and force-constant changes could not account for the small isotope shift.^{3,5} By additionally allowing for elastic relaxation of the K^+ first nearest neighbors (1nn) around the impurity site, the agreement between the calculated and experimental frequencies was improved.⁶⁻⁸ Relaxation of the 1nn affects both the impurity-1nn and the 1nn-4nn force constants.

In this paper we report the measurement of the Cl^- gap-mode absorption in KI at 1.2°K with a resolution of 0.11 cm^{-1} . These measurements reveal three absorption lines at 76.46 ± 0.05 , 76.75 ± 0.02 and $77.08 \pm 0.02 \text{ cm}^{-1}$ whose absorption

strengths can be explained by including the isotope effect of both the Cl^- impurity and its lnn. In addition the instrumental scanning function has been extracted from the highest frequency Cl^- gap mode to provide an estimate of its linewidth. The calculated linewidth is the same order of magnitude as that expected to result from defect-induced strain.

Fourier-transform spectroscopy was employed to provide the high resolution required for these measurements. The experimental apparatus consisted of a Michelson interferometer and a Ge:Ga detector which was cooled to 1.2°K.^{9,10} To obtain the absorption coefficient, spectra were measured for pure and Cl^- doped 1 mm thick KI crystals at 1.2°K. The pure KI crystal was grown by the Cornell Materials Science Crystal Growing Facility while the doped crystal was a nominally pure Harshaw grown crystal. From the observed absorption strength and previous experimental data, the Harshaw crystal has an estimated Cl^- impurity concentration of $5 \times 10^{17}/\text{cm}^3$.³

The results of our measurements of the absorption coefficient of the Cl^- gap mode in KI are shown in Fig. 1 with a Rayleigh resolution width of 0.11 cm^{-1} . The points indicate the experimental data while the solid line represents a fit to the data using a combination of three Lorentzian absorption peaks. The Lorentzian curves are given by

$$\alpha_i = \frac{A_i}{\frac{4(\nu - \nu_{oi})^2}{\Gamma_i^2} + 1} \quad (1)$$

and the total absorption is $\alpha = \alpha_1 + \alpha_2 + \alpha_3$ where the parameters for the curves are given in Table I. The frequencies ν_o shown in the Table have been corrected for the finite source size used in the interferometer.⁹ The frequencies of the second and third lines agree well with the values of 76.79 and $77.10 \pm 0.05 \text{ cm}^{-1}$ published elsewhere.³

In the Table the product $A\Gamma$ is proportional to the absorption strengths of the various lines. Since $A\Gamma$ for the two strongest lines is nearly in the ratio 2:1, the natural isotopic abundance of $\text{Cl}^{35}:\text{Cl}^{37} = 3:1$ is insufficient to account for the observed absorption strengths. To explain the three observed lines and the $A\Gamma$ ratios it is necessary to include the isotope effect of the lnn. Experimental and theoretical evidence for the K^+ isotope shift of the F-center gap mode in KI has been furnished by Bäuerle and Hübner.⁶ They demonstrated that the F-center triplet, which displays an isotope splitting of roughly 0.7 cm^{-1} between adjacent absorption lines, can be accounted for with a three-dimensional model and K^+ isotopic abundances of $\text{K}^{39}:\text{K}^{41} \equiv p:q = 93:7$. For a T_{1U} infrared-active mode a one-dimensional model in which $m = 0, 1$ or 2 of the K^{41} lnn are replaced by K^{39} is

sufficient to predict the relative absorption strengths of the low to high frequency lines of 1:27:177 using

$$\binom{2}{m} p^m q^{2-m} \quad (2)$$

to calculate the probabilities involved.

The relative isotope splittings resulting from Cl^- and its lnn can be estimated in a simple one-dimensional model in which the two lnn and the Cl^- vibrate as a functional unit against the I^- 4nn of the crystal lattice. Changing either the Cl^- or one of its lnn isotopes then produces the same isotope shift. This approximation is justified since the K^+ and the Cl^- vibrate with roughly the same amplitude⁷ and a one-dimensional calculation indicates little change in the frequency for inclusion of more than five atoms.¹¹ Not surprisingly the absolute isotope shift calculated in this simple rigid-coupling model is 40% too large when the force constants are adjusted to fit the Cl^- gap-mode frequency.

Hence assuming the splittings are the same for a change in the Cl^- or its lnn isotopes, we find that each of the Cl^- doublet lines are split by the K^+ triplet with equal spacing. Superimposing these isotope shifts results in a quadruplet with relative absorption strengths of 1:30:258:531 proceeding from low to higher frequency. The three lines we have observed display relative absorption strengths of 24 (+10):273(+30):531 providing good agreement with the predicted three strongest absorption

lines. The weakest Cl^- absorption line is expected to be unobservable for the impurity concentrations used here.

Of course equal isotope shifts are not in general expected and line 2 can be viewed as the combination of two lines with absorption strengths $(\text{K}^{39}\text{Cl}^{37}\text{K}^{39}) : (\text{K}^{41}\text{Cl}^{35}\text{K}^{39}) = 177:81$ and with slightly different central frequencies. For these relative absorption strengths, the addition of two Lorentzians with $\Gamma = 0.15 \text{ cm}^{-1}$ separated by 0.06 cm^{-1} produces a curve which approximates α_2 with $\Gamma = 0.18 \text{ cm}^{-1}$. Because of the number of adjustable parameters in the fit shown in Fig. 1, it is difficult to assess the sign of the 0.06 cm^{-1} difference. For a model without elastic relaxation of the lnn, Benedek has calculated the isotope shift for Cl^- to be 0.86 cm^{-1} and for its lnn to be 0.23 cm^{-1} .⁷ Hence on the reasonable assumption that the Cl^- isotope splitting is larger than that resulting from its lnn, we calculate isotope shifts of 0.34 ± 0.02 and $0.28 \pm 0.05 \text{ cm}^{-1}$ respectively. Absorption line 1 predominately results from the combination $(\text{K}^{41}\text{Cl}^{37}\text{K}^{39})$ and its isotope shift of $0.62 \pm 0.05 \text{ cm}^{-1}$ is just the sum of the calculated $(\text{K}^{39}\text{Cl}^{37}\text{K}^{39})$ and $(\text{K}^{41}\text{Cl}^{35}\text{K}^{39})$ shifts.

An additional interesting feature of the gap mode is the intrinsic linewidth of the highest-frequency line. This linewidth may, in part, result from anharmonic coupling to the lattice phonons. The line is expected to be narrow since it lies

in the band gap and no theoretical calculation of the linewidth has been performed because of the requirement of an extremely fine grid of points covering the Brillouin zone.⁵ The residual low-temperature linewidth can be determined experimentally by extracting the instrumental broadening. The width of the interferometer scanning function

$$(\sin (\pi \nu L) / \pi \nu L)^2 \quad (3)$$

is given by $\Gamma_L = 0.88/L = 0.10 \text{ cm}^{-1}$ where L is the optical path difference of the two interferometer arms and $1/L$ is the Rayleigh resolution width. In addition a correction of 0.02 cm^{-1} must be included because of broadening resulting from the finite aperture size.⁹ Water-vapor lines observed at 80 cm^{-1} with the same Γ_L have been found to have a linewidth of 0.12 cm^{-1} with our Michelson interferometer¹² so the linewidth that must be extracted is 0.10 to 0.12 cm^{-1} . Approximating the scanning function by a Gaussian and using convolution tables for a Gaussian and Lorentzian¹³ we estimate the linewidth of the Cl^- gap mode to be 0.08 to 0.04 cm^{-1} .

This residual linewidth can be accounted for by considering strain broadening which has been shown to give a Lorentzian lineshape for the N_1 -center.¹⁴ To estimate the strain-broadened linewidth we observe that for a volume V the Grüneisen constant

$$\gamma \equiv - \frac{d \ln \nu}{d \ln V} \quad (4)$$

is similar for the U-center in KBr ($\gamma = 1.63$) and Cl^- in KI ($\gamma = 1.0$).^{15,16} This similarity is expected if we ignore the difference between the bulk and local compressibilities and assume that the primary effect of compression is to change the frequency through comparable force-constant anharmonicities. The residual low-temperature linewidth of the U-center in KBr has been attributed to strain broadening.¹⁶ Hence for comparable strains resulting from both impurities and dislocations in KBr and KI, the similarity in Grüneisen constants implies

$$\left(\frac{\nu_0}{\Gamma}\right)_U = 1.4 \times 10^3 \approx \left(\frac{\nu_0}{\Gamma}\right)_{\text{Cl}^-} \quad (5)$$

so that $\Gamma_{\text{Cl}^-} \approx 0.05 \text{ cm}^{-1}$ is the expected strain-broadened linewidth. This is the correct order of magnitude to account for the observed Cl^- gap-mode linewidth.

In summary we have accounted for the linewidths and absorption strengths of the Cl^- gap-mode triplet in KI by a model including the isotope effect of both the Cl^- and its lnn. In a lattice of otherwise light isotopes, the isotope shift of the Cl^- is $0.34 \pm 0.02 \text{ cm}^{-1}$ and for a lnn the isotope shift is $0.28 \pm 0.05 \text{ cm}^{-1}$. The combined isotope shift for Cl^- and lnn is $0.62 \pm 0.05 \text{ cm}^{-1}$.

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Table I

Lorentzian Parameters for Cl^- Gap Mode in KI

Peak	$\nu_o (\text{cm}^{-1})$	$A (\text{cm}^{-1})$	$\Gamma (\text{cm}^{-1})$	$A\Gamma (\text{cm}^{-2})$
1	76.46 ± 0.05	0.4	0.26	0.10
2	76.75 ± 0.02	6.2	0.18	1.12
3	77.08 ± 0.02	14.5	0.15	2.18

FIGURE CAPTION

Fig. 1: Cl^- gap-mode absorption in KI at 1.2°K. The data are represented by points and the solid line results from fitting the data with the sum of three Lorentzians (dashes).

Figure 1