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Infrared-active localized pair modes in the gap region of KI[†]

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New infrared-active lattice gap modes due to Na^+ and Cl^- substitutional impurities in KI have been observed. The line strengths are shown to be proportional to the square of the impurity concentration, indicating the modes are due to associated *pairs* of ions. The previously reported Br^- gap mode at 73.8 cm^{-1} in KI is also shown to be due to *pairs* of Br^- ions. A new single-ion absorption mode due to Br^- has been observed at 88.47 cm^{-1} (for Br^{81}) with an isotopic frequency shift of 0.47 ± 0.05 cm^{-1}.

I. INTRODUCTION

Potassium iodide has long been a favorite host material for studying localized impurity modes, because of the relatively large gap in the frequency spectrum between the acoustic- and optical-phonon modes. From neutron-diffraction experiments, Dolling *et al.*[1] have shown that the gap extends from 69.7 to 95.6 cm^{-1}. Impurity-induced modes whose frequencies fall within this region are expected to give rise to very sharp well-defined absorption lines since the host-lattice phonons are not activated. Indeed this has been shown to be true for a variety of impurities in KI.[2-6]

Several recent experiments on a number of alkali-halide–impurity systems have shown that for high impurity concentrations (~ 1 mole%), interactions between impurity ions become important and modes due to *pairing* of ions have been observed. The first such mode due to Ag^+ ions NaCl was observed using Raman spectroscopy,[7] and infrared-active pair modes have been observed in KCl : Na^+,[8] NaCl : F^-,[9] and NaBr : Li^+.[10] Absorption lines due to aligned *U*-center pairs (containing H^- and D^- ions) have also been observed in KCl (Ref. 11) at frequencies well above the host-lattice phonon spectrum.

In this paper we report the first observation of several sharp gap modes due to substitutional Na^+ and Cl^- ions in KI. These new modes (two for Na^+ and three for Cl^-) are shown to be due to *pairing* of impurity ions. We have also studied the impurity-induced absorption due to Br^- ions in KI and find the mode previously reported by Nolt *et al.*[12] at 73.8 cm^{-1} is also due to impurity pairs. We have observed a new single-Br^--ion absorption peak at ~ 88.7 cm^{-1}. This line when examined under high resolution (0.2 cm^{-1}) is found to be a doublet with a separation of 0.47 cm^{-1}, which we attribute to the naturally occurring isotopic mixture of mass-79 and mass-81 bromine ions.

II. EXPERIMENTAL

The majority of the far-infrared absorption measurements were made using a modified[13] Beckman RIIC, FS-720 Michelson interferometer, with low-frequency (down to ~ 3-cm^{-1}) survey scans made using a Beckman RIIC, LR100 lamellar-grating interferometer. The instrumental resolution was typically 0.21 cm^{-1} and the sample temperature 4.2 K. The low-resolution interferograms were Fourier transformed in the laboratory on a Hewlett-Packard 2115A computer immediately after recording. High-resolution runs were transformed on the Simon Fraser University IBM 370-50 computer. The cryostat used was similar to the one described by Clayman *et al.*[14] with separate sample and detector compartments to facilitate isolation of the ^{3}He-cooled germanium bolometer.[14,15]

The single crystals used in this investigation were all grown in our laboratory using the Kryopoulos-Czochralski technique. The starting material for the melt was high-purity alkali-halide powders obtained from E. Merck, Darmstadt, Germany. To prevent OH^- contamination, the melt materials were baked at ~ 300 °C in an argon atmosphere for approximately 12 h previous to crystal growth. Spectra of several undoped KI crystals grown in this manner showed no absorption lines due to OH^- impurities.

The Na^+ concentrations were determined by flame-emission spectroscopy, in which aqueous solutions, prepared from the crystal samples, were compared with solutions containing known Na^+ concentrations. This technique gave an accuracy of ± 3%. The Cl^- and Br^- concentrations were determined using neutron-activation analysis. In the case of Cl^- an additional check of the relative impurity concentration was made from the single-ion far-infrared absorption in KI, whose strength is proportional to the impurity-ion concentration.

III. RESULTS

A. Sodium

The absorption spectra for samples of KI containing Na^+ impurities were measured from 3 cm^{-1} to the reststrahlen absorption edge at approximately 92 cm^{-1}. A continuous absorption spectrum ex-

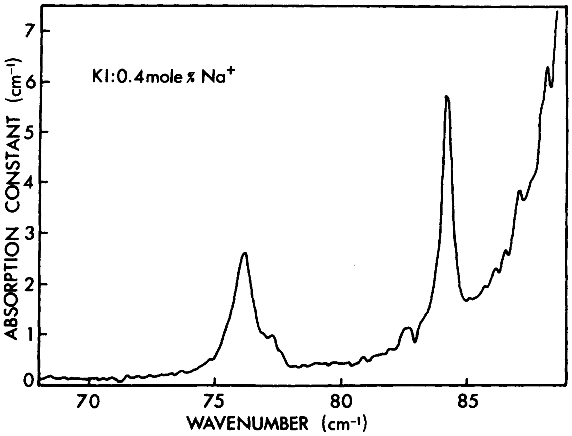

FIG. 1. Gap-mode absorption spectrum of KI : Na$^+$ at 4.2 K. The instrumental resolution is 0.21 cm^{-1}.

tending from about 20 to 70 cm^{-1} was observed in addition to the two sharp lines at 76.18 and 84.20 ± 0.05 cm^{-1} seen in Fig. 1. This continuous spectrum is due to host-lattice single-phonon absorption activated by the loss of translational symmetry when impurities are added to a perfect lattice.[16] Details of this absorption will be reported separately. The slight shoulder at 77 cm^{-1} on the high-frequency side of the 76.18-cm^{-1} line is due to a small amount of unwanted Cl$^-$ contamination in the samples. In addition to the two lines mentioned several weak lines were observed at 82.66, 85.2, 85.75, 86.21, 86.61, 87.19, and 88.25 ± 0.05 cm^{-1}. These lines are extremely weak and occur on the steeply rising reststrahlen edge, making their positive identification difficult, however, they were observed in more than half of the Na$^+$ samples studied.

In Fig. 2 the integrated absorption strength of the two sharp lines is plotted as a function of the square of the Na$^+$-ion density. The quadratic dependence of the line strengths on Na$^+$ concentration leads us to conclude that the two lines are due to Na$^+$ ion *pairs*.

The centroid frequency Ω of the two localized modes is found to increase linearly with increasing Na$^+$-ion concentration. We interpret this frequency shift as being due to changes in the average lattice constant[17] and find the relationship

$$\Delta\Omega/\Omega(0) = -A\ \Delta a/a_0 \tag{1}$$

to hold, where $\Omega(0) = 76.02$ and 84.14 cm^{-1} are the centroid frequencies extrapolated to zero Na$^+$-ion density, a_0 is the lattice constant of KI at $T = 0$ K, Δa is the change in average lattice constant as Na$^+$ ions replace K$^+$ ions, and A is a dimensionless constant found to be 5.8 ± 0.3 and 4.3 ± 0.3, respectively.

B. Chlorine

The absorption coefficient of KI containing 0.63-mole% Cl$^-$, in the gap region is shown in Fig. 3. A continuous absorption was also observed at lower frequencies. The absorption line at 77 cm^{-1}, which peaks off scale, has been previously determined to be a doublet with a separation of 0.31 cm^{-1} due to isolated Cl^{37} and Cl^{35} impurities.[12] Using high resolution (~ 0.21 cm^{-1}) we observe three new lines at 72.02, 80.26, and 82.84 ± 0.05 cm^{-1}. From Fig. 3 it can also be seen that the halfwidth of the 82.84-cm^{-1} mode is approximately a factor of 2 larger than either of the other two lines.

Figure 4 shows that the line strengths of the three lines depends quadratically on the Cl$^-$-ion concentration, indicating they are due to Cl$^-$–Cl$^-$ *pairs*. No appreciable frequency shift as a function of Cl$^-$ concentration was observed for any of the three modes.

C. Bromine

The KI: Br$^-$ system has been studied previously by Nolt *et al.*[12] who discovered a gap mode at 73.8 cm^{-1}. At that time the mode was assumed to be due to isolated Br$^-$ ions even though the mode differed in several respects from the Cl$^-$-induced absorption at 77 cm^{-1}. The line strength appeared abnormally low for a single-ion impurity and no Br$^-$ isotope splitting was observed at 0.20-cm^{-1} resolution even though a shift of 0.93 cm^{-1} was predicted from harmonic-oscillator theory for a single-ion absorption at this frequency. These peculiarities prompted us to reexamine the KI: Br$^-$ system.

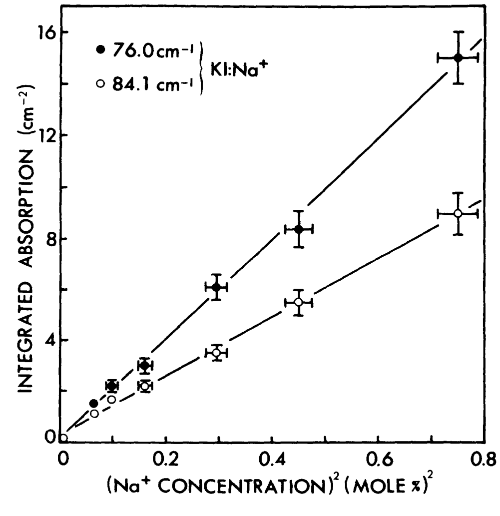

FIG. 2. Integrated absorption of the two Na$^+$ gap modes vs the square of the Na$^+$-ion density. The solid lines are a linear-least-squares fit to the data.

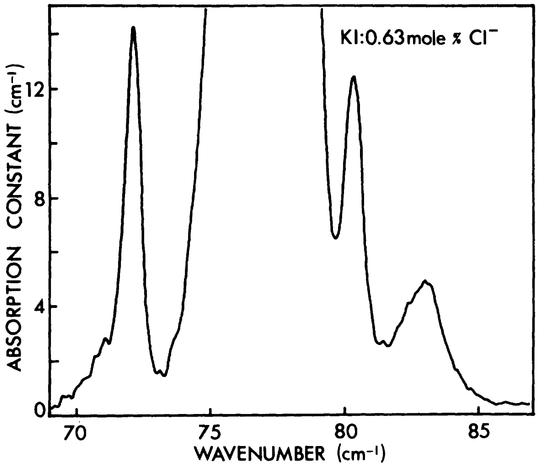

FIG. 3. Cl⁻-induced gap modes in KI at 4.2 K. The mode at 77 cm^{-1}, which peaks off scale, is a doublet due to isolated Cl^{37} and Cl^{35} impurities. The instrumental resolution is 0.21 cm^{-1}.

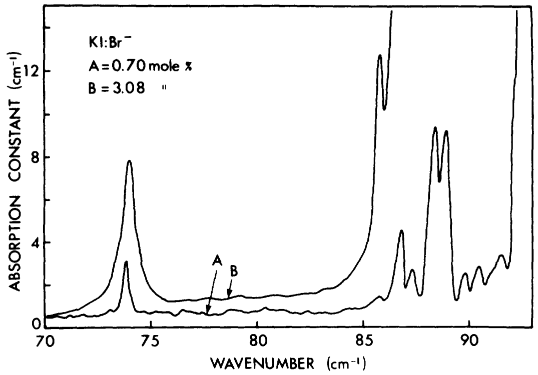

FIG. 5. Gap mode absorption spectrum of two concentrations of Br⁻ ions in KI at 4.2 K. At high Br⁻ concentrations the single ion mode at ~88 cm^{-1} becomes indistinguishable from the steeply rising reststrahlen background. The instrumental resolution is 0.21 cm^{-1}.

Figure 5 shows the impurity-induced absorption for two different concentrations of Br⁻ ions in KI between 70 and 90 cm^{-1}. In addition to the 73.8-cm^{-1} peak several new lines are observed at higher frequencies, the strongest of these being a doublet with center frequencies at 88.47 and 88.94 ± 0.05 cm^{-1}. This line is approximately a factor of 10 more intense than the 73.8-cm^{-1} line, with the line strengths of the components of the doublet approximately equal. From this we conclude that the doublet absorption is due to the two stable bromine isotopes, 79 and 81 in their naturally occurring ratio of approximately 1 : 1.[18]

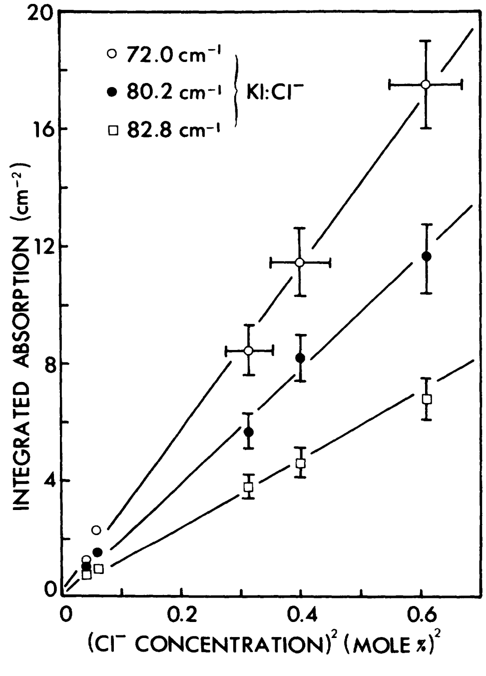

FIG. 4. Integrated absorption of the three Cl⁻ gap modes vs the square of the Cl⁻-ion density. The solid lines are linear least-squares fits to the data.

At 86.79 cm^{-1} a third new line whose strength is approximately equal to the 73.8-cm^{-1} mode is observed. Unfortunately, as the Br⁻-ion concentration is increased it becomes impossible to separate this mode from the doublet, so we are not able to definitely assign this absorption to either single or pairs of Br⁻ ions. However, we have included it in Table I, which lists all the gap pair modes observed in KI, as a possible pair mode because of its low intensity.

Figure 6 shows that the line strength of the 73.8-cm^{-1} peak had a quadratic dependence on the Br⁻-ion concentration and is thus due to Br⁻-ion *pairs*. Because of the closeness of the strong doublet to the steeply rising reststrahlen absorption edge the zero level of this absorption and thus the concentration dependence are difficult to determine. However, for a few low-concentration experiments with very thin (~0.5-mm) samples the line strength is found to depend linearly upon the Br⁻-ion density, and we conclude that it is due to *isolated* Br⁻ ions.

In addition to the lines mentioned so far we have also observed several very weak absorption lines at 85.78, 87.44, 89.73, 90.45, and 91.56 cm^{-1}. These lines are very similar in character to the weak Na^{+} lines observed previously, and are possibly due to more widely separated ion pairs or motions of the nearest-neighbor host ions surrounding the impurity pairs.

TABLE I. Localized pair modes in KI.

Impurity	Frequency (cm^{-1})	Integrated absorption (cm^{-2})	Full width at half-maximum (cm^{-1})[a]
0.26-mole%	76.02 ± 0.05	1.5 ± 10%	0.2 ± 10%
Na^+	84.14	1.2	0.2
0.21-mole%	72.02	1.19	0.6
Cl^-	80.26	0.97	0.6
	82.84	0.70	1.2
0.7-mole%	73.65	1.04	0.2
Br^-	86.79[b]	1.3	0.5

[a] Uncorrected for instrumental resolution of 0.21 cm^{-1}.

[b] Unconfirmed as due to pairs.

The centroid frequency Ω of the localized pair mode at 73.8 cm^{-1} is found to increase linearly with increasing Br^--ion concentration. As in the case of Na^+, we interpret this frequency shift as due to changes in the average lattice constant and again find expression (1) to hold with $\Omega(0) = 73.65$ cm^{-1} and $A = 4.1 \pm 0.4$.

IV. DISCUSSION

The two principal symmetry configurations for defect pairs in the alkali-halide lattice are "tetragonal" and "rhombic." In the case of tetragonal symmetry the defect pair is aligned along a [100] crystal axis with a host ion separating the defect pair. This has proven to be the case for the KCl : Na^+ system,[19] in which the two Na^+ ions are separated by a Cl^- ion. In general, when the two defect ions are allowed to vibrate in-phase, this configuration will yield two infrared-active modes, one longitudinal and one transverse, see Fig. 7(a). If the defects are coupled strongly to the nearest-neighbor host ions, then many more modes are

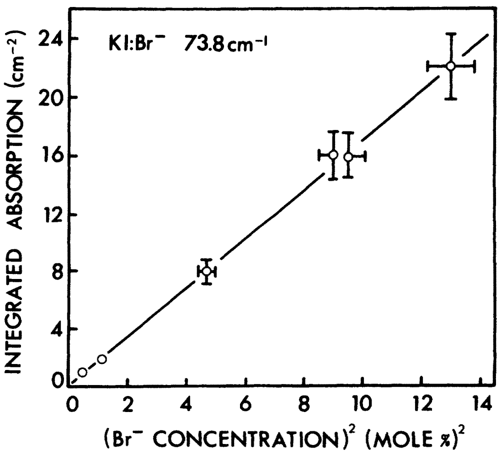

FIG. 6. Integrated absorption of the 73.8-cm^{-1} Br^- mode vs the square of the Br^- ion density. The solid line is a linear least-squares fit to the data.

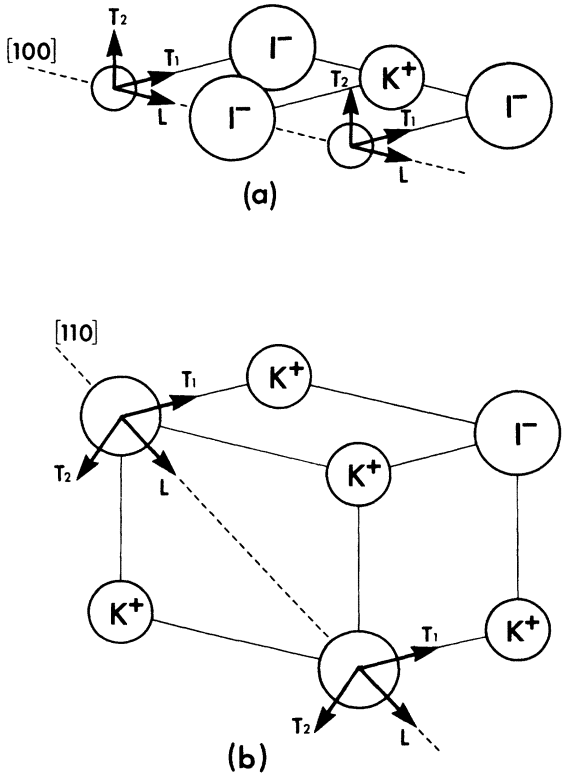

FIG. 7. Illustration of two possible impurity-pair configurations, showing the in-phase infrared-active modes. (a) In the tetragonal case the two transverse modes T_1 and T_2 are degenerate. (b) The rhombic configuration yields one longitudinal mode with the ions vibrating along the [110] axis and two nondegenerate transverse modes T_1 and T_2 vibrating perpendicular to the [110] direction.

possible, the total number depending upon the number of ions participating in the "defect molecule."

In the rhombic configuration the defect ions are separated by one nearest-neighbor distance in a [110] direction. If we consider only the defect ions to vibrate, this system yields three in-phase modes (infrared active), see Fig. 7(b), and three out-of-phase modes (Raman active). de Souza and Lüty[11] have recently reported a novel process for producing [110] aligned H^--ion pairs in KCl. They observed three infrared-active modes, one longitudinal, polarized in the [110] direction, and two transverse modes polarized in the two directions perpendicular to the longitudinal axis.

In this system, the H^- ion is known to be very weakly bound to the KCl lattice and thus vibrations of the neighboring ions are not likely to be of importance. Becker and Martin,[9] on the other hand, have reported the existence of six F^--ion pair modes in NaCl indicating the possibility that some of the host ions are in motion.

At the present time the vibrational symmetries of the three new systems we have described are unknown. Preliminary uniaxial-stress experiments of the type described by Templeton and Clayman[19] have met with little success. The maximum frequency shifts obtained with stress applied in the [100] direction and radiation polarized in the [100] direction, (this configuration is expected to show the highest frequency shifts), were ~ 0.23 cm^{-1} for a stress of 1.83 kg/mm^2 for both the Na^+ and Cl^- systems. The crystals, with our high dopant concentrations, were not able to withstand stresses greater than ~ 2.0 kg/mm^2. Since stress shifts in the other principal crystal directions are expected to be less than we have observed for the [100] direction, there appears to be little hope of determining the symmetry splitting patterns for these experiments.

As pointed out by Becker and Martin,[9] isotopic substitution would help determine if host ions are contributing to any of the observed localized modes. Such experiments are under way at the present time using the Cl^{35}, Cl^{37}, Br^{79}, and Br^{81} stable isotopes. Another approach for deciding between the possible symmetry alternatives can be made by comparing the experimentally observed frequencies with predictions of dynamical models of the defect and lattice.

Several such models have recently been developed to account for pair-mode systems. de Souza and Lüty[20] were able to fit their H^- and D^- [110] pair modes using a simple model of coupled localized oscillators. They assume a completely rigid lattice and allow only the impurity ions to move. This model adequately accounts for their experimentally observed infrared-active longitudinal pair mode below, and two infrared-active transverse-polarized pair modes above the corresponding single-impurity local-mode frequency. We have noted there is a similarity between our KI: Cl^- results and the above-mentioned system. For Cl^-, we also observe one mode below and two modes above the Cl^- single ion mode at 77 cm^{-1}. Another perhaps more striking similarity is the relatively large line width of the highest-frequency mode observed in both the H^- and Cl^- systems. de Souza and Lüty[20] have interpreted this line shape as possibly due to a decay of the mode via anharmonic coupling to a lattice phonon into another out-of-phase Raman-active pair mode. If the three lines we have observed are indeed due to [110] aligned Cl^--ion pairs, then a similar decay mechanism could be responsible for the linewidth of the 82.84-cm^{-1} Cl^- mode. Observation of the three conjugate out-of-phase Raman active modes would help clarify the situation.

In attempting to fit the KCl: Na^+ tetragonally oriented pair mode observed by Templeton and Clayman,[19] Jaswal[21] has developed a molecular model in which the Na^+ ions and the Cl^- ion between them and the 14 nearest neighbors to these three ions are allowed to vibrate in an otherwise rigid KCl lattice. The central repulsive spring constant between the Na^+ ions and their nearest-neighbors Cl^- ions was reduced until the lowest-frequency in-phase normal mode coincided with the experimentally determined frequency. As this force constant is reduced the mode becomes more and more localized. Since the pair modes we have observed are highly localized, we think this model should be suitable for describing our experimental results.

At the present time we are working on a Jaswal-type molecular model which takes into account both the tetragonal and rhombic pair symmetries. Estimates of the force constant changes between the defects and their neighbors can be obtained from fits of the calculated single-ion infrared absorption to the experimental one phonon continuum and resonant mode absorption. Such Green's-function calculations, similar to those carried out by Ward and Timusk for a variety of impurities in KBr and KCl,[16] are being carried out at the present time for Na^+, Cl^-, and Br^- impurity ions in KI. With force constant changes determined in this fashion, the predictions of the molecular pair model can then be compared with experiment without introducing any new adjustable parameters.

Finally, our new results on the KI: Br^- system help to account for the failure of theoretical models in describing the position and isotope splitting of the 73.8-cm^{-1} absorption mode.[6,22] As we have shown, this mode is due to absorption by Br^- ion pairs and is not due to isolated impurity ions as was previously supposed. Our measurements have shown that the single Br^- ion absorption mode is approximately 15 cm^{-1} higher in frequency with an isotope shift of 0.47 cm^{-1}.

V. SUMMARY

New far-infrared spectra of KI single crystals doped with several different substitutional impurities have revealed the existence of impurity pair modes in the gap between the optical- and acoustic-phonon branches. These new modes are very sharp, with halfwidths, in several cases, less than the instrumental resolution of 0.21 cm^{-1}. A new gap mode which exhibits an isotope shift due to Br^- impurity ions has also been observed.

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