ference in stopping power in the lower energy range, however, appears to deviate from the theory to some extent. Therefore it may be expected that the difference in stopping power is larger than the theoretical one calculated by Nelms below 100 keV. In order to clear up this point, a complete investigation of the stopping power of a NaI(Tl) crystal for positrons would be most desirable.

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Infrared Lattice Absorption by Gap Modes and Resonance Modes in KI

A. J. SIEVERS*
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

AND

A. A. MARADUDIN†
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

AND

S. S. JASWAL‡
Department of Physics, Michigan State University, East Lansing, Michigan

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Impurity-induced infrared absorption in KI containing Cl^- ions as substitutional impurities has been observed. A sharp line appears in the absorption spectrum in the neighborhood of 77 cm^{-1}, and at least three broad lines are observed near 61 cm^{-1}. The results of a theoretical calculation show that the identification of the former absorption peak with a localized mode whose frequency lies in the gap in the frequency spectrum of KI between the acoustic and optical branches is compatible with the experimental results. Similarly, the broad absorption peaks near 61 cm^{-1} can be identified with resonance modes in the acoustic continuum.

IT is our purpose in this note to present an experimental and theoretical demonstration of the existence of localized modes with frequencies in the gap between the acoustic and optical branches in the frequency spectrum of KI, as well as of resonance modes with frequencies in the acoustic continuum.

A powerful research tool for the study of the localized vibration modes introduced into the spectrum of crystal vibrations by impurity atoms has been infrared lattice absorption. Until very recently it has been used only in the investigation of the localized modes whose frequencies lie above the maximum frequency of the unperturbed host crystal.[1–7] It has been known for some time that if gaps occur in the frequency spectrum of a crystal it is possible for localized modes to exist whose frequencies lie in these gaps.[8] Moreover, it has been pointed out recently[9] that certain kinds of impurities, particularly very heavy ones, can give rise to resonance or quasilocalized modes whose frequencies lie in the range of normal-mode frequencies allowed to the perfect host crystal, and which are characterized by a greatly enhanced amplitude of vibration of the impurity atom.

The last two kinds of vibration modes should prove to be as interesting for theoretical and experimental study as the high-frequency localized modes. Up to the present time localized modes with frequencies in a

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forbidden gap in the frequency spectrum of the host crystal have been observed by means of infrared lattice absorption only in LiH containing deuteride ions as impurities.[10] Resonance modes have recently been observed by this method in KI containing Ag^+ ions as impurities.[11]

Of the several alkali-halide crystals whose frequency spectra have been calculated[12] only four, LiCl, NaBr, NaI, and KI, have a gap in the spectrum between the optical and acoustic branches. Of these, we have chosen to work with KI, containing KCl as an impurity. This choice was dictated by the fact that NaI and NaBr are hygroscopic and hence difficult to work with, while of the remaining two crystals KI has the larger gap. According to the results of our calculations of the eigenfrequencies and eigenvectors for KI, on the basis of Hardy's deformation dipole model of ionic crystals,[13] the gap in the frequency spectrum of KI lies between 64.1 cm^{-1} (the largest frequency for the longitudinal acoustic modes) and 79.4 cm^{-1}. The maximum frequency for the transverse acoustic modes is 50 cm^{-1}, and the maximum frequency of the crystal is 135.1 cm^{-1}.

In order to investigate the frequency region below the transverse optic branch in KI (T.O. = 108 cm^{-1} at 4.2°K),[14] we have used an incoherent source and optical techniques. The source is a high-pressure mercury arc. The large amount of unwanted high-frequency radiation from the arc is eliminated by a combination of sooted polyethelene windows, zero-order reflection plates, and transmission filters. The remaining radiation passes through a grating monochromator with 12-in. optics and on to a detector which consists of a liquid-helium-cooled bolometer.[15] The KI:Cl^- samples were located in the detector cryostat. By maintaining the samples at liquid helium temperatures, the host lattice absorption is minimized. In the frequency region of the chlorine-induced absorption, preliminary transmission measurements disclosed that 5% of the radiation at the detector was from higher orders of the grating. This higher frequency radiation was eliminated by a low-temperature filter composed of layers of sooted crystal quartz-KCl-NaCl-KBr and sooted crystal quartz placed in the cryostat directly before the sample chamber. The filter was transparent for frequencies less than 110 cm^{-1}. Our transmission measurements were confined to frequencies below 90 cm^{-1} because of the absorption from the infrared active transverse-optic mode in KI.

Potassium iodide single crystals with four different concentrations of chloride ions have been grown by the Kyropoulos technique in an argon atmosphere.[16] The impurity-induced absorption is determined by comparing the transmission obtained for a doped crystal with that obtained for a pure crystal. The absorption coefficient for each of the four cases is shown in Fig. 1. The reflectivity has been assumed to be the same for both the pure and doped crystals. The observed spectrum consists of a narrow line at 77±1 cm^{-1} and a band composed of at least three broad lines centered at 61 cm^{-1}. Below 30 cm^{-1}, the impurity-induced absorption becomes very small. The total (line plus band) integrated strength varies linearly with the chemically determined impurity concentration.[17] From higher resolution studies ($\nu/\Delta\nu \approx 80$) with samples *C* and *D*, see Fig. 1, the absorption at 77 cm^{-1} has a full-width-at-half-maximum absorption equal to 1% of the absorption frequency. Also, a weak absorption is resolved at 72 cm^{-1}. No narrow lines have been found within the broad band centered at 61 cm^{-1}.

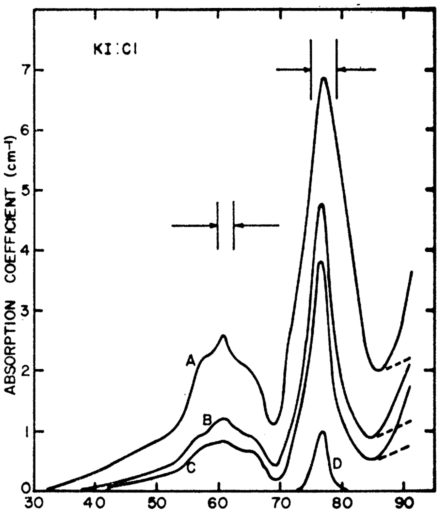

FIG. 1. Impurity-induced absorption in KI:Cl. By comparing the doped crystal with the pure crystal, the intrinsic lattice absorption has been divided out. The exact shape (compare solid and dashed curves) of the absorption at frequencies of 90 cm^{-1} and above is masked by the intrinsic absorption from the infrared-active transverse-optic branch. The four chloride concentrations are A: 1.2×10^{20}, B: 5.5×10^{19}, C: 3.9×10^{19}, and D: 2.8×10^{18} Cl^- ions per cm^3. (A, B, and C have been determined chemically, whereas D has been estimated from far-infrared measurements.) The resolution of the monochromator is given by the frequency intervals between the arrows.

The peak in the absorption spectrum at ≈77 cm^{-1} lies in the gap between the acoustic and optical branches in the frequency spectrum of KI. The three broad lines centered at 61 cm^{-1} lie in the acoustic continuum between the maximum frequencies for the transverse and longitudinal acoustic modes. On the basis of the follow-

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ing theoretical analysis we attribute the former peak to a localized mode with a frequency in the gap in the KI frequency spectrum, while the latter peaks are felt to be associated with resonance modes.

In the approximation in which the substitutional impurity is treated as a mass defect, the frequencies of localized modes and resonance modes are given by the solutions of the equation[18]

$$1/\epsilon_{\pm}=x^2A^{(\pm)}(x)\,, \tag{1}$$

where

$$\epsilon_{\pm}=1-M'/M_{\pm} \tag{2}$$

and

$$A^{(\pm)}(x)=\frac{1}{3N}\sum_{\mathbf{k}j}\frac{[W(\pm|\mathbf{k}j)]^2}{[x^2-\lambda_j^2(\mathbf{k})]_P}\,. \tag{3}$$

In these expressions the + index is used when the impurity substitutes for a positive ion, and the − index is used when the impurity substitutes for a negative ion. M' is the mass of the impurity, and we have introduced the dimensionless frequencies x and $\lambda_j\,(\mathbf{k})$ by

$$\begin{aligned}\omega&=\omega_L x\,,\\ \omega_j(\mathbf{k})&=\omega_L\lambda_j(\mathbf{k})\,,\end{aligned} \tag{4}$$

where ω_L is the maximum frequency of the host crystal. In Eqs. (3) and (4), the expression $\omega_j\,(\mathbf{k})$ is the frequency of the normal mode of the perfect crystal described by the wave vector κ and branch index j, while $\mathbf{W}(\kappa|\mathbf{k}j)(\kappa=+,\,-)$ is the associated unit eigenvector. It should be noted that $\mathbf{W}(\kappa|\mathbf{k}j)$ is the eigenvector associated with a phase factor $\exp i\mathbf{k}\cdot\mathbf{x}(l\kappa)$ rather than with $\exp i\mathbf{k}\cdot\mathbf{x}(l)$, where $\mathbf{x}(l)$ is the position vector of the lth unit cell, and $\mathbf{x}(\kappa)$ is the position vector of the κth ion in a limit cell. It is therefore real for crystals of the NaCl structure. Finally, N is the number of unit cells in the crystal.

When x lies in a range which is forbidden to the $\{\lambda_j(\mathbf{k})\}$, for example the gap between acoustic and optical branches or above the maximum frequency of the unperturbed crystal, the principal value restriction on the sum in Eq. (3) can be removed. The solutions of Eq. (1) in this case are the localized modes. When x lies in a range accessible to the $\{\lambda j(\mathbf{k})\}$ the principal value restriction in Eq. (3) is essential, and the solutions of Eq. (1) in this case are the resonance modes.

In the harmonic approximation the localized modes are eigenstates of the crystal Hamiltonian. They are therefore infinitely long-lived and have zero width. The resonance modes, on the other hand, can decay into the continuum of wave-like modes, and consequently have a finite width which for a resonance mode of frequency x is given by

$$\frac{\gamma^{(\pm)}(x)}{\omega_L}=\pi x^2\frac{B^{(\pm)}(x)}{|A^{(\pm)}(x)+(x/2)(d/dx)A^{(\pm)}(x)|}\,, \tag{5}$$

where

$$B^{(\pm)}(x)=\frac{1}{2x}\frac{1}{3N}\sum_{\kappa j}[W(\pm|\mathbf{k}j)]^2\delta[x-\lambda_j(\boldsymbol{\kappa})]\,,\quad 0\leqslant x\leqslant 1\,. \tag{6}$$

We have computed the functions $x^2A^{(\pm)}(x)$ and $\gamma^{(\pm)}(x)/\omega_L$ for the Hardy-Karo "deformation-dipole" model of KI.[12,13] In the sums over the wave vector $\mathbf{k}$ a grid of 8000 points in the Brillouin zone was employed. It may be worth remarking that $2xB^{(\pm)}(x)$ was evaluated first, as a histogram, in steps of $x=0.02$. A second histogram, shifted to the right from the first by $x=0.01$, was computed, and the mean of these was used as $2xB^{(\pm)}(x)$. The function $A^{(\pm)}(x)$ was evaluated from $2xB^{(\pm)}(x)$ by straightforward numerical integration according to

$$A^{(\pm)}(x)=\int_0^1 dy\frac{2yB^{(\pm)}(y)-2xB^{(\pm)}(x)}{(x^2-y^2)P}+B^{(\pm)}(x)\ln\frac{1+x}{1-x}\,,\quad 0\leqslant x\leqslant 1\,. \tag{7}$$

The function $C^{(\pm)}(x)=(x/2)(d/dx)A^{(\pm)}(x)$ was evaluated somewhat differently.[19] We have that

$$\begin{aligned}C^{(\pm)}(x)&=\frac{x}{2}\frac{d}{dx}\int_0^1 dy\frac{2yB^{(\pm)}(y)}{(x^2-y^2)P}\\ &\cong\frac{x}{2}\frac{d}{dx}\sum_{j=0}^{49}B^{(\pm)}(\xi_j)\int_{y_j}^{y_{j+1}}dy\frac{2y}{(x^2-y^2)P}\\ &=x^2\sum_j B^{(\pm)}(\xi_j)\left[\frac{1}{x^2-y_j^2}-\frac{1}{x^2-y_{j+1}^2}\right],\end{aligned} \tag{8}$$

where we have put

$$\xi_j=2j/100\,,\quad y_j=(2j+1)/100\,. \tag{9}$$

This function was computed for $x=0(0.02)1$.

The functions $x^2A^{(-)}(x)$ and $\gamma^{(-)}(x)/\omega_L$ for KI are plotted in Fig. 2, and the functions $x^2A^{(+)}(x)$ and $\gamma^{(+)}(x)/\omega_L$ are plotted in Fig. 3. For the present experimental conditions we have that $1/\epsilon_-=1.39$. We have drawn a horizontal line on Fig. 2 corresponding to this value of $1/\epsilon_-$. It is seen that this line intersects the curve of $x^2A^{(-)}(x)$ at $x=0.567$, corresponding to a frequency of 76.6 cm^{-1}, in the frequency range for which the frequency spectrum of KI has a gap. This solution, therefore, corresponds to a localized vibration mode. We see, in addition, that there are three more solutions for $x=0.375$, 0.388, and 0.422, corresponding to frequencies of 50.7, 52.3, and 57 cm^{-1}, respectively. These frequencies lie in the acoustic continuum in the fre-

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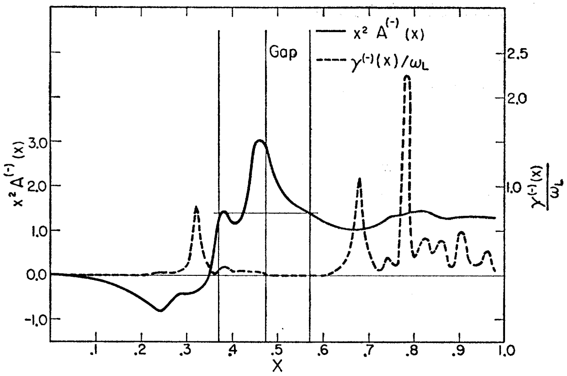

FIG. 2. A plot of the functions $x^2A^{(-)}(x)$ and $\gamma^{(-)}(x)/\omega_L$. The intersections of the former curve with a horizontal line drawn at a height of $(1/\epsilon_-)=M_-/(M_- - M_-')$ give the frequencies of the localized and resonance modes which can occur when an impurity of mass M_-' replaces one of the I^- ions (whose mass is M_-) in KI. The latter function gives the width of a resonance mode as a function of its frequency.

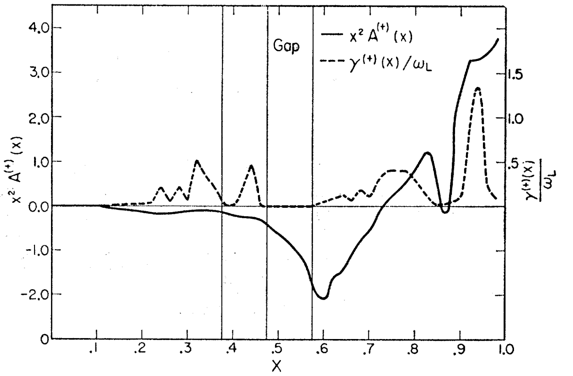

FIG. 3. A plot of the functions $x^2A^{(+)}(x)$ and $\gamma^{(+)}(x)/\omega_L$. The intersections of the former curve with a horizontal line drawn at a height of $(1/\epsilon_+)=M_+/(M_+ - M_+')$ give the frequencies of the localized and resonance modes which can occur when an impurity atom of mass M_+' replaces one of the K^+ ions (whose mass is M_+) in KI. The latter function gives the width of a resonance mode as a function of its frequency.

quency range between the maximum frequencies of the transverse acoustic and longitudinal acoustic modes. They therefore correspond to resonance modes. These four solutions correspond to vibration modes which are infrared active.

The good agreement between the theoretical value of 76.6 cm^{-1} for the frequency of the gap mode and the value of 77 cm^{-1} at which a sharp line is observed in the absorption spectrum of KI:Cl^-, leads us to attribute the latter to absorption associated with a gap mode at 77 cm^{-1}. The fact that the present simple theory predicts three resonance modes in a frequency range where three broad lines are observed in the absorption spectrum prompts us to attribute the latter to absorption by three resonance modes centered near 61 cm^{-1}. The theoretically computed widths ($\sim 0.1\omega_L$), for these resonance modes are somewhat broader than one would estimate from Fig. 1, but this may merely be a consequence of the simplicity of our model for Cl^- impurity. The fact that the calculated gap and resonance mode frequencies are somewhat lower than the experimental values suggests that the forces between the Cl^- ion and the host crystal are somewhat stiffer than the forces between the I^- ions and the rest of the crystal.

However, one must not take the quantitative results of the present theoretical discussion too literally. It is known that the frequencies of the localized modes due to hydride and deuteride U centers in NaCl and KCl come out too high by approximately 50% when computed on the basis of the assumption that these centers can be regarded as isotopic impurities.[20] These results show that an appreciable softening of the forces between the impurities and the surrounding lattice must occur. However, it may be argued that because of its small size, compared with the size of the ions it replaces, the hydride or deuteride ion is anomalous in this respect, and that the approximation of alkali or halide ion impurities in alkali-halide crystals by isotopic impurities may not be unjustified. Unfortunately, this does not seem to be always the case. It is found experimentally that when Na^+ ions are substituted for K^+ ions in KI, what appears to be a resonance mode occurs in the acoustic continuum near the maximum frequency of the longitudinal acoustic modes. According to Fig. 3 such a mode should not occur.

Nevertheless, the theoretical calculations do provide a qualitative explanation of the experimental results which are obtained when Cl^- ions replace I^- ions in KI, and they indicate that for quantitative agreement between theory and experiments in calculations of localized mode frequencies it will be necessary to take into account the changes in force constants which accompany the introduction of the impurity ion into the host crystal. Such calculations are now in progress.

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