in (26) is smaller than

$$[E_1^2/4\pi^2\hbar v^5 d\omega_e U(\omega_e/v)]$$

$$\times\int_0^{\omega_e}(\omega_e-\omega')\omega' U[(\omega_e-\omega')/v]U(\omega'/v)d\omega'. \quad (27)$$

The results of the numerical computations of (27) are given in Fig. 3. One can see from this figure that in *n*-Ge the two-phonon processes are unimportant as compared with the one-phonon processes. In *n*-Si the second term in (26) has the maximum at $\omega_e \approx 8\times10^{12}$ sec^{-1} (about $2\omega_{\max}'$). Thus the main contribution to the absorption with two-phonon emission will be given by the pairs at which $\omega_e \sim 8\times10^{12}$ sec^{-1}. One can see from Fig. 3 that at such values of ω_e the one-phonon process is about three times more frequent. Therefore, in *n*-Si also we can neglect the two-phonon processes as compared with the one-phonon processes.

It seems that the processes consisting of simultaneous absorption of a photon and emission of more than two phonons can also be neglected in both materials.

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Isotope Shift of a Low-Lying Lattice Resonant Mode*

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A sharp and very low-frequency lattice absorption due to a lithium resonant mode has been found in KBr:LiBr. A large frequency shift with lithium isotopes has been observed. The experimental results can be understood with a simplified lattice model in which both nearest-neighbor force constants and the mass of the impurity are varied. It is concluded that the resonant mode comes from a remarkable softening of the forces between the impurity and the surrounding lattice.

THE dynamics of a heavy substitutional isotopic impurity in a lattice has been approximately described in terms of two kinds of lattice modes, namely, approximate phonon modes and resonant modes.[1–3] The phonon modes are similar to modes in a pure crystal, while the resonant modes are localized around the impurity position. For an alkali halide lattice with the appropriate substitutional impurity, a resonant mode in which the impurity vibrates with a markedly different amplitude than does the corresponding atom in the host crystal is expected to be strongly infrared-active. The absorption of far-infrared radiation by a lattice mode activated by a heavy substitutional impurity has been reported.[4] Recently, a surprisingly low-frequency lattice absorption has been identified with the very light impurity Li^+ in KBr.[5]

In this note, we wish to report the observation and interpretation of a large frequency shift with lithium isotope of the resonant mode in KBr. The experimental results can be understood with a simplified lattice model in which both nearest-neighbor (n.n.) force constants and the mass of the impurity atom are varied. A fit gives n.n. force constants which are about 0.6% of the host-lattice force constants. Finally, for such large force-constant changes, the expression for the resonant-mode frequency simplifies to an Einstein oscillator form.

High-purity single crystals of KBr doped with small concentrations of Li^6Br and Li^7Br have been grown in an argon atmosphere by the Kyropoulos technique.[6] From thermal-conductivity measurements on both quenched and annealed crystals, the substitutional impurity centers appear to consist of individual lithium ions.[7] Far-infrared transmission measurements from a frequency of 90 to 12 cm^{-1} have been made on these doped crystals. The apparatus for these measurements has been described elsewhere.[4] The samples were maintained at 1.5°K by helium exchange gas in contact with the sample and with a liquid-helium reservoir.

The impurity-induced absorption coefficient has been

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obtained by comparing the transmission of a KBr:LiBr crystal with the transmission of a pure KBr crystal. The absorption coefficients found for both the Li^6 isotope and Li^7 isotope are shown in Fig. 1. For Li^6 ions a strong low-frequency absorption is observed at 17.9 ± 0.2 cm^{-1} with a full width at half-maximum absorption of approximately 1.4 cm^{-1}. In this frequency region, the bandwidth from our monochromator is approximately 0.7 cm^{-1}. Two concentrations have been measured: for curve A there are $1\pm0.1 \times 10^{19}$ Li^6 ions per cm^3 and for curve B there are $1.5\pm0.3 \times 10^{18}$ Li^6 ions per cm^3. With the higher concentration, A ,a prominent band is observed at 45.5 cm^{-1} and also at 83 cm^{-1}. For Li^7, a strong low-frequency absorption is located at 16.3 ± 0.2 cm^{-1} with a full width at half-maximum absorption of 1.2 cm^{-1}. Again two concentrations have been investigated: for curve C there are $1.2\pm0.1 \times 10^{19}$ Li^7 ions per cm^3 and for curve D there are $1.3\pm0.3 \times 10^{18}$ Li^7 ions per cm^3. A prominent band is observed at 43 cm^{-1} and another at 83 cm^{-1}.

Some qualitative statements about these experimental results are in order. The measured isotope shift for the low-frequency absorption ($\omega_6/\omega_7=1.10$) is larger than predicted by an Einstein oscillator $[(7/6)^{1/2}=1.08]$. Since the isotope shift will be large when the ion in question has a large amplitude in a normal mode, we picture, for the resonant mode, a threefold degenerate T_{1u} mode[8] in which the lithium ion is undergoing much larger excursions than the nearest-neighbor ions in the crystal. Most of the higher frequency absorption shown in Fig. 1 probably corresponds to the one-phonon absorption spectrum from the impurity-activated phonons.[9] The absorption coefficient should vary as a weighted one-phonon density of states; however, sufficient detail is not observed to verify this prediction. One unusual feature is the small but observable isotope shift of the band at 43 cm^{-1} for Li^7 to 45.5 cm^{-1} for Li^6. The band appears to be stronger for Li^6 than for Li^7. This absorption can either be identified with another slightly infrared-active impurity mode or as the second overtone of the low-frequency absorption. If anharmonic forces are important for this system, the second overtone can become infrared active in an octahedral environment.

Keeping these results in mind we shall now consider a specific model with which to interpret the isotope effect. Since the experimental modes are far down in the acoustic spectrum (resonant-mode frequency less than one-seventh the Debye frequency), we approximate the face-centered cubic diatomic lattice by the more tractable simple cubic monatomic lattice model. For this ordered S.C. lattice with mass M, the position of the substitutional impurity atom is taken as the origin. Each atom in the lattice is assumed to interact only with its nearest neighbors and the central and noncentral force constants are set equal to each other. With these simplifications the vibrational frequencies of the lattice can be described by the Green's function[10,11]:

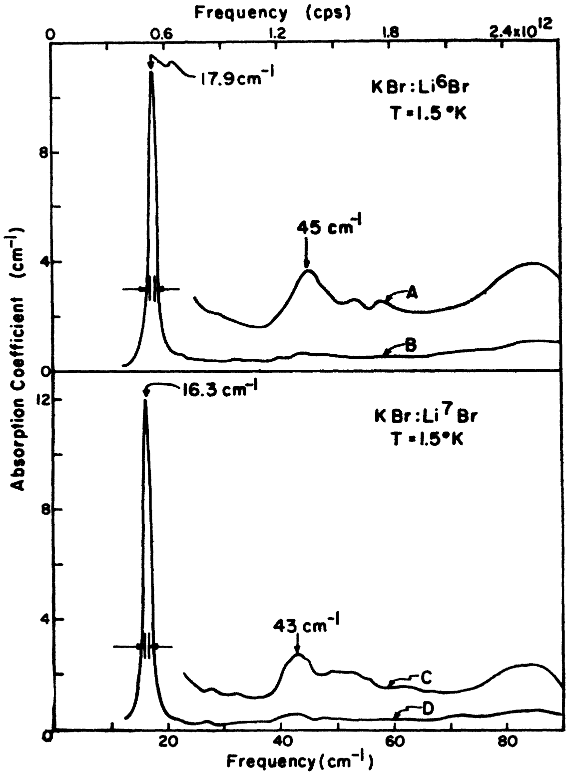

FIG. 1. Impurity-induced absorption coefficient versus frequency for the two lithium isotopes in KBr. For curves A and B, the concentrations of $KBr:Li^6Br$ are 1×10^{19} and 1.5×10^{18} Li^6 ions per cm^3, respectively. For curves C and D, the concentrations of $KBr:Li^7Br$ are 1.2×10^{19} and 1.3×10^{18} Li^7 ions per cm^3, respectively. The sample temperature for each measurement was approximately 1.5°K. In the low-frequency region the monochromator spectral bandwidth, about 0.7 cm^{-1}, is represented by the separation of the two arrows and is comparable to the resonant-mode linewidth at half-maximum absorption.

$$g(\omega^2;n_1n_2n_3)$$

$$=\frac{1}{N}\sum_{k_1k_2k_3}\frac{\exp[i(n_1k_1+n_2k_2+n_3k_3)]}{\omega^2-2(K/M)(3-\cos k_1-\cos k_2-\cos k_3)},\quad(1)$$

where N is the number of atoms in the lattice, K the force constant for the perfect lattice, $k=(k_1k_2k_3)$ is the wave vector (the lattice constant is taken to be unity), n_1,n_2,n_3 are a set of integers specifying sites, and the sum extends over the first Brillouin zone. For this case there exists three types of vibrational modes associated with the motion of the impurity: S-like (A_{2u}), P-like (A_{1g},E_g), and D-like modes (B_{2u}).[12] Among these types, only the first is infrared active. This mode is charac-

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terized by the equation $u(100)=u(-100)=u(010)=u(0-10)=u(001)=u(00-1)$, where $u(n_1n_2n_3)$ is one component, say the x component, of the displacement vector of the atom at $(n_1n_2n_3)$. The secular equation which determines the eigenfrequency of this mode is described by four kinds of Green's functions, $g(\omega^2;000)$ $g(\omega^2;100)$, $g(\omega^2;110)$, and $g(\omega^2;200)$. However, if we make use of some identity relations satisfied by the Green's functions of a S.C. lattice,[13] the resulting secular equation can be expressed entirely in terms of $g(\omega^2;000)$. The result is that

$$D(\omega^2)=1+\mu+2\mu(1+\lambda)(\omega/\omega_D)^2 +\{\lambda(1+\mu)-2\mu(1+\lambda)(\omega/\omega_D)^2\}\omega^2 g(\omega^2;000)=0, \quad (2)$$

where $\lambda=(M'/M)-1$ and $\mu=(K'/K)-1$ in which M' is the mass of the impurity and K' is the n.n. force constant and $\omega_D=12K/M$ is the maximum eigenfrequency of the perfect lattice.

Let us pay particular attention to the low-frequency region. We take the limit $N\rightarrow\infty$ and replace ω^2 by $\omega^2+i\epsilon$ (ϵ is positive and infinitesimal). Here the Debye approximation is used for the evaluation of the Green's function. To the lowest order in ω/ω_D it is given by $\mathrm{Re}\,g(\omega^2+i\epsilon;\ 000)=-3/\omega_D{}^2$ and $\mathrm{Im}\,g(\omega^2+i\epsilon;\ 000)=-i(3\pi/2)(\omega/\omega_D{}^3)$. Equation $\mathrm{Re}D(\omega^2+i\epsilon)=0$ (the resonant-mode solution is designated by ω_0) determines the resonant-mode frequency of the S-like mode with a width Γ given by

$$\Gamma/2=|\mathrm{Im}D(\omega_0{}^2+i\epsilon)/\{(d/d\omega)\,\mathrm{Re}D(\omega^2+i\epsilon)\}_0|\,,$$

where $\{\ \}_0$ is the value of the derivative at $\omega=\omega_0$. Using these facts we find that

$$(\omega_0/\omega_D)^2=(1+\mu)/(3\lambda+\lambda\mu-2\mu)$$

or (3)

$$\omega_0{}^2=12KK'/(2M'K+M'K'-3MK')$$

and

$$\Gamma/2=(3\pi/4)\omega_D|M'-M| \times K'^2M/(2M'K+M'K'-3MK')^2 \quad (4)$$

which is correct to order $(\omega_0/\omega_D)^2$. (For $K'=K$, ω_0 and Γ reduce to the Brout Visscher expressions.[1]) The change in force constant K'/K can be estimated by using our experimental values of ω_0. With a Debye temperature of 174°K we find $K'/K=0.0064$ for KBr:Li^{6}Br crystal and $K'/K=0.0062$ for KBr:Li^{7}Br crystal. These results show that a remarkable softening of the forces between the impurity and the surrounding lattice must occur. The isotope shift of the resonant-mode frequency has been studied by considering the ratio $\omega_0(6)/\omega_0(7)$, where $\omega_0(6)$ and $\omega_0(7)$ are, respectively, the values of ω_0 for the Li^6-doped and the Li^7-doped samples. Taking $K'/K=0.0063$, we find $\omega_0(6)/\omega_0(7)=1.085$ which is in fair agreement with the experimental value of 1.10 ± 0.01. Somewhat more physical insight can be gained if we neglect K' compared with K in (3). We then obtain $\omega_0{}^2=6K'/M'$. Hence in the limit $K'/K\ll1$, the resonant mode is well described by the Einstein model. In this same limit (4) becomes $\Gamma/2=(3\pi/16)\omega_D(M|M'-M|/M'^2)(K'/K)^2$. With the experimental value of K'/K given above fairly good agreement between theory and experiment is found for the linewidth. The ratio of the linewidths has also been estimated and the result is $\Gamma(6)/\Gamma(7)=1.4$ which is again in reasonable agreement with our experimental results.

In summary, a study of the isotope effect for KBr:LiBr has allowed a detailed comparison of theory and experiment. An appreciable softening of the forces between the Li ion and its surroundings is indicated by the sharp low-frequency resonant modes. An Einstein oscillator model can approximately describe the properties of such a low-frequency mode. Finally, in addition to the heavy impurity, the light impurity coupled with weak forces is also an important activator of a low-frequency infrared-active resonant mode.

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