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Far Infrared Properties of Lattice Resonant Modes. I. Isotope Shifts*

R. D. Kirby, I. G. Nolt,† R. W. Alexander, Jr., and A. J. Sievers
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

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The frequency shift of a lattice resonant mode associated with the isotopic substitution of an impurity ion has been measured for NaCl:Cu$^+$, KI:Ag$^+$, and KBr:Li$^+$. For all three systems, the experimental frequency shifts can be described satisfactorily by an Einstein oscillator representation for the resonant mode with the oscillator mass set equal to the impurity-ion mass. The model of Benedek and Nardelli and also Klein does not account for the experimental results of NaCl:Cu$^+$ or KBr:Li$^+$. The inclusion of anharmonic forces does improve the agreement between theory and experiment, but a large discrepancy still exists for KBr:Li$^+$.

I. INTRODUCTION

Although the isotope frequency shift associated with a lattice resonant mode[1] has been known for some time, the experimental results are not yet really understood. To account for the frequency shift in ^{6}Li$^+$- and ^{7}Li$^+$-doped KBr, Sievers and Takeno[1] used a simple lattice model in which long-range forces were neglected. Recently, calculations of the isotope shift have been attempted by Benedek and Nardelli,[2] using Hardy's deformation dipole model, and by Klein,[3] using the shell model to describe the perfect lattice. In both of these calculations long-range forces are included only in the description of the perfect lattice. The impurity is still coupled to the lattice with short-range forces. With these models a much smaller isotope shift has been calculated than was found previously either with simple lattice models[1,4] or by experiment. If the agreement of the simple model with experiment is fortuitous, then the resonant mode must be associated with a very anharmonic potential to account for the discrepancy between theory and experiment. However, because the Li$^+$ ion has a small radius and also a small mass, the resonant mode associated with this particular impurity may be anomalous in nature and not a characteristic feature of the coupled system. We have tested this possibility by studying the isotope shifts for the alkali halides NaCl and KI containing the heavy Cu$^+$ and Ag$^+$ impurity ions, respectively. Improved data for the KBr:LiBr system also have been obtained. Although the measured shifts for these three dopant-lattice systems differ by more than an order of magnitude, the isotope effect indicates that the three systems are indeed similar. The degree of anharmonicity associated with each resonant mode has not been resolved satisfactorily.

In Sec. II, the experimental shifts and resonant-mode linewidths are reported. Included here is a description of the far infrared absorption associated with the unwanted OH$^-$ impurity in NaCl.

In Sec. III, the experimental shifts are compared with the shifts predicted by both the simple model with only short-range forces and also with the model of Benedek and Nardelli and of Klein. Anharmonic forces are then discussed. When a large coupling between the resonant mode and other phonon modes is introduced, some agreement between the models and experiment can be realized if the coupling is assumed to be independent of the impurity mass.

II. EXPERIMENTAL RESULTS

A. Copper-Ion Impurity

Far infrared transmission spectra of the doped alkali-halide crystals were measured with a Strong-type lamellar interferometer.[5,6] The radiation was detected with a liquid-helium-cooled germanium bolometer. By comparing the transmission of the doped samples with the transmission of the pure crystal, the impurity-induced absorption coefficients were obtained. The same crystal-growing techniques were used to obtain all single crystals, i.e., the Kryopolous technique with an argon atmosphere.

The NaCl:CuCl transmission measurements were made with the samples at 4.2°K and an instrumental resolution of 0.09 cm^{-1}. This resolution is about a factor of 3 better than was available to Weber and Nette in their original investigation of the NaCl:CuCl system.[7] By using isotopically pure ^{63}Cu$^+$ and ^{65}Cu$^+$, the isotope shift has been resolved, and the impurity-induced absorption coefficient for the two isotopes is shown in Fig. 1. The numerical values for the two center frequencies are given in Table I, and the full width at one-

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† Present address: Institute for Astronomy, University of Hawaii, Honolulu, Haw.

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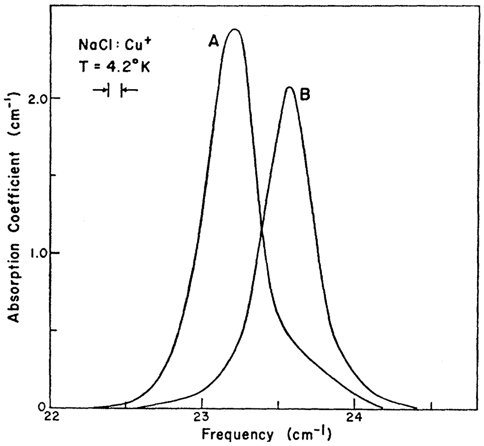

FIG. 1. Impurity-induced absorption coefficient versus frequency for $^{63}Cu^+$ and $^{65}Cu^+$ impurities in NaCl. Curve A has 1.15×10^{17} ($^{65}Cu^+$ ions)/cm^3, and curve B has 1.06×10^{17} ($^{63}Cu^+$ ions)/cm^3. The interferometer resolution is indicated by the separation of the two arrows.

half-maximum-absorption coefficient Γ is given in Table II. Because we have not yet found a consistent method of unfolding the instrumental linewidth from the measured width, only the measured value is given in the table. However, the experimental values of Γ probably should be reduced by about 0.02 cm^{-1} because of the finite instrumental resolution.

A more serious experimental problem has been the identification of unwanted impurities in NaCl. When the natural abundance of CuCl was added to the melt, an absorption line at 9.2 cm^{-1} also was observed. Moreover, when isotopic copper in the form of CuO was added to the melt, a number of additional low-frequency lines appeared. Most of the low-frequency absorptions are due to the OH^- impurity. The identification was made by studying NaCl doped with OH^- ions.[8] The induced absorption in NaCl for an OH^- concentration of 60 ppm[9] is shown in Fig. 2. Not all of this absorption is necessarily due to the OH^- impurity itself, as our samples showed an absorption at about 7 μ,[9] indicating CO_3^- impurities. However, the absorption spectrum shown in Fig. 2 does seem to scale roughly with OH^- concentration. An oscillator strength[10] $f=0.02$ has been assigned to the strongest absorption at 9.2 cm^{-1}.

Recently, Bosomworth[11] has reported an NaCl:OH^- absorption spectrum which is substantially different from that shown in Fig. 2. He observed a broad peak at 12 cm^{-1}, with a weak absorption at 9.5 cm^{-1}, for an OH^- concentration of 1900 ppm. The difference between Bosomworth's absorption spectrum and ours probably results from the large difference in OH^- concentration. A strong concentration-dependent absorption associated with the internal stretching mode of the OH^- ion in the near infrared has been observed by Wedding.[12]

An NaCl:OD^- crystal gave essentially the same spectrum as that shown in Fig. 2, but the OD^- stretching mode was not observed by Wedding in the near infrared.[9] We conclude that the resultant spectrum was associated with the OH^- impurity and that the OD^- dopant did not enter the crystal.

Fortunately, the absorption at 22 cm^{-1} in Fig. 2 is weak. Our NaCl:Cu^+ samples contained much less than 60 ppm OH^-, and no distortion of the Cu^+ absorption was observed. As a matter of practical interest, we found that a Harshaw[13] NaCl sample showed a far

TABLE I. Center frequencies for isotopic impurities. A comparison of the experimental resonant-mode frequency ratios with the ratios predicted by the ST model, the BNK model, and with an Einstein oscillator $[(\Omega_l/\Omega_h)=(M_h/M_l)^{1/2}]$. Here Ω_l and M_l are the resonant-mode frequency and mass of the lighter impurity, and Ω_h and M_h are the frequency and mass of the heavier impurity.

Resonant-mode system	Experimental resonant frequency (cm^{-1})	Ω_l/Ω_h (expt.)	Ω_l/Ω_h (ST)	$(M_h/M_l)^{1/2}$	Ω_l/Ω_h (BNK)
NaCl:$^{63}Cu^+$	23.57±0.02	1.016±0.002	1.017	1.0158	1.013[a]
NaCl:$^{65}Cu^+$	23.20±0.02				
KI:$^{107}Ag^+$	17.37±0.02	1.008±0.002	1.0099	1.0093	1.0065[b]
KI:$^{109}Ag^+$	17.23±0.02				
KBr:$^6Li^+$	17.71±0.05	1.105±0.004	1.085	1.0801	1.019[a,c]
KBr:$^7Li^+$	16.07±0.05				

[a] M. V. Klein (Ref. 3).
[b] G. Benedek (private communication).
[c] Benedek and Nardelli estimated this ratio to be about 1.05 on the basis of their model.

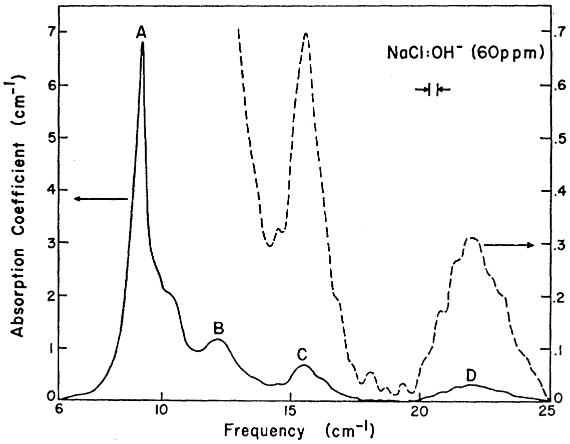

FIG. 2. Impurity-induced absorption coefficient versus frequency for NaCl:OH^-. Note the factor-of-10 change in the absorption coefficient scale for the dotted curve. The small "wiggles" on the dotted curve are instrumental. Line A is at 9.2 cm^{-1}, line B is at 12.2 cm^{-1}, line C is at 15.6 cm^{-1}, and line D is at 22.0 cm^{-1}. The interferometer resolution is indicated by the separation ot the two arrows. The sample temperature was 4.2°K.

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[8] These NaCl:OH^- crystals were kindly supplied by M. V. Klein and B. Wedding.

[9] B. Wedding (private communication).

[10] A. J. Sievers, Phys. Rev. Letters **13**, 310 (1964).

[11] D. R. Bosomworth, Solid State Commun. **5**, 681 (1967).

[12] B. Wedding, Ph.D. thesis, University of Illinois, 1967 (unpublished).

[13] The NaCl crystal was obtained from the Harshaw Chemical Co., Cleveland, Ohio.

infrared spectrum similar to that of Fig. 2, corresponding to a few ppm OH$^-$.

B. Silver-Ion Impurity

The KI:AgI system[10] exhibits an impurity-induced absorption at about 17.3 cm^{-1}. While the relative-mass ratio of the two isotopes (107/109) is considerably smaller than for the copper ion, it has been possible to detect the isotopic frequency shift by using isotopically pure ^{107}Ag$^+$ and ^{109}Ag$^+$ in the form of Ag metal as a dopant.[14,15] Again the far-infrared-transmission measurements were made with the samples at 4.2°K and an instrumental resolution of 0.09 cm^{-1}. The impurity-induced absorption coefficients for the two isotopes are shown in Fig. 3. The center frequencies are recorded in Table I, and the full width at one-half-maximum absorption is given in Table II. Note that the linewidth is much smaller than had been estimated previously.[10]

All transmission measurements were made soon after the crystals were grown because this dopant-lattice combination has the curious property of not being stable at room temperature. By monitoring the strength of the far-infrared absorption at low temperature as a function of the length of time that the crystal is at room temperature, a marked decrease in the line strength has been measured over a three-month period. The conversion process can be increased by heating the crystals to 140°C. At this temperature, the crystal turns a distinct yellow color. Upon cooling to room temperature, the sample returns to a normal clear appearance.

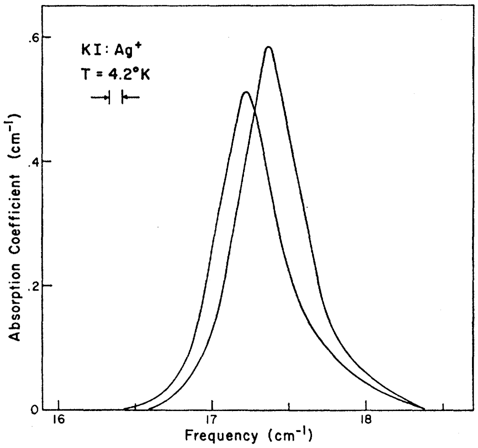

FIG. 3. Impurity-induced absorption coefficient versus frequency for ^{107}Ag$^+$ and ^{109}Ag$^+$ impurities in KI. No Ag$^+$ concentrations are given because of the uncertainty about what fraction of the Ag$^+$ ions are actually participating in the resonant mode. (See Sec. II B of this paper.) The interferometer resolution is indicated by the separation of the two arrows.

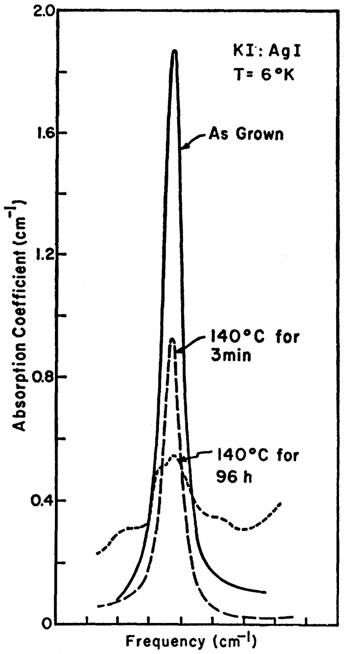

FIG. 4. Temperature instability of the silver-activated resonant-mode in KI. The far-infrared transmission was measured with the crystal at 6°K between each cycle to 413°K. For this low-resolution study, the line shape is determined by the instrumental width of 1 cm^{-1}.

When the sample is then cooled to liquid-helium temperatures, the strength of the resonant mode is less than before the heating cycle. The line strength at different stages of the heating cycle is shown in Fig. 4. As the absorption at 17.3 cm^{-1} disappears, a new absorption line appears at about 78 cm^{-1}. Although the kinetics of this transformation have not yet been studied in detail, one possible explanation of these results is that AgI domains may be formed in the crystal at room temperature and above, resulting in a decrease in the resonant-mode strength. The 78-cm^{-1} absorption line is in the appropriate frequency region to be associated with the infrared-active transverse optic mode for the small AgI crystallites.

C. Lithium-Ion Impurity

The observation of the ^{6}Li$^+$ and ^{7}Li$^+$ resonant-mode frequency shift in KBr was reported in 1965.[1] The

TABLE II. Linewidths for isotopic impurities. A comparison of the experimental resonant-mode linewidths with the linewidths predicted by the ST model.

Resonant-mode system	Γ (cm^{-1}) Experimental	Γ (cm^{-1}) (ST)
NaCl:^{63}Cu$^+$	0.38±0.05	0.57
NaCl:^{65}Cu$^+$	0.40±0.05	0.56
KI:^{107}Ag$^+$	0.47±0.05	0.72
KI:^{109}Ag$^+$	0.45±0.05	0.72
KBr:^{6}Li$^+$	0.60±0.05	0.21
KBr:^{7}Li$^+$	0.43±0.05	0.15

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[14] The isotopic copper, silver, and lithium used to dope our samples were obtained from Oak Ridge National Laboratory, Oak Ridge, Tenn.

[15] The crystals were grown by the Materials Science Center Crystal Growing Facility at Cornell University.

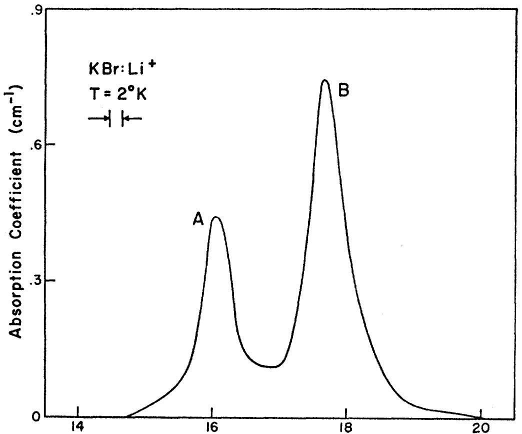

FIG. 5. Impurity-induced absorption coefficient versus frequency for ^{6}Li$^+$ and ^{7}Li$^+$ impurities in KBr. Peak A corresponds to 1.9×10^{16} (^{7}Li$^+$ ions)/cm^3, and peak B corresponds to 3.7×10^{16} (^{6}Li$^+$ ions)/cm^3. The interferometer resolution is indicated by the separation of the two arrows.

resolution of the grating monochromator was barely sufficient to distinguish the experimental frequency shift from a mass$^{1/2}$ dependence. Measurements obtained with the interferometer have increased the precision of both the frequency shift and the linewidths. An impurity-induced absorption spectrum which contains an enriched ^{6}Li$^+$ and ^{7}Li$^+$ mixture is shown in Fig. 5. The sample was maintained at 2°K, and the instrumental resolution was 0.18 cm^{-1}. A careful investigation of these two absorption lines for a variety of lithium concentrations has revealed a concentration effect. By varying the lithium concentration from 2×10^{15} Li$^+$ ions/cm^3 to 2.4×10^{18} Li$^+$ ions/cm^3 (three orders of magnitude), a change has been detected for both the linewidth and the center-frequency position. Heretofore such concentration effects have been overlooked.

The center frequency of the resonance absorption varies linearly with Li$^+$ concentration. A frequency shift of 0.07 cm^{-1} is observed when the concentration is changed from 2×10^{17} to 2×10^{15} ions/cm^3 for ^{7}Li$^+$ in KBr. The value of the experimental frequency ratio Ω_6/Ω_7 in Table I was obtained from crystals of the lowest concentrations measured. We now estimate the frequency shift due to the concentration dependence of the average lattice constant.

By measuring the frequency shifts of a resonant mode with static stress applied to the crystal, the coupling of the first excited state to long-wavelength phonons can be measured.[16] The stress perturbation produces a crystal strain which can be resolved into strain components transforming according to the irreducible representations of the octahedral point group. Three coefficients A, B, and C prescribe the dependence of the resonant-mode frequency upon the fully symmetric (A_{1g}), the tetragonal (E_g), and the trigonal (T_{2g}) strain components, respectively. The three coefficients have been determined in Ref. 16 for KBr:Li$^+$. The coefficient for the strain component which transforms as the A_{1g} representation exhibits directly the dependence of the resonant-mode frequency upon unit volume change. The transition energy is

$$E=\hbar\Omega+A(\Delta V/V). \qquad (1)$$

We estimate the frequency shift by first calculating the average lattice constant $\bar{a}$ from the known impurity concentration by using Vegard's relation[17]

$$\bar{a}=a_1+(a_2-a_1)x, \qquad (2)$$

where a_1 and a_2 are the lattice constants of KBr and LiBr, respectively, and x is the molar concentration of LiBr. For $a_1=6.58$ Å, $a_2=5.50$ Å, and 2×10^{17} Li$^+$ ions/cm^3, the calculated frequency shift due to the volume change is 0.006 cm^{-1}. This number is about an order of magnitude smaller than the observed shift. Such a large discrepancy might be resolved if, in addition to the strain interaction, there was a dynamic coupling between Li$^+$ ions.

The concentration dependence of the full width at half-maximum absorption is shown in Fig. 6. The data have been corrected for the instrumental width, assuming a Gaussian absorption line and slit function. The slope of the line in Fig. 6 indicates that the linewidth depends quite weakly upon the concentration, varying as the concentration to the 0.1 power approximately. From earlier measurements on the stress-induced shifts of the lithium resonant mode an estimate of the random strain broadening can be made.[16] For random static stresses on the order of $\frac{1}{2}$ kg/mm^2 in the crystal, an increased width of about 0.1 cm^{-1} can be expected. A good estimate of the true resonant-mode width will not be possible until the problem of lattice

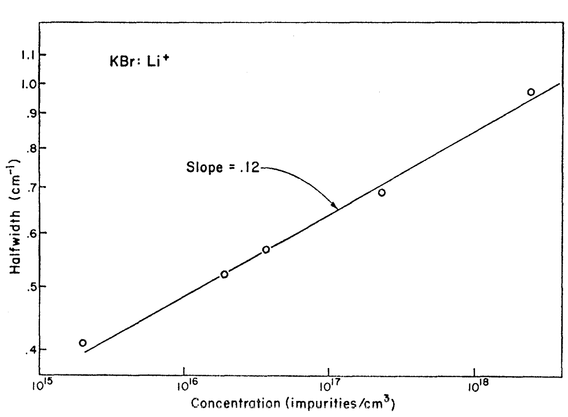

FIG. 6. Concentration dependence of the full width at half-maximum absorption for KBr:Li$^+$. The experimental widths have been corrected for the instrumental width, assuming a Gaussian absorption line and slit function. Note the log-log coordinates.

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[16] I. G. Nolt and A. J. Sievers, Phys. Rev. Letters **16**, 1103 (1966).

[17] L. Vegard, Z. Physik **5**, 17 (1921).

strains has been studied in detail, but the experimental value of 0.43 cm^{-1} in Table II is clearly an upper bound.

III. DISCUSSION OF RESULTS

A. Isotope Shift in the Harmonic Approximation

In the model which Sievers and Takeno (hereafter called ST) used for low-frequency resonant modes, only nearest-neighbor forces were considered. The central and noncentral force constants of the host crystal were set equal to each other, while both the impurity mass M' and its nearest-neighbor force constant K' were taken to be different than those of the host lattice. From their Eq. (3) we can obtain a simple expression for the ratio of the resonant-mode frequencies for two isotopic impurity ions. If the light isotope is labeled M_l with resonant-mode frequency Ω_l, and the heavy isotope M_h with frequency Ω_h, then the ratio of the frequencies is

$$\frac{\Omega_l}{\Omega_h}=\left(\frac{M_h}{M_l}\right)^{1/2}\left[1-3\left(\frac{M_h}{M_l}-1\right)\left(\frac{\Omega_h}{\omega_D}\right)^2\right]^{-1/2}, \tag{3}$$

where ω_D is the Debye frequency for the lattice. Note that Eq. (3) predicts that the frequency ratio is always larger than that obtained with an Einstein oscillator, namely, larger than $(M_h/M_l)^{1/2}$.

The values for ω_D were taken to be 164 cm^{-1} for NaCl, 101 cm^{-1} for KI, and 121 cm^{-1} for KBr, and the ratios are compared to the experimental results in Table I.

Our experimental results may also be compared with the predictions of the model containing long-range Coulomb interactions which was formulated by Benedek and Nardelli.[2] Here a monovalent impurity with a different mass and nearest-neighbor central force constant is substituted for a host ion. Using Hardy's deformation dipole model to obtain the perfect-lattice–phonon spectrum, Benedek and Nardelli (hereafter called BN) have estimated the frequency ratio for isotopic Li^+ in KBr. Also, Benedek has made a similar computer calculation for Ag^+ in KI.[18] This result is given in Table I.

Starting with the BN model, Klein has derived an expression for the resonant-mode frequency of a positive impurity for the limit of low frequencies. If the same force constants are assumed for both isotopic impurities, then the frequency ratio of the two resonant modes is[3]

$$\frac{\Omega_l}{\Omega_h}=\left[\frac{M_h+\delta M_+}{M_l+\delta M_+}\right]^{1/2}, \tag{4}$$

where δM_+ is an effective mass representing a host-lattice contribution to the impurity mass. Since $\delta M_+>0$, this frequency ratio is always less than the Einstein oscillator value, in contrast with the ST model described earlier. Klein has calculated the resonant-mode parameters, using the BN model, but with the perfect-lattice spectrum obtained from the shell model. He finds $\delta M_+=15.72$ amu for Cu^+ in NaCl and $\delta M_+=20.4$ amu for Li^+ in KBr. The calculated frequency ratio is compared with the experimental numbers in Table I.

We see that the ST model is in somewhat better agreement with the experimental results than the BN model. The ST model gives the correct isotope shift (within the experimental error) for NaCl:Cu^+ and KI:Ag^+, and gives about 80% of the experimental shift for KBr:Li^+. The BN model agrees with experiment for KI:Ag^+, gives about 80% of the experimental shift for NaCl:Cu^+, and only about 20% for KBr:Li^+.

B. Anharmonic Effects

Clearly, a model such as that of Benedek and Nardelli and Klein (BNK), which includes both long-range Coulomb forces as well as short-range repulsive forces, should be a good approximation to the actual impurity-lattice system. We now look for anharmonic contributions to the resonant-mode frequency which could influence the isotope shift.

Two different anharmonic effects are described here. One contribution to the isotope shift can arise from the anharmonic nature of the potential which describes the resonant-mode oscillator. Another contribution can arise from the modulation of this potential by other lattice modes. To be more specific, we describe the resonant mode by an oscillator coordinate Q; then, in the harmonic approximation, the Hamiltonian for the mode is

$$H=(1/2M)P^2+\tfrac{1}{2}M\Omega^2Q^2, \tag{5}$$

where M is the effective mass of the oscillator, and Ω is the oscillator frequency. A perturbation which does not depend on the other lattice-mode coordinates (we label this a static perturbation) is

$$H'=CQ^4, \tag{6}$$

where C is a constant. This static effect will be contrasted with the dynamic perturbation which shall be treated shortly. By first-order perturbation theory the 0-1 transition energy for the anharmonic oscillator is

$$E=\hbar\Omega+\epsilon/M, \tag{7}$$

where $\epsilon=3C\hbar^2/M\Omega^2$ is independent of the oscillator mass M. Therefore the anharmonic contribution to the transition energy is proportional to $1/M$. From the known values of the resonant-mode frequencies in Table I, ϵ can be calculated. For the ST model, the oscillator mass is the impurity-ion mass. Inserting these masses in Eq. (7), we find that the anharmonic contribution to the resonant-mode frequency is about 37% of the harmonic contribution for KBr: $^6\text{Li}^+$. In other words, large anharmonic effects are necessary to explain

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[18] G. Benedek (private communication).

the isotope shift on the basis of the ST model. For larger mass-impurity ions, the anharmonic contribution to the isotope shift becomes smaller. In fact, if we assume that the coefficient ϵ in Eq. (7) determined for Li$^+$ in KBr also roughly describes the anharmonic contribution for Cu$^+$ in NaCl, then the calculated frequency ratio becomes

$$\Omega(63)/\Omega(65)=1.018\,.$$

This value is still within the experimental error of the measured value in Table I.

The BNK model requires a much larger anharmonic coefficient ϵ because of the large effective mass in Eq. (7). In fact, as we now show, even a very anharmonic potential such as a square well cannot remove the disagreement with experiment. For the square well the transition energy varies as $1/M$, rather than $1/\sqrt{M}$ as for the harmonic oscillator. Klein[3] found $\Omega(6)/\Omega(7)=1.02$ for Li$^+$ in KBr in the harmonic approximation. Then, for the square-well potential, this ratio should only change to $\Omega(6)/\Omega(7)\approx 1.04$, which is only 40% of the experimental shift. By itself, then, this static perturbation cannot remove the discrepancy.

Another effect can arise from the dynamical motion of the lattice, and we now consider this possibility. To illustrate this problem, the perturbation to the harmonic-oscillator resonant mode is now

$$H'=\tfrac{1}{2}Q^2\frac{1}{\sqrt{N}}\sum_k b_k q_k\,, \tag{8}$$

where Q is again the coordinate of the resonant mode, and q_k is the coordinate of the kth lattice mode. (Later, we shall approximate these lattice modes by phonon modes of the unperturbed lattice.) The anharmonic coupling coefficient of this mode to the resonant mode is b_k, and N is the number of degrees of freedom of the lattice. Because of the linear coupling, the transition energy is

$$E=\hbar\Omega+\frac{1}{2M\Omega}\frac{1}{\sqrt{N}}\sum_k b_k q_k\,. \tag{9}$$

We shall now estimate the magnitude of this effect for Li$^+$ in KBr by using the static-stress results discussed earlier. The dependence of the resonant-mode frequency upon a unit-volume change of the lattice has already been given by Eq. (1). We assume that the modes in the perturbed lattice can be represented by the unperturbed phonons of the perfect crystal. Noting that the local strain for long-wavelength plane waves of wave vector k varies as kq_k,[19] we set $b_k=bk$ in Eq. (9). The lattice dilation is then[20]

$$\frac{\Delta V}{V}=\frac{1}{N}\sum_k kq_k\,, \tag{10}$$

and from Eq. (1)

$$A=\hbar b/2M\Omega\,. \tag{11}$$

Putting this value for b back into Eq. (9), the mean-square breadth associated with the transition is

$$\langle(E-\hbar\Omega)^2\rangle=\Delta^2>\frac{A^2}{\mathrm{N}}\sum_k k^2\langle q_k{}^2\rangle\,. \tag{12}$$

The inequality sign is used because the tetragonal and trigonal contributions have been neglected. At 0°K

$$\langle q_k{}^2\rangle=\hbar/2m\omega_k\,.$$

Thus, using the Debye approximation, we find for the second moment

$$\Delta^2>\frac{A^2\hbar}{2mv^2}\int_0^{\omega_\mathrm{D}}\omega^3\frac{d\omega}{\omega_D{}^3}\,, \tag{13}$$

where $k=\omega/v$, and v is the velocity of sound. Also, $\hbar\omega_D=k\Theta_D$, where Θ_D is the Debye temperature, and ω_D is the cutoff frequency. For this case

$$\Delta>\tfrac{1}{2}A\,(\hbar\omega_D/2mv^2)^{1/2}\,. \tag{14}$$

If we assume that m is the acoustic mass, i.e.,

$$m=\tfrac{1}{2}[m(\mathrm{K}^+)+m(\mathrm{Br}^-)]\,,$$

and take the measured value of $A=830$ cm^{-1}, then $(\hbar\omega_D/2mv^2)^{1/2}=0.057$, and

$$\Delta>24\ \mathrm{cm}^{-1}$$

for Li$^+$ in KBr. From Table II the measured width of the resonant mode is at least a factor of 60 smaller than the value of Δ above. Thus the square root of the second moment is not directly related to the linewidth of the resonant mode. Because of the large linear coupling of the resonant mode to long-wavelength phonons, the modulation of the resonant-mode energy levels does introduce characteristic properties into the absorption spectrum. The second moment which we have estimated above is to be associated with the breadth of the resonant mode plus phonon sideband. In fact, modulation which is linear in the phonon coordinates does not contribute to the width of the resonant mode in first order.[19] The sharp zero-phonon lines which have been studied in the optical spectrum are a much better known example of this motional effect of the lattice.[19,21] There has been some confusion

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[19] R. H. Silsbee, Phys. Rev. **128**, 1726 (1962); R. H. Silsbee, in *Proceedings of the Third International Congress on Quantum Electronics*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 774; R. H. Silsbee and D. B. Fitchen, Rev. Mod. Phys. **36**, 423 (1964); R. H. Silsbee, in Lectures on Optical Properties of Solids, NATO Advanced Study Institute, Freiburg, Germany, 1966, edited by S. S. Mitra (to be published).

[20] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 23.

[21] T. Timusk and M. V. Klein, Phys. Rev. **141**, 664 (1966).

about the credibility of identifying low-frequency transitions with zero-phonon lines because the adiabatic approximation is usually used in the optical problem. However, a number of investigators[3,19,22] have indicated that if the phonon-impurity interaction shifts but does not mix the impurity states, then the adiabatic approximation is not required.

Because of the strong coupling between the resonant mode and the phonons, the zero-phonon resonant-mode transition E° will be shifted from the value given by a harmonic oscillator. Linear coupling to the phonon field will give a shift in second order, while quadratic coupling produces a shift in first order. As we are mainly interested in the magnitude of this shift, we continue with our study of the linear coupling. In second order the center frequency E° is given by

$$E^\circ = \hbar\Omega - \frac{A^2}{2mN}\sum_k \frac{k^2}{\omega_k^2}. \tag{15}$$

In the Debye approximation

$$E^\circ = \hbar\Omega - \tfrac{1}{3}A(A/2mv^2), \tag{16}$$

and for $^7\text{Li}^+$ the correction term becomes

$$\Delta E^\circ = \tfrac{1}{3}A(A/2mv^2) = 6.2\ \text{cm}^{-1}.$$

As only the hydrostatic coupling term has been used, this ΔE° probably represents a lower bound. For both the ST model and also the BNK model, ΔE° will only reduce the calculated isotope shift from that given by the harmonic approximation. That is, the correction we have found is in the wrong direction. The reduction occurs because the coupling constant A^2 varies inversely as the oscillator mass itself [see Eq. (11)].

A second-order dipole-moment coupling of the resonant mode to the lattice phonons could produce a coupling term which would not depend on the impurity mass; hence the correction would then be in the right direction. Such a coupling would increase the isotope shift over that given by a harmonic oscillator. No evidence for such a coupling mechanism has as yet been found, but perhaps accurate stress measurements on the $^6\text{Li}^+$ and $^7\text{Li}^+$ resonant modes will demonstrate whether or not the linear coupling coefficient does indeed depend on the impurity mass.

In order to better understand some of the other contributions to the isotope effect, the temperature-dependent properties of these resonant modes are now being measured. Apparently, only dynamic perturbations such as the one considered above can lead to agreement between the BNK model and the large experimental isotope shifts observed for Li^+ and Cu^+. For Ag^+ the experimental errors for the frequency shifts are still large enough to mask any detailed comparison with theory.

IV. SUMMARY

For both KBr:Li^+ and NaCl:Cu^+ the resonant-mode isotope shifts are at least as large as given by an Einstein oscillator, with the mass of the oscillator given by the impurity ion mass itself. This experimental result has been contrasted with the BNK model which predicts isotope shifts which are always smaller than those given by the Einstein oscillator. The introduction of anharmonic forces has not improved significantly the agreement between theory and experiment. We have shown that dynamic coupling of the resonant mode to the lattice is important, but a satisfactory answer has not been found. Recently, Krumhansl[23] has pointed out that the disagreement between the BNK model and experiment may occur for yet a different reason. Consistent solutions do not follow necessarily from a model in which the impurity is coupled to the lattice by short-range forces while the other ions are coupled together by both short-range and long-range forces. To be self-consistent, a model should treat all ions on an equal basis.

In the course of our investigation, a number of additional properties of lattice resonant modes have been uncovered. The resonant-mode widths are found to be much smaller than previously reported. For KBr:Li^+ a concentration dependence of the linewidth and also the resonant-mode frequency has been observed. Also, the resonant mode has been measured for concentrations as low as 2.5×10^{15} (Li^+ ions)/cm^3. Although the concentration dependence of the resonant modes for Cu^+ and Ag^+ has not yet been investigated, similar concentration effects are expected.

Linewidth values must still be regarded with a degree of caution. For although the contribution from concentration broadening and also from the finite resolving power of the interferometer can be estimated, the broadening from inhomogeneous lattice stains has not been studied yet. The true width of the resonant mode is no doubt still smaller than the widths which we have reported here.

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