

purest crystals we could make (Fig. 18). The addition of Na^+ ions results in the appearance of three new bands at 101, 83.5, and 71.5 cm^{-1} (Fig. 18), of the same frequencies as the three maxima in the lattice-mode density,⁹ and corresponding approximately to characteristic TO, LA, and TA phonons. Except for Na^+ , all impurities give only a general background absorption. The same is true for neutron irradiation, except in the narrow phonon gap of KBr around 93 cm^{-1} , where the absorption does not increase.²⁷ Chlorine seems to induce a localized vibration at the limit of the gap: this should explain the residual peak at 93 cm^{-1} we found in the purest crystal, which still contained a small amount of chlorine.

²⁷ A. Hadni, G. Morlot, and F. Brehat, *Compt. Rend.* **264**, 164 (1967).

VII. CONCLUSIONS

The optical constants of potassium bromide (ν_T , δ_1 , ρ_1 , k_M , ϵ_{R0} , and χ_T) vary linearly with temperature within the experimental accuracy. Lorentz theory permits us to consider two linear oscillators, which represent quite well the behavior of KBr, if they are modified to include a temperature dependence. The damping of the fundamental oscillator decreases when T decreases. On the other hand, its strength does not vary much, while the strength of the second oscillator decreases strongly.

ACKNOWLEDGMENTS

We are grateful to Bernard Jacques and Robert Thomas, who did the laser measurements at 336μ , and wish also to thank Dr. J. N. Plendl of the Cambridge Research Laboratories for his interest in the investigation.

Scattering of Phonons by Monatomic Impurities in Potassium Halides*

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The thermal conductivity of doped KCl, KBr, and KI has been measured between 1 and 200°K . Below $\sim 5^\circ\text{K}$, the phonon scattering by the defects obeys a Rayleigh law in most cases. The magnitude of the scattering is determined by the mass difference alone. In Ag^+ -doped crystals, however, the Rayleigh scattering is much weaker than predicted by the mass difference. This is explained through the weak coupling between the Ag^+ and its neighbors. Above 5°K , in the region of the resonance scattering, the conductivity can be qualitatively described with the model of elastic phonon resonant scattering by quasi-localized modes. In $\text{KCl}:\text{Tl}$, I , Rb , and Br , the mass difference alone suffices to qualitatively describe the data, which means that the resonant mode is odd. The resonant scattering observed in Li^+ - and Ag^+ -doped crystals is ascribed to excitations of even resonant modes. It is noted that in many cases thermal-conductivity measurements are complementary to optical-absorption measurements, since the former observe defects strongly coupled to the lattice, whereas the latter observe the ones which are weakly coupled.

I. INTRODUCTION

THE increasing recognition of the importance of lattice vibrations for many solid-state phenomena has stimulated numerous theoretical and experimental studies of lattice vibrations in defect crystals.¹ Defects change the vibrational spectrum of the lattice by causing new modes which can not be described as plane waves, but which are centered around the defect and whose amplitude decreases with increasing distance

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¹ I. M. Lifshitz, *Rept. Progr. Phys.* **29**, 277 (1966); A. A. Maradudin, *ibid.* **28**, 332 (1965); M. V. Klein, in *Physics of Color Centers*, edited by W. Beall Fowler (Academic Press Inc., New York, 1968). These review articles contain references to earlier work.

from the defect. Such impurity modes can have frequencies which lie in the frequency spectrum of the unperturbed lattice. If they are strongly coupled to the plane-wave phonons, they will impede the heat flow in the crystal and can thus be detected through measurements of the lattice thermal conductivity.²⁻⁶ By investigating a large number of foreign alkali or halogen ions dissolved in the host lattices KCl, KBr, and KI, and by comparing the results with those obtained by far

² C. T. Walker and R. O. Pohl, *Phys. Rev.* **131**, 1433 (1963); interpretation by M. C. Wagner, *ibid.* **131**, 1443 (1963).

³ C. T. Schwartz and C. T. Walker, *Phys. Rev.* **155**, 959 (1967). We refer to this and the following two references for a historical review of the field.

⁴ R. F. Caldwell and M. V. Klein, *Phys. Rev.* **158**, 851 (1967).

⁵ R. O. Pohl, in *Lectures on Elementary Excitations and their Interactions in Solids* (NATO Advanced Study Institute, Cortina d'Ampezzo, Italy, 1966), p. VIII, 1.

⁶ F. C. Baumann, J. P. Harrison, R. O. Pohl, and W. D. Seward, *Phys. Rev.* **159**, 691 (1967).

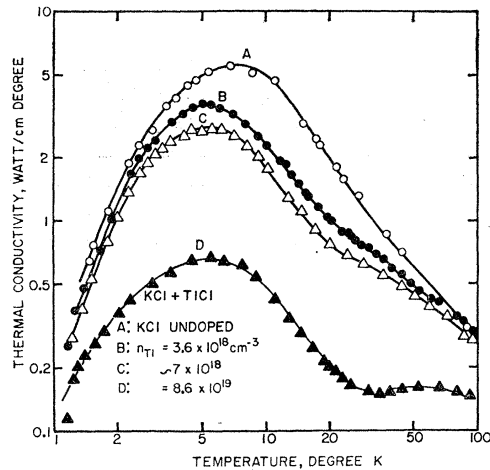


FIG. 1. Thermal conductivity of KCl:Ti. All crystals used in this work had sandblasted surfaces, were 5×5 mm wide and 40 mm long, and the separation between the thermometers was ~ 20 mm. Ti^+ concentrations n_i : A, undoped; B, $n_i = 3.6 \times 10^{18} \text{ cm}^{-3}$; C, n_i estimated to be $7 \times 10^{18} \text{ cm}^{-3}$; and D, $n_i = 8.6 \times 10^{19} \text{ cm}^{-3}$.

infrared techniques,^{7,8} we have tried to gain a deeper insight into the nature of these impurity modes.

II. EXPERIMENTAL RESULTS

The techniques for measuring the thermal conductivity and the sample preparation have been de-

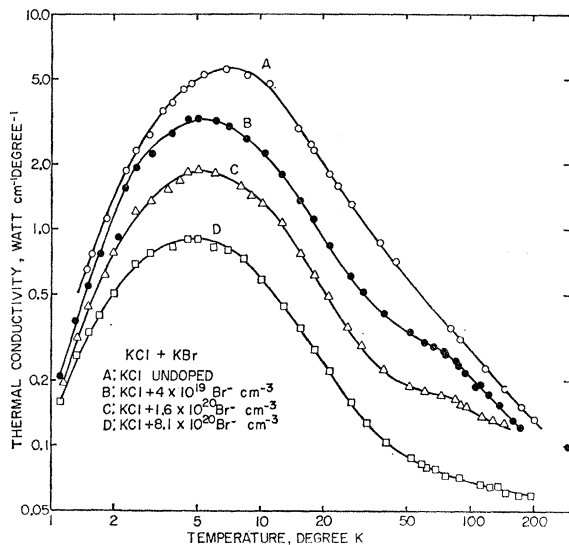


FIG. 2. KCl:Br. Br^- concentrations n_i : A, undoped, B, $n_i = 4 \times 10^{19} \text{ cm}^{-3}$; C, $n_i = 1.6 \times 10^{20} \text{ cm}^{-3}$; D, $n_i = 8.08 \times 10^{20} \text{ cm}^{-3}$. These chemically determined concentrations are equal to the concentrations in the melt from which the crystals were pulled. This result is expected because of the complete miscibility of the two salts. We take this agreement as indication of the quality of the chemical analysis used for all the crystals studied in this work (see Skogerboe, Ref. 9). The thermal conductivity of the system KCl:Br has been studied before between 3 and 20°K by W. S. Williams, Phys. Rev. **119**, 1021 (1960).

⁷ L. Genzel, in Lectures on Impurity Induced Lattice Absorption, in NATO Summer Institute in Physics, Freiburg, Germany, 1966 (unpublished).

⁸ A. J. Sievers, in Ref. 5, p. VI, 30.

TABLE I. Summary of results obtained on KCl containing various monatomic, monovalent impurities. Frequencies given in wave numbers (cm^{-1}). 1 cm^{-1} corresponds to $\omega = 1.88 \times 10^{11} \text{ rad sec}^{-1}$.

Impurity	n_i (cm^{-3})	A_{expt} Eq. (1) ($10^{-23} \text{ cm}^2 \text{ sec}^{-3}$)	A_{theor} Eq. (3)	T_0 (°K)	ω_0 From T_0 Eq. (2) (cm^{-1})	ω_0 , theor Eq. (6) (cm^{-1})	Sym- metry of ω_0
Ti^+	7×10^{18} 8.6×10^{19}	29 48	100	19	45	45	T_{1u}
I^-	1.25×10^{19} 5×10^{19}	26 ^a 26	32	24	57	57	T_{1u}
Ag^+	1×10^{19}	<6	17	22	53	69	E_g
Br^-	4×10^{19} 1.6×10^{20} 8.1×10^{20}	6.2 5.2 3.1	7.5	36	86	82	T_{1u}
Rb^+	1.5×10^{20}	5.5	4.5	36	86	85	T_{1u}
Na^+	2.3×10^{19}	14 ^a	1.0	32	77	144 ^c	
F^-		b		34	82	136 ^c	
Li^+		b		21	51 ^d	100 ^c	E_g

^a From Ref. 2, but corrected for incorrect sound velocity used in that reference.

^b No Rayleigh region observed. See Ref. 11.

^c For an estimate of the error introduced by using the simple Eq. (6) for light impurities we list the frequencies calculated by K. Lakatos and J. A. D. Matthew using the general formula for arbitrary mass difference (see Refs. 22, 23, and 26); Na: 160 cm^{-1} ; F: 175 cm^{-1} ; Li: 290 cm^{-1} .

^d The values for Li in KCl and in KBr differ from those given in Ref. 6, where a different scaling factor between T_0 and ω_0 had been used. This disagreement characterizes the uncertainty encountered with this type of phonon spectroscopy. See text.

scribed before.^{2,9} In order to conserve space, we show only a selection of the data (Figs. 1-6). The rest of the data is contained in an appendix to the unpublished

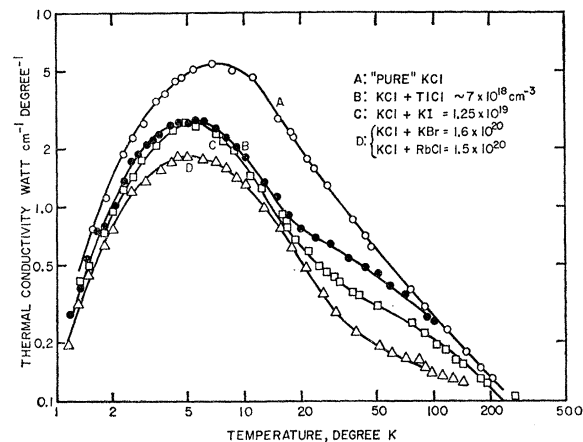


FIG. 3. Comparison of conductivity of KCl containing Ti^+ , I^- (from Ref. 2), Rb^+ , and Br^- . Concentrations: $n_{\text{Ti}} \sim 7 \times 10^{18} \text{ cm}^{-3}$; $n_{\text{I}} = 1.25 \times 10^{19} \text{ cm}^{-3}$; $n_{\text{Rb}} = 1.5 \times 10^{20} \text{ cm}^{-3}$; $n_{\text{Br}} = 1.6 \times 10^{20} \text{ cm}^{-3}$. The data for KCl:Rb and KCl:Br were identical over the entire temperature range. This graph shows that all three curves (Ti, I, Br) are very similar at low temperatures up to a certain temperature T_0 which is defined in the text and which depends on the doping. Above this temperature, the conductivity rapidly approaches that of the pure crystal.

⁹ For a recent description of the crystal-growth techniques used at Cornell see J. M. Peck, D. A. Bower, and R. O. Pohl, J. Appl. Phys. **38**, 2166 (1967). The spectrochemical determination of the concentration of the doping in the crystals was made by Dr. R. Skogerboe of the Analytical Facility of the Cornell Materials Science Center. We would like to thank him again at this point for his constant help and advice. A description of the cryostats used for thermal conductivity measurements at Illinois was recently given by M. V. Klein and R. F. Caldwell, Rev. Sci. Instr. **37**, 1291 (1966).

TABLE II. Summary of results obtained on KBr.

Impurity	n_i (cm^{-3})	A_{expt} Eq. (1) ($10^{-63} \text{ cm}^3 \text{ sec}^3$)	A_{theor} Eq. (3)	T_0 ($^{\circ}\text{K}$)	ω_0 From T_0 Eq. (2) (cm^{-1})	Sym- metry of ω_0
Tl ⁺	2.93×10^{18}	110	110	30 ^a	72	T_{1u}
I ⁻				34 ^b	82	T_{1u}
Ag ⁺	1.5×10^{19}	<4.4	19	19	46	E_g
Rb ⁺	1×10^{20}	6.4	8.4	30	72	T_{1u}
Cl ⁻	1.4×10^{20}	4.6	8.0	43 ^c	104	
Na ⁺	1.2×10^{20}	7.1 ^d	1	30	72	
F ⁻		d		18	43	
Li ⁶		d		13	31	E_g
Li ⁷				13	31	

^a Another dip was observed at $\sim 80^{\circ}\text{K}$, similar to KBr:Rb. See Fig. 5.
^b Data from R. O. Pohl, Z. Physik 176, 358 (1963). Position of the dip is not well defined.

^c Position of dip is not well defined. Low-temperature data are not good. Is there contamination?

^d See Ref. 11.

report of this paper. It can be obtained upon request.¹⁰ Most of the monatomic impurities in KCl and KBr produce the same characteristic shape of the conductivity curve which at low temperatures [$< 5^{\circ}\text{K}$, corresponding to $\omega < 2 \times 10^{12} \text{ sec}^{-1}$, (10 cm^{-1})] is describable with a Rayleigh-type scattering mechanism.¹¹ Above

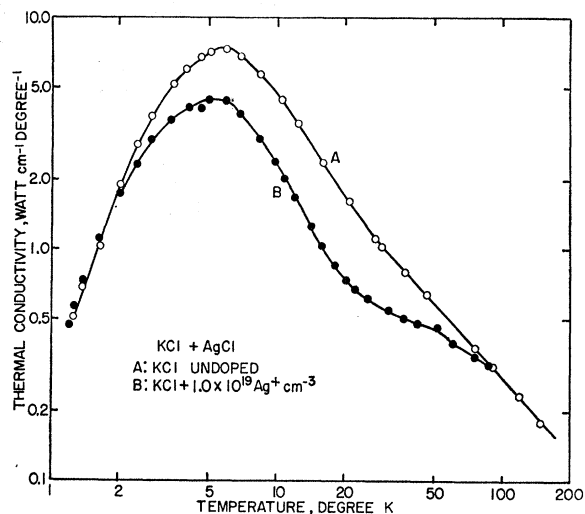


FIG. 4. Thermal conductivity of KCl:Ag. $n_{\text{Ag}} = 1 \times 10^{19} \text{ cm}^{-3}$. Data are identical to those shown in Ref. 14. The concentration given in that reference was obtained by chemical analysis of a piece close to that on which the conductivity was measured. Both the undoped and the doped crystals were seedpulled under Cl_2 protective atmosphere. The conductivity of the undoped crystal at the lowest temperature is about 10% lower than that of a crystal seedpulled after zonerefining, see Peech *et al.*, Ref. 9. The conductivity of the doped sample, therefore, is exactly identical below 2°K to that of highest purity KCl. The two curves were measured twice over a period of several years. Identical results were obtained.

¹⁰ Available from Cornell Materials Science Center, Clark Hall, Ithaca, New York 14850, Report No. 671.

¹¹ Li^+ is an exception and has therefore been discussed separately in Ref. 6. Li^+ produces a low-lying resonance in the boundary scattering region. A similar resonance has recently been found in KCl:F, with the temperature of the dip $T_0 = 1.2^{\circ}\text{K}$, corresponding to $\omega_0 = 2.9 \text{ cm}^{-1}$, see Eq. (2); G. Lombardo (private communication). Evidence for similar resonances can be seen in KBr:F and

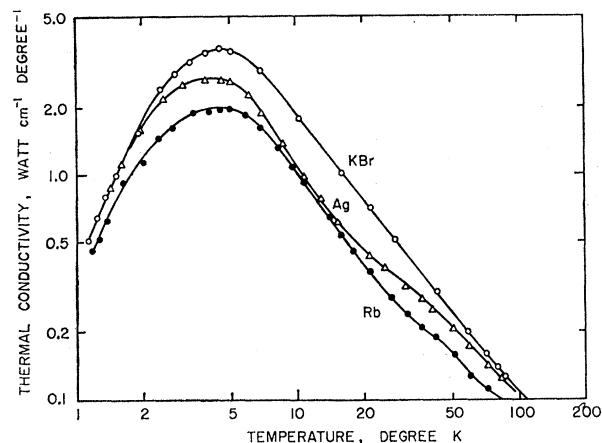


FIG. 5. Thermal conductivity of KBr:Ag and KBr:Rb. $n_{\text{Ag}} = 1.5 \times 10^{19} \text{ cm}^{-3}$; $n_{\text{Rb}} = 1 \times 10^{20} \text{ cm}^{-3}$. Note the second dip around 80°K in the Rb-doped crystal. An almost identical curve was obtained with KBr:Na ($n_{\text{Na}} = 1.2 \times 10^{20} \text{ cm}^{-3}$). Only difference: below 3°K the Na^+ scatters more; see also Ref. 11.

the conductivity maximum a sudden drop of the conductivity is noticed, a "dip" indicating a resonance scattering process, and at high temperatures ($\sim 100^{\circ}\text{K}$) the conductivity recovers towards that of the pure sample. The results are summarized in Tables I and II.

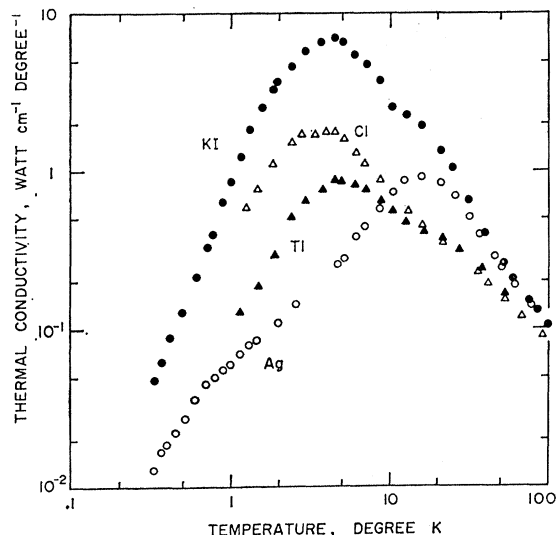


FIG. 6. KI with Cl^- , Tl^+ , and Ag^+ . The data below 1°K were obtained by W. D. Seward, whom we would like to thank at this time. See also W. D. Seward, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. V. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 1130. Concentrations: $n_{\text{Cl}} = 5 \times 10^{19} \text{ cm}^{-3}$; $n_{\text{Tl}} = 6.2 \times 10^{18} \text{ cm}^{-3}$; $n_{\text{Ag}} = 1.5 \times 10^{19} \text{ cm}^{-3}$. The undoped KI crystal shows evidence for residual impurities between 3 and 20°K . We do not believe that they play an important role in the doped samples. No precaution was taken to prevent the peculiar coagulation observed on KI:Ag, Ref. 8. The temperatures T_0 are approximately 4°K for Ag^+ and 15°K for Tl^+ and Cl^- .

KBr:Na. The temperature range of our measurements does not allow a proper identification. See also the discussion of the KI data below.

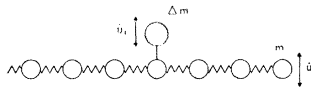


FIG. 7. One-dimensional model of crystal containing an isotopic impurity.

Of particular interest are columns 3 and 5. Column 3 contains the Rayleigh scattering strength, i.e., the quantity A_{expt} in the phonon relaxation rate,

$$\tau_{\text{def}}^{-1} = n_i A_{\text{expt}} \omega^4 \quad (1)$$

(n_i is the defect concentration), determined through curve fitting using the Debye model of thermal conductivity.^{2,6} In column 5 is listed the temperature T_0 of the dip, determined as the temperature at which the two tangents to the conductivity curve, above and below the dip, intersect. From T_0 , a so-called resonance frequency ω_0 (column 6) is determined using the following empirical relation:

$$\hbar\omega_0 = 3.4kT_0 \quad (2)$$

[i.e., 1°K corresponds to 4.5×10^{11} rad sec⁻¹, (2.4 cm⁻¹)] where \hbar and k are Planck's and Boltzmann's constants, respectively. Previously,^{5,6} we had used 4.25 as the proportionality constant in Eq. (2). It had been derived from a comparison of low-temperature resonances (i.e., resonances occurring at temperatures near or below the conductivity maximum) with spectroscopic and other independent observations. The smaller constant 3.4 appears to be more appropriate for the dips above the conductivity maximum. It must be realized, however, that the connection between T_0 and a resonance frequency will depend on the shape of the scattering cross section. This becomes immediately obvious if the latter is assumed to be temperature-dependent. It has been our experience, though, that regardless of what the specific resonance term used to fit the data, the resonance frequencies always come out within 20% of each other. (See end of Sec. III, and in particular Ref. 35.) We therefore believe that this is the accuracy of Eq. (2).

III. DISCUSSION

The discussion will be divided into three parts: the strength of the Rayleigh scattering, the nature of the impurity mode or modes to which we ascribe the resonance scattering, and a critical inspection of the frequency and temperature dependence of the phonon-defect scattering cross section.

In the limit of long wavelengths, the scattering by a point defect can be described as an elastic scattering of one plane wave (energy ω , wave vector q_1) into another plane wave (ω, q_2) with a phonon relaxation rate proportional¹² to ω^4 . If mass-defect scattering alone (isotope effect) is considered, the perturbation is simply given by the kinetic energy of the excess mass, as indicated in Fig. 7. The defect of mass $m_i = m + \Delta m$ is drawn as a

host atom to which an additional particle of mass Δm is rigidly attached.

For a diatomic lattice in which a small number of the atoms of one kind are replaced by atoms of a different mass only, the well-established phonon scattering rate for mass defects is¹³ (written for foreign alkali ions)

$$\tau_{\text{def}}^{-1} = n_i A_{\text{theor}} \omega^4 = \frac{\Omega_0}{4\pi v^3} \frac{n_i}{n} \left(\frac{m_a - m_{ai}}{m_a + m_h} \right)^2 \quad (3)$$

Here Ω_0 is the volume of the alkali halide (ah) molecule, v is the velocity of sound in the Debye approximation (in which the difference between the a and the h ions is ignored), n_i and n are the number densities of the ah and the ah molecules, respectively ($n_i \ll n$), and m is the mass of the ions designated by the subscript. From the Debye temperature $\Theta = 230^\circ\text{K}$ (at 0°K) and $\Omega_0 = (1.6 \times 10^{22})^{-1}$ cm³ for KCl we obtain $v_{\text{KCl}} = 2.45 \times 10^5$ cm/sec. Correspondingly, for KBr, $\Theta = 174^\circ\text{K}$, $\Omega_0 = (1.39 \times 10^{22})^{-1}$ cm³, $v_{\text{KBr}} = 1.9 \times 10^5$ cm/sec. Equation (3) holds in the limit of $\omega \rightarrow 0$ (i.e., $\omega \ll \omega_D$); however, it holds for arbitrary $\Delta m = (m_{ai} - m_a)$. In Tables I and II, column 4, we list A_{theor} calculated from Eq. (3). A comparison with the experimentally determined quantity A_{expt} [Eq. (1)] reveals an interesting result: For most of the heavy impurities, the low-temperature Rayleigh-type scattering agrees amazingly well with that calculated for isotopic scattering alone, regardless of the force constants or the ionic radii of the impurity. In view of the quality of the low-temperature fit (as an example, we refer to the fit to the KCl:I data of Ref. 2), the accuracy with which A_{expt} can be determined from experiment is not expected to be better than 50%. Nevertheless, the fact that A_{expt} and A_{theor} agree that well for a number of defects suggests that mass-defect scattering is, indeed, at low frequencies, the dominant process in most cases.

A striking discrepancy is found for Ag^+ , which scatters far less than predicted from Δm alone. Krumhansl and Matthew¹⁴ suggested that mass and spring changes around the imperfection may give compensating contributions to the scattering amplitude. They demonstrated this for a one-dimensional chain and showed that for a certain combination of positive Δm and negative $\Delta\lambda$ (change in force constant) the back-scattered amplitude can have a minimum. Yussouff and Mahanty¹⁵ found the same result for a three-dimensional lattice. However, a numerical evaluation¹⁶ of their result [for a body-centered cubic lattice, their Eq. (43)] shows that the lowest scattering rate produced by such an interference is still 67% of the mass-defect

¹² P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

¹⁴ J. A. Krumhansl and J. A. D. Matthew, Phys. Rev. **140**, A1812 (1965).

¹⁵ M. Yussouff and J. Mahanty, Proc. Phys. Soc. (London) **87**, 689 (1966). The same authors have also recently studied the influence of phonon polarization on the scattering by point defects [Proc. Phys. Soc. (London) **90**, 519 (1967)].

¹⁶ We would like to thank Dr. J. A. D. Matthew for calling this to our attention.

¹³ P. Debye, in *Vorträge über die Kinetische Theorie der Materie und der Elektrizität* (B. G. Teubner, Berlin, 1914), p. 46; R. E. Peierls, Ann. Physik **3**, 1055 (1929).

scattering alone, and therefore is much less of a reduction than observed experimentally.¹⁷ Furthermore, it follows from their calculations that even for $\Delta\lambda = -\lambda$, i.e., for complete decoupling of the defect, the scattering rate still depends on the mass defect and not on the force constants alone, and this raises some doubt about the validity of their result. We therefore conclude that the interference effects alone, at least as treated so far, cannot explain the weak Rayleigh scattering in Ag-doped KCl and KBr at low temperatures, and that the model needs further inspection. We shall later come back to this point.

In the second part of our discussion we ask what we can learn about impurity modes from thermal conductivity. In an attempt to understand phonon-resonant scattering, a number of authors¹⁸ carried the discussion of isotopic scattering into a frequency region where, for sufficiently large Δm , the response of the lattice to the reaction force of the periodically driven excess mass Δm changes the vibrations of the host lattice: The incoming plane wave gets scattered, causing an outgoing spherical wave. The resulting phonon scattering cross section has resonance character: The relaxation rate is given by the Rayleigh expression [Eq. (3)] only at the lowest frequencies. As the frequency increases, the scattering rate increases faster than ω^4 , goes through a maximum at a resonance frequency ω_0 , and then decreases. The same resonance-scattering rate is obtained quite generally if a wave hits an obstacle capable of resonating. As an example, we mention the scattering of sound waves in a fluid containing gas bubbles.¹⁹ For wavelengths much larger than their diameters, the bubbles will perform a symmetric breathing motion, hence the resonant frequency ω_0 will correspond to a so-called *s* mode, and the scattering will be *s* scattering. This simple analogy leads us to inquire about the resonant mode in the lattice containing the heavy isotope and about its symmetry. Figure 7 suggests the answer: \dot{u}_i will be parallel or antiparallel to \dot{u} the velocity of the surrounding ions, but the amplitude will be different, depending on the magnitude of Δm . The symmetry of the impurity mode excited will therefore be T_{1u} , i.e., in the isotope case the resonant frequency ω_0 will belong to the same mode which is expected to be infrared active in the diatomic lattice. The following argument may help to clarify this point: Conceptually, the simplest impurity mode is produced by a very light substitutional impurity, as discovered by Pick and coworkers in alkali halides containing H^- ions (*U* centers).²⁰ This infrared active impurity mode has a

¹⁷ To give a specific example: The minimum in the scattering rate occurs if $\Delta m = 2m$, for $\Delta\lambda = -0.8\lambda$.

¹⁸ We refer to Refs. 3-5. For the novice in Green's-function techniques we refer in particular to McCombie and Slater, Ref. 26.

¹⁹ See, e.g., P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York 1953), Chap. 11.3.

²⁰ See, e.g., W. Barth and B. Fritz, *Phys. Status Solidi* **19**, 515 (1967), and references therein.

frequency much higher than the maximum frequency of the pure host and can therefore be described as an oscillation of the H^- against a quasistatic lattice. If only the difference in mass is considered, this Einstein oscillator has a frequency $\omega_E^{1,21,22}$

$$\omega_E^2 = \langle \omega^2 \rangle M / M', \quad (4)$$

where $\langle \omega^2 \rangle$ is the second moment of the frequency distribution of the undisturbed lattice, and M and M' are the masses of the host and impurity atoms, respectively. For a Debye lattice,

$$\omega_E^2 = \frac{3}{5} \omega_D^2 M / M'. \quad (5)$$

The impurity modes which are believed to be the important phonon scatterers in our experiments have low frequencies, $\omega_0 < \omega_D$, and are produced by heavy impurities, $M' > M$. Their occurrence was first predicted for isotopic defects by Kagan and Iosilevskii.²³ The frequency $\omega_{0,\text{theor}}$ of these modes is

$$\omega_{0,\text{theor}}^2 = \frac{1}{3} \omega_D^2 M / (M' - M), \quad (6)$$

which becomes, for $M' \gg M$,

$$\omega_{0,\text{theor}}^2 = \frac{1}{3} \omega_D^2 M / M'. \quad (7)$$

In spite of their entirely different ranges of application, ω_E [Eq. (5)] and $\omega_{0,\text{theor}}$ [Eq. (7)] agree to within 25%. This emphasizes the similarity between the two types of modes. What it means physically is that the heavy isotope oscillates with low frequency against a large portion of the surrounding lattice, which is considered to respond in a quasistatic manner, so that its effective mass again is much larger than the mass of the defect.²⁴

It is necessary at this point to anticipate a little bit of the third part of this discussion: It was shown by Elliott and Taylor²⁵ and by McCombie and Slater²⁶ that, using a relaxation rate determined along the lines just sketched,²⁷ a good qualitative fit of the KCl:I data could be obtained over the temperature range 1-100°K. They found, in particular, a dip at the same temperature as was observed experimentally. Hence, they con-

²¹ I. M. Lifshitz, *Zh. Eksperim. i Teor. Fiz.* **17**, 1017 (1947); **17**, 1076 (1947); see also Ref. 26.

²² J. A. D. Matthew, *J. Phys. Chem. Solids* **26**, 2067 (1965).
²³ Yu. Kagan and Ya. A. Iosilevskii, *Zh. Eksperim. i Teor. Fiz.* **42**, 259 (1962) [English transl.: *Soviet Phys.—JETP* **15**, 182 (1962)]. See also R. Brout and W. Visscher, *Phys. Rev. Letters* **9**, 54 (1962); Yu. Kagan and Ya. A. Iosilevskii, *Zh. Eksperim. i Teor. Fiz.* **45**, 819 (1963) [English transl.: *Soviet Phys.—JETP* **18**, 562 (1964)].

²⁴ M. C. Wagner (private communication).

²⁵ R. J. Elliott and D. W. Taylor, *Proc. Phys. Soc. (London)* **83**, 189 (1964).

²⁶ C. W. McCombie and J. Slater, *Proc. Phys. Soc. (London)* **84**, 499 (1964).

²⁷ A serious shortcoming of this model is that it ignores the dispersion of the phonons in the frequency region of the resonance. Or in the form of a question: Is it permissible in cases of very strong scattering, as observed in our crystals, to talk about plane waves travelling through the lattice with velocity v , until they hit a scattering center? We refer to L. Brillouin, *Wave Propagation and Group Velocity* (Academic Press Inc., New York, 1958). See also the experimental study by N. Shiren, *Phys. Rev.* **128**, 2103 (1962).

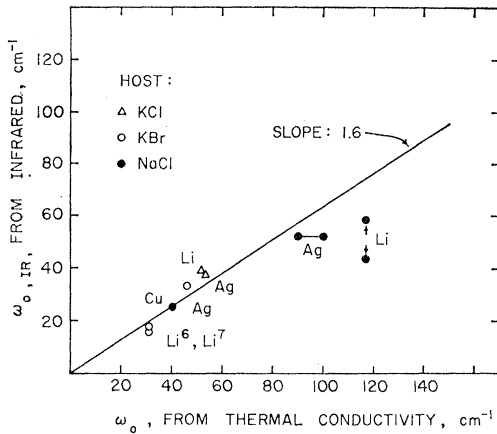


FIG. 8. Comparison of the infrared active T_{1u} impurity mode (Weber, Ref. 32 and Sievers, Ref. 8) with the impurity mode seen in thermal conductivity. The data for the phonon resonance in NaCl:Li, NaCl:Cu, and NaCl:Ag were taken from Caldwell and Klein, Ref. 4. The left circle for NaCl:Ag was obtained from T_0 using Eq. (2); the right circle is the maximum of $\tau(\omega)^{-1}$ from Ref. 4. The magnitude of the slope depends on the choice of the proportionality constant in Eq. (2), connecting the temperature of the dip and the resonant frequency (see text). It appears certain, however, that the slope is greater than unity, which means that the two resonant frequencies belong to different resonances.

cluded that the assumption of the I^- behaving essentially as a heavy isotope of the Cl^- ion was a good one. The experimental curves for KCl:Tl, Br, and Rb are qualitatively similar. The dip produced by the heavier Tl^+ ion lies at a lower temperature, and the dips caused by the lighter Rb^+ and Br^- ions occur at a higher temperature, as expected from the theory. We take the fact that the curves for KCl:Rb and KCl:Br are exactly identical over the entire temperature range studied as further evidence that only Δm is important for this scattering. If the scattering were sensitive to the force constant and lattice deformations, the equality of the two curves would seem to be too much of an accident. Rather than trying to fit the KCl:Tl⁺, Rb⁺, and Br⁻ with a resonance expression (this will be done in the third part of this discussion), we associate the temperature T_0 of the dip with a resonance frequency ω_0 , by using the empirical relation, Eq. (2). The proportionality constant was adjusted so that the equation was correct for KCl:I ($\omega_0 = \omega_{0, \text{theor}}$). Columns 6 and 7 in Table I show a comparison of ω_0 and $\omega_{0, \text{theor}}$. The agreement is very good for Tl⁺, Rb⁺, and Br⁻ and less good for Ag⁺, Li⁺, Na⁺, and F⁻. A qualitative understanding of this different behavior comes from measurements of the far infrared absorption. In his search for low-lying infrared active impurity modes, Sievers²⁸ found no absorption bands in KCl doped with Tl, I, Rb, and Br. We argue that the T_{1u} mode is strongly damped in these cases, and hence the absorption band is too broad to be detectable in the infrared. The mode

²⁸ A. J. Sievers (private communication). For KCl:Tl, he found the following limits: $n_i = 10^{18} \text{ cm}^{-3}$, no additional absorption peak ($k < 0.1 \text{ cm}^{-1}$) at 2°K, for $100 \mu < \lambda < 1000 \mu$. One slight bump ($k \sim 0.2 \text{ cm}^{-1}$) at 110μ .

can be seen, however, through the broad-band phonon spectroscopy which thermal conductivity affords. On the other hand, Sievers²⁹ did find absorption bands in KCl containing Ag (at 38.8 cm^{-1}) and Li (at 40 cm^{-1}).⁸ Hence these T_{1u} modes are less strongly damped, and therefore can not be observed in thermal conductivity. This may also be part of the reason for the vanishing of the Δm Rayleigh scattering in KCl:Ag at low temperatures, noted earlier. We then explain the phonon resonant scattering observed at higher temperatures through scattering by even impurity modes, which do not require a motion of the impurity. Hence the difference between the infrared active resonance frequency and the one observed in thermal conductivity. The same arguments hold for KBr:Ag and KBr:Li, where Sievers also saw a narrow T_{1u} mode absorption. The model of phonon scattering by even modes in the KBr:Li is confirmed by the absence of an isotope effect in the thermal conductivity of KBr:Li,⁶ in contrast to the isotope effect of the infrared active T_{1u} mode.³⁰

Resonances caused by vacancies were studied theoretically by Krumhansl.³¹ Using the model of elastic phonon scattering, he found that strong scattering was to be expected for the fully symmetric breathing mode A_{1g} and also for the E_u mode. The scattering rate had the same form as found for isotopic impurities, with the resonance frequency determined by the softening $\Delta\lambda$ of the force constants. For the A_{1g} mode he showed that for 50% softening ($\Delta\lambda/\lambda = -0.5$) a resonance dip occurred in the conductivity curve of KCl at $\sim 33^\circ\text{K}$. In a recent experimental study of this process, Schwartz and Walker³ produced vacancies by adding divalent impurities to alkali halides. They argued that for divalent impurities with mass and ionic radius sufficiently close to the alkali ion they replaced, the dynamics of the lattice defect was very similar to that of a vacancy, the nearest-neighbor divalent impurity behaving essentially as an alkali ion of the host lattice. In their work on NaCl containing foreign alkali or halogen ions, Caldwell and Klein⁴ computed the elastic scattering for T_{1u} , A_{1g} , and E_g impurity modes considering changes in both mass and force constant. They found that in general the T_{1u} mode gave the strongest contribution, next came the mode E_g , and the scattering by A_{1g} turned out to be weakest. On the basis of their detailed calculation, we suggest that the quasivacancies in the case of Ag- and Li-doped KCl and KBr crystals, scatter predominantly through the mode E_g . Their frequencies ω_0 are given in Tables I and II. They are compared to the infrared active T_{1u} modes observed in the infrared^{7,8,32} in Fig. 8. In the first approximation, the

²⁹ A. J. Sievers, Phys. Rev. Letters 13, 310 (1964).

³⁰ A. J. Sievers and S. Takeno, Phys. Rev. 140, A1030 (1965).

³¹ J. A. Krumhansl, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York 1965), p. 523.

³² R. Weber, Phys. Rev. Letters 12, 311 (1964); and private communication.

E_g frequency is 60% larger than the T_{1u} frequency for any given defect system. The softening of the force constants determined from the position of the T_{1u} absorption was found to be 70% and over 99% for Ag^+ and Li^+ , respectively.⁸ On the basis of Krumhansl's calculation for A_{1g} modes, we conclude that the E_g frequencies found in the present work are not unreasonable.

We have claimed that in some instances the T_{1u} mode is too strongly damped, and hence can not be seen in the infrared, but can be seen in thermal conductivity. In other cases ($\text{Ag};\text{Li}$) the damping is weak, and the resonance shows up in the infrared (IR) but not in thermal conductivity. Why is the damping that different? In the harmonic approximation, the damping of resonances occurring at the same frequency should differ only by a factor³³ of $(\lambda + \Delta\lambda)/\lambda$, which does not seem to be enough to explain the difference, except perhaps for Li. Strong anharmonicities suggest themselves, therefore, for the strongly damped resonances. We shall come back to this point in the third part of the discussion. Let us add one additional piece of evidence: Caldwell and Klein⁴ found considerable T_{1u} mode phonon scattering in $\text{NaCl}:\text{Ag}$, and the low-temperature Rayleigh scattering was almost as large as predicted for Δm scattering (perhaps 20% less). Nevertheless, Weber saw an infrared active T_{1u} mode. But this absorption band was broader than in $\text{KCl}:\text{Ag}$, and, in particular, it did not narrow upon cooling to 4°K.³⁴ We suggest that $\text{NaCl}:\text{Ag}$ is a borderline case: coupled weakly enough to the phonons to be visible in the infrared, yet strongly enough to be also phonon active in the Rayleigh region. The two frequencies are shown in Fig. 8 to agree with the general relation between T_{1u} and E_g frequencies. The same seems to hold for $\text{NaCl}:\text{Li}$. The low-temperature Rayleigh scattering⁴ is slightly less than predicted for isotopic scattering, and Sievers⁸ reports absorption in the far IR (actually two lines, Fig. 8).

There remain the resonances in $\text{KCl}:\text{Na}^+$ and F^- and most of the KBr resonances (except for Ag^+ and Li^+) to be discussed. We believe that the resonances for heavy impurities in KBr , as in KCl , are connected with simple isotopic resonance scattering, i.e., in Tl^+ , I^- , and possibly Rb^+ -doped KBr . In the other cases, we do not see how we can expect reasonably simple circumstances; instead, a situation similar to that found by Caldwell and Klein⁴ is more likely.

We now come to the last part of our discussion, the question of the phonon relaxation rate or the scattering mechanism. From what has been said so far, the reader may have received the impression that at least for the case of the quasi-isotopic defects, viz., $\text{KCl}:\text{Tl}$, I , Br , and Rb , this problem has been solved exactly.

³³ See, e.g., A. J. Sievers and S. Takeno, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite (John Wiley & Sons, Inc., New York, 1968).

³⁴ R. Weber (private communication). The $\text{KCl}:\text{Ag}$ band was measured at 2°K only (Ref. 29).

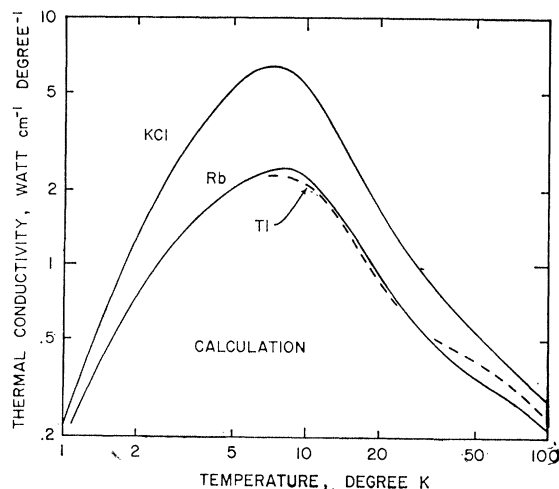


Fig. 9. Computed conductivity for $\text{KCl}:\text{Tl}$ and $\text{KCl}:\text{Br}$. The computed curves for $\text{KCl}:\text{I}$ (Refs. 25 and 26) lie between Tl and Br . Elastic phonon scattering, mass difference only, Debye model. The curves reproduce the position of the dip fairly well, but their general shape differs from that of the measured curves (Fig. 3).

Unfortunately, this is not so except at low temperatures. Elliott and Taylor²⁵ and McCombie and Slater²⁶ in their work had noticed that the depression of the dip was too weak. This is demonstrated in Fig. 9, which was computed with the relaxation rate given in Eqs. (10), (24), and (25) of Ref. 26, with the Debye model of thermal conductivity, for Tl and $\text{Rb}(\text{Br})$ doping of some arbitrary concentration. The temperature of the dip shifts at least close to the experimental T_0 , but the high-temperature scatter (above 7°K) is far too weak compared to the Rayleigh scatter. Moreover, and this is more important, the computed curves vary far less abruptly near the dip than the experimental curves (see Fig. 3 and also Fig. 1, curve D). Numerous attempts were made with other frequency-dependent, and theoretically unjustified, relaxation rates. All these efforts were similarly unsuccessful in producing the observed abrupt changes of the conductivity curves. We also refer to the work by Caldwell and Klein,⁴ who encountered similar difficulties, although they carried the model of elastic scattering to considerably higher sophistication than was done previously (see, for instance, their results on $\text{NaCl}:\text{Br}$ and $\text{NaCl}:\text{Ag}$).

We therefore conclude that a relaxation rate depending only on the frequency without a term containing some rapid variation with temperature, like an exponential term, will not be able to describe the data, at least within the relaxation time approximation. The same holds, apparently even more strongly, for E_g -type scatterers, like Ag^+ and Li^+ .⁶ Possibly such a scattering rate can be obtained from Wagner's inelastic three-quantum scattering processes.^{2,35} They can

³⁵ One might wonder whether such a scattering mechanism should not completely alter the connection between T_0 and ω_0 (Eq. 2). The resonance frequencies determined for $\text{KCl}:\text{I}$ and $\text{KCl}:\text{Na}$, however, were 69 and 85 cm^{-1} (Ref. 2) which is within the limit of 20%.

arise through the strong anharmonic contributions to the binding forces for the phonon active defects which we suspected earlier in this discussion. Strong anharmonicities around the quasivacancies could conceivably originate from the increased overlap of the nearest neighbors relaxing around the small defect. Unfortunately, Wagner's model presently contains too many *ad hoc* assumptions to justify more computational efforts than were made in Ref. 2. Furthermore, the relaxation-time approximation may need a very careful reinspection, at least in cases where the conductivity in the doped sample is much smaller than in the undoped sample. It appears doubtful that the umklapp processes should continue to act in doped samples in the same way as they did in the pure ones. A very simple and highly speculative model which treats Umklapp- and Wagner-type collisions in some similar fashion has been suggested before⁵ and shall not be repeated here.

In reporting the very weak Rayleigh scattering in Ag-doped KCl and KBr, we had suggested that this might not be entirely the result of a cancellation of two scattering amplitudes.^{14,15} Instead we suggested in part two of this discussion that the Δm scattering vanishes for weakly bound defects. In that case we should be left with the phonon scattering by quasivacancies. If this model is correct, it follows from the data that their scattering too must vanish at low temperatures. This is possible if the even modes scatter predominantly through three-quantum processes. On the other hand, Krumhansl²³ was able to demonstrate that Rayleigh scattering was possible at low frequencies resulting from elastic-phonon scattering by vacancies, and he determined the magnitude of this process with the softening of the binding forces as the only parameter. According to his calculations and to the softening of the binding forces determined by Sievers,⁸ this Rayleigh scattering should be visible in our cases. The entire question must be left open. We do believe, though, that its answer must be connected somehow with the presence or absence of far-IR absorption bands.

So far our discussion has dealt with doped KCl and KBr. The data available on KI look entirely different and somewhat reminiscent of the data on KBr:Li.⁶ There it had been suggested that the nearest neighbors around the impurity ion relax in an asymmetric fashion, resulting in, crudely speaking, an off-center AB_6 molecule. Such a model might well apply also to the highly polarizable KI lattice. It is disturbing that the host lattice, which from the point of view of far-IR absorption work is the most attractive one (besides, say, KBr:Li), is so confusing as far as phonon scattering is concerned. We refer in this connection to the peculiar behavior of the molecular impurity NO_2^- in KI observed by Narayanamurti *et al.*³⁶ in near-IR absorption.

³⁶ V. Narayanamurti, W. D. Seward, and R. O. Pohl, Phys. Rev. 148, 481 (1966).

More work will be needed on the thermal properties of doped KI.

IV. CONCLUSION

In spite of the considerable changes in force constant and volume expected when an impurity ion is introduced, Rayleigh scattering, as caused by the mass difference alone, is seen to be adequate to describe the low-temperature ($T < 5^\circ\text{K}$) thermal conductivity in most of the doped crystals. The model of elastic phonon resonant scattering by heavy isotopic impurities is adequate for a qualitative description of the high-temperature conductivity in KCl containing Tl^+ , I^- , Rb^+ , and Br^- . The observation that force constants and nearest-neighbor relaxation play such a small role is contrasted by the drastic changes observed for in-band resonances seen in the far IR, where considerable softening of the force constants was observed. Hence, thermal conductivity appears to be the appropriate tool for the study of those in-band resonances in which the force constants are less drastically altered. Unfortunately, this type of phonon spectroscopy has a poor resolution. It is impossible to deduce from thermal-conductivity experiments the resonance frequency to an accuracy better than $\pm 20\%$, as long as the frequency and temperature dependence of the scattering rate is not known. Thermal conductivity, on the other hand, makes up for this disadvantage by also being able to see the impurity modes which are not IR active and are therefore not visible in optical spectroscopy. We propose that E_g modes are the important phonon scatterers in Ag^+ - and Li^+ -doped crystals, where narrow absorption lines in the far IR indicate that the T_{1u} mode is weakly coupled to the lattice. We believe that in these cases the phonons cannot impart kinetic energy to the Ag (and Li) ions, and hence mass-difference (isotopic) scattering cannot occur. Consequently, only the modes which otherwise scatter less strongly, of the E_g type, are seen in thermal conductivity. In Tables I and II we list the frequencies and symmetries of the impurity modes as determined from thermal conductivity. Another problem is pointed out in these experiments: The phonon-defect interaction appears to be rather complex. We have shown that elastic-phonon scattering alone cannot describe the observed conductivity in quantitative detail.

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