normally conducting state it has been proposed[12] that K_d is proportional to the d-electron spin susceptibility, χ_d. By assuming that the strong temperature dependence of the measured susceptibility is due to χ_d, the influence of χ_d on K_{V} has been deduced. A sharp peak in the density-of-states curve for the d band was offered as one possible explanation for the influence of temperature on χ_d. This argument does not appear useful for V-Fe alloys in the composition range 0 to about 20 at.% Fe, or for V-Cr and V-Tc alloys, for which a strong temperature dependence in the susceptibility and in the Knight shift is not found. It may be significant that the d band in these alloys is not characterized by sharp curvature.

If it were assumed that the composition dependence of K_{V} is due entirely to K_s, the variation of the latter must enter through the probability density of the s electrons at the Fermi surface rather than through the measured density of states and atomic volume, both of which decrease with Fe concentration in the composition range concerned.

It seems likely that an algebraic summing of the three terms in Eq. (1) must be invoked to explain the observed results. For example, the peak in K_{V} could be due to an increase in K_s and/or K_{VV} on the one hand and a decrease in K_d on the other as e/a increases. However, the occurrence of the peak in K_{V} in the vicinity of $e/a=5.6$ for three different systems seems to be more than fortuitous. An analysis combining the three terms must account for this electron concentration dependency.

In the composition region where moments and ferromagnetism appear and where the γ term in the specific heat has a large peak, a more detailed study of susceptibility, NMR parameters and saturation magnetization is currently in progress with the purpose of clarifying the nature of the spin interactions which give rise to the observed properties.

ACKNOWLEDGMENTS

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Phonon Scattering by Point Defects*

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Phonon scattering by point defects was studied by measuring the thermal conductivity of KCl containing known amounts of KI, NaCl, and $CaCl_2$ in solid solution. By also measuring the conductivity in crystals in which the impurities were allowed to coagulate, it was possible to distinguish between the effect of atomically dispersed defects and precipitates.

The experimental data cannot be described by a Rayleigh-type scattering mechanism alone. An additional phonon scattering by impurity modes, as discussed by Wagner in the following paper, is shown to describe the experimental data. The angular frequencies of the impurity modes thus determined are of the order of 10^{13} sec^{-1} for the defect systems investigated here. A discussion of the magnitude of the Rayleigh scattering is also given.

1. INTRODUCTION

THE strong influence of lattice defects on the low-temperature thermal conductivity of solids was first demonstrated by Berman,[1] and has since been observed in many experiments. In electrically insulating crystals, energy is carried predominantly by elastic waves or phonons, and, therefore, measurements of the lattice thermal conductivity at low temperatures are a useful tool for the study of the interaction between phonons and defects. For a review of this field we refer to the articles by Klemens,[2] Carruthers,[3] and Bross.[4]

Among the defects which have been most carefully studied are those whose size is comparable to that of the host lattice atoms. In spite of considerably theoretical and experimental effort, the problem of the phonon scattering by these "point defects" must still be considered as unsolved.

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* Supported in part by the Advanced Research Projects Agency and the U. S. Atomic Energy Commission.

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[2] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951); Proc. Phys. Soc. (London) **A68**, 1113 (1955); also in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

[3] P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

[4] H. Bross, Physica Status Solidi, **2**, 481 (1962).

At present it appears that the only phonon scattering that is well understood is that by randomly distributed mass-fluctuations in an otherwise undisturbed lattice. This so-called isotope effect has been discussed by Pomeranchuk[5] and later by Slack[6] and Berman *et al.*[7] It was demonstrated by Geballe and Hull[8] who compared two Ge crystals which presumably differed in nothing but their isotopic composition. One specimen consisted of isotopically enriched Ge^{74}, whereas the other consisted of the natural isotopic mixture. Callaway[9] showed that the decrease in thermal conductivity in the crystal containing the natural mixture could be described with a Rayleigh-type scattering mechanism, i.e., a phonon relaxation time $\tau \propto \omega^{-4}$ in quantitative agreement with the existing theory. Measurements in crystals of LiF containing different concentrations of Li^6 and Li^7 by Berman *et al.*[10] also agreed with this theory, even though the limited temperature range over which the thermal conductivity had been determined reduced somewhat the reliability of the theoretical analysis.

Walker and Fairbank[11] have investigated isotopic mixtures of He^3 and He^4, but their results are complicated somewhat by uncertainties concerning the randomness of the impurity distribution as well as the physical perfection of the samples.[12] Zero-point motion is also important here.[13]

In summary, one can probably say that the isotope effect is basically understood, even though further experimental studies certainly would be desirable. One cannot be nearly so sanguine concerning any other point defects.

In the original theoretical treatment[2] of the phonon scattering by a static point defect only the effect of a difference in mass, ΔM, a difference in force constant, ΔF, and a difference in unit cell volume, ΔV, were considered. In all three cases it was found that in the long-wavelength limit the relaxation time should be proportional to ω^{-4}. It was therefore generally assumed that point defects even of the most general type always scatter phonons with a Rayleigh-type mechanism. None of the experiments performed to test this assumption, however, could prove its validity. In fact most of them yielded very different phonon relaxation times. As examples we mention experiments on radiation damage,[14-16] semiconductors with acceptors,[17,18] or crystals in which one atom was replaced by a molecule.[19] In defense of the theoretical model it could always be said that the defects studied in these experiments basically did not qualify as point defects in the above mentioned sense and that additional scattering mechanisms had to be considered.

In the remaining group of experiments this saving grace could not be invoked. Slack[20] studied KCl containing small concentrations of $CaCl_2$. The point defects in this case were Ca^{++}, positive ion vacancies, or pairs of both. The data could not be explained by Rayleigh scattering, and therefore Slack concluded that some of the calcium had precipitated in the form of $CaCl_2$:KCl clusters, which produced additional scattering. Another experiment performed by Williams[21] on mixed crystals of KCl:KBr did not give conclusive information because the temperature range was too small. Toxen[22] and Abeles *et al.*[23] studied mixed crystals of Ge and Si in the temperature ranges of 2 to 50 and 300 to 1200°K, respectively. Their results agreed roughly with the Rayleigh scattering model, although the conductivity at temperatures above the conductivity maximum decreased faster with defect concentration than predicted. In both investigations, therefore, a modification of three-phonon processes by isotopic scattering as discussed by Carruthers[24] was considered as a possible explanation. Finally, the last experiment to be mentioned in this series of attempts to study point defects was done by Klein.[25] He studied NaCl crystals containing small concentrations of $MnCl_2$. As in Slack's experiment the $MnCl_2$ tends to precipitate at room temperature; however, the clustering can be observed independently with electron spin resonance measurements and can be avoided if the sample is quenched rapidly. In such crystals Klein found a rather strong decrease in conductivity in the temperature range between 20 and 50°K. He could not explain his data with a pure Rayleigh-type scattering process.

In summary, there seems to exist strong evidence that even for this comparatively simple class of defects Rayleigh scattering alone is not sufficient to explain the

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[24] P. Carruthers, Phys. Rev. **126**, 1448 (1962).

[25] M. V. Klein, Phys. Rev. **123**, 1977 (1961).

experimental data. However, not enough information seems to be available to make a positive statement about the scattering processes involved.

In an attempt to clarify this situation we have undertaken an investigation of alkali halides doped with other alkali halides or alkaline earth halides, and we report here the first results of this investigation. In none of the systems investigated have we found a pure Rayleigh-type scattering mechanism. It will be shown that our data can be understood if in addition to the Rayleigh scattering one assumes a resonance-like scattering of phonons due to modifications of the normal lattice modes by introduction of the impurity. The same explanation will be invoked to explain Klein's data as well as the more recent data of Worlock[26] for the system NaCl:AgCl.

II. EXPERIMENTAL METHOD

The technique for measuring low-temperature thermal conductivity has been described in great detail elsewhere,[20,25] and will not be repeated here. The only departure from standard practice was the use in some cases of carbon resistance thermometry over the entire temperature range up to 150°K, rather than the use of the more usual differential thermocouples. 100-Ω-Allen-Bradley resistors were used for the range 1–20°K, and 1000 Ω-Allen-Bradley resistors were used for the range 3–150°K. In the region of overlap the data obtained by the two sets of resistors always agreed to well within experimental error.

The crystals measured were grown by a Kyropoulos technique[27] from Cl_2-treated reagent grade material with the proper amount of doping added to the melt. In the furnace high-purity argon was used as a protective atmosphere; the crucibles used were made of sintered alumina. The thermal conductivity specimens were all cleaved in [100] directions. They had the same size, 40×5×5 mm, and their surfaces were sandblasted to insure identical conditions for diffuse phonon scattering by the crystal boundaries (Casimir scattering).

The determination of the impurity concentration in the samples will be discussed individually for the various defect systems in the next section.

III. EXPERIMENTAL RESULTS

1. KCl Doped with KI

The optical properties as well as the segregation coefficient of this system have recently been studied in great detail by Mahr.[28] He also determined the oscillator strength for the first exciton band of the KI in solid solution using a chemical method. He concluded from his investigations that the KI molecules do not coagulate and are probably randomly distributed in "as-grown" crystals (i.e., unannealed). In the present experiment a Cary Model No. 14 spectrophotometer was used to measure the tail of the KI exciton band. By comparing these measurements with Mahr's, the I^- concentration could be determined. The thermal conductivity results are shown in Fig. 1; a preliminary report of these data has been given elsewhere.[29] The data are for the crystals as grown.

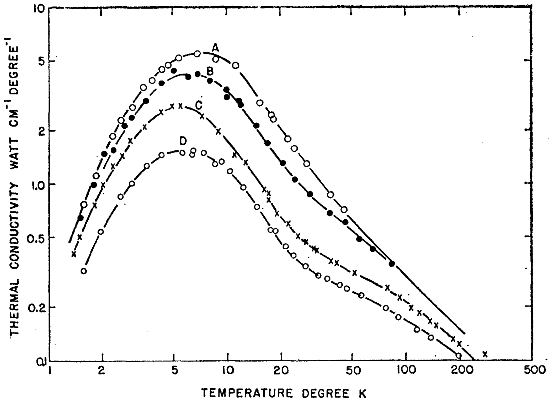

FIG. 1. Thermal conductivity of KCl doped with KI; A, undoped KCl; B, I^- concentration $N_v = 1.0\times10^{18}$ cm^{-3}; C, $N_v = 1.25\times10^{19}$; D, $N_v = 5.0\times10^{19}$.

2. KCl Doped with NaCl

The concentration of Na^+ was determined using a flame photometric method. This and all the following analyses were done by Professor G. Morrison of the Cornell University Chemistry Department. The measurements for this system are shown in Fig. 2, and again

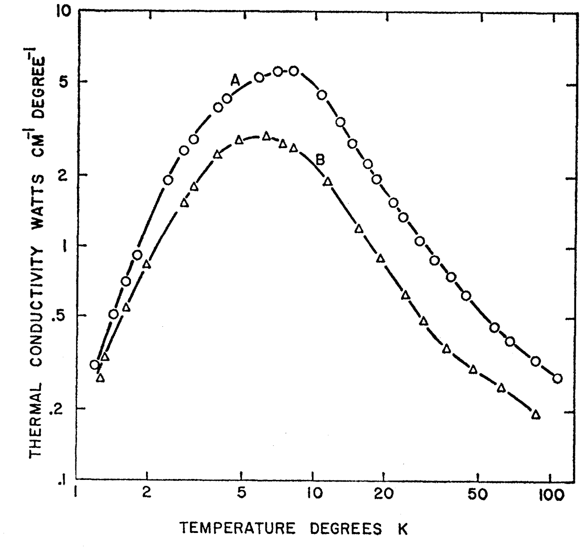

FIG. 2. Thermal conductivity of KCl doped with NaCl; A, undoped KCl; B, Na^+ concentration $N_v = 2.3\times10^{19}$ cm^{-3}.

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[26] J. M. Worlock, thesis, Cornell University, 1962 (unpublished).

[27] S. Kyropoulos, Z. Anorg. Allgem. Chemie **154**, 308 (1926).

[28] H. Mahr, Phys. Rev. **125**, 1510 (1962).

[29] R. O. Pohl, Bull. Am. Phys. Soc. **7**, 192 (1962).

are for the crystal as-grown. The ratio of the NaCl in the melt to the NaCl in the crystal was about 3:1.

3. KCl Doped with $CaCl_2$

The concentration of Ca^{++}, again determined using a flame photometric method, turned out to be roughly 15% of that in the melt.

As pointed out earlier, Slack's work on this same system demonstrated the difficulty in keeping the calcium in solid solution. The x-ray diffraction work of Suzuki[30] showed that the calcium in heavily doped NaCl crystals precipitated out into platelets of $CaCl_2$:NaCl even at room temperature. However, Suzuki also showed that if the crystals were heated to 400°C and rapidly quenched to room temperature, then the precipitates were dissolved and did not re-form immediately (~1 week).

On the assumption that the behavior of $CaCl_2$ in KCl would be roughly similar, a comparable heat treatment was used in the present investigation. The three most heavily doped samples were annealed at 400°C for 2 h and quenched by quickly removing them from the oven and blowing on them with a jet of room temperature air. The time needed for the crystals to reach room temperature was 2–3 min. The samples were immediately mounted in the cryostat and cooled. The total time lapse between removing from the oven and passing below dry ice temperature was of the order of 3 h.

The data for this system are given in Fig. 3. They are very similar to those obtained for the KCl:KI and KCl:NaCl cases. In the Ca-doped crystals a somewhat greater effect on the conductivity at temperatures below the conductivity maximum can perhaps be seen. This is probably due to two effects. The first is that in spite of the careful heat treatment, some "microprecipitates" still form, in the manner suggested by Klein.[25] The second effect causing the somewhat greater low-temperature depression is the rapid quench itself. Such a treatment is known to introduce dislocations, and to determine the magnitude of the effect for KCl, the pure crystal was subjected to the same thermal history. The results are shown in Fig. 4 in which it is seen that the quench produces a small low-temperature effect. However, there is no high-temperature effect and the "dips" in the curves at about 30°K in Fig. 3 cannot be ascribed to the quench.

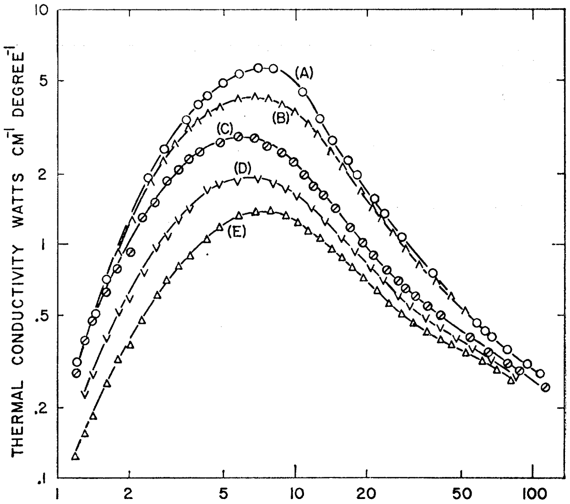

FIG. 3. Thermal conductivity of KCl doped with $CaCl_2$; A, undoped KCl; B, Ca^{++} concentration $N_v=2.4\times10^{17}$ cm^{-3}; C, $N_v=1.9\times10^{18}$; D, $N_v=2.7\times10^{18}$; E, $N_v=4.7\times10^{18}$. Crystals C, D, E, were quenched to room temperature from 400°C.

It is quite apparent that the data in Fig. 3 disagree rather remarkably with Slack's[3,20] data. One must bear in mind, however, that Slack's crystals were very carefully slow-cooled from 700°C and allowed to age at room temperature before measurement. The thermal history of his crystals was thus entirely opposite to the history of our crystals. In order to demonstrate that the behavior seen by Slack can be reproduced, our heaviest doped crystal (curve E in Fig. 3) was annealed for 2 h at 400°C and slow-cooled (~20°C/h) to room temperature. The results of the measurements are seen in Fig. 5, where the behavior of both the quenched (curve B) and slow-cooled (curve C) samples is seen. Also shown in Fig. 5 (curve D) is the result of our remeasurement of Slack's heaviest doped sample, his crystal *S*. This crystal was kindly provided by Dr. Slack. Before the measurements were made the sample was slow-cooled from 700°C. The ×'s in Fig. 5 are

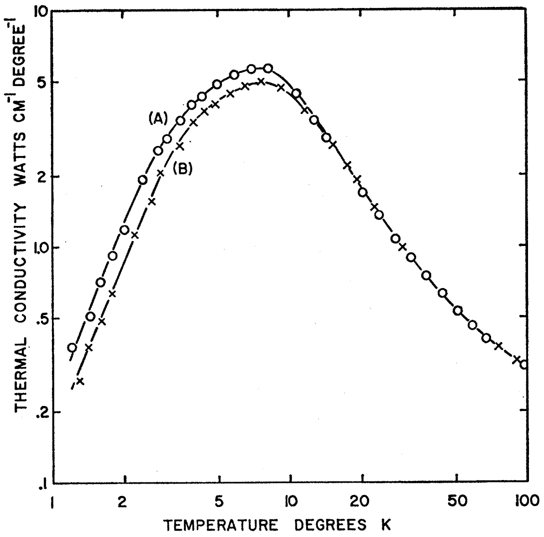

FIG. 4. Thermal conductivity of pure KCl quenched from 400°C; A, KCl as-grown; B, after quenching. Average dislocation density of quenched crystal was 2×10^6 cm^{-2} except within 0.25 mm of surface where density was $>10^7$ cm^{-2}.

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[30] K. Suzuki, J. Phys. Soc. Japan **13**, 179 (1958).

Slack's original measurements on this sample. The agreement between the measurements taken 6 yr apart by different people is, indeed, remarkable. The data in Fig. 5 also show that a slow cool from 400°C produces precipitates as efficiently as one from 700°C, and that both result in a complete obliteration of the behavior seen in Fig. 3, where the bulk of the calcium has remained in solution.

The most striking feature of the experiments reported here is the pronounced decrease in the thermal conductivity curves around 30°K in crystals with presumably no coagulation. The same "dip" can be seen in Klein's data for the system NaCl:MnCl$_2$ and was also found recently by Worlock in NaCl containing small concentrations of AgCl. It is worth emphasizing at this point that these five cases, all showing similar behavior, in fact emcompass five somewhat different types of point defects. The KCl:KI system has a heavier monovalent negative ion for the defect. The KCl:NaCl system has a lighter monovalent positive ion for the defect, while the NaCl:AgCl system has a heavier monovalent positive ion substituting for the host ion. In the KCl:CaCl$_2$ system one has a foreign ion of negligible mass difference but accompanied by a positive ion vacancy. Finally, and possibly most complex, in NaCl:MnCl$_2$ one has both a heavier ion and an associated vacancy. All of these defects are of atomic dimensions, and all of them give the same effect in the thermal conductivity. The latter fact suggests that all obey the same scattering law. Its determination is the objective of the next section.

IV. DETERMINATION OF THE RELAXATION TIMES

In first, or Debye, approximation, the lattice thermal conductivity K is given by the following equation:

$$K=\frac{1}{3}\int_0^{\omega_D} v^2\tau(\omega,T)\frac{dC}{d\omega}d\omega\,, \qquad (1)$$

with

$$\tau^{-1}(\omega,T)=\textstyle\sum_i \tau_i^{-1}(\omega,T)\,, \qquad (2)$$

where ω_D is the Debye frequency, v is the sound velocity, τ_i is the relaxation time for the ith phonon scattering mechanism, T the temperature, and $dC/d\omega$ the specific heat per unit angular frequency. The limits on the validity of these equations have been discussed in detail elsewhere,[2,9] but for the present discussion they shall be assumed to hold.

In the analysis of data for systems containing deliberately added defects it is useful to rewrite Eq. (2) as

$$\tau^{-1}(\omega,T)=\tau_p^{-1}(\omega,T)+\tau_d^{-1}(\omega,T)\,. \qquad (3)$$

Here τ_p contains all the information describing the undoped crystal and τ_d contains the information concerning the phonon scattering by the defect(s).

There are at least three separate scattering mechanisms acting in the pure KCl crystals. These are the scattering by the crystalline boundaries, the scattering by the natural isotopes of K and Cl, and the intrinsic or phonon-phonon scattering. We consider each term separately.

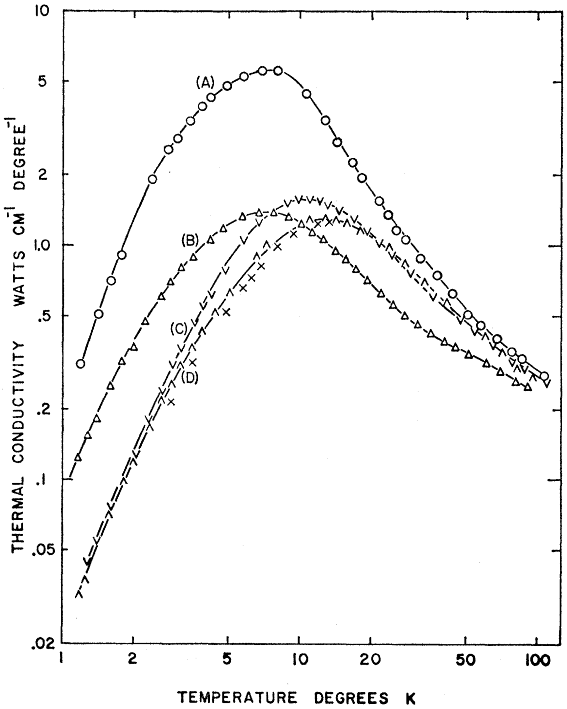

FIG. 5. KCl doped with CaCl$_2$; A, undoped KCl; B, $N_v=4.7\times10^{18}$ cm^{-3} after quenching from 400°C (same as curve E of Fig. 3); C, same crystal after slow cool from 400°C; D, Slack's crystal S, our measurements after slow cool from 700°C. x's are Slack's original measurements on crystal, S.

(*a*) *Boundary scattering.* The relaxation time for boundary scattering is given by

$$\tau_B^{-1}=v/L\,, \qquad (4)$$

where L is the Casimir scattering length.[31] For crystals of square cross section and roughened surfaces, such as ours, L is defined as the diameter of a circle with an area equal to the cross-sectional area of the crystal. For a crystal of width d, then, $L=1.12d$.[3] For KCl, the low-temperature Debye temperature is 233°K,[32] and from this one calculates the average sound velocity $v=3.1\times10^5$ cm/sec. The cross-sectional area of our crystals was 0.25 cm^2 and, thus, one would expect the boundary scattering term to be

$$\tau_B^{-1}=5.6\times10^5\ \text{sec}^{-1}.$$

The low-temperature data are fitted best with $\tau_B^{-1}=5.8\times10^5$ sec^{-1} in excellent agreement with Casimir's model.

(*b*) *Natural isotope scattering.* According to Pomeranchuk,[5] as amended by Klemens,[2] the relaxation time for

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[31] H. B. Casimir, Physica **5**, 495 (1938).

[32] P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1354 (1953).

the scattering by the natural isotopes is given by

$$\tau_{\text{Isot}}^{-1}=\frac{V_0\Gamma}{4\pi v^3}\omega^4, \tag{5}$$

where V_0 is the molecular volume and Γ is given by

$$\Gamma=\sum_i f_i(1-m_i/\bar{m})^2. \tag{6}$$

Here m_i is the mass of the ith species of molecules, $\bar{m}$ is the average molecular mass, and f_i is the relative concentration of the ith species. Substituting the appropriate quantities for KCl one obtains

$$\tau_{\text{Isot}}^{-1}=3.0\times10^{-44}\ \text{sec}^3\ \omega^4. \tag{7}$$

(*c*) *Phonon-Phonon scattering*. In order to explain the data of Geballe and Hull,[8] Callaway[9] used the following expressions for Umklapp and normal phonon-phonon processes

$$\tau_U^{-1}=B_1\omega^2T^3e^{-\theta/aT}, \tag{8}$$

$$\tau_N^{-1}=B_2\omega^2T^3, \tag{9}$$

where θ is the Debye temperature and a is a constant of order 2 or 3. The same expressions were used by Agrawal and Verma[33] in their attempt to explain the previously published data on pure KCl. The basic feature of Eqs. (8) and (9) is that the general behavior for temperatures above the conductivity maximum is $K\propto T^{-2}$, especially if the exponential term is ignored, and the normal processes are included in Eq. (2) merely as an additional scattering mechanism.[9]

Using these relaxation processes (τ_B, τ_{Isot}, τ_U, and τ_N), we have examined our data for the pure KCl. One sees immediately that at high temperatures, where phonon-phonon interactions become the dominant scattering mechanism, the conductivity changes proportionally to T^{-1}. This excludes the use of Eqs. (8) and (9). A good fit at high temperatures requires a different relaxation time:

$$\tau_{U,N}^{-1}=B\omega^2Te^{-b/T}, \tag{10}$$

where $b=40$°K and $B=2.92\times10^{-18}$ sec deg^{-1}. For a detailed study of the conductivity, Eq. (1) was calculated with the relaxation times described in Eqs. (4), (5), and (10) combined according to Eq. (2). The integration was done using the Burroughs-220 digital computer of the Cornell Computing Center. To obtain a good fit near the conductivity maximum, it was necessary to use a somewhat larger Rayleigh scattering term, namely $A=11.2\times10^{-44}$ sec.^{3} This is perhaps not surprising in view of the impurities present in the undoped crystal ($\sim$20 ppm). The total relaxation time, τ, used to describe the undoped crystal thus is given by

$$\tau^{-1}=5.8\times10^5\ \text{sec}^{-1}+11.2\times10^{-44}\ \text{sec}^3\omega^4 +2.92\times10^{-18}\ \text{sec deg}^{-1}T\omega^2e^{-40\text{°K}/T}. \tag{11}$$

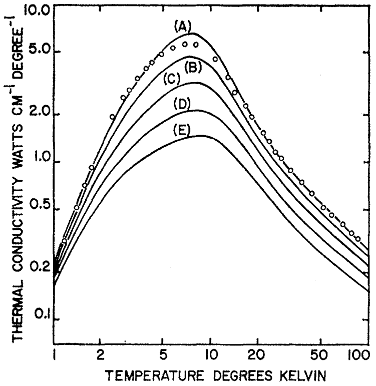

FIG. 6. Calculated curves. A, calculated for KCl using Eq. (11), circles are measured data; B, calculated using Eq. (11) plus additional relaxation time $\tau^{-1}=A\cdot\omega^4$, $A=1\times10^{-43}$ sec^{-3}; C, $A=3\times10^{-43}$; D, $A=7\times10^{-43}$; E, $A=14\times10^{-43}$.

The resultant curve is shown as the top curve in Fig. 6; also included are the data for the pure KCl crystal. We do not attempt to justify Eq. (11) physically, but merely assert that it is the form needed to provide the best fit to our data and accept it without comment. For a serious discussion of the theoretical justification of Eq. (11), we believe that it will be important to improve the physical perfection of the undoped KCl, i.e., essentially to reduce the background impurities. We note parenthetically that the previously mentioned analysis of Agrawal and Verma[33] is completely inapplicable in our case, and, in fact, the use of Eq. (10) is a considerable improvement for the previously published pure KCl data which they considered.

We turn now to the heart of the problem, the determination of the defect scattering term in Eq. (3). According to the theories of Klemens and Carruthers, the defects which we have studied should obey a scattering law of the form $\tau^{-1}=A\omega^4$, i.e., a Rayleigh scattering law. Our experiments were designed specifically to test this conclusion. If the Rayleigh law held true, then one could predict the shape of the experimental curves for the doped crystals. One would simply add an ω^4 term to the total relaxation time describing the pure crystal and calculate the result. This has been done for increasing strength of the scattering term and the results are seen as the bottom four curves in Fig. 6. A comparison of the curves in Fig. 6 with the experimental curves shows that the computed curves agree with the experimental ones only at very low temperatures. The significant feature of our data, the "dip" in the conductivity around 25–30°K, cannot be described with Rayleigh scattering. This structure of the conductivity curves is somewhat similar to the structure found in KCl crystals containing KNO_2 in solid solution,[19] in which case the defect scattering could be described with a resonance expression of the form

$$\tau_{\text{defect}}^{-1}=A\omega^2/(\omega_0^2-\omega^2)^2. \tag{12}$$

We have found, however, that a term of the same form does not fit our present data because it does not die off fast enough at low temperatures. A rather remarkable fit of the present data has been achieved with a modified

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[33] B. K. Agrawal and G. S. Verma, Phys. Rev. **126**, 24 (1962).

resonance expression:

$$\tau_{\text{defect}}^{-1}=A\omega^2T^2/(\omega_0^2-\omega^2)^2\,, \tag{13}$$

where T is the temperature. The result of the calculation is seen in Fig. 7. For KCl:KI, the resonance frequency was determined to be

$$\omega_0=1.0\times10^{13}\ \text{sec}^{-1}.$$

For an I^- concentration of 5×10^{19} cm^{-3} (curve D in Fig. 1), the proportionality factor A was found to be:

$$A=8\times10^{32}\ \text{sec}^{-3}\ \text{deg}^{-2}.$$

Even though Eq. (13) yields calculated curves which roughly resemble the experimental data we use it only as a crude example of the type of relaxation term which one needs to explain the data and shall not consider it further. The chief difficulty with Eq. (13), in addition to the fact that it has no physical justification, is that it does not show explicitly any phonon scattering of the Rayleigh type expected at least as a result of the mass difference between the I$^-$ and the Cl$^-$. However, one may conclude at this point that any theoretical interpretation of the experimental phenomena for the system KCl:KI must contain a characteristic frequency ω_0 of the order of 10^{13} sec^{-1}.

V. THEORY

We now consider in detail the consequences of introducing a point defect into an alkali halide crystal. As pointed out in the introduction, the perturbation of the periodicity of mass, force constants, and volume will give rise to a Rayleigh-type scattering mechanism. Its effect on the thermal conductivity was demonstrated in Fig. 6, and it was concluded that this mechanism did not suffice to explain the experiments.

The incorporation of point defects, however, also causes other effects. Alkali halide crystals are composed of diatomic molecules and the well-known dispersion relations for this system show that the frequency spectrum is split into two bands, acoustic and optical, with a gap between. If a point defect satisfying certain criteria is introduced into this system, new modes are produced which do not lie in either band. For example, an impurity substituting for the lighter of the two host ions and with a mass greater than the ion it replaces (as I$^-$ for Cl$^-$ in KCl) produces a new mode which lies in the gap between the acoustic and optical bands. A quantitative determination of the impurity mode also requires a knowledge of the binding forces and strain field around the defect. This problem has been discussed in detail by several investigators.[34–38] Since these new modes exist in energetically forbidden regions they must be highly localized and will have little interaction with the phonons.

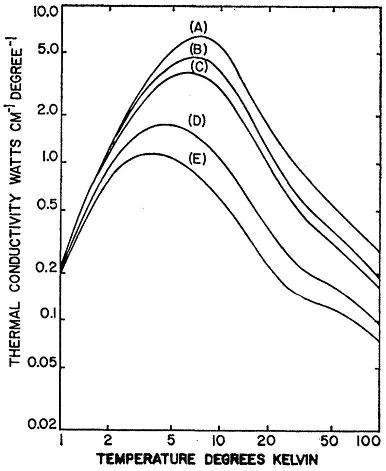

FIG. 7. Calculated curves. A, calculated for KCl using Eq. (11); B, calculated using Eq. (11) plus Eq. (13), coefficient of resonance term $=A_0$; C, coefficient $=2A_0$; D, coefficient $=10\ A_0$; E, coefficient $=20\ A_0$.

In addition to creating these new local modes, the defects will also disturb the phonon spectrum present in the pure crystal. In a crystal of N diatomic molecules there can be only $3N$ normal modes. If by introducing an impurity M new modes have come into play, it can only be at the expense of M of the old modes. Further, it is probable that the phonon spectrum may be modified more radically than by the simple loss of M of the unperturbed normal modes to make up for the M localized modes. McCombie *et al.*[38] have considered the effect on the frequency spectrum of introducing an F center into an alkali halide. They found that several new (or at least enhanced old) modes are produced in both the acoustic and optical bands. These modes seem to average to a frequency which is the same frequency needed to explain the F-band half-width. It is probable that an argument similar to McCombie's would show a similar modification for the type of point defects which we consider. It is possible that the portion of these modes lying in the heat-carrying part of the spectrum (acoustic band) would be sufficiently closely spaced that a gross average over frequency, such as thermal conductivity, would show only an "average" mode. All of these modes in the acoustic spectrum can no longer really be called localized because they will interact strongly with the remaining acoustic modes.

Wagner[39] has studied the scattering of phonons by localized modes and we shall sketch his method briefly in the following. Let us assume a local mode (i.e., a mode outside the acoustic and optical continuum) of angular frequency, ω_s, and wave vector $\mathbf{k}_s$. Let two phonons of frequencies ω_1 and ω_2 and wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ collide to form a third phonon of frequency ω_3 and wave vector $\mathbf{k}_3$. If $\omega_3=\omega_s$ and $\mathbf{k}_3=\mathbf{k}_s$ and if there is any interaction at all between the phonons and the localized mode, then the possibility exists that phonon

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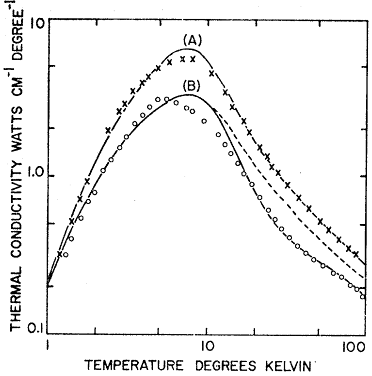

FIG. 8. Influence of impurity mode scattering for Na$^+$ impurity. A, curve calculated from Eq. (11) and fitted to ×'s. (Same as curve A of Fig. 6); B, calculated using Eq. (11) $+2.7\times10^{-43}$ ω^4 +Eq. (14) and fitted to O's, impurity mode frequency $\omega_s=1.6\times10^{13}$ rad/sec.

3 will simply be absorbed by the localized mode. When the mode de-excites, the probable result would resemble phonon-phonon scattering if the excited state of the localized mode has a lifetime short compared to a typical phonon period ($\sim10^{-13}$ sec). If the lifetime of the excited state is comparable to or longer than a phonon period, the process of excitation should be independent of the process of de-excitation and one would not have a resonance-flourescence type of scattering but simply a resonance absorption of phonons followed by a later reemission. Since ω_s lies in an energetically forbidden region, the collision between phonons 1 and 2 must be of the Umklapp type. That is, if the impurity mode were not there, phonon 3 would quickly undergo the process $\mathbf{k}_3+\mathbf{K}=\mathbf{k}_3'$, where $\mathbf{K}$ is a reciprocal lattice vector. Thus, if this process is going to occur and be detectable in the thermal conductivity, it must occur in a temperature region where umklapp collisions are abundant; i.e., for temperatures greater than the conductivity maximum. It also follows that this process will be most important in the thermal conductivity for localized modes lying between the acoustic and optical branches and will decrease strongly for larger impurity mode energies.

Quantitatively, Wagner finds that the process can be described by the following phonon scattering relaxation time:

$$\tau^{-1}(\omega,T)=Ef(\omega,T)g(\omega)\,, \tag{14}$$

where

$$E=\frac{9}{16}\,\frac{\pi^2}{\rho}\,\frac{\gamma^2\hbar}{v}\,\frac{(M\alpha)n}{\omega_s}\,,$$

$$g(\omega)=\left(1+4\frac{\omega_\alpha}{\omega_s}\right)\ln\left\{\frac{(\omega/\omega_s)(1-\omega/\omega_s)+\omega_\alpha/\omega_s}{\omega_\alpha/\omega_s}\right\}-4\frac{\omega}{\omega_s}\left(1-\frac{\omega}{\omega_s}\right),$$

and

$$f(\omega,T)=\frac{(\omega_s-\omega)^2e^{\hbar(\omega_s-\omega)/kT}(e^{\hbar\omega/kT}-1)}{(e^{\hbar\omega_s/kT}-1)(e^{\hbar(\omega_s-\omega)/kT}-1)}\,.$$

Here ω_s is the frequency of the localized mode, n is the concentration of defects, γ is Grüneisen's constant, ρ is the density of the crystal, v is the sound velocity, and $\omega_\alpha=\alpha v$, where α is the exponential damping factor of the localized mode. M is the number of localized modes created by one impurity. The properties of Eq. (14) have been discussed by Wagner.[39] The important results are that τ^{-1} peaks roughly at $\omega_s/2$ and is large over less than a decade of frequency, and that the height of the peak increases roughly exponentially for low temperatures, as T^2 for intermediate temperatures, and as T for high temperatures. Although the scattering process [Eq. (14)] was derived for the interaction between phonons and a localized mode, Wagner has shown that the same result can be obtained when the interaction occurs with impurity modes that lie in the acoustic or optical continuum. In this case M in Eq. (14) is the number of "quasilocalized" modes lying in the band. Single-phonon processes can still be neglected.

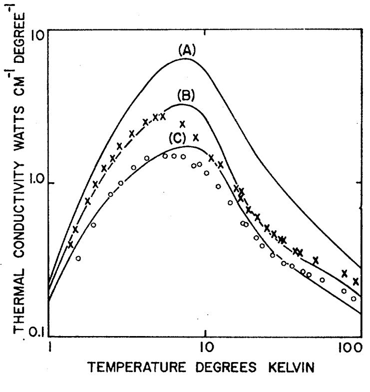

FIG. 9. Influence of impurity mode scattering for I$^-$ impurity. A, same as curve A of Fig. 8; B, caclulated using Eq. (11)+Eq. (14) $+2.7\times10^{-43}$ sec^3 ω^4 and fitted to X's, Impurity mode frequency $\omega_0=1.3\times10^{13}$ rad/sec; C, Same as B except that coefficient of ω^4 term is 10.8×10^{-43} sec^3.

In the following it will be shown how the experimental data were fitted using a combination of a Rayleigh scattering term and Wagner's term [Eq. (14)]. Since it turns out that the resonance term has no low-temperature effect the coefficient of the ω^{-4} term was adjusted to fit the low-temperature data. The two variables in the resonance term, the impurity mode frequency and the damping coefficient, were then adjusted to provide a "dip" of the proper position and depth to explain the high-temperature data. This calculation was carried out on the Control Data-1604 electronic computer and the result for the system KCl:NaCl is shown in Fig. 8. The top curve in Fig. 8 is the pure KCl curve and the bottom curve is for the doped crystal. The circles are the actual data and the dashed line shows the calculated curve using an ω^{-4} law only. The coefficient of the excess ω^{-4} needed for curve B is $A=2.7\times10^{-43}$ sec^3. The impurity mode frequency is $\omega_s=1.6\times10^{13}$ sec^{-1}, while the coefficient of the resonance term is $E=8.8\times10^{-17}$ sec. From the expression for E in Eq. (14) one determines $(M\alpha)=2.5\times10^7$ cm^{-1}.

The relevant parameters for all three defect systems are given in Table I. Fig. 9 shows the result of the calculation for KCl:KI. It has not been possible to

TABLE I. Parameters needed to explain thermal conductivity data including Rayleigh and resonance scattering effects.

Defect concentration (cm^{-3})	A in Eq. (5) calculated from mass difference (10^{-43} sec^3)	A needed to fit data (10^{-43} sec^3)	A_{exp}/A_{theory}	ω_s in Eq. (14) (10^{13} sec^{-1})	E in Eq. (14) (10^{-17} sec)	$(M\alpha)^{-1}$ in Eq. (14) (Å)
2.3×10^{19} Na^+	0.301	2.7	9.0	1.6	8.8	4.0
1.0×10^{18} I^-	0.155	...	...	...	...	...
1.25×10^{19} I^-	1.80	2.7	1.4	1.3	8.8	5.0
5.0×10^{19} I^-	7.52	10.8	1.4	1.3	4.4	40.0
2.4×10^{17} Ca^{++}	0.00343	0.34	99	1.7	<0.4	2.3
1.92×10^{18} Ca^{++}	0.0275	2.2	81	1.7	1.6	2.3
2.74×10^{18} Ca^{++}	0.0392	3.2	81	1.7	2.3	2.3
4.67×10^{18} Ca^{++}	0.0668	5.0	75	1.7	3.5	2.3

fit the two most highly doped KCl:$CaCl_2$ crystals very well because of the previously mentioned low-temperature depression presumably caused by the onset of precipitation. Accordingly, the coefficients in Table I for these two cases are merely surmises and are probably accurate only to 50%. The impurity mode frequency, however, is reasonably accurate. Also in Table I it is seen that E for the highest concentration of KI is smaller than for the lower concentration.

VI. DISCUSSION

1. Rayleigh-Type Scattering

In Table I we have seen that the coefficient of the ω^{-4} term seems to be proportional to the concentration, and that the size of the coefficient, A, in every case is larger than that calculated for mass-difference scattering only. This suggests that the theory of point-defect scattering is at least qualitatively correct insofar as it concerns the elastic (Rayleigh) scattering. Klemens[2] describes this scattering in terms of a dimensionless parameter S^2 where the coefficient of the ω^{-4} term is given by

$$A=\frac{3a^3}{\pi v^3}S^2 f,$$

where v is the sound velocity, a^3 is the molecular volume, and f is the mole fraction of impurity. For mass-difference scattering only one has $(S_1)^2=(1/12)(\Delta M/M)^2$ and for scattering by a change in atomic linkages only one has $(S_2)^2=\frac{1}{6}(\Delta F/F)^2$. For scattering by a change in linkages accompanied by a lattice distortion (i.e., volume changes) one has $(S_3)^2=24(\Delta R/R)^2$. S^2 for a general type defect is given by $S^2=S_1^2+(S_2+S_3)^2$.

Klemens has tabulated calculated values of S^2 for various systems.[2] The values relevant to our experiments are listed in Table II. The values of S^2 needed to explain our data are also given in Table II.

Carruthers[40] describes the scattering by the strain field around point defects and obtains $S^2=80\gamma^2\epsilon^2$, where γ is Grüneisen's constant and ϵ is a "misfit parameter" giving the fractional amount of volume misfit for the impurity ion relative to the host ion. The values for ϵ needed to give our experimentally determined values of S^2 are given in Table II.

From Table II we conclude that the agreement with either theory is fair for the case of Na doping. For the I and Ca doping, Klemens' S^2 is much too small and Carruthers' theory seems more applicable. The biggest discrepancy with Klemens' calculation is found for Ca. Here one is dealing with a strain dipole and it is, therefore, understandable that Carruthers' approach is more appropriate.

2. Impurity-Mode Scattering

From Restrahlen and elastic data[41] one determines the upper limit of the acoustic band in KCl to be greater than $\omega=2.0\times10^{13}$ sec^{-1}. A comparison with Table I shows that all the frequencies ω_s needed to explain our data lie well below this value. According to Wagner's theory, then, we do not see the effect of localized modes in the band gap, but rather the effect of impurity modes or quasilocalized modes in the acoustic continuum. Their damping factor α can be estimated if we assume that the number M of quasilocalized modes connected with each impurity atom is small, say four or five. In the case of the Na^+ impurity with a concentration of 2.3×10^{19} cm^{-3}, the mean distance between impurity sites

TABLE II. Comparison between experimental and calculated Rayleigh-scattering parameters.

Defect concentration (cm^{-3})	A_{exp} needed to fit data (10^{-43} sec^3)	S^2_{exp}	S_{theory}[a]	Misfit parameter
2.3×10^{19} Na^+	2.7	0.34	0.29	0.041
1.0×10^{18} I^-	...	...	0.43	0.093
1.25×10^{19} I^-	2.7	1.7	0.43	0.093
5.0×10^{19} I^-	10.8	1.7	0.43	0.093
2.4×10^{17} Ca^{++}	0.34	1.1	<0.2	0.07
1.92×10^{18} Ca^{++}	2.2	0.9	<0.2	0.07
2.74×10^{18} Ca^{++}	3.2	0.9	<0.2	0.07
4.67×10^{18} Ca^{++}	5.0	0.9	<0.2	0.07

[a] From Klemens (Ref. 2), corrected by calculating $\Delta M/M$ using molecular masses rather than atomic masses.

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[40] Equation (4.43) of Ref. 3 corrected numerically by Carruthers (private communication).

[41] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956).

is of the order of 36 Å. The value of $(M\alpha)^{-1}$ needed to explain the data is 4 Å; thus, α^{-1} would be of the order of 15–20 Å. Therefore, one could still consider the defects as isolated, as postulated by Wagner.

The same argument holds for the lower I^- impurity concentration. However for the highest I^- concentration, 5×10^{19} cm^{-3}, the mean separation between impurity sites is only about 27 Å. In this case four or five quasilocalized modes would give α^{-1} of the order of 20–25 Å and one would be dealing with an impurity band rather than isolated impurities. The theory is probably not applicable under this condition and this may explain the very high value of $(M\alpha)^{-1}$ needed for the highest I^- case.

It appears that Wagner's theory indeed gives a plausible description of the experimental data. It is important to point out, however, the problem of whether resonances in the band are to be expected for all the impurity systems we have discussed. Arguments considering mass difference only suggest that the Na^+ impurity should not produce a quasilocalized mode. However, Lifshitz[34] has set up the problem for arbitrary mass difference and one can see that a lighter mass, such as Na for K, could indeed produce a quasilocalized mode. Our observed resonance frequencies span the range 1.3–1.7×10^{13} sec^{-1}. Since it is not yet clear how much effect force constant changes will have on localized mode frequencies, we cannot comment on whether our observed frequency range is reasonable. At this stage, then, several questions remain open, such as the magnitude of ω_s and its dependence on host lattice and impurity atoms as well as the concentration dependence of the scattering term. These questions are presently under further investigation.

VII. SUMMARY

We can summarize the results of the present investigation as follows:

(1) Measurements of the thermal conductivity of KCl crystals containing known amounts of KI, NaCl, and $CaCl_2$ in solid solution were used to study the interaction between phonons and point defects. In all cases the doped crystals showed a pronounced decrease in the thermal conductivity around 30°K. Similar observations were reported earlier by Klein for the system $NaCl{:}MnCl_2$ and by Worlock for NaCl:AgCl. This "dip" disappeared in the $KCl{:}CaCl_2$ system when the Ca^{++} was allowed to precipitate, indicating that the effect is to be attributed to the atomically dispersed defects.

(2) It was not possible to describe these results solely with a Rayleigh-type phonon scattering mechanism. This suggested the occurrence of an additional scattering mechanism which had not been considered in previous theories.

(3) A phonon-phonon excitation of an impurity mode as discussed by Wagner is shown to be a possible source for the "dip" in the thermal conductivity curve. The angular frequencies ω_s of the impurity modes, determined from the experiments under this assumption, are of the order of 10^{13} sec^{-1} for the three defect systems investigated here. This means they lie in the acoustic continuum. The same holds true for the systems discussed by Klein and Worlock. Further experiments will be required to test this theory and in particular the dependence of ω_s on host lattice and impurity atom will have to be studied.

(4) The experiment also permitted a quantitative determination of the Rayleigh relaxation time and the data were used to study the effect of the strain around the point defect. In agreement with Slack's result it was found that the Rayleigh scattering for the Ca-doped crystals is much stronger than Klemens' estimate; this might be expected for a strain dipole as formed by the Ca^{++} vacancy aggregate. This result, combined with the results for the Na^+ and I^- doping, suggest that Carruthers' strain-field model is more applicable than Klemens'.

ACKNOWLEDGMENTS

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