Phonon Scattering by Point Defects in CaF_2, SrF_2, and BaF_2†

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Low-temperature thermal-conductivity measurements have been made on pure CaF_2, SrF_2, and BaF_2, and on all three hosts containing Li^+ or Na^+ impurities. Concentrations of these impurities near 10^{18} cm^{-3} were found to have no effect on the thermal conductivity, suggesting a weak phonon scattering due to point defects in these systems. Sm^{++} and U^{3+} impurities in the 10^{19}-cm^{-3} range and H^- in the 10^{20}-cm^{-3} range were studied in CaF_2, and two effects were observed. Nonresonant point-defect scattering of the Rayleigh type was seen. Mass-difference scattering alone was shown to be sufficient to explain the data for all three impurities. The strength of this Rayleigh scattering is in accord with the lack of an effect at low concentrations of Li^+ and Na^+. In addition, the low-temperature side of the conductivity curves for all three dopants was found to vary as T^3. This behavior has been ascribed to phonon scattering by precipitates. Since Sm^{++} and U^{3+} are magnetic, the possibility of phonon-spin interactions for these systems was investigated as an explanation for the low-temperature data. This possibility was shown to be excludable.

I. INTRODUCTION

OVER the past 20 years, many investigators have used low-temperature thermal-conductivity measurements as a technique for studying phonon interactions. Phonon interactions in pure crystals and in crystals containing controlled amounts of defects have been studied. In this paper we report our results from a study of phonon scattering by point defects in insulators with the fluorite structure. Our greater attention will be confined chiefly to CaF_2 as a host material, although SrF_2 and BaF_2 were also used as hosts.

Point defects have been found to scatter phonons in several interesting ways. As was first shown by Pomeranchuk,[1] the introduction of atoms whose mass differs from that of the host atoms leads to a phonon-scattering cross section which varies as the fourth power of the phonon frequency (Rayleigh scattering of phonons). This result was later calculated in more detail by Klemens,[2] who also showed that impurity atoms bound by force constants which differed from those of the host lattice also resulted in a Rayleigh-like scattering cross section. The mass-difference-only case (isotope effect) has been well verified, even into the short-wavelength region where one might expect the Rayleigh scattering to be severely altered. The most complete study of the isotope effect has been described by Berman and Brock.[3]

The case of point defects bound by different force constants is a much more complicated one. As has been shown by many studies in alkali-halide host lattices, such defects usually produce a resonant scattering of phonons. One must distinguish at least three different resonant effects. As was first shown by Pohl,[4] defects composed of molecules have a resonant interaction with phonons. This resonant interaction has been found to be quite complicated,[5] with the molecules undergoing free rotations, librations, tunneling, etc., in the solid. In general, this resonant interaction arises from the presence of an internal structure of the molecule.

A second type of resonant behavior comes from point defects which are composed of single atoms or ions but which are so small that their equilibrium site is off center. Such defects have been heavily studied by Pohl[6] and his students and colleagues. Neither the molecular nor the off-center defects will be discussed in this paper.

Our attention here is on monatomic point defects of the sort discussed theoretically by Klemens in the paper described above. From the time of the paper by Walker and Pohl,[7] with the accompanying theoretical model of Wagner,[8] such defects have been known to perturb the lattice vibrational spectrum in a resonant manner. These resonant states have, in fact, come to be expected almost as a general rule. They manifest themselves as "dips" in the thermal-conductivity–versus–temperature plots, with the dip generally occurring near or above the peak in the conductivity curve. Baumann and Pohl[9] have reported a broad spectrum of results in the alkali halides. On the theoretical side, the study of such lattice resonances has been a theorist's playground; a review of the theoretical scene has been given by Klein.[10]

A summary of the theoretical endeavors would read as follows. Point defects whose masses differ from the host atom's mass, or which are bound by different force constants, or both, have phonon-scattering cross sections with large resonant peaks. The frequencies of such resonant peaks do not follow a simple set of rules.[11] However, all the scattering cross sections from all models,

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whether evaluated analytically or numerically, go over to a Rayleigh-like behavior at long wavelengths. This fact has been documented experimentally by Baumann and Pohl.[9]

Almost all of the experimental studies mentioned above have been done using alkali halides as host materials. On the grounds that one would like theoretical models to have a validity which extends beyond alkali halides, one would like to see experimental data for other host lattices. The recent work of Moore and Klein[12] is quite interesting in this regard. They observed *no* resonant scattering for several different impurities in CdS. One might explain away this rather unexpected result by noting that the concentration of impurities in their samples (~500 ppm) may have been marginal for observation of resonant effects, and an additional scattering due to dislocations in their samples may have partially masked any point-defect scattering.

This much background explains our choice of crystal systems. CaF_2, in its nominally pure state, has a reasonably high thermal conductivity. Thus, it would be expected to show point-defect scattering for reasonable concentrations. In addition, it can be grown reproducibly with a fairly constant level of purity. But most importantly it allows introduction of a broad spectrum of impurities, to quite high impurity concentrations. We have picked impurity types which are known to produce resonant effects in alkali halides and have gone on to include two other fluorite-type hosts, SrF_2 and BaF_2. As will be seen, in *no case* has a phonon resonance been observed. Phonon scattering in these hosts is seen to be relatively weak and, where we have made detailed fits to the data, explainable essentially completely by mass-difference Rayleigh-like scattering acting alone.

Section II of this paper contains the experimental results, while Sec. III contains an outline of the theory and data-fitting procedures. In Sec. IV we shall discuss our results.

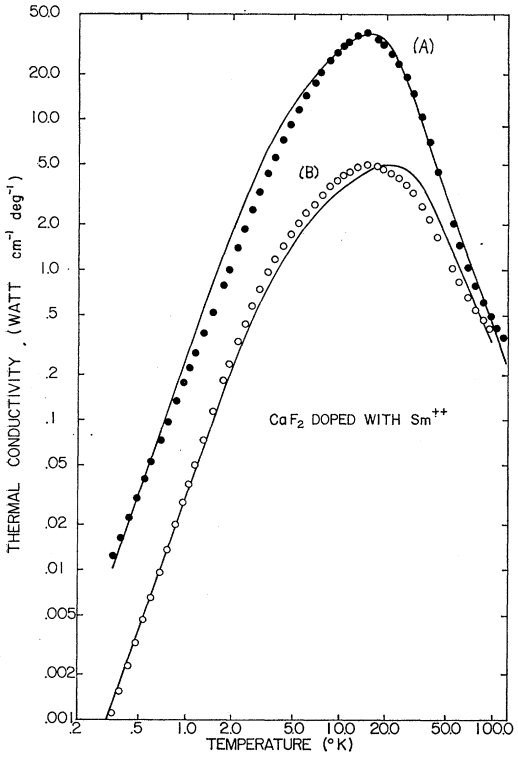

FIG. 1. Thermal conductivity versus temperature for pure and doped CaF_2. (A) Pure CaF_2; (B) CaF_2 containing 3×10^{19} cm^{-3} Sm^{++} as an impurity. The solid lines are theoretical curves whose calculation is described in the text.

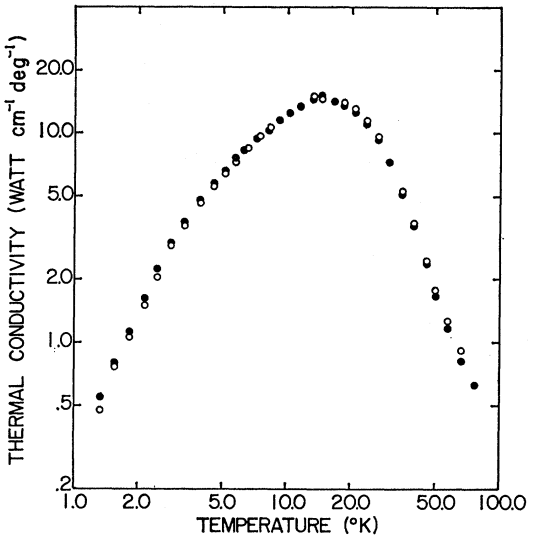

FIG. 2. Thermal conductivity versus temperature for pure and doped SrF_2. Closed circles, pure SrF_2; open circles, SrF_2 containing about 5×10^{18} cm^{-3} Na^+ as an impurity.

II. EXPERIMENTAL RESULTS

A. Pure Crystals

The pure CaF_2, SrF_2, and BaF_2 crystals used in these experiments were purchased from the Harshaw Chemical Co. Their determination of background impurities gave less than 20 ppm for CaF_2, and less than 50 ppm for SrF_2 and BaF_2. The colloidal matter in CaF_2, presumably CaO, reported earlier by Moss,[13] appears no longer to be present. All crystals were in the shape of rectangular parallelepipeds, measuring about $40\times5\times5$ mm. The heat flow was along the long axis, a $\langle111\rangle$ direction. All crystal surfaces, for pure and doped crystals, were sanded with 600-grit carborundum cloth to ensure diffuse scattering of phonons at the crystal surfaces. Thermal-conductivity data for pure CaF_2, SrF_2, and BaF_2 are shown in Figs. 1–3, respectively. CaF_2 has been measured from 0.32 to 100°K, while SrF_2 and BaF_2 have only been measured down to 1.3°K. As will become clear below, it did not seem to be necessary to

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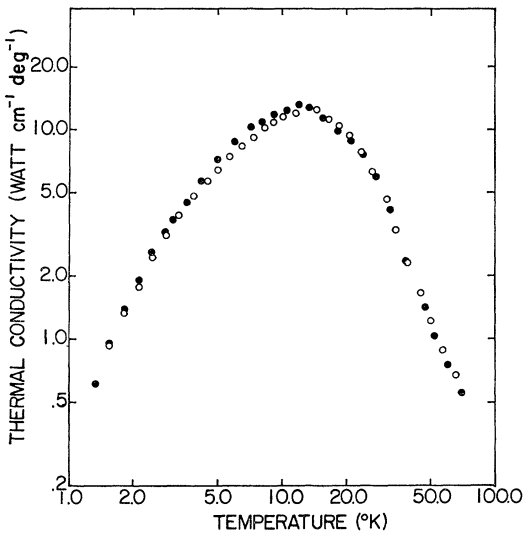

FIG. 3. Thermal conductivity versus temperature for pure and doped BaF_2. Closed circles, pure BaF_2; open circles, BaF_2 containing about 5×10^{18} cm^{-3} Li^+ as an impurity.

make measurements below 1°K for SrF_2 and BaF_2. Our CaF_2 data on the high-temperature side of the peak are in good agreement with those measured and referred to by Slack.[14] Our BaF_2 data do not extrapolate to the high-temperature data of McCarthy and Ballard,[15] but the rather unrealistic temperature dependence of their data leads us to suspect some ambiguity in their experiment.

The thermal conductivity for pure CaF_2 varies as $T^{2.6}$ on the low-temperature side of the peak, rather than as T^3 if the only phonon-scattering mechanism were boundary scattering. SrF_2 and BaF_2 have not been measured to sufficiently low temperatures to allow verification of T^3 dependence. The peak conductivities are 38 W/cm deg for CaF_2 and 15 and 13 for SrF_2 and BaF_2, respectively. These values would suggest that the crystals are of at least moderate quality, in terms of phonon interactions.

B. Sm^{++} Doping

The simplest point defect on the Ca^{++} sublattice is a substitutional divalent ion. Direct substitutional impurities, requiring no charge compensation, are known to produce phonon resonances in alkali halides.[7,9,11] In fact, this type of defect almost always produces a phonon resonance. Sm^{++} was selected as an impurity in CaF_2 because of its much heavier atomic mass (150.45 versus 40.08 for Ca^{++}). One might expect a low-lying resonance due to the much heavier mass. The Sm^{++} ion is larger than the Ca^{++} ion (1.18–1.00 Å), and thus presumably gives an increased force constant. The force constant change would not be expected to produce a resonance in the acoustic band.

It is known that Sm^{++} enters CaF_2 substitutionally[16] and produces an optical-absorption spectrum in the visible region, which can be used for determination of the impurity concentration. Thermal-conductivity data for CaF_2 containing 3×10^{19} cm^{-3} Sm^{++} ions is shown in Fig. 1. The crystal was cut from a boule purchased from Harshaw. As can be seen, there is no evidence of a phonon resonance, but instead there is both a low- and a high-temperature depression of the doped-crystal data relative to the pure-crystal data.

Sm^{++} was not used as an impurity in SrF_2 or BaF_2 since neither the size nor mass differences were felt to be dramatic enough.

C. Alkali-Ion Doping

Alkali ions carry a unit positive charge, and when introduced into CaF_2 must be accompanied by a negative-ion vacancy for charge neutrality. An equivalent dopant in an alkali halide would be an alkaline-earth ion accompanied by a positive-ion vacancy. The latter defect is known to produce a phonon resonance, which has been attributed to the vacancy.[17] It was felt desirable to search for vacancy effects in alkaline-earth halides using Li^+ and Na^+ dopings. Since both Li^+ and Na^+ are lighter than Ca^{++}, Sr^{++}, or Ba^{++} one would not expect a mass-difference resonance in the acoustic band. However, both are smaller ions, would probably have lower force constants, and might lead to low-lying force-constant resonances.

Boules of CaF_2, SrF_2, and BaF_2 containing Li^+ and Na^+ (separately) were especially grown by Harshaw Chemical Co. The boules were grown by a Bridgeman method, and the melt contained 500 ppm of impurity. The final crystals are estimated to contain no more than half that amount or 5×10^{18} cm^{-3} of impurity. (It has not proved possible to obtain reliable numerical values for these particular dopants.)

Thermal-conductivity data for SrF_2 containing Na^+ and BaF_2 containing Li^+ are given in Figs. 2 and 3, respectively. As can be seen, the data are indistinguishable from the "pure"-crystal data. Li^+ in SrF_2 and Na^+ in BaF_2 demonstrate precisely the same behavior. Li^+ and Na^+ in CaF_2 are not shown, but again there is no difference between the doped- and pure-crystal data. The impurities are known to be in the crystals. It is obvious that at these concentrations they have no effect on the conductivity. This may not be surprising for SrF_2 and BaF_2 since the pure-crystal quality there leaves a bit to be desired and low impurity concentrations might not produce visible effects. Such is not the case for CaF_2. The peak conductivity there is high enough that impu-

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rity concentrations of 1×10^{18} cm^{-3} or even lower might be expected to give visible changes in conductivity.

The peak conductivity for KCl is almost a factor of 10 lower than that of CaF_2. Yet 1×10^{18} cm^{-3} of the analogous impurity in KCl (say Ca^{++}, Sr^{++}, or Ba^{++}) is easily observable. It would appear that the phonon scattering is much weaker in the alkaline-earth halides. This conclusion will be borne out below.

D. H^--Ion Doping

The *U* center in CaF_2, SrF_2, and BaF_2 has been well studied.[18] H^- ions are known to enter the crystal substitutionally and constitute a simple impurity in the F^- sublattice. While the *U* center in alkali halides is known to give a phonon resonance,[11] a conclusion in agreement with infrared (IR) data,[19] such is not necessarily expected in advance for the *U* center in alkaline-earth fluorides. The IR studies by Elliott *et al.*[18] resulted in data which could be fitted without invoking resonances to explain the sidebands of the localized mode.

U centers were produced by two separate methods. The first was the "aluminum method" described by Hall and Schumacher,[20] in which the sample is heated in hydrogen gas while in contact with molten aluminum. However, this method neither allows a high enough concentration to be reached, nor leaves one confident that the crystals contain only H^- ions. The second technique was a two-step method utilizing additive coloration in hot Ca^{++} vapor followed by *F*-center conversion in hot hydrogen gas.

Thermal-conductivity data for CaF_2 containing 6.1×10^{20} cm^{-3} H^- impurity ions are shown in Fig. 4. The data have qualitatively the same shape as those for Sm^{++} in CaF_2. It has been possible to obtain H^- concentrations in the mid-10^{21} range. However, at these concentrations our IR studies (which will be separately published) show clearly that one is no longer dealing with isolated noninteracting point defects. The lack of a thermal-conductivity resonance dip for this system is in agreement with the IR data of Elliott *et al.*[18]

U centers in SrF_2 and BaF_2 were also produced in the low 10^{19}-cm^{-3} range. The data are not reproduced here, but were characterized chiefly by a low-temperature depression similar to that for CaF_2 containing H^-. No significant high-temperature depressions were observed.

E. CaF_2 containing U^{3+}

This defect is the most complicated of all. The ratio of U^{3+} mass to Ca^{++} mass (238 to 40) is enormous. If ever a heavy mass resonance were expected it would be here. But the charge imbalance requires either vacancies in the Ca^{++} sublattice or extra fluorines for maintainance of charge neutrality. The work of Bleaney *et al.*[21] has shown that the U^{3+} ion enters the lattice substitutionally for the Ca^{2+} host ion, and is accompanied by an extra fluorine ion which occupies an interstitial site at the center of the neighboring cube of fluorines. Possible resonances due to interstitial ions have been discussed by Brice.[22]

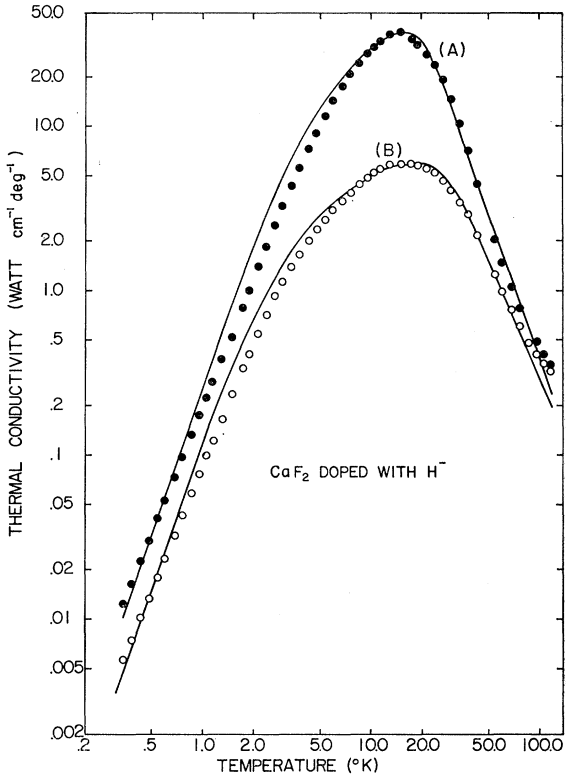

FIG. 4. Thermal conductivity versus temperature for pure and doped CaF_2. (A) Pure CaF_2 containing 6.1×10^{20} cm^{-3} H^- as an impurity. The solid lines are theoretical curves whose calculation is described in the text.

U^{3+} in CaF_2 gives rise to an optical-absorption spectrum in the visible range,[23] which can be used for determination of concentration. This particular substance has technical value as a laser material,[24] as does Sm^{++} in CaF_2.

Thermal-conductivity data for a crystal containing 1×10^{19} cm^{-3} of U^{3+} are shown in Fig. 5. The crystal was purchased from Harshaw Chemical Co. As can be seen, the data closely resemble those for Sm^{2+} in CaF_2. U^{3+} in SrF_2 or BaF_2 was not studied.

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[24] G. D. Boyd, R. J. Collins, S. P. S. Porto, A. Yariv, and W. A. Hargreaves, Phys. Rev. Letters **8**, 269 (1962).

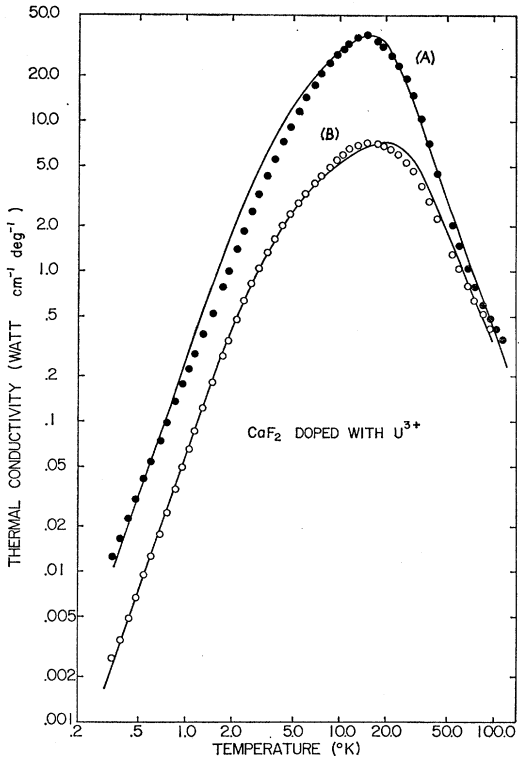

FIG. 5. Thermal conductivity versus temperature for pure and doped CaF_2. (A) Pure CaF_2; (B) CaF_2 containing 1×10^{19} cm^{-3} U^{3+} as an impurity. The solid lines are theoretical curves whose calculation is described in the text.

III. THEORY

A. General

When solved within the framework of certain approximations and assumptions, the linearized phonon Boltzmann equation leads one to the following expression for the lattice thermal conductivity:

$$K=\frac{1}{2\pi^2 v}\int_0^{\omega_D}\tau(\omega,T)\frac{\hbar^2\omega^4}{kT^2}\frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}d\omega. \quad (1)$$

In this expression v is the sound velocity, ω_D is the Debye frequency, $\hbar$ and k are Planck's and Boltzmann's constants, respectively, T is the temperature, ω is the phonon frequency, and $\tau(\omega,T)$ is the total phonon relaxation time. This expression and the approach to analysis of thermal-conductivity data are due to Callaway.[25] Within the framework of the Callaway model one writes the total relaxation time as a sum of reciprocal relaxation times for the separate scattering processes:

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

There are as many τ_i as individual scattering mechanisms. Equation (2) is an equivalent way of stating that one adds scattering rates.

[25] J. Callaway, Phys. Rev. **113**, 1046 (1959).

Two central approximations underlying Eq. (1) are the assumption of isotropy, in converting a conductivity tensor to a conductivity scalar, and the introduction of the Debye density of states, in converting a summation over phonon states into an integral. The first approximation has been examined experimentally by Moss,[13] who found no anisotropy in the thermal conductivity for CaF_2. However, there is still some lack of legitimacy in using an "average" sound velocity since it is known that this quantity is anisotropic. To take account of this and other issues properly one should break the conductivity integral up into a longitudinal part and a transverse part, as was done by Holland[26] for silicon and germanium. Such an analysis would be desirable, but contains rather more parameters than we feel our data warrant.

Validity of the Debye approximation has been examined empirically by Pohl,[27] who found it to hold even in materials such as KBr, with a 2-to-1 mass ratio between the ions. It would seem to be valid as well for CaF_2, based on the very small gap between acoustic and optic branches of its dispersion curves.[28]

As was shown in Callaway's first paper on this subject,[25] Eq. (1) does not constitute a complete description of the problem of calculating the thermal conductivity. Even though normal-process phonon-phonon interactions cannot produce a thermal resistance when acting alone, one includes an N-process relaxation time in Eq. (2), and in turn in Eq. (1). This process would not seem to introduce serious errors as long as the N-process relaxation time is greater than the relaxation time due to resistive scattering processes. When this is not the case it is necessary to add a "correction term" to Eq. (1). The correction term is a rather formidable integral which can have a very large effect on the computed thermal conductivity. A rough rule of thumb for insulators is that one need never use the correction term if the peak conductivity is 10 W/cm deg or less, and need always use the correction term if the peak exceeds 100 in these units. CaF_2 is clearly in the range where one should begin to think about the correction term. We shall not use the term here because we feel that the full-blown Callaway model should only be used when one feels his pure-crystal data to be truly representative of the intrinsic phonon-scattering rates. We do not feel that the pure materials used in our experiments have high enough quality to warrant taking seriously any results obtained from the correction term. Some error will perforce be introduced in determining the impurity relaxation times if the correction term is ignored. Our experience in playing with these integrals suggests that the maximum error introduced in the impurity relaxation times, obtained by data fitting, will be a factor of 2. A 30% error seems more likely, and is no larger than

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[27] R. O. Pohl, Z. Physik **176**, 358 (1963).
[28] S. Ganesan and R. Srinivasan, Can. J. Phys. **40**, 74 (1962).

the uncertainty in determining the impurity relaxation rates by any method.

B. Pure Crystal

We shall discuss, and fit, only the data for pure and doped CaF_2. Inspection of Figs. 1–5 reveals this to be an obvious choice.

There are three dominant scattering mechanisms active in pure CaF_2. These are boundary scattering, phonon-phonon scattering, and defect scattering from the isotopes of Ca^{++} and the background chemical impurities.

Boundary scattering is well understood. At low enough temperatures the dominant scattering mechanism is the collisions of phonons with the crystal surfaces. As shown by Casimir,[29] the relaxation rate for this process is (for crystals of square cross section)

$$\tau_{\text{boundary}}^{-1}=v/1.12L, \tag{3}$$

where v is the phonon velocity and L is the width of the crystal. The "average" sound velocity for CaF_2, computed[14] from the low-temperature elastic constants, is 3.51×10^5 cm/sec. Our CaF_2 sample measured 0.51 cm in width, and thus one computes a boundary scattering rate of 6.14×10^5 sec^{-1}. However, as shown by Berman *et al.*,[30] crystals of finite length require that Eq. (3) be multiplied by a factor which depends on the ratio of sample width to length. For our sample size, 0.51 cm wide by 4.0 cm long, the correction factor is 1/0.8, which gives a boundary-scattering rate of

$$\tau_{\text{boundary theory}}^{-1}=7.68\times10^5 \text{ sec}^{-1}. \tag{4}$$

In practice, one treats the boundary-scattering rate as an adjustable parameter which is determined by fitting the data at low temperatures. The value needed was

$$\tau_{\text{boundary experiment}}^{-1}=4.50\times10^5 \text{ sec}^{-1}. \tag{5}$$

Comparison of Eqs. (3), (4), and (5) suggests that instead of the factor 1.12 in Eq. (3), one should have used 1.53. That is, the crystal could be thought to appear larger than it really was, at least to phonons. Alternatively, one might tamper with the average sound velocity. But only with the unphysical assumption that transverse phonons carry all the heat is it possible to make the theoretical and experimental values coincide.

Phonon-phonon interactions are rather more awkward to handle. As shown by Herring,[31] one would expect the following expressions in the *long-wavelength limit.*

$$\begin{aligned}\tau_{\text{normal process}}^{-1}&=B_1\omega^2T^3,\\ \tau_{\text{umklapp}}^{-1}&=B_2\omega^2T^3e^{-\theta/aT},\end{aligned} \tag{6}$$

where B_1, B_2, and a are constants and Θ is the Debye temperature. It must be emphasized that these expressions are only expected to be valid at long wavelengths (i.e., low temperatures). At high temperatures, when the specific-heat contribution to the conductivity integral becomes constant, Eqs. (6) do not give the expected T^{-1} dependence to the conductivity. In fact, it is usually not possible to fit data by using Eqs. (6) as written. It is generally necessary to change the form to ω^2T^2 or even ω^2T to effect a fit to pure-crystal data.[3,7,11–13] However, in the present case the most efficacious choice is Eqs. (6) as written without, however, using any N-process term. B_2 and a are determined by fitting the high-temperature data, and the values needed are

$$\begin{aligned}B_2&=3.6\times10^{-22} \text{ sec deg}^{-3},\\ a&=7.25.\end{aligned} \tag{7}$$

A Debye temperature of 500°K was used as an average between the low- and medium-temperature extremes.

Isotopes of the host material, and chemical background impurities which scatter through mass difference only, have a scattering rate as follows[2]:

$$\tau_{\text{mass difference}}^{-1}=\frac{a^3}{4\pi v^3}\omega^4\sum\left(\frac{m_i-\bar{m}}{m_{\text{Ca}^{++}}+2m_{\text{F}}}\right)^2 f_i. \tag{8}$$

This equation is written explicitly for CaF_2, and a^3 is the molecular volume (4.04×10^{-23} cm^3), f_i is the fractional concentration of isotopic or impurity mass m_i, $\bar{m}$ is the average mass of the species in question which is being replaced, $\bar{m}_{\text{Ca}}$ is the atomic mass of Ca^{++}, and $\bar{m}_{\text{F}}$ is the atomic mass of F^-. Ca^{++} has six isotopes which occur naturally, while F^- has one isotope. The solution to Eq. (8) is

$$\tau_{\text{CaF}_2,\text{ isotopes}}^{-1}=5.86\times10^{-45}\omega^4 \text{ sec}^{-1}. \tag{9}$$

In practice, one treats the coefficient in Eq. (9) as an adjustable parameter and determines the best value needed to fit the data. The conductivity near the peak is most sensitive to this value. Our empirically determined term is

$$\tau_{\text{isotopes, experiment}}^{-1}=1.30\times10^{-44}\omega^4 \text{ sec}^{-1}. \tag{10}$$

That is, we needed an additional 7.14×10^{-45} "isotope" scattering. This is presumably due to background chemical impurities. If these impurities had an average mass 50 amu different from Ca^{++} or F^-, then a concentration of 200 ppm would give the needed extra Rayleigh-like scattering. This calculation is based on the assumption that chemical impurities scatter phonons only through their mass difference (to be borne out below) and that heavy metal ions or halogen ions are the most likely impurities. The stated crystal purity is a factor of 10 below this concentration. However, 30 ppm of impurities as heavy as Pb would be enough to give the observed excess chemical scattering.

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TABLE I. Experimental and theoretical parameters for doped-crystal data.

System	Impurity concentration (cm^{-3})	Value of C in Eq. (11) needed to fit data (sec^{-1})	Value of D in Eq. (11) needed to fit data (sec^{-1})	Value of D computed from Eq. (8) (sec^{-1})	Column 5 divided by column 4
CaF_2: Sm^{++}	3×10^{19}	32.5×10^{5}	10.7×10^{-44}	17.9×10^{-44}	1.7
CaF_2: H^-	6.1×10^{20}	4.0×10^{5}	15.7×10^{-44}	9.74×10^{-44}	0.6
CaF_2: U^{3+}	1×10^{19}	14.5×10^{5}	7.9×10^{-44}	19.3×10^{-44}	2.4
				5.8×10^{-44}	0.7

Equations (5)–(7) and (10) were combined according to the prescription of Eq. (2) and substituted into Eq. (1). The resulting thermal-conductivity curve is shown as the solid line through the pure CaF_2 data in Figs. 1, 4, and 5. As can be seen, the fit to the data is acceptable but not compellingly excellent. Any attempts to improve the fit rest on the use of phonon-scattering mechanisms for which we have no experimental evidence. Our values for the boundary and Rayleigh scattering rates are close to those deduced by Agrawal and Verma[32] in attempting to fit Slack's CaF_2 data. However, they neglected to use an exponential umklapp term.

C. Doped Crystals

Again, we shall consider only the doped CaF_2 data. These are surprisingly easy to fit. A consideration of the regularities of the data suggests the needed terms. In Figs. 1, 4, and 5 one notes the doped-crystal data to be depressed below the pure-crystal data over the entire temperature range. Below the peak the conductivity of the doped crystals varies approximately as T^3, while above the peak the data are parallel to the pure-crystal data. These features suggest the use of an impurity relaxation time of the form

$$\tau_{\text{impurity}}^{-1}=C+D\omega^4. \tag{11}$$

That is, we assume first that two separate scattering mechanisms are present. One is characterized by a constant scattering rate while the other is characterized by a Rayleigh-like scattering. Equation (11) turns out to be enough to fit the doped-crystal curves. When Eq. (11) is added to the total relaxation rate used for the pure crystals, one computes the conductivity curves passing through the doped-crystal data in Figs. 1, 4, and 5. The fit is as good as, if not better than, that of the pure crystal itself. Values of C and D in Eq. (11) for the various impurities are listed in Table I.

It has not been necessary to invoke any relaxation rates of a resonant character in order to explain the data. Thus, we do not discuss such terms here.

IV. DISCUSSION

We discuss first the awkward part of the data—the low-temperature depression. What could cause this frequency-independent scattering? The first answer which one might give would be precipitates. Phonon scattering from precipitates is reasonably well understood.[33] For a precipitate of diameter d, when one is in the region $qd\gg1$ (where $q=2\pi/\lambda$ is the phonon wave vector) the scattering cross section leads to a thermal conductivity which varies as T^3. This is the temperature dependence of our doped-crystal data below the peak. Since one sees no deviation from T^3 behavior down to 0.32°K, the $qd\gg1$ criterion leads one to conclude that any precipitates are 500–1000 Å or so in size.

The data from Ref. 33 on the strength of precipitate scattering can be combined with the values of C in Table I to obtain an estimate of the concentration of precipitates. Values range from 1×10^{12} cm^{-3} for H^- in CaF_2 to 6×10^{12} cm^{-3} for U^{3+} in CaF_2. These concentrations are marginal for detection by Rayleigh scattering of light. Unfortunately, both the Sm^{2+}- and U^{3+}-doped crystals have optical-absorption bands which span most of the visible region. It is thus not possible to attempt a Rayleigh-scattering study using white light or the light from a laser in the visible region. We did attempt to study the H^--doped CaF_2 with the 6328 Å line of a He-Ne laser. A good deal of light scattering did occur, but it is not clear whether this is Rayleigh scattering from precipitates, or scattering from surface damage produced in the additive coloration. What is clear is that all three doped-crystal systems are near their region of maximum solubility and some precipitation is to be expected. True, we can produce H^- concentrations more than a factor of 10 higher than used here. But in those crystals the scattering of He-Ne laser light is fantastic.

One might wonder whether the Sm^{++}- or U^{3+}-doped crystals would have any magnetic scattering of phonons as the cause of their low-temperature depressions. Sm^{++} is isoelectronic with Eu^{3+}, and thus is a non-Kramers ion. In the cubic field of CaF_2 the Sm^{++} ion should have a ground state which is a singlet of $^7F_0$ character. The optical data[16] reinforce this view and suggest that the first excited state, a $^7F_1$ state, lies 263 cm^{-1} above the ground state. 263 cm^{-1} is equivalent in temperature to 375°K. Phonons of this energy would be the dominant heat carriers near 375°K/3.83, or 100°K. No effect is observed there and, in any case, this is rather high for the sub-1°K effects we are after. Since the ground state of Sm^{++} is a singlet there is no zero-field strain splitting

[32] B. K. Agrawal and G. S. Verma, Physica **28**, 599 (1962).

[33] J. W. Schwartz and C. T. Walker, Phys. Rev. **155**, 969 (1967).

to bother us, and we conclude that magnetic effects are unlikely for Sm^{++}.

U^{3+} is a Kramers ion and, in its tetragonal environment, the $^4I_{9/2}$ ground state is split into a number of Kramers doublets. There must be five such doublets. It is known[24] that the sequence of five doublets is at least 609 cm^{-1} wide. The doublets are not expected to be uniformly spaced at 609/4, or 152 cm^{-1}, but rather the bottom end should be compressed. It is possible that the two lowest doublets are separated by as little as 40 or 50 cm^{-1}. This is equivalent in temperature to 55–70°K, which means any effect would be observed at about 15–20°K, far too high for the sub-1°K effects we are discussing. Neither is there any evidence near 15–20°K for a resonant phonon absorption between doublets. However, since the ground state for U^{3+} is a Kramers doublet, it is possible to evaluate the coupling between magnetic levels and phonons directly. The average g value[21] for U^{3+} in CaF_2 is about 2.7, and in a field of 17.5 kG the Kramers doublet should split by about 2.3 cm^{-1}. This splitting should be evident in thermal conductivity near 0.6°K, if phonons couple to the magnetic levels. We have measured the thermal conductivity of CaF_2 containing U^{3+} in a field of 17.5 kG between 0.40 and 1.2°K. There is no change from the zero-field conductivity values.

We conclude that magnetic scattering of phonons cannot be invoked for the low-temperature Sm^{++} or U^{3+} data.

We turn now to the second half of Eq. (11), the Rayleigh scattering produced by all three impurity ions. We have used Eq. (8) to calculate the strength of the Rayleigh scattering expected from the mass difference between Sm^{++} or U^{3+} and Ca^{++}, and between H^- and F^- at our concentrations. The results are tabulated in Table I. Two separate values are given for U^{3+}. The higher value was computed for U^{3+} substituting for Ca^{++} in a single molecule, ignoring the interstitial fluorine ion. The lower value was computed with U^{3+} in one Ca^{++} ion site and the interstitial F^- added to a second CaF_2 molecule. When one considers that the value of D from Eq. (11), needed to fit the data, is at best determined to within 30%, then column 6 of Table I becomes quite interesting.

With a realistic model of the U^{3+}-F^- combination, the scattering is essentially explained by mass-difference scattering alone. The H^- impurity in CaF_2 is also almost completely explained by mass-difference scattering alone. The Sm^{++} impurity is seen to scatter *more weakly* than mass-difference scattering alone. This situation is reminiscent of the interference between mass-difference and force-constant difference scatterings explained by Krumhansl and Matthew.[34] However, Sm^{++} is a larger ion than the Ca^{++} which it replaces, so it is likely to have a positive change in force constants. It obviously has a positive change in mass, so an interference effect would seem to be ruled out. Samarium can also enter CaF_2 as Sm^{3+}, but exact concentrations are difficult to determine experimentally. Inclusion of Sm^{3+}, with its accompanying interstitial, into the Rayleigh calculation would bring the theoretical value closer to the experimental.

Thus, to a very good first approximation, including all the uncertainties in our analysis, it would seem that all three impurities scatter phonons only through their mass difference. We shall not attempt a calculation of force-constant change scattering since it would seem to be so unnecessary.

The situation in CaF_2, then, is very different from the case of alkali halides. The rules of thumb acquired so laboriously there would not appear to be transferable *in toto*. In particular, no resonant effects are seen, and, since only mass-difference scattering seems to appear, phonon scattering by point defects is very weak. We would note that mass-difference-only scattering explains heavy-mass data in alkali halides,[9] although it does not explain light-mass data. However, in Baumann and Pohl's work[9] it is the resonances which dominate.

This result leads to some interesting conclusions. Na^+ and Li^+ ions in CaF_2, SrF_2, and BaF_2 were seen not to display any effects on heat conductivity, at the concentration studied. Neither did H^- in SrF_2 and BaF_2 display point-defect scattering. The low-temperature depressions there are probably also due to precipitates, as in CaF_2. Now we see why. The scattering is so weak that concentrations in the 10^{18}-cm^{-3} range, with impurity masses differing little from the host mass, will not be observed. From the data in Table I, one can estimate that a concentration of 1×10^{20}-cm^{-3} Li^+ or 5×10^{20}-cm^{-3} Na^+ would be necessary for an easily identifiable effect to occur.

Equally interesting is a consideration of the relatively low-peak thermal conductivity of pure SrF_2 and BaF_2 (in comparison with CaF_2). The coefficient of the Rayleigh term for the natural-isotope scattering in SrF_2 and BaF_2 is about the same size as that for CaF_2. Further, the conductivity at higher temperatures is not much different from that of CaF_2. One is tempted to argue that the reduced peak and low-temperature conductivity is caused by background chemical impurities. If we use the point-defect strengths deduced for CaF_2, and further assume that "ideally pure" SrF_2 and BaF_2 would have peak conductivities near that of CaF_2, then one can estimate the background impurity level necessary to give the observed peak values in SrF_2 and BaF_2. The result is about 3000 ppm of impurities with average mass of 100 amu, or 300 ppm of atoms as heavy as uranium. It would be hard to miss these amounts in analyses.

Alternatively, one might argue that the SrF_2 and BaF_2 crystals are badly strained, with the lower peak conductivity and lack of T^3 behavior at low tempera-

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

tures being due to dislocation scattering. Moss's values for the scattering strength of dislocations in CaF_2 [13] can be used to estimate the dislocation density necessary to produce the observed conductivity. The value needed is 10^7 cm^{-2}. This density requires that the crystals at some stage of their existence were compressed by about 4%.

A combination of weak point-defect scattering, lack of resonant effects due to a broad spectrum of point defects, and relatively bad thermal conductivity in the pure materials suggests that the fluorite structure requires some further study. At present it is rather different from alkali halides.

V. SUMMARY

(1) Thermal-conductivity measurements have been made on CaF_2, SrF_2, and BaF_2, both in the pure state and when doped with a wide variety of point defects.

(2) The conductivity of pure SrF_2 and BaF_2 was lower than might be expected, but is difficult to understand in terms of limitations due to background chemical impurities.

(3) Li^+ and Na^+ impurities in all three hosts were seen to have no influence on the thermal conductivity. This is probably due to the low concentration (10^{18} cm^{-3}) of impurity. Failure to observe any effect at this concentration suggests that point-defect scattering is weak in these host materials.

(4) H^-, Sm^{++}, and U^{3+} point defects in CaF_2 were seen to scatter phonons by mass-difference scattering alone. No phonon resonances were observed, even at concentrations exceeding 10^{20} cm^{-3}. The strength of the scattering confirms the conclusion in point (3) above.

(5) H^-, Sm^{++}, and U^{3+} point defects in CaF_2 were also seen to produce a low-temperature thermal conductivity varying as T^3. This effect is tentatively ascribed to scattering by precipitates. Scattering of phonons from magnetic states was ruled out.

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Lifetime Studies on the Relaxed Excited State of Color Centers*

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The improved precision and accuracy of lifetime measurements allowed by the technique of detecting the single-photon delay distribution has been utilized in lifetime studies on F, M, and R centers in alkali halides. $\tau_R(F)$, the F-center radiative lifetime, was measured in KCl at 80°K and at different F-center concentrations. Even though the luminescence quantum yield η_R varies with concentration, $\tau_R(F)$ is shown to remain constant. This fact has been explained in terms of a tunneling process among nonrandomly distributed F centers. The radiative lifetime of excited M centers has been measured at 80°K in different alkali halides (in nsec): $\tau_R(M)=28\pm1$ in KCl; 26.2 ± 1 in NaCl; 17.2 ± 1 in LiF; 12.3 ± 1 in NaF. From the temperature behavior of $\tau(M)$ in KCl, the relaxed excited-state deexcitation energy ΔE_d has been evaluated: $\Delta E_d=0.21\pm0.01$ eV. The observed values of $\tau_R(M)$ and ΔE_d are discussed.

1. INTRODUCTION

SINCE Swank and Brown's early work[1] on the relaxed excited-state radiative lifetime $\tau_R(F)$, of F centers, considerable attention—both theoretical and experimental—has been devoted to certain problems common to F centers and to their aggregates M and R centers. These problems, which also constitute the general subject of the present paper, include (i) the exact energy-level scheme in the relaxed situation; (ii) the symmetry of the levels among which the emission transitions take place; (iii) the magnitude of τ_R and the influence on it of the host matrix and local relaxation; (iv) the possible influence of perturbations, such as foreign ions, concentration, and external fields. Our knowledge of the relaxed excited states of the F center and its aggregates is still unsatisfactory and not yet substantiated by conclusive statements. For instance, the proposals that have been made to explain the

* A preliminary report on this work has been given at the 1968 International Symposium on Color Centers in Alkali Halides, Rome (unpublished).

[1] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).