

where the integrand is not an analytic function. A little analysis immediately shows that (I4) can be rewritten

$$I = \int_{\Gamma} \frac{(1-z^2)(\sin Bz)}{(A^2+z^2)^2} \ln\left(\frac{z+1}{z-1}\right) dz, \quad (\text{A5})$$

where the contour  $\Gamma$  runs along the real axis from  $-\infty$  to  $\infty$  except in the region of a cut lying on the real axis from  $-1$  to  $1$ . The contour  $\Gamma$  may be taken either just

above or just below the cut. The next step is to write the  $(\sin Bz)$  in terms of exponentials and to write  $I$  as the sum of two integrals, where the contours for both integrals must be taken on the same side of the cut. By the use of Jordan's lemma and deformations of the contours of integration, the integral in (A5) is reduced to the evaluation of two residues and an integral around the cut. The latter integral is the source of the integral appearing in the final form (A3), and the residues are readily evaluated. This completes the outline.

## Thermal Conductivity of Some Alkali Halides Containing $F$ Centers\*

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Thermal conductivity measurements are used to study phonon scattering by  $F$  centers in NaF, KCl, KBr, and KI.  $F$  centers were produced by additive coloration and by  $x$  and  $\gamma$  irradiation. The total effect on the thermal conductivity is seen to be different for the two methods of preparation. The additively colored data display two features: a low-temperature depression due to phonon scattering by colloids and quench-induced defects, and a high-temperature effect due to phonon scattering by  $F$  centers. The irradiated samples also display two features, a high-temperature effect due to  $F$  centers and a different low-temperature depression of unknown origin. The high-temperature data in irradiated samples can be explained if one assumes that  $F$  centers are formed in regions of high concentration during irradiation. Several mechanisms are discussed for the low-temperature depression in irradiated crystals, including interstitials and the effect of dislocations on  $F$ -center formation. The  $F$  center is shown to produce quasilocalized impurity modes with frequencies of the order of  $10^{13}$  sec<sup>-1</sup>, and is seen to scatter phonons elastically primarily through its strain field.

### I. INTRODUCTION

AS was first demonstrated by Berman<sup>1</sup> low-temperature thermal conductivity measurements provide a sensitive method for investigating the scattering of phonons by lattice defects. In the decade since Berman's original work the technique has been applied to study many defect systems, running the gamut from simple isotopic impurities,<sup>2-4</sup> substitutional chemical impurities,<sup>5-8</sup> molecular impurities,<sup>9</sup> dislocations,<sup>10</sup> colloids<sup>11</sup>

up to such esoteric studies as phonon-spin interactions<sup>12</sup> and acoustic phonon-optic phonon interactions.<sup>13</sup> During this time there has been continued interest in the scattering of phonons by point defects, where "point" has the usual meaning of an object whose size is of atomic dimensions. The early interest in point defects arose from the fact that the initial theories<sup>14,15</sup> predicted an especially simple scattering law for point defects, namely a Rayleigh-type law. The more recent interest arises from the experimental<sup>16</sup> and theoretical<sup>17-19</sup> evidence for a resonant phonon scattering by quasilocalized impurity modes in addition to the elastic Rayleigh scattering.

The  $F$  center, an electron occupying a negative ion vacancy, satisfies all the criteria for a point defect since its mass is certainly different from the mass of

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<sup>1</sup> R. Berman, Proc. Roy. Soc. (London) **A208**, 90 (1951); Suppl. Phil. Mag. **2**, 103 (1953).

<sup>2</sup> T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

<sup>3</sup> R. Berman, P. T. Nettley, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) **A253**, 403 (1959).

<sup>4</sup> E. J. Walker and H. A. Fairbank, Phys. Rev. **118**, 913 (1960).

<sup>5</sup> G. A. Slack, Phys. Rev. **105**, 832 (1957).

<sup>6</sup> W. S. Williams, Phys. Rev. **119**, 1021 (1960).

<sup>7</sup> B. Abeles, D. S. Beers, G. D. Cody, J. P. Dismukes, Phys. Rev. **125**, 44 (1962).

<sup>8</sup> M. V. Klein, Phys. Rev. **123**, 1977 (1961).

<sup>9</sup> R. O. Pohl, Phys. Rev. Letters **8**, 481 (1962).

<sup>10</sup> R. L. Sproull, M. Moss, H. Weinstock, J. Appl. Phys. **30**, 334 (1959).

<sup>11</sup> J. M. Worlock, Ph.D. thesis, Cornell University, 1962 (unpublished).

<sup>12</sup> I. P. Morton and H. M. Rosenberg, Phys. Rev. Letters **8**, 200 (1962); R. Berman, J. C. F. Brock, and D. J. Huntley, Phys. Letters **3**, 310 (1963).

<sup>13</sup> A. J. Sievers, III, Bull. Am. Phys. Soc. **8**, 208 (1963).

<sup>14</sup> P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

<sup>15</sup> P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

<sup>16</sup> C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1428 (1963).

<sup>17</sup> M. Wagner, Phys. Rev. **131**, 1443 (1963).

<sup>18</sup> J. A. Krumhansl, Bull. Am. Phys. Soc. **8**, 207 (1963).

<sup>19</sup> M. V. Klein, Bull. Am. Phys. Soc. **8**, 207 (1963). S. Takeno, Progr. Theoret. Phys. (Kyoto) **29**, 191 (1963); **29**, 328 (1963).

the ion it replaces, and its different "ionic radius" causes a strain field to be set up around it. In addition, it is a system which is relatively easy to prepare and can be prepared in more than one way. There have been only four studies of the low-temperature thermal conductivity of alkali halides containing  $F$  centers; a qualitative study by Cohen<sup>20</sup> on neutron and  $\gamma$ -irradiated materials and the quantitative studies by Pohl<sup>21</sup> of room temperature x- and  $\gamma$ -irradiated LiF, by Gebhardt<sup>22</sup> of helium temperature x-irradiated KCl and KBr, and by Devyatkova and Stilbans.<sup>22</sup> None of these studies has shown an effect which even remotely resembles the predicted effect of  $F$  centers. This in itself is sufficient reason for further studies, since if the earlier work is shown to be due solely to  $F$  centers then it is clear that the  $F$  center is an unusual "point defect" indeed.

Section II of this paper will detail the samples used in these experiments. The experimental results for crystals which have been additively colored and for crystals which have been x and  $\gamma$  irradiated at or above room temperature will be given in Sec. III. It will be seen that the results for the two methods do not agree. In Sec. IV the scattering laws describing the data will be determined, and it will be seen that at least two separate laws are necessary for each method of sample preparation. The results will be discussed in Sec. V where it will be seen that additive coloration or very light x irradiation come closest to demonstrating the behavior of truly random  $F$  centers only. The results for the irradiated specimens, including Pohl's re-evaluated LiF data, will be shown to be in quantitative agreement. In particular, it will be shown that the dramatic low-temperature depression of the conductivity in irradiated samples is not due to  $F$  centers, but is due to other damage produced during irradiation. Gebhardt's helium-temperature irradiation data will be shown to be in qualitative agreement.

## II. SAMPLES

A total of seven samples was investigated, three of KCl, two of NaF, one each of KBr and KI. The KCl and KBr samples were grown at Cornell using the Kyropolous<sup>23</sup> technique. The starting material was  $\text{Cl}_2$  treated KCl powder and  $\text{Br}_2$  treated KBr powder, and the crystals were grown under an inert argon atmosphere. The NaF and KI samples were purchased from the Harshaw Chemical Company. One sample of NaF was purchased in December 1961, and the second in July 1962, while the KI was purchased in October 1962. All crystals were used either as grown or as received with no further heat treatment.

<sup>20</sup> A. F. Cohen, *Proceedings of the Fifth International Conference on Low-Temperature Physics* (University of Wisconsin Press, Madison, 1958), p. 385.

<sup>21</sup> R. O. Pohl, *Phys. Rev.* **118**, 1499 (1960).

<sup>22</sup> W. Gebhardt, *J. Phys. Chem. Solids* **23**, 1123 (1962); E. D. Devyatkova, L. S. Stilbans, *Zh. Tekhn. Fiz.* **22**, 968 (1952).

<sup>23</sup> S. Kyropolous, *Z. Anorg. u. Allgem. Chem.* **154**, 308 (1926).

Optical absorption measurements on the pure samples were made between  $15\ \mu$  (the long-wavelength end of the standard interchange for the Beckman Model IR-7) and either  $1950\ \text{\AA}$  (the short-wavelength end of the Cary Model 14) or the exciton edge. There were no absorption bands (absorption constant less than  $0.001\ \text{cm}^{-1}$ ) over this entire range except for rudimentary ultraviolet "OH" bands in KCl, KBr, KI. The absorption constants of these OH bands were about  $0.1\ \text{cm}^{-1}$  for all three. No OH band could be detected in the NaF samples since the band lies beyond the range of the Cary Model 14.

All samples used measured  $5 \times 5 \times 40\ \text{mm}$ , with all faces being cleavage planes. The actual samples colored by additive coloration were slightly larger than  $5 \times 5\ \text{mm}$  in cross section. The surfaces are damaged in the coloration process and it is necessary to color a larger sample so that the desired size is left after abrading away the surface damage. All samples were sandblasted to insure diffuse phonon scattering at the crystal boundaries.

After coloration all samples were handled only under the light from a Sylvania 25 W "Ruby-Red" lamp. The efficacy of this treatment in the case of KI is questionable since the short-wavelength cutoff of the lamp is about  $6800\ \text{\AA}$  and the peak wavelength of the  $F$  band in KI is  $6890\ \text{\AA}$ . However, there was no other alternative since there are absorption bands in the blue for all x-rayed samples, and since it has not proved possible to mount specimens in the conductivity apparatus under conditions of complete darkness.

The concentration of  $F$  and other centers was determined optically (using the Cary Model 14). For the x- and  $\gamma$ -rayed samples the absorption measurements were made on thin slices of crystal which had the same radiative and thermal history as the conductivity samples. At the conclusion of a sequence of irradiations the conductivity specimen was cleaved into thin slices and checked against the absorption specimens. No discrepancy was found. The additively colored samples were optically checked directly after the conductivity runs. The  $F$ -center concentration for all samples was calculated using Dexter's<sup>24</sup> correction of Smakula's formula, assuming in all cases an oscillator strength of 1.0.

## III. EXPERIMENT

The technique for measuring low-temperature thermal conductivity has been described in great detail elsewhere,<sup>5,8</sup> and will not be repeated here. The only innovation in our measurements was the use in the later stages of a Minneapolis-Honeywell Type II germanium resistor as a primary temperature standard over the range of 1 to  $77^\circ\text{K}$ . Over a period of 20 thermal conductivity runs it has been found to be reproducible to within the uncertainty of measuring the temperature by the more usual methods. The simplicity of the

<sup>24</sup> D. Dexter, *Phys. Rev.* **101**, 48 (1956).

germanium thermometer in contrast to the cumbersome gas thermometer is obvious. Additionally it eliminates the necessity of stopping periodically while pumping on the helium bath in order to calibrate the carbon thermometers.

### A. Additive Coloration Experiments

Two samples of KCl were colored additively using a modification of the technique detailed by van Doorn.<sup>25</sup> The crystals were colored at 700°C. One crystal was cooled to room temperature by removing it from the oven and holding it in front of a high-speed air blower. In 30 sec the crystal was cool to the touch. This quench treatment has proved to be the most rigorous which can be given a KCl crystal of the desired size without causing the crystal either to shatter on cooling or crack in the cryostat. Even this method was successful only once in thirteen attempts. The thermal conductivity results for this crystal are given in Fig. 1 along with the results for pure KCl. The solid line through the pure crystal data is a theoretical curve calculated by a method to be detailed later. The solid line through the data for the colored crystal is also a theoretical curve, with the low-temperature portion of this curve being calculated from a scattering law characterized by a phonon relaxation time which is *frequency-independent*. We note also the presence of a "dip" in the conductivity around 17°K. This dip is barely discernible in small scale graphs such as Fig. 1. However, it is quite clear on larger scale curves particularly if one compares the data with the expected Rayleigh-like behavior.

The second additively colored crystal was cooled by removing the nickel coloring bomb from the oven and

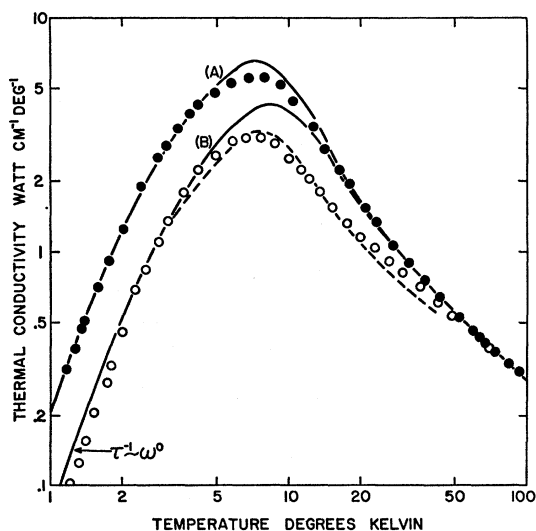


FIG. 1. Thermal conductivity of additively colored KCl; (A) pure KCl; (B),  $N_{V,F} = 9.3 \times 10^{17} \text{ cm}^{-3}$ , quenched from 700°C in 30 sec. Solid and dashed lines are theoretical curves.

<sup>25</sup> C. Z. van Doorn, Rev. Sci. Instr. **32**, 755 (1961).

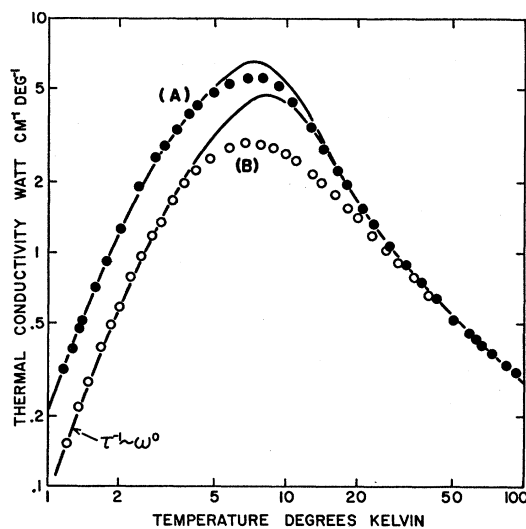


FIG. 2. Thermal conductivity of additively colored KCl; (A) pure KCl; (B)  $N_{V,F} = 1.1 \times 10^{18} \text{ cm}^{-3}$ , slow cooled from 700°C. Solid lines are theoretical curves.

letting it sit in the room. Using this method it took about 10 min for the sample to reach room temperature. The data for this crystal are given in Fig. 2 where the solid lines through the data are again theoretical curves. The low-temperature part of the theoretical curve through the colored sample data is again calculated using a frequency-independent scattering law.

For both crystals the optical absorption measurements showed that the  $F$ -center concentration was about 20% higher near the surface than in the middle of the sample. The concentrations quoted are averages of the surface and center values. The optical absorption curve for the slowly cooled sample is given in Fig. 3, curve A. The small band at 1.67 eV has been identified by Scott and Smith<sup>26</sup> as a colloid band. The optical

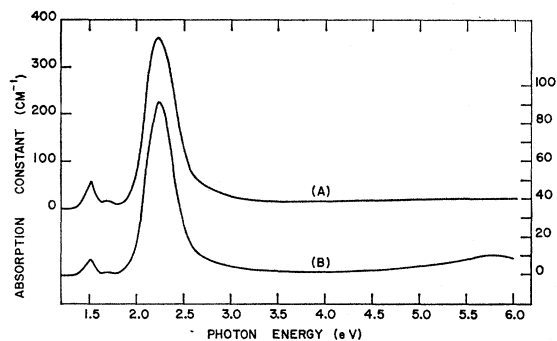


FIG. 3. Optical absorption curves for KCl with  $F$  centers; (A) additively colored and slowly cooled from 700°C,  $N_{V,F} = 1.1 \times 10^{18} \text{ cm}^{-3}$ ; (B) x rayed at 310°K,  $N_{V,F} = 2.2 \times 10^{17} \text{ cm}^{-3}$ . Both curves measured at room temperature. Left scale is for curve (A), right scale for curve (B). In both cases there are small bands at about 1.7 eV. Detailed examination of large scale graphs shows these bands to have different shapes and peak wavelengths. The bands are identified as the colloid band in the additively colored sample and as one of the  $R$  bands in the x-rayed sample.

<sup>26</sup> A. B. Scott, W. A. Smith, Phys. Rev. **83**, 982 (1951).

TABLE I. Irradiation conditions for x- and  $\gamma$ -irradiated samples.

Specimen	Concentration of $F$ centers $N_v(\text{cm}^{-3})$	$F$ -Absorption constant		Mode of production	Irradiation temperature ( $^{\circ}\text{C}$ )	Compton cross section <sup>a</sup>	
		$M$ -Absorption constant $k_F/k_m$				Photoelectric cross section $\sigma_e/\sigma_P$	
KCl	$3.7 \times 10^{16}$	15.5		68 min at 70 keV $\frac{1}{16}$ in. Al shield	35		0.9
KCl	$9.1 \times 10^{16}$	13.2		100 more min at 70 keV	35		0.9
KCl	$22.0 \times 10^{16}$	11.0		24 more h at 70 keV	35		0.9
KCl	$70.0 \times 10^{16}$	9.4		Additional $10^8$ R in $\text{Co}^{60}$ source <sup>b</sup>			> 500
KBr	$1.7 \times 10^{17}$	25.8		22 h at $2 \times 10^6$ R/h $\text{Co}^{60}$ source <sup>c</sup>	35		86
KBr	$4.7 \times 10^{17}$	17.9		120 more h $\text{Co}^{60}$ $\gamma$ ray <sup>c</sup>	55		86
KI	$2.2 \times 10^{17}$	33.4		22 h at $2 \times 10^6$ R/h $\text{Co}^{60}$ source <sup>c</sup>	35		17
KI	$4.0 \times 10^{17}$	22.0		120 more h $\text{Co}^{60}$ $\gamma$ ray <sup>c</sup>	55		17
NaF # 1	$1.2 \times 10^{16}$	19.7		11 min at 130 keV $\frac{1}{16}$ in. Al shield	35		74
NaF # 1	$2.0 \times 10^{16}$	12.1		24 more min at 130 keV	35		74
NaF # 1	$5.7 \times 10^{16}$	4.1		24 more h at 130 keV	35		74
NaF # 2	$5.4 \times 10^{16}$	7.0		3 h at 120 keV $\frac{1}{16}$ in. Al shield	35		57
NaF # 2	$9.6 \times 10^{16}$	3.9		72 more h at 120 keV	35		57
LiF <sup>d</sup>	$4.2 \times 10^{17}$	26.3		20.5 h at 60 keV 2 mm Al shield	30		6.7
LiF <sup>d</sup>	$7.1 \times 10^{17}$	17.8		38.5 more h at 60 keV	30		6.7
LiF <sup>d</sup>	$20 \times 10^{17}$	5.1		Additional $2 \times 10^7$ R in $\text{Co}^{60}$ $\gamma$ source			> 500

<sup>a</sup> See Ref. 41.

<sup>b</sup> Irradiated by Dr. James H. Schulman of the U. S. Naval Research Laboratory.

<sup>c</sup> Irradiated in Cornell  $\text{Co}^{60}$  facility operated by Professor Robert von Berg.

<sup>d</sup> Data kindly supplied by Professor R. O. Pohl.

absorption of the rapidly quenched sample is the same except that no colloid band is seen.

The data from the two samples may be compared as follows. The low-temperature region ( $T < 4^{\circ}\text{K}$ ) is characterized by a frequency-independent scattering law. The data for both crystals fall considerably below the calculated curves around and above the conductivity

maximum. The slowly cooled sample shows no "dip" in the conductivity while the rapidly quenched sample does show a dip. This dip is stable: after leaving the sample in the dark for two weeks at room temperature a remeasurement of the conductivity gave again curve (B) of Fig. 1.

### B. x- and $\gamma$ -Irradiation Experiments

One sample each of KCl, KBr, and KI and two samples of NaF were colored by ionizing radiation. The x-irradiated samples were colored using a Müller MG 150 x-ray machine. This is a high-intensity unit allowing, for example, 12 mA tube current at 150 keV and 22 mA at 70 keV. This high intensity is necessary to produce the deep, uniform body coloration desired in reasonable irradiation times. The samples were x rayed through a  $\frac{1}{16}$ -in. aluminum filter to prevent heavy surface coloration. The samples were x rayed through their short dimensions with the x-ray beam illuminating each side for  $\frac{1}{4}$  of the time. A very uniform coloration resulted from this procedure with the  $F$ -center concentration in the center of the sample being only 10% less than at the surface. These precautions were not necessary in the  $\gamma$ -irradiation parts of the experiment since the radiation is so penetrating. The conditions of irradiation for all samples are listed in Table I, with Pohl's original work included for completeness.

The thermal conductivity results for successive irradiations of KCl are given in Fig. 4. We note five significant features. (1) Curve (B) was obtained for two different concentrations of  $F$  centers. Thus, at least in KCl, the low-temperature depression in the early stages is independent of the fact that the crystal contains  $F$  centers.

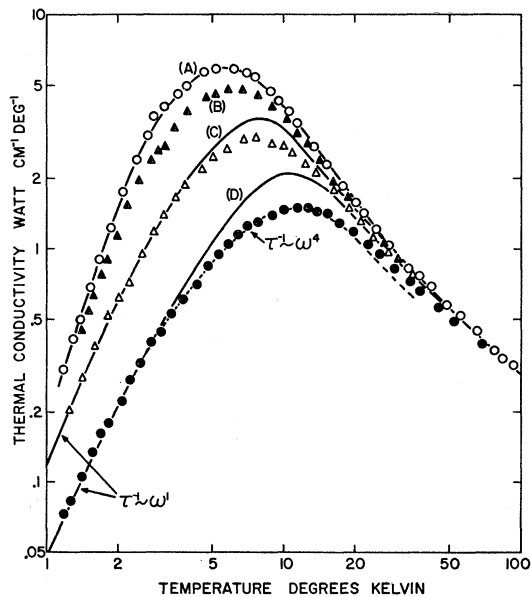


FIG. 4. Thermal conductivity of KCl after successive irradiations; (A) pure KCl; (B) after x raying at 70 keV,  $N_{v,F} = 3.7 \times 10^{16}$  and  $9.1 \times 10^{16} \text{ cm}^{-3}$ ; (C)  $N_{v,F} = 2.2 \times 10^{17}$ ; (D) after  $\text{Co}^{60}$  irradiation,  $N_{v,F} = 7.0 \times 10^{17}$ . Solid lines through curves (C) and (D) are theoretical curves.

(2) The solid curve through the pure crystal data is not a theoretical curve, while the solid curves through the data for the two highest  $F$ -center concentrations are theoretical curves. In this case, however, the theoretical curves are calculated using a relaxation time inversely proportional to the *first* power of the phonon frequency.

(3) The data around the conductivity maxima fall below the calculated curves, with the deviation being greater for higher  $F$ -center concentration. (4) There is no "dip" in the conductivity. (5) The low-temperature depression for the irradiated sample is greater than for the same concentration of  $F$  centers produced additively.

The optical absorption curve for x-rayed KCl is shown in Fig. 3, curve (B). We note the presence of an  $M$  band, a barely discernible  $R$  band, the  $F$  band, and a band at about 5.8 eV. The latter band, known previously as the  $V_3$  band, has recently been shown by Lüty<sup>27</sup> to be in fact the  $U$  band, produced when the ionizing radiation splits up  $\text{OH}^-$  impurities leaving  $U$  centers behind. It was thus necessary to correct the measured conductivity curves for the  $U$  centers' contribution, with the corrected curves being the ones presented here. The influence of  $U$  centers on the thermal conductivity of several alkali halides has been measured and will be published separately. The correction is small. The crystal corresponding to Fig. 3, curve (B) contains  $2.2 \times 10^{17} \text{ cm}^{-3}$   $F$  centers and  $3.6 \times 10^{16} \text{ cm}^{-3}$   $U$  centers. The correction to the conductivity turns out to be about 5% for KCl, 10% for KI and 20% for KBr. Comparison of curves (A) and (B) in Fig. 3 discloses nothing to account for the profound differences in the conductivity results shown in Figs. 1 and 4.

The conductivity results for irradiated KBr are given in Fig. 5. Comments 2, 3, and 4 made for KCl also apply for the KBr data. The KI results are shown in Fig. 6. The same comments pertain again, except that the low-temperature scattering law seems to be intermediate between frequency independent and frequency to the first power. This point will be considered later.

There are two sets of NaF data. The results for successive irradiations of the first sample (hereafter referred to as NaF #1) are given in Fig. 7 and the results for NaF #2 are given in Fig. 8. We notice again a low-temperature depression describable by a relaxation time inversely proportional to the first power of the phonon frequency, with the effect being stronger in NaF #2 than in NaF #1. Again there is a deviation around the conductivity maximum, with a small "dip" occurring at about 17°K for  $F$ -center concentrations of

<sup>27</sup> F. Lüty, J. Phys. Chem. Solids **23**, 677 (1962); Lüty's observations have been verified in this laboratory. We find that the 5.8 eV band in KCl is not repeatable from crystal to crystal, being in fact absent in one very pure crystal which was  $\gamma$  rayed. The parameter which seems to be most intimately connected with the height of the 5.8 eV band is the irradiation time and not the  $F$  concentration. This observation is also true for the analogous bands at 2270 Å in KBr and 2440 Å in KI. The band in KI has been measured down to 10°K and shifts with temperature in exactly the same manner as does the  $U$  band.

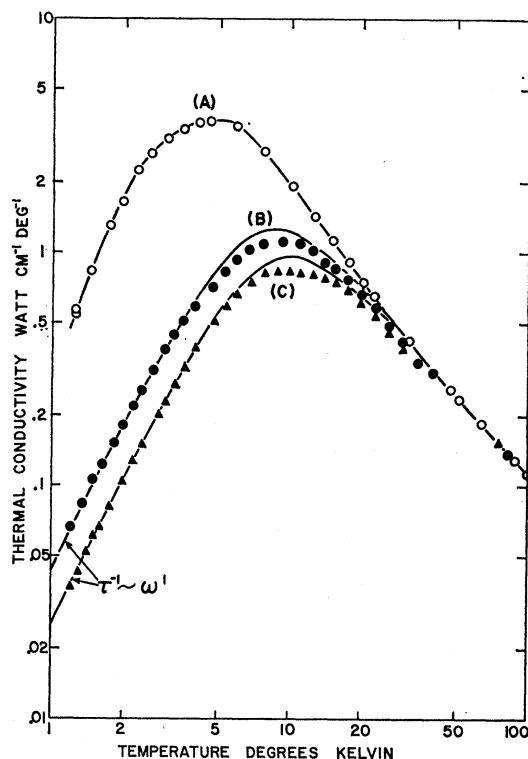


Fig. 5. Thermal conductivity of KBr after successive  $\text{Co}^{60}$  irradiations; (A) pure KBr; (B)  $N_{V,F} = 1.7 \times 10^{17} \text{ cm}^{-3}$ ; (C)  $N_{V,F} = 4.7 \times 10^{17}$ . Solid lines through curves (B) and (C) are theoretical curves.

about  $5 \times 10^{16} \text{ cm}^{-3}$ . Again the dip is stable. Curve (D) of Fig. 7 was measured three times, once after warming to room temperature for several weeks, and the same

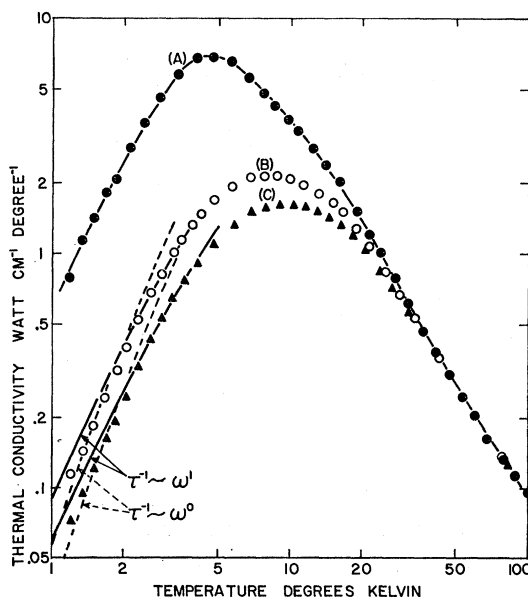


Fig. 6. Thermal conductivity of KI after successive  $\text{Co}^{60}$  irradiations; (A) pure KI; (B)  $N_{V,F} = 2.2 \times 10^{17} \text{ cm}^{-3}$ ; (C)  $N_{V,F} = 4.0 \times 10^{17}$ . Solid and dashed lines through curves (B) and (C) are theoretical curves.

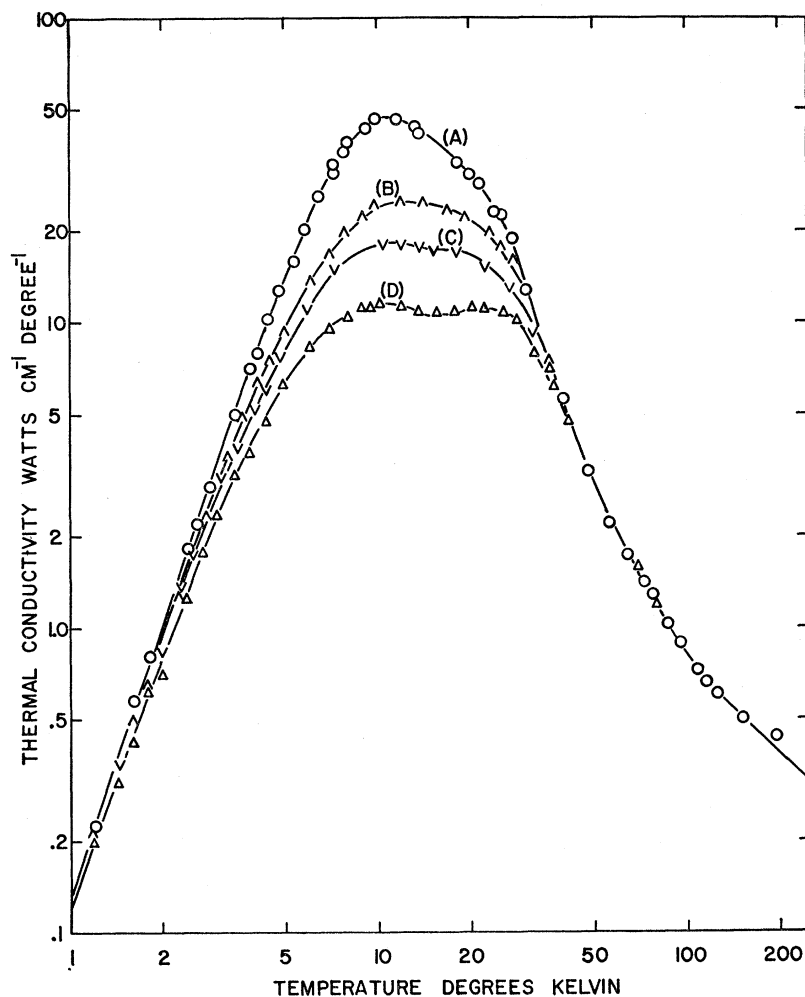


FIG. 7. Thermal conductivity of NaF #1 after successive x irradiations at 130 keV; (A) pure NaF; (B)  $N_{V,F} = 1.2 \times 10^{16} \text{ cm}^{-3}$ ; (C)  $N_{V,F} = 2.0 \times 10^{16}$ ; (D)  $N_{V,F} = 5.7 \times 10^{16}$ .

curve was obtained each time. The dip is also evident in Fig. 8, curve (B). In Fig. 8 it is seen that as the concentration is raised further the dip disappears. Since the  $F$ -center concentration is so low it might be remarked that had the dip never been seen to disappear one might choose to ascribe it to an unfortunate combination of background impurities, which became extremely effective resonant scatterers of phonons upon being "activated" by the radiation (e.g.,  $\text{OH}^-$  converting to  $U$  centers). However, since the dip disappears and since it is produced by such widely different irradiation times (cf. Table I) one would need a very unfortunate background impurities combination indeed since they must suddenly stop scattering strongly and become virtually undetectable [cf. Fig. 8, curves (B) and (C)].

The thermal conductivity data are summarized, then, as follows. Both additive coloration and x- or  $\gamma$ -irradiation produce a strong low-temperature ( $T < 4^\circ\text{K}$ ) effect. In the first case the scattering is described by  $\tau^{-1}\alpha\omega^0$ , and in the second case by  $\tau^{-1}\alpha\omega^1$ . In both cases the measured conductivity falls below the calculated curves with the deviation increasing with increasing  $F$ -center

concentration. The rapidly quenched additively colored and very low-concentration irradiated specimens display a resonance scattering behavior. The slowly cooled additively colored and higher concentration irradiated specimens show no resonance behavior. In the latter cases the deviation between calculated  $\omega^1$  scattering or  $\omega^0$  scattering and the measured data looks remarkably like a  $\tau^{-1}\alpha\omega^4$  scattering.

At this point, then, without even a detailed analysis of the data one is faced with the following alternative. Either the low-temperature effect ( $T < 4^\circ\text{K}$ ) in at least one of the methods of preparation is not due to  $F$  centers, or one kind of strain field is produced by an additively colored  $F$  center and another kind by an x-ray produced  $F$  center. We reject the latter alternative and shall argue shortly that in neither case is the low-temperature effect due to  $F$  centers.

#### IV. THEORY AND CURVE FITTING

##### A. Pure Crystals

Debye's classical expression for calculating lattice thermal conductivity has been generalized by Klemens<sup>14</sup>

and Callaway<sup>28</sup> to the form

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

where  $v$  is the sound velocity,  $\hbar$  and  $k$  are Planck's and Boltzmann's constants,  $\omega_D$  is the Debye frequency, and  $\tau$  is the phonon-relaxation time. The only problem with using Eq. (1) is that one must know precisely what is meant by the relaxation time, particularly in view of the fact that in a real crystal there is usually more than one scattering mechanism operative at a single temperature. The situation becomes especially perilous when one decides to take into account the "normal" three-phonon processes. The problem has been considered in detail by Callaway<sup>28</sup> and Carruthers,<sup>15</sup> and it is Callaway's phenomenological formalism which is adopted here. Callaway assumes that the total relaxation time is given by

$$\tau_c^{-1} = \sum_i \tau_i^{-1}, \quad (2)$$

where the sum is over the various scattering mechanisms. If one includes Normal processes then the thermal conductivity becomes

$$K = \frac{k}{2\pi^2 v} \left( \frac{kT}{\hbar} \right)^3 (I_1 + \beta I_2), \quad (3)$$

where  $I_1$  is Eq. (1) expressed in the dimensionless variable  $x = \hbar\omega/kT$ .  $\beta$  is given by

$$\beta = \frac{\int_0^{\theta/T} \frac{\tau_c}{\tau_N} \frac{e^x}{(e^x - 1)^2} x^4 dx}{\int_0^{\theta/T} \frac{1}{\tau_N} \left( 1 - \frac{\tau_c}{\tau_N} \right) \frac{e^x}{(e^x - 1)^2} x^4 dx}. \quad (4)$$

$I_2$  is given by the numerator of  $\beta$ . Here  $\tau_c$  is the total relaxation time given by Eq. (2) including Normal processes and  $\tau_N$  is the Normal process relaxation time. The term  $\beta I_2$ , hereafter called the correction term, must be calculated when Normal process scattering is important. When Normal scattering is unimportant, i.e.,  $\tau_N$  becomes very large, then  $\beta I_2$  can be ignored and Eq. (3) reduces to Eq. (1).

Quantitative estimates of  $\beta I_2$  for pure KCl, KBr, and KI show it to be unimportant ( $\approx 20\%$ ), and so the theoretical curves for these samples have been calculated using Eq. (1) only. We shall discuss the correction term further below for the case of NaF.

The methodology for finding the "correct"  $\tau$  to describe the pure crystal has been given previously.<sup>16</sup> One uses a boundary scattering term, an intrinsic or phonon-phonon term, a term describing the random

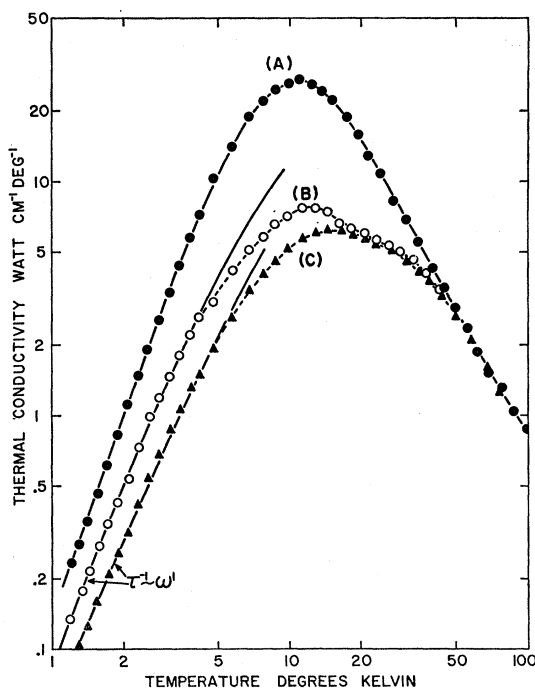


Fig. 8. Thermal conductivity of NaF #2 after successive x irradiations at 120 keV; (A) pure NaF; (B)  $N_{v,F} = 5.4 \times 10^{16} \text{ cm}^{-3}$ ; (C)  $N_{v,F} = 9.6 \times 10^{16}$ . Solid lines through curves (B) and (C) are theoretical curves.

disorder produced by the naturally occurring isotopes, and an additional point defect term describing the background impurities. The individual terms found for the samples discussed in this paper are given in Table II. The numerical integrations were carried out on the Control Data Corporation 1604 computer at the Cornell Computing Center. The sound velocities in all cases were calculated from the Debye temperatures<sup>29</sup> at  $T = 0^\circ\text{K}$ .

There was some difficulty for KI in finding an intrinsic scattering term which gave any hope of fitting the data. The combination of an exponential law plus a power law could not be made to work at all. What finally proved necessary was the following combination:

$$\tau_{\text{intrinsic}}^{-1} = 8.2 \times 10^{-21} T^{2.5} \omega^2, \quad \text{for } \omega < 6.0 \times 10^{12},$$

$$\tau_{\text{intrinsic}}^{-1} = 1.4 \times 10^{-19} T^{1.75} \omega^2, \quad \text{for } \omega \geq 6.0 \times 10^{12}.$$

We note that the cutoff frequency of  $6.0 \times 10^{12}$  is the transverse acoustic mode cutoff calculated by Karo and Hardy.<sup>30</sup> At this time we attach no significance either to the scattering laws needed, or to the presence of a cutoff. The reasons for this diffidence will become clear in the next paragraph.

Table II shows that two rather different sets of intrinsic scattering laws are needed to fit the two different NaF samples. However, examination of Figs. 7

<sup>28</sup> J. Callaway, Phys. Rev. **113**, 1046 (1962).

<sup>29</sup> P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1354 (1953).  
<sup>30</sup> A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

TABLE II. Inverse relaxation times needed to fit pure crystal data.

Sample	Debye temperature (°K)	Calculated casimir term (sec <sup>-1</sup> ×10 <sup>6</sup> )	Actual boundary scattering term (sec <sup>-1</sup> ×10 <sup>6</sup> )	Isotope plus "extra point defect" term (sec <sup>-1</sup> )	Intrinsic term (sec <sup>-1</sup> )
KCl	230	5.6	5.8	3.0×10 <sup>-44</sup> ω <sup>4</sup> + 8.2×10 <sup>-44</sup> ω <sup>4</sup>	2.9 ×10 <sup>-18</sup> Tω <sup>2</sup> e <sup>-40°K/T</sup>
KBr	165	4.1	5.0	3.7×10 <sup>-44</sup> ω <sup>4</sup> +13.7×10 <sup>-44</sup> ω <sup>4</sup>	5.8 ×10 <sup>-21</sup> T <sup>2</sup> ω <sup>2</sup> +6.0 ×10 <sup>-18</sup> Tω <sup>2</sup> e <sup>-30°K/T</sup>
KI	120	2.7	3.1	1.2×10 <sup>-44</sup> ω <sup>4</sup> + 3.4×10 <sup>-44</sup> ω <sup>4</sup>	See text
NaF # 1	470	7.3	5.6	None	2.8 ×10 <sup>-21</sup> T <sup>3</sup> ω <sup>2</sup> +1.87×10 <sup>-18</sup> Tω <sup>2</sup> e <sup>-140°K/T</sup>
NaF # 2	470	7.3	5.4	0.0ω <sup>4</sup> + 2.7×10 <sup>-46</sup> ω <sup>4</sup>	8.8 ×10 <sup>-22</sup> T <sup>2</sup> ω <sup>2</sup> +1.1 ×10 <sup>-18</sup> Tω <sup>2</sup> e <sup>-98°K/T</sup>

and 8 shows clearly that the data for temperatures above the maximum are different for the two samples. The fact that one cannot proceed from NaF # 1, the higher conductivity sample, to NaF # 2 by simply adding in some point defect scattering betrays the fact that the method for taking intrinsic scattering into account is not yet clear. For this reason, the "intrinsic" terms listed in Table II are simply accepted for what they are, namely that term which is necessary to fit the high-temperature data.

The problem of intrinsic scattering laws for NaF is compounded further by considering the correction term  $\beta I_2$ . For NaF # 1 if one identifies the  $T^3\omega^2$  term as the  $N$ -process term, then a calculation of  $\beta I_2$  shows that at the conductivity maximum the small correction amounts to 400%! For NaF # 2 the correction is about 200%. The significant difference in intrinsic laws for the two NaF samples could perhaps be alleviated by attempting to fit the data using Eq. (3) throughout the process. However, since so little is known about intrinsic processes generally it was not felt that the results would be significantly more meaningful than the results listed in Table II. This experience with NaF should serve as a clear warning for all attempts to fit the data from high-conductivity samples. Fortunately, the correction term is negligible above about 35°K and below 7°K. Thus, the low-temperature data for the colored NaF crystals can be fit with some confidence.

### B. Crystals Containing $F$ Centers

Now that the reciprocal relaxation times have been obtained for the pure crystals the problem is reduced to one of adding on different types of scattering laws until the colored crystal data are reproduced. This procedure was tried until it became apparent that in neither the additively colored nor irradiated cases was a single scattering law sufficient. At least two laws were necessary for each case.

The low-temperature data for the additively colored KCl can be fitted using a defect scattering law given by

$$\tau^{-1} = A\omega^0. \quad (5)$$

For the rapidly quenched sample  $A = 1.0 \times 10^6 \text{ sec}^{-1}$  and for the slowly cooled sample  $A = 9.0 \times 10^5 \text{ sec}^{-1}$ . The resultant curves calculated using this defect scattering law and the pure crystal relaxation times are shown as the solid lines through Fig. 1, curve (B) and Fig. 2, curve (B).

The low-temperature data for the irradiated KCl, KBr, and NaF can be fitted using a defect scattering law given by

$$\tau^{-1} = B\omega^1. \quad (6)$$

The resultant curves calculated using this scattering law are drawn through the appropriate data in Figs. 4, 5, and 8. As mentioned previously and as seen in Fig. 6 the low-temperature KI data fall some place in between the behaviors predicted by Eqs. (5) and (6). The coefficients of Eq. (6) needed to fit all the low-temperature data for the irradiated samples are given in Table III. In an attempt to determine the strength per scattering center and to see whether the  $\omega^1$  scattering is due to  $F$  centers we have included in Table III the ratio of the coefficient of Eq. (6) to the  $F$ -center concentration. It is seen that the coefficients,  $B$ , do not scale with  $F$ -center concentration. For KCl, LiF, and NaF  $B/N_v$  increases as  $N_v$  increases, while the reverse is true for KBr and KI. The numbers in Table III for KI are included on the assumption that Eq. (6) provides a better fit to the data than Eq. (5).

For completeness we have included in Table III the LiF data re-evaluated by Pohl.<sup>31</sup> Also included is the result of our fit to Gebhardt's helium temperature irradiation data for KCl. The latter fit is probably only accurate to about 30% because of the limited temperature range covered in his experiments and because his pure KCl crystal had a conductivity significantly lower than ours. In Gebhardt's case  $N_v$  refers to the  $\alpha$ -center concentration.

The scattering laws needed to fit the data around the conductivity maxima (more specifically for  $T > 4^\circ\text{K}$ ) fall into three categories. The slowly cooled additively colored KCl sample data can be fitted using a scatter-

<sup>31</sup> R. Pohl (private communication).



ing law of the form

$$\tau^{-1} = C\omega^4, \quad (7)$$

where  $C = 12.0 \times 10^{-44} \text{ sec}^3$ . Thus, the total defect scattering law needed to describe the slow-cooled KCl sample is

$$\tau^{-1}_{\text{defect}} = 9.0 \times 10^5 \text{ sec}^{-1} + 12.0 \times 10^{-44} \text{ sec}^3 \omega^4. \quad (8)$$

The data around the maxima for x- and  $\gamma$ -rayed KCl, KBr, and KI also require the use of Eq. (7). For the KCl crystal with the highest concentration of  $F$  centers the coefficient of Eq. (7) is  $C = 20.0 \times 10^{-44} \text{ sec}^3$ . The calculated curve is shown as the dashed line in Fig. 4, curve D. We do not quote any further values of  $C$  in Eq. (7) since, as will be seen in the next section, it is not clear how meaningful the numbers are. Pohl<sup>31</sup> has also found that the same quantitative remarks pertain for his LiF data.

Finally, we must now try to fit the data around the maxima for the fast quenched additively colored KCl and the x-rayed NaF. These are the data which show a "resonance dip." (Cf. Figs. 1, 7, and 8.) A similar behavior has been seen by Walker and Pohl<sup>16</sup> for alkali halides deliberately doped with chemical impurities. There the data were explained by invoking a resonance scattering of phonons by quasilocalized modes produced by the impurities. The scattering is a three-quantum process in which two phonons combine to excite the mode. The inverse process also occurs but only after a lifetime long compared with typical phonon periods. The de-excitation of the quasilocal mode is thus independent of the excitation. The formalism of Wagner<sup>17</sup> was applied in this case with a fair degree of success. We shall apply the Wagner formalism to the  $F$ -center data. In so doing we are making the explicit assumption that the resonance dips in the  $F$ -center data are due to a resonant scattering of phonons by quasilocalized impurity modes produced by the  $F$  center. There is at present no reason to presume that these modes are any less likely to be formed by  $F$  centers than by chemical defects.

Krumhansl<sup>18</sup> has also calculated the phonon scattering by impurity modes, and has specialized his calculation to the case of  $F$  and  $U$  centers. The net effect on the thermal conductivity of his result is the same as Wagner's. Both predict resonance dips. However, since Krumhansl's calculation has not yet been generalized to include anharmonic effects, and since in Wagner's result the adjustable parameters are easily identified, we choose to use Wagner's calculation.

Wagner's calculation<sup>17</sup> shows that the phonon scattering by point defects is a sum of two terms. One is the elastic Rayleigh scattering term and the other is a resonance-like term. Thus

$$\tau^{-1}_{\text{point defect}} = C\omega^4 + Ef(\omega, T)g(\omega), \quad (9)$$

TABLE III. Parameters for fitting irradiated crystal data below 4°K.

Sample	$F$ -center concentration $N_v$ (cm <sup>-3</sup> )	Coefficient $B$ in Eq. (6) (dimensionless)	$B/N_v$ (10 <sup>-24</sup> cm <sup>-3</sup> )	$S/D^a$
KCl	$2.2 \times 10^{17}$	$9.9 \times 10^{-7}$	4.5	0.598
KCl	$7.0 \times 10^{17}$	$4.4 \times 10^{-6}$	6.3	0.598
KCl (Gebhardt)	$4 \times 10^{16}$	$9.1 \times 10^{-7}$	23.0	0.598
KBr	$1.7 \times 10^{17}$	$6.9 \times 10^{-6}$	40.7	0.467
KBr	$4.7 \times 10^{17}$	$12.3 \times 10^{-6}$	26.2	0.467
KI	$2.2 \times 10^{17}$	$3.3 \times 10^{-6}$	14.5	0.326
KI	$4.0 \times 10^{17}$	$5.5 \times 10^{-6}$	12.5	0.326
NaF #1	$5.7 \times 10^{16}$	$2.7 \times 10^{-7}$	4.7	0.693
NaF #2	$5.4 \times 10^{16}$	$6.1 \times 10^{-7}$	11.3	0.693
NaF #2	$9.6 \times 10^{16}$	$13.0 \times 10^{-7}$	13.6	0.693
LiF <sup>b</sup>	$4.2 \times 10^{17}$	$1.3 \times 10^{-6}$	3.1	0.486
LiF <sup>b</sup>	$7.1 \times 10^{17}$	$2.2 \times 10^{-6}$	3.1	0.486
LiF <sup>b</sup>	$2 \times 10^{18}$	$7.3 \times 10^{-6}$	3.7	0.486

<sup>a</sup> See text.

<sup>b</sup> Data kindly supplied by Professor Robert D. Pohl.

where

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

Here  $\rho$  is the crystal density,  $\gamma$  is Grüneisen's constant,  $v$  is the sound velocity,  $k$  and  $\hbar$  are Boltzmann's and Planck's constants,  $n$  is the concentration of defects and  $\omega_s$  is the frequency of the quasilocal mode.  $M$  is the number of quasilocal modes created by one impurity and  $\alpha$  is the exponential damping factor of the mode, which is assumed to be a damped spherical wave. In terms of the dimensionless variable  $x = \hbar\omega/kT$

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

and

$$f(\omega, T) = \frac{T^2 (x_s - x)^2 e^{(x_s - x)} (e^x - 1)}{(e^{x_s} - 1) (e^{(x_s - x)} - 1)}.$$

Here  $\omega_\alpha = \alpha v$ . In Eq. (9) the adjustable parameters are  $C$ ,  $\omega_s$  and the combination  $(M\alpha)$ .

Equation (9) has been used to fit the fast-quenched additively colored KCl data with the result shown in Fig. 1, curve (B) as the dashed line. To fit this curve the following parameters are needed:

The coefficient of the Rayleigh term,

$$C = 6.8 \times 10^{-44} \text{ sec}^3.$$

The quasilocal mode frequency,

$$\omega_s = 9 \times 10^{12} \text{ rad sec}^{-1}, \quad (M\alpha) = 8.5 \times 10^7 \text{ cm}^{-1}.$$

Equation (9) has also been applied to find the quasilocal mode frequency for the  $F$  center in NaF. The result is  $\omega_s = 1.4 \times 10^{13} \text{ rad/sec}$  for both NaF samples in spite of the different shapes of the dip in the two cases.

Because of the previously discussed problems in fitting the pure NaF data a detailed fit to the colored crystal data was not attempted.

The results of fitting the colored crystal data can be summarized as: (a) The additively colored data can be fitted for low temperatures using a relaxation time of the form  $\tau^{-1} = A\omega^0$ . The slowly cooled sample needs an additional term of the form  $\tau^{-1} = C\omega^4$  to fit the higher temperature data, while the quenched sample needs both the Rayleigh law and a localized mode resonance term. (b) The irradiated samples can be fitted at low temperatures using a relaxation time of the form  $\tau^{-1} = B\omega^1$ . The lightly colored samples require the combination of Rayleigh scattering and quasilocalized mode resonance for the higher temperature data. The heavily colored samples also require the use of  $\tau^{-1} = C\omega^4$  to fit the higher temperature data.

## V. DISCUSSION

From the summary at the end of the last section it is clear that the interpretation of the data will be somewhat complicated. We repeat the argument at the end of Sec. III, to wit: either additive coloration produces one kind of  $F$  center and irradiation produces another, or at least one of the types of behavior is not caused by  $F$  centers alone. We adopt the latter point of view and shall argue that the behavior below 4°K is not caused by  $F$  centers in either case. What else could be contributing to the phonon scattering? Examination of Tables I and III suggests quite strongly that  $M$  centers are not the answer. For example, the low-temperature effect in irradiated KBr is the strongest of all the samples, and yet the  $M$ -center concentration is very low in this sample. The answer must be more deep seated than this obvious choice. The two methods of coloration shall be discussed separately.

### A. Additively Colored Samples

It is known<sup>26</sup> that when a crystal is colored additively the final state of the crystal depends quite strongly on the rate at which it is cooled from the coloring temperature. In addition to  $F$  centers the crystal will contain colloids of alkali metal with the number and size of the colloids depending on the heat treatment. The optical absorption due to colloids as a function of heat treatment has been studied by Scott *et al.*<sup>26,32</sup> who have identified a colloid band at 1.65 eV in KCl. This is the same band observed in the slow cooled sample. Simon and Sproull<sup>33</sup> have studied electron micrographs of KCl crystals containing  $10^{18}$ – $10^{19}$   $F$  centers per  $\text{cm}^3$  as a function of quench rate. Their work suggests that even our rapidly quenched sample, which displays no

optical colloid band, was not cooled rapidly enough to prevent formation of some potassium colloids. Worlock<sup>11</sup> has studied the thermal conductivity of NaCl crystals containing Ag colloids and colored KCl crystals which show strong colloid bands, and has found that a frequency-independent scattering law is sufficient to describe the data. Thus, we conclude that the low-temperature effect in additively colored KCl is due to the fact that the crystal contains potassium metal colloids. The quenched sample has the additional complication that such a quench treatment applied to pure KCl produces a similar but smaller low-temperature effect.<sup>16</sup> This factor probably explains the need for a slightly larger  $\omega^0$  term for the quenched sample when, as will be seen below, one might expect a slightly smaller term.

The data around the conductivity maximum for the quenched sample have been fitted using a resonance plus Rayleigh term. Since this is precisely the effect expected for randomly distributed point defects we identify this effect as being caused by  $F$  centers. A coefficient of  $6.8 \times 10^{-44} \text{ sec}^3$  was found for the Rayleigh term. Calculating from the mass difference effect only one would expect a coefficient of  $0.215 \times 10^{-44} \text{ sec}^3$ , or a factor of 30 lower. This result suggests that  $F$  centers elastically scatter phonons predominantly through their strain field and not through their mass difference, in agreement with chemical defects,<sup>8,16</sup> and as suggested by theory.<sup>14,15</sup>

The statement that the resonance plus Rayleigh effect is caused by  $F$  centers is given strong support by the slowly cooled sample data. Here there are sufficient colloids for an optical colloid band to appear, albeit a small one, and there is now no doubt that the crystal contains potassium colloids. But if the crystal contains measurable amounts of colloid then it must also contain the early stages of colloid formation such as  $F$  centers which have begun to move together but have not yet coagulated. From the parameter  $(M\alpha) = 8.5 \times 10^7 \text{ cm}^{-1}$  one calculates a  $1/e$  distance for the quasilocalized  $F$ -center mode to be about 10 Å. When significant quantities of  $F$  centers have moved to within about 10 Å of each other, then, by analogy with chemical defects<sup>16</sup> one would expect the resonance effect to disappear since one no longer has isolated impurity modes. This is precisely the effect seen in the slowly cooled sample.

A rapidly quenched additively colored sample would thus seem to come as close to a "pure"  $F$ -center effect as one can get. Even this rigorous treatment leaves some colloidal metal in the sample, and the heat treatment itself provides some low-temperature effect. Any departure from the rapid quenching treatment, such as the slow cooling treatment, results in more colloid formation and the obliteration of the resonance effect. The Rayleigh effect which persists is the cumulative effect of phonon scattering from the now lower background concentration of isolated  $F$  centers and from small clusters of  $F$  centers.

<sup>32</sup> A. B. Scott, W. A. Smith, and M. A. Thompson, *J. Phys. Chem.* **57**, 757 (1953).

<sup>33</sup> R. E. Simon and R. L. Sproull, *J. Appl. Phys.* **31**, 2224 (1960).

### B. Irradiated Samples

The data around the conductivity maxima are considered first. The key to understanding these data is provided by the NaF. At low concentrations there is a resonance effect. As the concentration approaches  $10^{17}$   $F$  centers per  $\text{cm}^3$  the dip disappears; this is the most significant fact. The KCl, KBr, KI, and LiF were all studied for concentrations above this apparently critical concentration. The presence of the resonance is easy to understand, but why does it go away as the concentration is increased? By analogy with the slowly cooled additively colored KCl and with chemical impurities<sup>16</sup> one expects the resonance effect to disappear with *increasing* concentration when the concentration is high enough so that there is significant spatial overlap of the impurity modes. But in view of the fact that the  $1/e$  distance for an additively colored  $F$  center has been seen to be about 10 Å one cannot argue that  $10^{17}$  is a sufficiently high concentration for this overlap to occur. On the other hand a calculation using Eq. (9) suggests that even in NaF a concentration of  $5 \times 10^{16}$  distributed randomly is too low to expect any observable resonance effect, assuming that the strength per center is the same as for an additively colored center. To explain the observed resonance and its disappearance, then, we conclude that the crystal must contain regions of abnormally high  $F$ -center concentration. The concentration in these local regions must be high enough ( $10^{19}$ – $10^{20}$ ) that the resonance scattering is enhanced to the point that a dip, arising from the local regions, can be observed. As the average concentration, determined optically, is increased the local concentrations also increase to the point where they are so high the resonance washes out. The balance between a local concentration high enough for an enhanced resonance but low enough to avoid spatial overlap is expected to be quite delicate. This would explain the abrupt disappearance of a resonance with increasing concentration.

The nature of the local regions can be characterized as follows. The regions must be microscopically small so as to be undetectable by optical absorption measurements, and must themselves be uniformly distributed through the crystal since optical measurements show no concentration gradients. To agree with ESR studies of  $F$  centers, which measure interactions out to the 7th or 8th neighbors, the overwhelming majority of the crystal volume must be filled with randomly distributed centers. For the NaF crystal containing about  $10^{17} \text{ cm}^{-3}$  centers there is no resonance dip, so the concentration of the local regions must be about  $10^{20} \text{ cm}^{-3}$  or greater. For the random background to provide no detectable resonance effect itself, the background must contain less than about  $5 \times 10^{16} \text{ cm}^{-3}$ . From these considerations it is estimated that the high concentration regions occupy only about 0.1% of the crystal volume and contain about 50% of the  $F$  centers. If each region contains three or four  $F$  centers then

there would be about  $10^{16}$  such regions in the crystal. The statistical probability of finding such density fluctuations is insignificant<sup>34</sup> so that these regions must be characteristic of  $F$ -center formation by irradiation.

Independent evidence for regions of high concentration has been summarized by Mitchell *et al.*<sup>35</sup> The most compelling evidence hinges on the observation that optical bleaching of  $F$  centers proceeds in two stages. There is an initial rapid bleach accompanied by a high quantum efficiency and a subsequent slow bleach with a low quantum efficiency.<sup>36</sup> The rapid bleach is associated with the background and the slow bleach with the high concentration regions. The ESR measurements by Kaplan and Bray<sup>37</sup> on neutron irradiated LiF show direct evidence for regions of high concentration. However, similar experiments have not yet been performed on x- or  $\gamma$ -irradiated samples.

The data around the conductivity maxima for irradiated samples thus seem to require the explanation that  $F$  centers do not form uniformly in a crystal upon irradiation. Instead there are local regions of high concentration which manifest themselves as a resonance effect in low average concentration samples. As the average concentration increases the resonance effect disappears because the local concentrations become too high, and all that remains is the Rayleigh-like scattering from the impoverished background (whose concentration is too low for detectable resonance) and the Rayleigh-like scattering from the high concentration regions. A resonance scattering from the background itself might be expected for still higher average concentrations provided two conditions hold. The background concentration must increase with increasing average concentration (a moot point<sup>35</sup>) and the ever-present low-temperature effect must not become so strong as to obliterate the resonance effect.

We now come to the most difficult question of all. What is the source of the  $\omega^1$  scattering law which describes the low-temperature data in the irradiated crystals? We shall see that the question cannot be answered at this time. We now consider why.

One way of obtaining an  $\omega^1$  law is to assume that the scattering is due to point defects arranged in such a way that there is coherent elastic scattering from the array. An example of such an array would be  $F$  centers distributed around a dislocation line. The argument is that each impurity, if isolated, would scatter in a well-defined way describable by a Rayleigh-like behavior, but that the single center scattering cross section is increased because of coherent addition of scattered amplitudes from neighbors in the array, and its fre-

<sup>34</sup> R. B. Lindsay, *Physical Statistics* (John Wiley & Sons, Inc., New York, 1941), Chap. 2.

<sup>35</sup> P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, *Phys. Rev.* **121**, 484 (1961).

<sup>36</sup> E. E. Schneider, *Fundamental Mechanisms of Photographic Sensitivity* (Butterworths Scientific Publications, Ltd., London, 1951).

<sup>37</sup> R. Kaplan and P. J. Bray, *Phys. Rev.* **129**, 1919 (1963).

quency dependence is reduced. Let  $f(\mathbf{r})$  be the function which specifies the spatial arrangement in the array. In order to obtain  $\tau^{-1} \propto \omega^1$  it is easy to show that  $f(\mathbf{r}) \propto r^{-3/2}$  if  $f(\mathbf{r})$  is assumed to be spherically symmetric,<sup>38,15</sup> and  $f(\mathbf{r}) \propto r^{-1}$  if  $f(\mathbf{r})$  is assumed to have cylindrical symmetry.<sup>38</sup> The latter spatial distribution is physically quite plausible, but calculation of the coefficient of an  $\omega^1$  law [ $B$  in Eq. (6)] using either symmetry gives a value about 100 times smaller than the observed value. Further the calculation predicts that  $B$  should vary as the square of the concentration of defects, when in fact Table III shows that  $B$  varies little faster than linearly. Thus, any explanation of an  $\omega^1$  law based on this simplified model of coherent scattering does not work. This is unfortunate since such a model could have explained all the irradiated data in terms of the degree of clustering of defects.

Since coherent arrangements of  $F$  centers do not seem to provide an answer let us consider whether there are any defects which have been overlooked and examine their possible behavior. Two such possible defects are suggested, interstitials and dislocations.

Up to this point we have not asked how the vacancy now occupied by the  $F$  electron was formed. If the Varley-type mechanism<sup>39</sup> has any validity then one would expect interstitials to be formed during irradiation. How stable they would be during room temperature irradiation is problematical; evidence suggesting interstitial formation at room temperature has been presented by Wiegand.<sup>40</sup> A consideration of Table III shows that Gebhardt's helium temperature irradiation produced an effect about five times stronger than the room temperature effect in KCl. Coloration of KBr and KI at 35° and 55°C shows that the  $\omega^1$  effect becomes still weaker at the latter temperature. This is at least qualitatively what would be expected from interstitials. Further the low-temperature KI effect can be understood in terms of iodine atoms coagulating rather than going into interstitial sites. The well-known  $S/D$  ratio for  $F$ -center formation, where  $S$  is the space between adjacent halide ions along a face diagonal and  $D$  is the diameter of a halide atom, shows KI to be the least favorable case for interstitial formation. However, there are three arguments which militate against interstitials. The first is that  $A/N_v$ , given in Table III might be expected to scale in some way with the  $S/D$  ratio. The  $S/D$  ratios for our samples are listed in Table III, and as can be seen there is no apparent relation between  $A/N_v$  and  $S/D$ . The second problem is that in order to obtain an  $\omega^1$  law for interstitials one must postulate that the interstitials are arranged in a linear array and that the displacement field produced by interstitials varies as  $1/r$ . The first postulate is not unreasonable particularly if  $F$  centers are formed near

dislocations. As another possibility for a linear array we see from Table I that in most of our cases the scattering of the  $X$  or  $\gamma$  photon was a Compton process rather than photoelectric.<sup>41</sup> The Compton electron comes off with significant energy<sup>42</sup> and since its scattering is mostly small angle<sup>43</sup> it is not inconceivable that  $F$  centers, and thus, interstitials, could be formed in short lines. The  $F$  centers being more mobile could diffuse away leaving a chain of interstitials behind. The requirement on the length of the chain is modest; it must appear to be a line to typical phonon wavelengths ( $\sim 100$  Å). However, the assumption of a displacement field varying as  $1/r$  is at present untenable.<sup>15</sup> Adopting the more realistic  $1/r^2$  field leads one right back to the coherent scattering discussion above in order to obtain  $\tau^{-1} \propto \omega^1$ . The third problem is that, as seen in Table III, the two NaF samples show quite different strengths for the  $\omega^1$  effect. Since both were irradiated at the same temperature this fact is quite difficult to reconcile with an interstitial effect. Instead it argues that the  $\omega^1$  effect is probably connected with the intrinsic state of the crystal prior to irradiation.

The NaF problem, in addition to all the low-temperature irradiated data except KI, can be understood in terms of our last possibility which is dislocation effects. If  $F$  centers are formed near dislocations, either by the Seitz-Markham<sup>44,45</sup> mechanism or by the mechanism proposed by Mitchell *et al.*<sup>36</sup> then one might conceive of an "enhanced" dislocation scattering mechanism. The long-range strain field of a dislocation has been shown on theoretical grounds<sup>14,15</sup> to scatter phonons according to the law in question, namely  $\tau^{-1} \propto \omega^1$ .

If one assumes that the  $F$  centers "decorate" a dislocation and that a decorated dislocation has a long-range strain field a factor of 10 stronger than the undecorated dislocation then all the low-temperature data except for the KI fall into place immediately. The different strengths for the two NaF crystals can be understood as arising from different dislocation densities in the two crystals. The influence of temperature on the strength of the  $\omega^1$  depression can be understood in terms of diffusion of  $F$  centers away from the dislocations. The fact that there seems to be no order to the effect as one proceeds to various alkali halides is also consistent. However, it is not yet clear whether a decorated dislocation scatters phonons more strongly or more weakly than an undecorated one. Carruthers<sup>15</sup> suggests the latter. Also, the more recent work by Moss,<sup>46</sup> and by Pohl and Taylor<sup>47</sup> on alkali halides containing dislocations has shown that the predicted

<sup>41</sup> G. W. Grodstein, Nat. Bur. Std. U. S. Circ. 583 (1957). Also *ibid.* Suppl. Circ. 583 (1959).

<sup>42</sup> A. T. Nelms, Nat. Bur. Std. U. S. Circ. 542 (1953).

<sup>43</sup> R. D. Evans, *The Atomic Nucleus* (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 19.

<sup>44</sup> F. Seitz, Phys. Rev. 80, 239 (1950).

<sup>45</sup> J. J. Markham, Phys. Rev. 88, 500 (1952).

<sup>46</sup> M. Moss, Ph.D. thesis, Cornell University, 1962 (unpublished).

<sup>47</sup> R. O. Pohl, and A. T. Taylor (to be published).

<sup>38</sup> M. V. Klein, Phys. Rev. 122, 1393 (1961).

<sup>39</sup> J. H. O. Varley, Nature 174, 886 (1954).

<sup>40</sup> D. A. Wiegand, in International Symposium on Color Centers in Alkali Halides, Stuttgart 1962 (unpublished).

$\tau^{-1} \propto \omega^1$  law for dislocations is not yet verified experimentally. The KI data can only be included in this picture if some precipitation of defects is assumed. We note that this was also required in the interstitial model.

We mention in conclusion that the most obvious possibility of all has not been discussed, namely, that there is some new scattering process, not covered by standard theories or revealed in the standard experiments, which is taking place in the irradiated crystals. Probably the fairest statement is that the nature of the low-temperature depression is the same as discussed three years ago by Pohl—unknown.

#### VI. SUMMARY

(1) Thermal conductivity measurements were made to study the scattering of phonons in crystals containing  $F$  centers. Both additively colored and  $x$ - or  $\gamma$ -irradiated crystals were studied and the results of the two methods were seen not to agree.

(2) The additively colored data divided into two parts. The data for temperatures below about 4°K could be explained by invoking a scattering law of the form  $\tau^{-1} \propto \omega^0$ . This depression in the conductivity was attributed to the crystal containing colloids of potassium metal and to quench-induced imperfections. The data for temperatures above about 4°K could be explained by invoking a Rayleigh-type scattering law and a resonance-like scattering of phonons due to quasi-localized impurity modes created by  $F$  centers.

(3) The data from irradiated samples also divided into two parts. The data above 4°K could be understood in the same terms as the additively colored data

if the  $F$ -center concentration was low. For higher  $F$ -center concentrations the resonance effect disappeared. This effect was explained by assuming that  $F$  centers are not randomly produced in the sample.

(4) The data for temperatures below 4°K in the irradiated samples could be characterized by a  $\tau^{-1} \propto \omega^1$  scattering law. The nature of the mechanism causing this effect is unknown at present, but may be explained by interstitials or by the influence of dislocations on  $F$ -center formation.

(5) The quasilocalized mode frequency was found to be  $9 \times 10^{12}$  rad/sec for the  $F$  center in KCl and  $1.4 \times 10^{13}$  rad/sec for the  $F$  center in NaF. The strength of the Rayleigh-type scattering by the  $F$  center in KCl was found to be 30 times stronger than predicted by mass-difference scattering only. This suggests that the  $F$  center scatters phonons elastically predominantly through its strain field.

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