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# Change in Thermal Conductivity upon Low-Temperature Electron Irradiation: GaAs†

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Measurements of the change in thermal conductivity of high-purity single-crystal GaAs were made upon 2-MeV electron irradiation and annealing. Two GaAs samples were irradiated at maximum temperatures of 100 and 80°K. A linear increase in the additive thermal resistivity near 50°K is observed upon bombardment. The results yield $1/K-1/K_0=(3.15\pm0.2)\times10^{-19}$ cm-deg/W per 2-MeV electron/cm². The experimental ratio of the point-defect thermal resistivity to the induced lattice strain at 50°K is $(1/K-1/K_0)/(3\Delta L/L)=(1.0\pm0.2)\times10^4$ cm-deg/W. Using estimates for the introduced defect concentration (based upon the change in strain rate as a function of electron energy) together with the observed increase in thermal resistivity, one obtains $1/K-1/K_0=(94\pm10)\times10^2C$ cm-deg/W, where $C$ is the fractional point-defect concentration. This value is intermediate between those predicted by the point-defect scattering theories of Klemens and Ziman. Isochronal anneals carried out above 50°K with all measurements made at 50°K demonstrate low-temperature annealing in GaAs. Annealing is observed to begin near 55°K and accelerate near 190°K. About 70% of the additive thermal resistivity stable at 50°K anneals below 325°K. Definite minima are observed in the temperature dependence of the thermal conductivity, suggesting localized-impurity-mode scattering. The annealing, however, takes place over too large a temperature range to be due to a single thermally activated process. The change in shape of the temperature dependence of the thermal conductivity upon annealing indicates that below 325°K the defects anneal as point defects. For anneal temperatures between 325 and 575°K the point defects no longer remain isolated, and clustering or precipitation is suggested.

## I. INTRODUCTION

THE great sensitivity of low-temperature thermal conductivity to lattice defects was first demonstrated by Berman for neutron-irradiated quartz.[1] Recent reviews of thermal conductivity are given by Klemens,[2] Carruthers,[3] and Bross.[4] Following the initial work of Berman, further studies of the change in thermal conductivity upon neutron irradiation were reported for many materials, especially for the dielectric crystals quartz,[1,5] diamond,[6] and sapphire.[6,7] Thermal conductivity measurements following x-ray and $\gamma$-ray irradiations of ionic crystals[8–11] and electron irradiation of graphite[12] have been performed. Recently, the change in thermal conductivity of semiconductors on irradiation has been studied.[13,14]

Since simple primary defects introduced into semiconductors anneal[15–18] and interact with impurities[17,18] well below room temperature, the usual method of irradiating at room temperature and measuring the thermal conductivity at low temperature will give no direct information on simple primary defects. Accordingly, it is important to study the effects of irradiation *in situ*—that is, to irradiate and measure the thermal conductivity at low temperature.[19]

The purpose of this paper is to report the change in thermal conductivity of GaAs upon the low-temperature introduction and annealing of point defects produced by 2-MeV electron irradiation. The change in thermal conductivity is correlated with the previously measured strain (length change) of 2-MeV electron-irradiated GaAs,[13,20] and compared with theories of point-defect-strain scattering. Isochronal annealing measurements demonstrating low-temperature annealing and defect reordering in high-purity GaAs are also presented.

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## II. EXPERIMENTAL

The GaAs samples were irradiated near 70°K. Measurements of the change in thermal conductivity were performed at 50°K in the same apparatus without warmup. Since the samples had the same temperature environment for each measurement, the relative change in thermal conductivity both on bombardment and on annealing could easily be measured, avoiding the complications inherent in absolute measurements necessary for irradiations and measurements not performed in the same apparatus.

Two samples, G-1 and G-3, were fabricated from single-crystal $n$-type material grown by the Czochralski technique and obtained from Merck and Company. The carrier concentration was $1.41\times10^{16}/\text{cm}^3$, and the Hall mobility was 4720 $\text{cm}^2/\text{V-sec}$. The samples G-1 and G-3 were bar shaped; respectively, 0.150 and 0.127 cm wide, 0.042 and 0.060 cm thick, with irradiated lengths of 1.0 cm. The long dimensions of the samples were in the ⟨112⟩ direction for G-1 and the ⟨110⟩ direction for G-3. Each sample was soldered at one end to a sample block which in turn was conduction cooled in an irradiation cryostat. Wire heaters were attached to the other ends of the samples. Two copper-constantan thermocouples measured the temperature difference across each sample. The change in the temperature difference on bombardment is independent of the precise location of the thermocouples. A schematic diagram of the sample and thermocouple geometry, which was slightly different for G-1 and G-3, is shown in Fig. 1. During irradiation, energy in the form of ionization heat was deposited uniformly in the irradiated volume of the sample. The maximum temperature range across sample G-1 during bombardment was from $<100$°K near the sample tip to 50°K at the sample block. The maximum temperature range across sample G-3 was from $<80$°K near the sample tip to 50°K near the sample block. The temperature ranges across the samples during the beam and heater measurements were in general much smaller than these and were proportional to the particular beam current or heater input power that was used.

The samples were irradiated with 2-MeV electrons in separate irradiations in the ⟨111⟩ direction through the small dimensions of the crystals, thus giving a fairly uniform production of defects per unit volume. Sample G-1 was irradiated to a total flux of $8.8\times10^{18}$ $e/\text{cm}^2$; sample G-3 was irradiated to $5.0\times10^{18}$ $e/\text{cm}^2$. At 50°K, boundary scattering of phonons was not deemed to be important even for the small sample size. This was confirmed since sample G-1, having a lapped surface, and G-3, having a polished surface, gave essentially the same results.

The increase in thermal resistivity on bombardment was measured by two methods. The first utilized the uniform heat input of the electron beam. The second used the heat of the small wire heater attached to the end of the sample. For the beam method, the increase in thermal resistivity is given by Eq. (1).

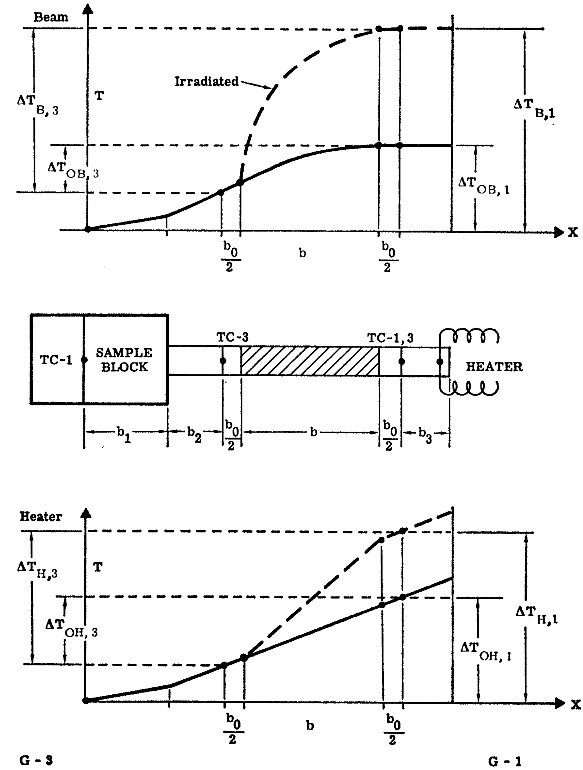


FIG. 1. Schematic diagram of the sample geometry indicating the temperature along the sample for the beam measurements (above) and heater measurements (below). The solid curves give the initial conditions, and the dashed curves show the change in temperature profile following some irradiation.

$$W-W_0=\frac{1}{K}-\frac{1}{K_0}=\frac{2}{Hb^2}(\Delta T_B-\Delta T_{0B}), \quad (1)$$

where

$$H=J\frac{\mu\text{A}}{\text{cm}^2}\frac{\Delta E}{\Delta x}\frac{\text{MeV}}{\text{cm}}. \quad (2)$$

Here $K_0$ and $\Delta T_{0B}$ are the thermal conductivity and the temperature difference, respectively, for the sample as initially irradiated. $K$ and $\Delta T_B$ are the corresponding quantities for the irradiated sample. $H$ is the heat per second per unit volume introduced into the irradiated portion of the sample ($b=1.0$ cm). $J$ is the current density of the electron beam, and $\Delta E$ is the energy lost by the electron in passing through a sample of thickness $\Delta x$. The upper portion of Fig. 1 gives a schematic representation of the temperature profile across the samples for the beam measurements. Beam current densities of 2.5 $\mu\text{A/cm}^2$ and 5.0 $\mu\text{A/cm}^2$ corresponding to total currents of 1.0 $\mu$A and 2.0 $\mu$A were used.

Measurements utilizing the 0.005-in. Chromel wire heaters were made both on bombardment and anneal-

ing. Equation (3) gives the increase in thermal resistivity for the heater measurements.

$$\frac{1}{K}-\frac{1}{K_0}=\frac{1}{Mb}(\Delta T_H-\Delta T_{0H}), \qquad (3)$$

where

$$M=\frac{I^2Rf_I}{A}\text{W/cm}^2. \qquad (4)$$

Here $K_0$ and $\Delta T_{0H}$ are the thermal conductivity and temperature difference for the unirradiated sample. $K$ and $\Delta T_H$ are the corresponding quantities for the irradiated sample. $M$ is the heat per second per unit cross-sectional area that is conducted through the sample; $I$ is the current through the sample heater (either 200 mA or 100 mA); $R$ is the heater resistance; $A$ is the cross-sectional area of the sample; and $f_I$ is the fraction of the heater power that is conducted down the sample. The lower portion of Fig. 1 presents a schematic representation of the temperature profile across the samples for the heater measurements.

Following irradiation, isochronal annealing measurements were performed by thermally isolating the samples from the refrigerant through the use of a heat switch and then heating the sample with a block heater to each desired anneal temperature. The sample was held at each temperature for 15 min. It was then rapidly cooled to 50°K for each thermal conductivity measurement by reconnecting the sample to the refrigerant. All the measurements following anneals were made using the sample heater method. No measurements using the beam ionization were made on annealing since the beam would have introduced further damage and complicated the analysis. In addition, for sample G-3, the temperature dependence of the thermal conductivity was measured between 10°K and the anneal temperature, and anneals were carried out to 575°K.

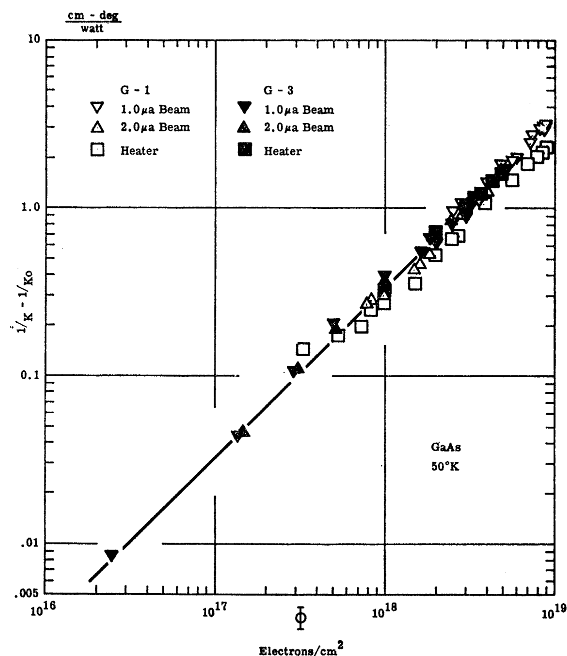


FIG. 2. Increase in the additive thermal resistivity at 50°K as a function of the number of 2.0-MeV electrons/cm² passed through the sample.

## III. RESULTS

### 1. Bombardment

The linear increase in thermal resistivity for both samples is shown in Fig. 2. Measurements using the ionization of the 2.0-MeV electron beam as well as the sample heaters are given. In general, all the measurements agree with each other to within experimental errors. The measurements for sample G-3 are more precise than those for G-1 due to a more favorable thermocouple geometry.

The beam data were obtained using Eq. (1). The value of $\Delta E/\Delta x=10.05$ MeV/cm used for GaAs was obtained from the range-energy formula of Katz and Penfold.[21] The heater data were obtained using Eq. (3). For sample G-1, the ratio of $f_{200}$ to $f_{100}$ was obtained directly by assuming $(1/K-1/K_0)_{200}=(1/K-1/K_0)_{100}$. The absolute values of the $f$'s were estimated by making the further approximation that for small $\Delta T_{0H}$, $f$ approaches unity as a linear function of $\Delta T_{0H}$. A more precise determination of $f_I$ was possible for G-3. Prior to bombardment the thermal conductivity of sample G-3 was measured as a function of temperature at heater currents of 50, 100, 150, and 200 mA. The values of $f_I$ were determined at each current using a value for the unirradiated thermal conductivity of GaAs at 50°K of 6.0 W/cm-deg, in agreement with the data of Holland.[22] The values of $f_I$ were found to be constant and temperature-independent since one value

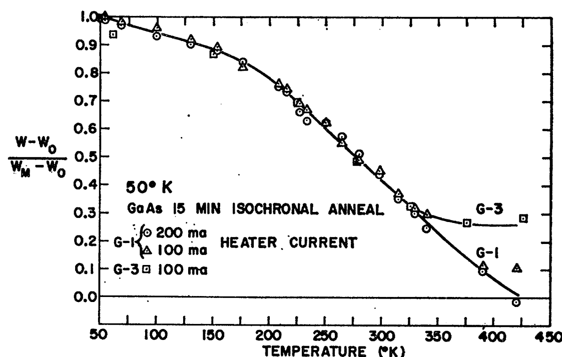


FIG. 3. Fraction of the additive thermal resistivity at 50°K that remains unannealed after successive 15-min anneals at each indicated temperature. All measurements made at 50°K after each anneal.

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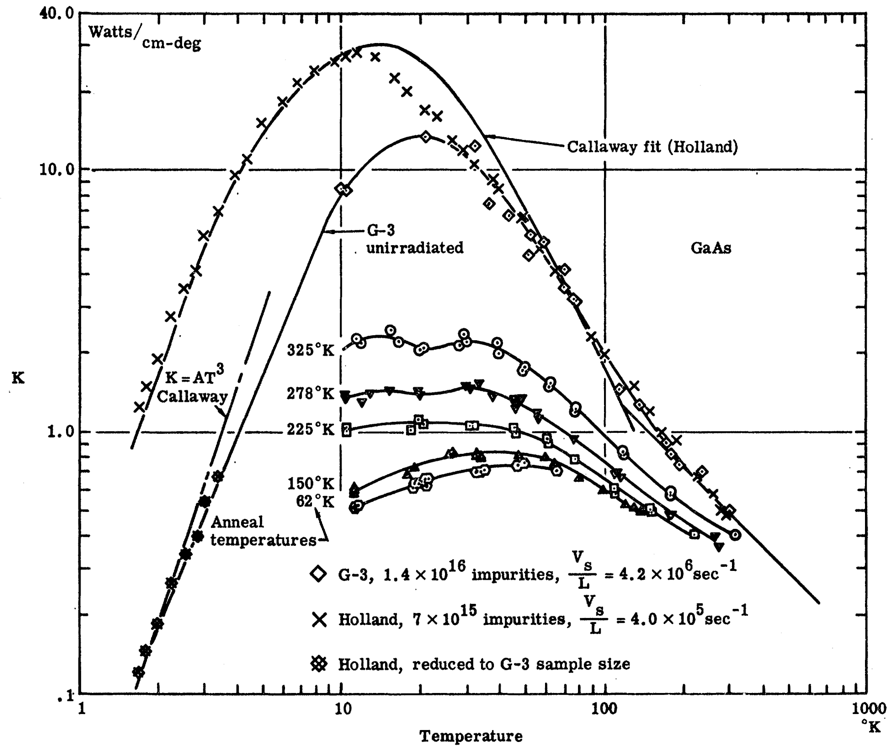


FIG. 4. Temperature dependence of the thermal conductivity of GaAs, G-3 before irradiation and after irradiation below each of the indicated 15-min anneal temperatures. Annealing temperatures between 62 and 325°K.

of $f_I$ yielded values of $K_0$ in agreement with Holland's data for all temperatures between 50 and 300°K.

The best fit to both the heater and beam data in Fig. 2 is $1/K-1/K_0=(3.15\pm0.2)\times10^{-19}$ cm-deg/W per 2 MeV-electron/cm². The agreement between the two methods of measuring thermal conductivity implies that there is no large change in the thermal conductivity of GaAs when ionization is introduced by the electron beam. One may therefore use the two methods interchangeably. As a practical matter, the beam measurement is easier to perform on bombardment, but the heater method is necessary for annealing studies.

### 2. Annealing

Since the thermal resistivity increase, $W-W_0$, is linearly proportional to the integrated flux of 2-MeV electrons passed through the sample, $(W-W_0)/(W_m-W_0)$ would give the fraction of the damage which is unannealed for simple recombination of defects. Here $W_m$ is the maximum thermal resistivity observed at the end of the bombardment. Figure 3 shows this fraction for G-1 and G-3 for 15-min anneals at each temperature with all measurements made at 50°K. The temperature dependence of the thermal conductivity as observed for G-3 below each anneal temperature is shown in Fig. 4 for anneals below 325°K, and in Fig. 5 for anneals above 325°K. Figure 6 shows the analogous temperature dependence of the thermal resistivity of G-3 for anneals below 325°K on a linear scale.

## IV. DISCUSSION

The electrical conductivity of the GaAs samples studied here is so small that the thermal conductivity must be attributed to lattice thermal conductivity. The lattice thermal conductivity of a crystal at low temperature exhibits a maximum at temperatures of the order of 1/30 the Debye temperature, which for GaAs is 346°K.[23] At lower temperatures the phonon mean free path is limited by boundary scattering and although it is long, few phonons are excited so that the conductivity is low. At higher temperatures three phonon (anharmonic) umklapp processes become important and decrease the mean free path, and therefore the thermal conductivity is also low. In the intermediate region of the maximum, the thermal conductivity is extremely sensitive to the presence of point defects.

The interpretation of experiments on phonon scattering of point defects is difficult because treatments of the point-defect scattering must include the other scattering mechanisms. It is clear that the resulting theoretical thermal conductivity will depend on just exactly how this is done. We do not wish to engage in a detailed discussion of the various theories and approximations that have been made, but will restrict ourselves to a discussion of (1) previous experimental observations on point-defect thermal conductivity, (2)

[23] Recent survey: J. R. Drabble and H. J. Goldsmid, *Thermal Conduction in Semiconductors* (Pergamon Press Ltd., London, 1961).

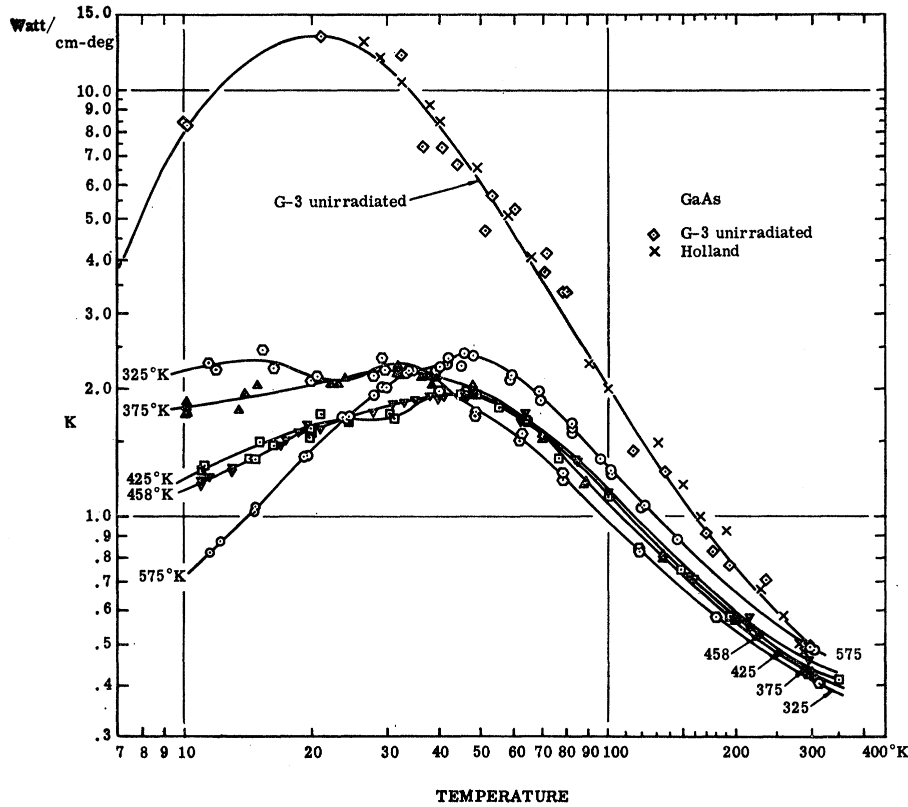


FIG. 5. Temperature dependence of the thermal conductivity of GaAs, G-3 before irradiation and after irradiation for successive 15-min isochronal anneals between 325 and 575°K.

discussion of the concentration dependence of the point-defect thermal conductivity, and (3) simple calculations of the magnitude of the effects.

Previous experiments of point-defect phonon scattering may be conveniently divided into two categories. The first is isotope scattering, in which the main perturbation arises through a change only in mass. The second is a stronger perturbation in which the point defect perturbs the lattice with a localized change in force constants (e.g., by lattice strain or chemical bonding) as well as a change in mass. An example of isotope scattering is the data on enriched $Ge^{74}$ and

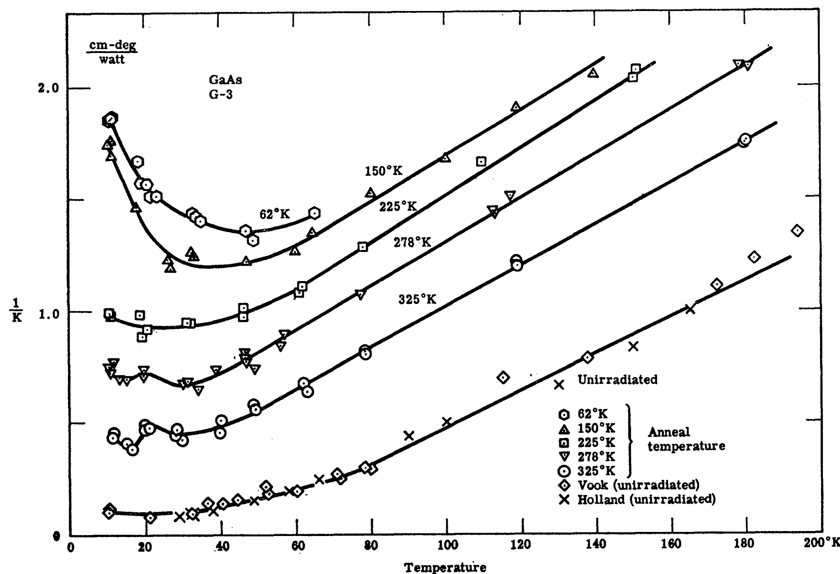


FIG. 6. Temperature dependence of the thermal resistivity of GaAs, G-3 before irradiation and after irradiation below each of the indicated 15-min anneal temperatures. Annealing temperatures be-between 62 and 325°K.

isotopically normal germanium measured by Geballe and Hull.[24] Another example is the data of Berman *et al.*[25] on the isotope effect in LiF. These results are characteristic of Rayleigh scattering and exhibit a decreasing thermal conductivity with little or no shift in the position of the maximum as the isotopic purity is decreased.

A typical example of the second type of point defect is contained in the data of Pohl[9] for $F$ centers in LiF. Here the conductivity decrease is larger on the low-temperature side of the maximum than on the high-temperature side resulting in a progressive shift of the maximum to higher temperatures as the impurity content is increased. The latter behavior, although common, violates the Rayleigh-type scattering found for isotopes.

Theoretical studies to explain isotope scattering have been made. A Deybe-model treatment by Klemens[26] and a variational approach by Ziman[27] lead to a formula $1/K-1/K_0\propto C(1-C)$, where $C$ is the fractional concentration of one species of isotope or impurity whose mass differs from the average mass. Klemens later extended his theory[28] to include scattering due to a change in force constants (strain and bonding) as well as by a difference in mass. It is not expected that the result above should hold for large concentrations. Experimental data of Berman *et al.*[25] agreed with this theory for $C\rightarrow 0$; but for appreciable concentrations of imperfections, the actual thermal resistivity rose with concentration much less rapidly than $C(1-C)$. In a more general variational treatment in which the contribution of three-phonon normal processes is calculated explicitly, Berman *et al.*[25] predict that the thermal resistance should become proportional to the square root of the effective defect concentration at large concentrations. This trend agrees with that deduced by Toxen[29] from a collection of thermal conductivity data by several workers. Pohl[9] has explained the nonlinearity pointed out by Toxen on the basis of Callaway's theory,[30] using a combined relaxation time together with the fact that the boundary can act as a cutoff mechanism for low-frequency phonons. For the case of a single kind of impurity at low temperature where the impurity scattering is dominant, Callaway's theory[30,31] leads to an expression for the total thermal resistivity which is approximately proportional to the square root of the concentration.

[24] T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).
[25] R. Berman, P. T. Nettley, F. W. Sheard, A. N. Spencer, R. W. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) **A253**, 403 (1959).
[26] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).
[27] J. M. Ziman, Can. J. Phys. **34**, 1256 (1956).
[28] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).
[29] A. M. Toxen, Phys. Rev. **110**, 585 (1958).
[30] J. Callaway, Phys. Rev. **113**, 1046 (1959).
[31] J. Callaway, in *Proceedings of the International Conference on Semiconductor Physics, Prague 1960* (Academic Press Inc., New York, 1961), p. 627.

At high temperatures ($T>\theta$) and small defect concentrations, Berman *et al.*[32] and Ambegaokar[33] have derived a contribution to the thermal resistivity $\propto C$ the concentration of defects. However, if defect scattering is dominant even at high temperature, Klemens[34] and Callaway[31] have shown the thermal resistivity is proportional to the square root of the defect concentration. In summary, most theories predict that the defect thermal resistivity is proportional to the concentration of defects for small concentrations and proportional to the square root of the concentration for larger concentrations.

### 1. Bombardment

In light of the above discussion it is interesting that we do observe a linear increase in defect thermal resistivity versus integrated flux and therefore versus defect concentration. This behavior does agree with the prediction of Klemens and Ziman for small concentrations of defects.

Since it is always difficult to determine the absolute defect concentration in any radiation damage experiment, we wish to first present those results which depend the least on any one particular theory. If we take an average thermal resistivity of $(1/K)-(1/K_0)=3.1\times10^{-19}$ cm-deg/W per 2.0-MeV electron/cm$^2$ and use the strain (length-change) measurements reported previously[13,20] for 2.0-MeV electron bombarded GaAs, the resulting experimental ratio of thermal resistivity to lattice strain at 50°K is

$$\frac{1/K-1/K_0}{3\Delta L/L}=\frac{3.1\times10^{-19}\text{ cm-deg/W}}{3.0\times10^{-23}}=(1.0\pm0.2)\times10^{4}\text{ cm-deg/W}. \quad (5)$$

If we now estimate the number of defects produced, we can calculate the thermal resistivity per defect in the additive resistance approximation. Using the Seitz-Koehler displacement theory[35] and the effective threshold displacement energy of 45 eV obtained from the length measurements,[20] the fractional concentration of defects is $C=3.3\times10^{-23}\Phi$, where $\Phi$ is the number of 2.0-MeV electron/cm$^2$ passed through the sample.

$$W_d=\frac{1}{K}-\frac{1}{K_0}=3.1\times10^{-19}\Phi=\frac{3.1\times10^{-19}\times C}{3.3\times10^{-23}}=(94\pm10)\times10^{2}C\text{ cm-deg/W}. \quad (6)$$

The above results can be compared with the defect scattering theories of Klemens[2,34] and Ziman.[25] Klemens

[32] R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956).
[33] V. Ambegaokar, Phys. Rev. **114**, 488 (1959).
[34] P. G. Klemens, Phys. Rev. **119**, 507 (1960).
[35] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 305.

gives the following formula for point defect scattering:

$$\frac{W_d}{T}=\frac{3(2\pi)^2a^3S^2}{hv^2 0.90G}, \qquad (7)$$

where $W_d$ is the thermal resistivity due to the point defects; $T$ is the absolute temperature; $1/G=C$ is the fractional concentration of defects; $1/a^3=N_0$ the number of atoms per unit volume; $(a^3G)^{-1}$ is the number of imperfections per unit volume; $h$ is Planck's constant; $v$ is the sound velocity, and $S^2$ is a dimensionless scattering parameter. Klemens[34] made estimates of the scattering arising from point imperfections in simple cubic lattices in the limit of long waves.

Approximately, $S^2=S_1^2+(S_2+S_3)^2$. Here $S_1$, $S_2$, and $S_3$ take account, respectively, of scattering due to mass difference, change in elastic constant, and lattice strain.

$$S_1^2=\tfrac{1}{12}(\Delta M/M)^2, \qquad (8a)$$

$$S_2=\frac{1}{\sqrt{6}}\frac{\Delta f}{f}=\frac{1}{\sqrt{6}}\frac{\Delta(v^2)}{v^2}, \qquad (8b)$$

$$S_3=-(\tfrac{2}{3})^{1/2}Q\gamma(\Delta R/R). \qquad (8c)$$

$M$ is the average mass of a unit cell and $M+\Delta M$ is the mass of the defect. Similarly, $f$ is the force constant of a linkage, $v^2$ is the square of the sound velocity, $R$ is the nearest-neighbor distance, and $\Delta M$, $\Delta f$, $\Delta(v^2)$, $\Delta R$ are the changes in them. $Q\simeq 4.2$ if the nearest linkages have the same anharmonicity as all other links, but $Q=3.2$ if the anharmonicity of the nearest links is excluded, e.g., for a vacancy. Here $\gamma$ is the Grüneisen constant obtained from thermal-expansion data. The value used was $\gamma=0.1$, the measured low-temperature value for germanium.[36]

Calculations of $S^2$ and $W_d$ were made using the Klemens theory [Eqs. (7) and (8)] applied for the case of vacancies assuming $\Delta M/M=-1$, $\Delta(v^2)/v^2=-1$, $Q=3.2$ and each defect has a volume expansion of $3\Delta R/R=\Delta V/V=0.94$ atomic volume.[20] The results yield $S_1^2=0.083$, $S^2=0.32$, and $W_d=3.2\times 10^2$ cm-deg/W where $C$ is the fractional concentration of defects. Klemens emphasizes that the estimates of $S^2$ are very uncertain since the effects of lattice distortion and foreign bonds are difficult to treat. Experience[34,37–41] has shown that the calculated values using Eq. (7) tend to be too low. Carruthers[3] suggests that the scattering of phonons by static strain fields can be much larger than predicted by Klemens.[28] Using the model of a point defect represented by a sphere of radius $r_0$ embedded in an isotropic elastic medium, Carruthers concludes that for relative atomic misfits, $\epsilon r_0$ evaluated at $r=r_0$, the strain field scattering is much greater than the corresponding Rayleigh scattering for values of $\epsilon>0.1$. Such values for $\epsilon$ are certainly expected for volume expansions of $\Delta V/V=0.94$ atomic volume.

Ziman's variational treatment,[25] although leading to the same functional form for $W_d$, predicts a numerical coefficient 54 times larger than Klemens' value. Ziman's treatment should hold where phonon-phonon scattering is extremely strong with respect to defect scattering. Ziman's calculations considered only mass-difference scattering. Since it is a variational treatment, it gives a lower limit on $K$ or an upper limit on $W_d$. If Ziman's coefficient holds for all three types of scattering, then $W_{d\,\mathrm{Ziman}}\leq 173\times 10^2C$. Our experimental value of $94\times 10^2C$ is well within these two theoretical predictions. In addition, the thermal resistivity, as seen in Fig. 6 for G-3, exhibits a linear temperature dependence between 60 and 180°K for anneals below 325°K in agreement with the dominance of point-defect scattering.

### 2. Annealing

Since the thermal resistivity is a linear function of defect concentration on bombardment, one might make the simple assumption that it is also a linear function on annealing. The fraction of defects remaining after a 15-min isochronal anneal at each temperature would then be shown in Fig. 3. The following points are evident: (a) Annealing begins as low as 55°K. (b) About 70% of the increased thermal resistivity stable at 50°K anneals out by 325°K.[41a] (c) Annealing begins to accelerate near 190°K in agreement with similar results[20] for length change annealing. (d) The annealing that is observed for GaAs takes place over too large a temperature range to be due to a single thermally activated process.

The last conclusion in particular is supported by the observed temperature dependence of the thermal conductivity of G-3 below each annealing temperature. Figure 4 shows the temperature dependence of the thermal conductivity below each isochronal anneal for anneals below 325°K. The original unbombarded thermal conductivity curve is also shown together with the dashed line, giving the theoretical[32] boundary scattering curve which would apply for our sample size. Holland's data for GaAs having $7\times 10^{15}$ impurities and $v_s/L=4.0\times 10^5$ sec$^{-1}$ is also included. The velocity $v_s$ is the average of the transverse and acoustical mode velocities derived from elastic constant data, and $L$ is defined as the diameter of a circle having the same

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cross-sectional area as the sample. Below 10°K we have plotted Holland's data reduced to our sample size, which had $v_s/L=4.2\times10^6$ sec$^{-1}$ and contained approximately the same number of impurities. The anneal curve following irradiation, marked 62°K, shows the large decrease in the thermal conductivity produced by the introduction of the defects. A noticeable shift in the peak temperature to higher temperatures is evident. This dependence is not characteristic of Rayleigh scattering. A progressive shift in the position of the maximum to higher temperatures as the impurity content is increased has, however, been observed frequently[9,37,41] for "point-defect" scattering that involves a change in localized force constants (strain and/or bonding) as well as a change in mass. The thermal conductivity increases at all temperatures for anneals below 325°K as the maximum of the thermal conductivity curve shifts back to lower temperatures.

A further striking observation is the formation of distinct minima near 20°K in the thermal conductivity curves of the 278, 325, and also 425°K anneals. A similar inflection is observed in Fig. 4 near 20°K in Holland's data for unirradiated GaAs. This inflection does not appear in the Callaway fit to his data which is shown as the smooth curve. Such inflections, seen recently in ionic crystals, have been ascribed by Walker and Pohl,[42] and Wagner[43] to resonant scattering from localized impurity modes. The identity of the defect responsible for this localized mode is as yet unknown and requires further investigation.

Figure 5 shows the annealing curves above 325°K. Here the thermal conductivity curves for increasing anneal temperatures cross previous curves. The thermal conductivity above 40°K increases corresponding to normal annealing, whereas the thermal conductivity below 40°K decreases corresponding to "reverse" annealing. This behavior unambiguously means that the defects are changing their phonon-frequency scattering dependencies, and in particular that one no longer has only point defects. The direction of the changes in the temperature dependence suggests that the point defects are clustering into colloids or precipitates to provide a scattering nearer to boundary scattering. Indeed, extremely similar behavior was observed by Klein[44] in the precipitation and clustering of dissolved $MnCl_2$ in NaCl crystals which had been quenched from 300°C, and by Walker and Pohl[42] in the precipitation of dissolved $CaCl_2$ in KCl crystals. The larger defect concentration of G-1 could produce a higher precipitation rate and account for the deviation in the anneal curves of G-1 and G-3 above 325°K as shown in Fig. 3. After the highest anneal at 575°K the low-temperature thermal conductivity exhibits a $T^{1.0}$ dependence suggesting a scattering mechanism with a phonon-frequency dependence of $\omega^2$ characteristic of thin sheets of precipitate imbedded in a single crystal.[2]

These annealing effects should be distinguished from the large concentrations of defects observed only after high-temperature annealing of as-grown GaAs by Blanc *et al.*[45] ($450<T<800$°C). They measured bulk density, trap densities, and thermal conductivity before and after annealing. A bulk density increase was observed for anneals above 700°C. Measurements by Vook[20] of the length change of unirradiated GaAs on annealing to 325°C showed no density change in agreement with the above results. The anneal, however, of 2.0-MeV electron irradiated GaAs did show a length change decrease (density increase) between 250 and 325°C. This anneal is very likely associated with the clustering of the point defects as seen in thermal conductivity.

The results presented here demonstrate that low-temperature irradiations and measurements are indeed necessary to study primary defects in GaAs. They imply that the 500°K annealing step observed by Aukerman[46] and Vook[20] is not, as previously suggested,[46] associated with close-pair interstitial vacancy recombination for high purity *n*-type GaAs. These annealing data show that although electron irradiations very likely produce point defects on bombardment, the defects do not necessarily remain point defects throughout the annealing.

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