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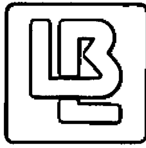

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Presented at the IR Detector Technology
Workshop, Mountain View, CA,
August 13-14, 1985

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August 1985

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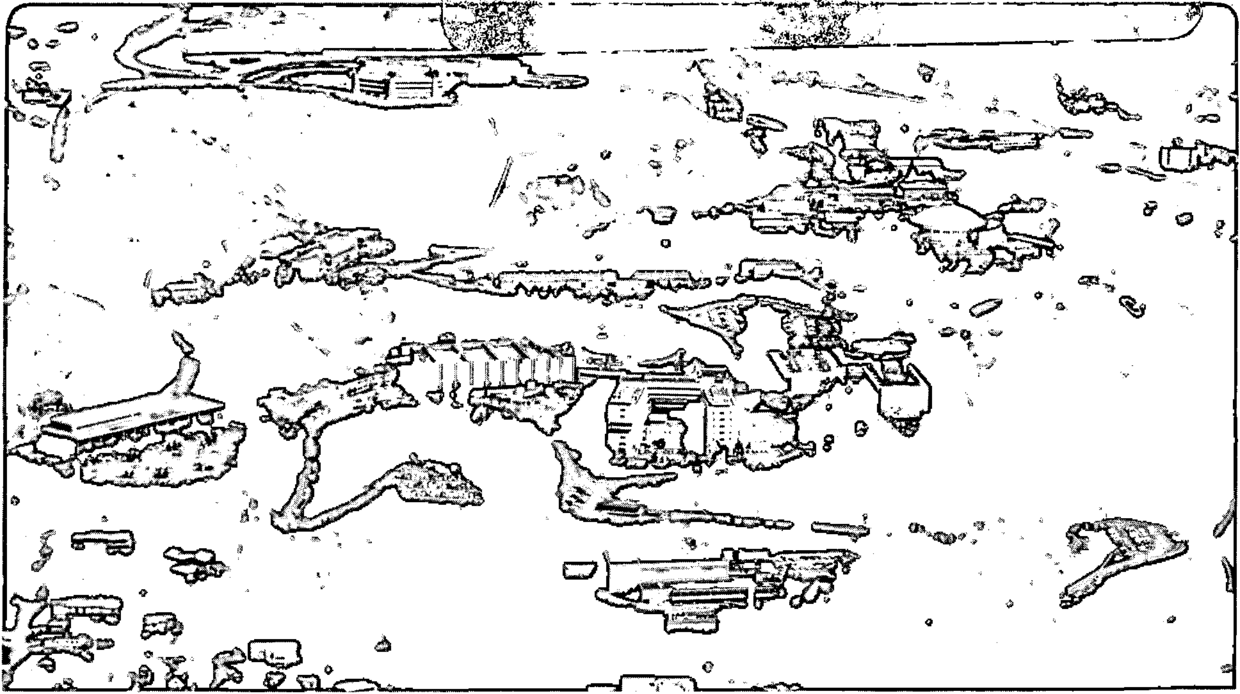

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STATUS OF NTD Ge BOLOMETER MATERIAL AND DEVICES

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Lawrence Berkeley Laboratory and
University of California

Summary-Abstract

This status report is a direct follow up to the presentation given at the first IR Detector Technology Workshop which took place at NASA Ames Research Center on July 12 and 13, 1983 (1). The conclusions which we presented at that meeting are still fully valid. In the meantime we have learned more about the physics of hopping conduction at very low temperatures which will be important for bolometer design and operation at ever decreasing temperatures. Resistivity measurements have been extended down to 50 mK. At such low temperatures, precise knowledge of the neutron capture cross sections σ_n of the various Ge isotopes is critical if one is to make an accurate prediction of the dopant concentrations and compensation, and therefore resistivity, that will result from a given irradiation. We describe an empirical approach for obtaining the desired resistivity material and are in the process of conducting a set of experiments which will improve the knowledge of the effective σ_n values for a given location in a particular reactor. A wider range of NTD Ge samples is now available. Noise measurements on bolometers with ion implanted contacts show that no 1/f noise component appears down to 1 Hz and probably lower.

1. Introduction

High performance bolometers for far infrared, low background applications (2) typically utilize a semiconductor thermistor and are operated at very low temperatures (T < 4.2 K). At such temperatures, the electrical conductivity

of a doped and compensated semiconductor is dominated by the hopping mechanism: charge carriers tunnel from occupied to empty energy levels in the semiconductor bandgap. The hopping mechanism is thermally activated and depends exponentially on the hopping distance, which in turn depends strongly on the dopant concentrations and the compensation. The majority dopant provides the tunneling charge carriers whereas the minority dopant creates the empty majority sites due to compensation.

Incorporation of dopant impurities during growth of a semiconductor crystal from a melt typically leads to impurity concentration fluctuations which are called striations. At room temperatures these striations may lead to macroscopic fluctuations of the electrical conductivity of a few percent. In the hopping conduction regime these variations become much more important and local variations of several orders of magnitude in resistivity are not uncommon. The problem becomes worse as the temperature is lowered.

A much more uniform dopant distribution can be achieved with the neutron transmutation doping (NTD) process (3). This technique is based on the decay of a host crystal isotope into a dopant impurity after capture of a thermal neutron. Nuclear reactors are used as the source of thermal neutrons. The NTD process has been developed commercially for doping silicon with phosphorus donors for high voltage, high power devices. No acceptors are created in Si by NTD. This makes the process useless for doping Si for bolometer applications. Germanium, in contrast, contains isotopes which decay into acceptors as well as isotopes which decay into donors. Table 1 contains the information on the NTD reactions which are relevant for doping. The transformations of one Ge isotope into another stable Ge isotope are not listed. Because the natural isotopic abundance of a given element is fixed, the dopant concentration ratios and the compensation will be fixed as well.

2. Low Temperature Conductivity of NTD Ge

Since the last workshop, a number of new NTD Ge samples have been processed. Two groups have made electrical conductivity measurements down to ~ 250 mK and ~ 50 mK. Figure 1 displays the results obtained by E. Kreysa, MPI Bonn, using five of our NTD Ge samples. Figure 2 shows the results obtained by J. Krause, Lake Shore Cryotronics, Inc. The excellent fit of straight lines to the results displayed as an Arrhenius plot with modified temperature dependence $(1/T)^{1/2}$ supports the theoretical model of Shklovski and Efros (4) for low temperature hopping conduction. Their model leads to the following resistivity dependence:

$$\rho = c \exp(\Delta/T)^{1/2} \qquad \text{Eq. (1)}$$

The constants c and Δ in Eq. 1 can be theoretically estimated. The accuracy is, however, not sufficient for useful predictions of the resistivity in the temperature range of interest. Table II contains the experimentally determined preexponential factors c and the exponent constants Δ for the various samples. The measurements done by J. Krause on our NTD sample No. 12 do not permit the determination of c because the precise geometry of the Ge samples was not known. The deviations of the data at very low temperatures from the hopping conduction as described by Eq. 1 are currently attributed to resistive heating of the devices. Further measurements are required to verify this point. The resistivity dependence given by Eq. 1 is asymptotically approached at low temperatures and represents the ultimate low temperature dependence. All of our samples give results which are well described by Eq. 1 over several orders of magnitude which means that resisitivity values can be predicted accurately to much lower temperatures. This is useful for the design of bolometers to be operated at even lower temperatures.

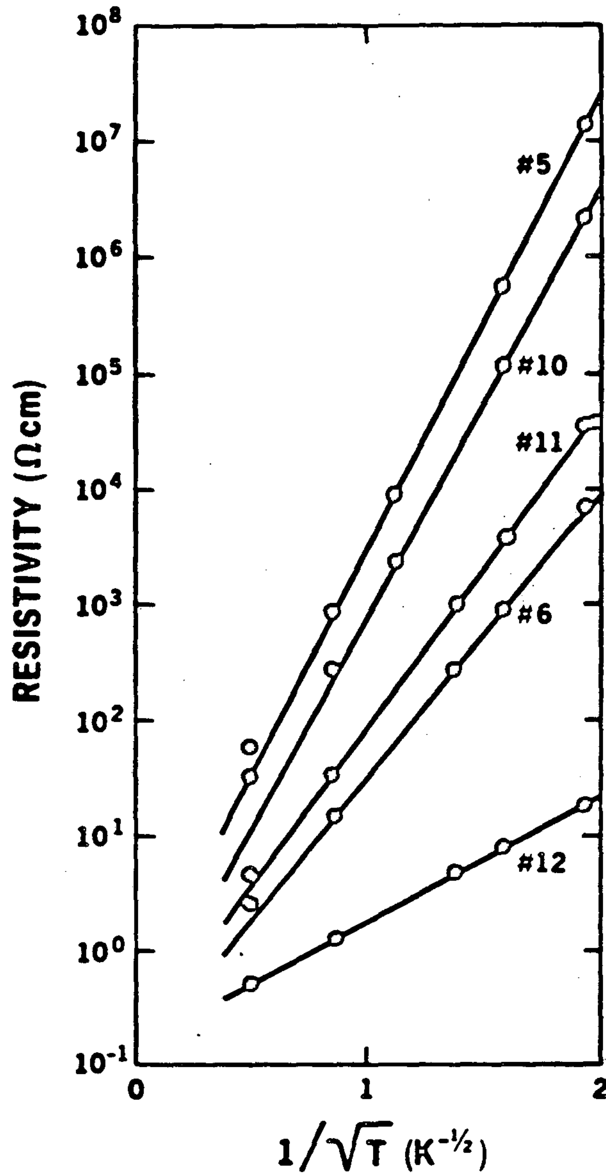

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Figure 1. Modified Arrhenius plot of the resistivity and the temperature of five neutron-transmutation-doped Ge samples. The excellent fit of straight lines to the experimental points supports the law described by Eq. 1.

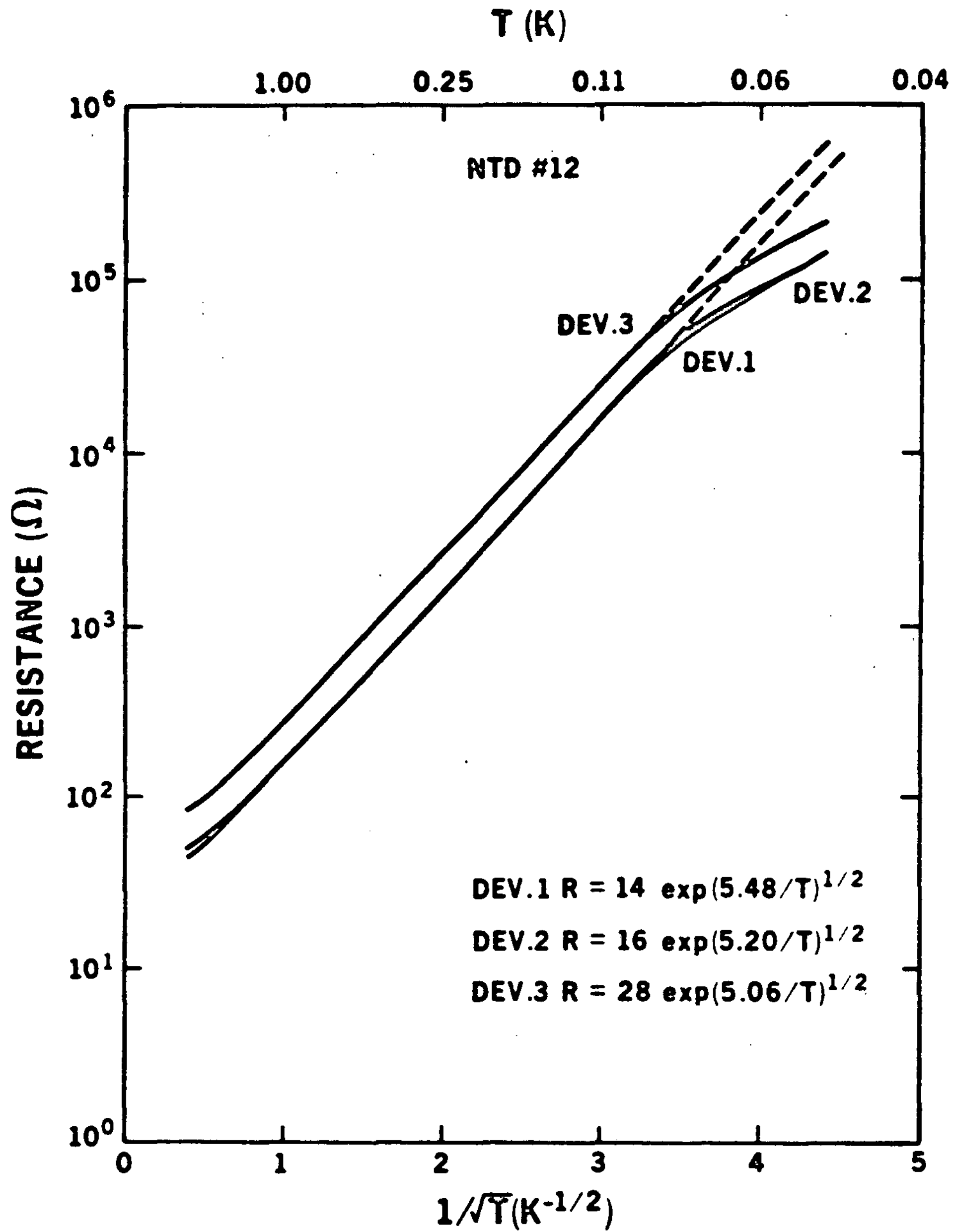

Figure 2. Modified Arrhenius plot of the resistance and the temperature of three resistors fabricated from NTD Ge sample No. 12. The deviation of the experimental data from the straight line is assumed to be due to self heating.

Figure 3 shows the range of resistivity and temperatures for which we currently have NTD Ge samples. We are interested in collaborating with groups who are interested in studying some of the samples, particularly at temperatures below 1 K.

3. Thermal Neutron Capture Cross Sections

The concentrations of the dopants obtained by the NTD process depend on isotopic abundance, neutron flux and the neutron capture cross sections. While the first two parameters are known to high precision, the value of the latter parameter shows large fluctuations from one reference to another. Table III summarizes cross sections σ for the relevant Ge isotopes from four reference sources. The difficulty in obtaining accurate values for σ lies in the fact that σ is an integral over the neutron energy dependent differential cross section $d\sigma/dE$. It appears difficult to obtain a perfectly "thermal" neutron energy spectrum with which a precise value of σ can be determined. Even if this could be achieved, it would be of little help to the experimenter who wants to dope a crystal at a given reactor which may not produce a perfectly thermal spectrum. From our experience with work done at the Missouri Research Reactor we find that NTD done always in the same location leads to reproducible results. A number of closely spaced neutron exposures will "box-in" the range of interest. One to two iterations have always been sufficient to create material with the required properties.

We are in the process of determining experimentally the neutron cross sections by measuring the net-carrier concentrations as a function of time after neutron exposure. The total exposure time for the NTD is negligibly short compared to the decay times of interest. Since the various dopants are produced with very different time constants, it is possible to observe the

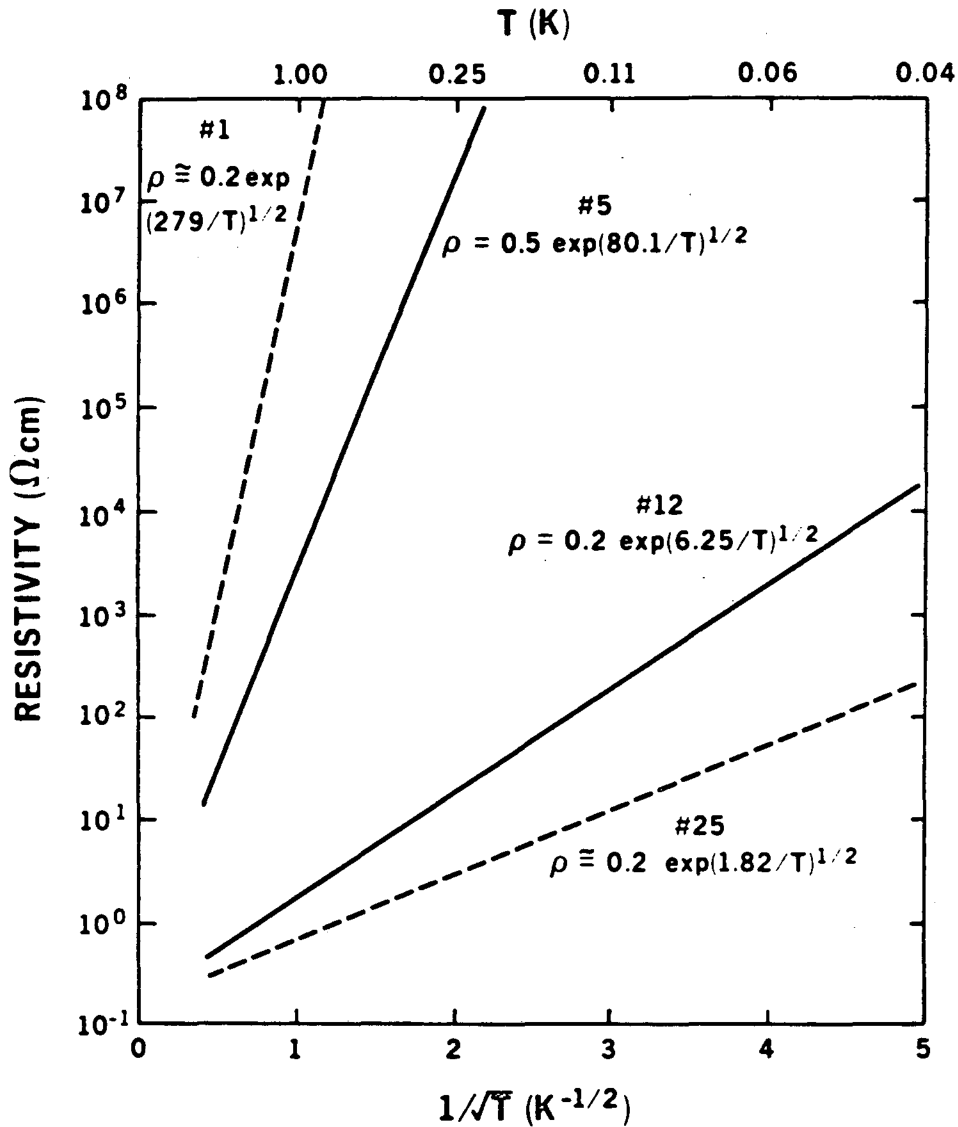

Figure 3. NTD Ge in the range between #1 and #12 are currently available. More heavily doped samples (up to #25) are being processed.

generation of the arsenic donors ($T_{1/2}$ = 82.2 min) almost independently of the gallium acceptors ($T_{1/2}$ = 11.2 d) and the selenium double donors [$T_{1/2}$(dominant) = 38.8 hrs]. Figure 4 shows the dependences of the dopant concentrations as a function of time calculated for the cross sections reported in Ref. 1 of Table III. The net dopant concentration $N = N_{Ga} - N_{As} - 2N_{Se}$ is shown as well. The selenium concentration is counted twice because

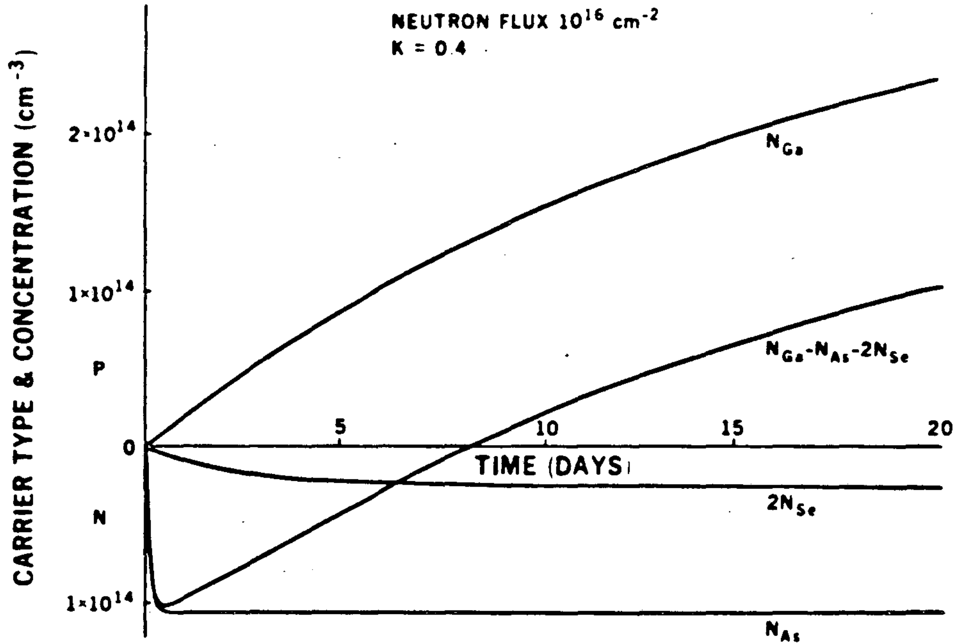

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Figure 4. The evolution of the Ga, As and Se concentrations as a function of time after a brief neutron irradiation cycle. The net-dopant concentration is shown as well. Cross sections given in Ref. 1 in Table III have been used.

each selenium double donor gives up two electrons to compensate two shallow gallium acceptors. The maximum of N on the n-type side occurs after 9.6 hrs and it reaches 96% of the ultimate arsenic concentration. After ~ 8.2 days, a type change occurs from n to p. After several half lives of ^{71}Ge creating ^{71}Ga, one reaches the ultimate net-acceptor concentration. Figure 5 shows how sensitive the net-dopant curve is to changes in cross sections. Depending on the set of cross sections, the time for the change of type changes from ~ 8.2 days (K = 0.40, Ref. 1, Table III) to ~ 6.3 days (K = 0.32, Ref. 2, Table III). The net-dopant concentration changes as well. The change of type occurs at a certain time, t_0, independent of the total neutron flux. This provides an additional restriction for a set of experimental curves. They all must cross on the x-axis at t_0. Thermal annealing of the residual fast

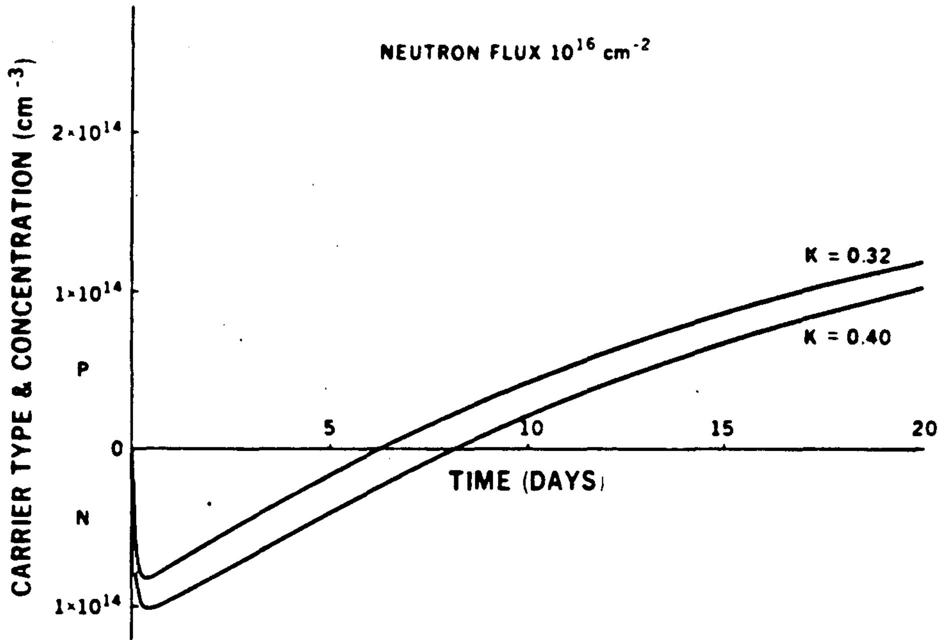

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Figure 5. The cross-over time from n- to p-type is very sensitive to the particular set of neutron cross sections. An experimental study of the net-carrier concentration as a function of time will determine whether the curve labelled with compensation K = 0.4 (Ref. 1 of Table III) or with K = 0.32 (Ref. 2 of Table III) or neither is appropriate for the reactor used in our case.

neutron radiation damage after irradiation can introduce rapidly diffusing impurities such as copper, a triple acceptor. When the Cu is in a substitutional position, the crossing point of the experimental curves will be offset to the p-type side if Cu contamination occurs. We are currently in the process of generating such curves to extract a much more accurate set of cross section values for a particular reactor.

4. Conclusions

Experimental and theoretical results show that NTD Ge can be used successfully as bolometer material down to 50 mK and most probably much lower. Predictions of resistivity at lower temperatures can be made with good accuracy because the law described by Eq. 1 is of asymptotic nature at low

temperatures. Despite the small dependence of the neutron capture cross sections of the various germanium isotopes on the neutron energy spectrum, one can achieve predictable doping by first "bracketing" the target neutron flux range and then using the same location in a given reactor for further doping cycles.

The question of heat capacity, C_v, of NTD Ge at very low temperatures has not been addressed. It seems probable that at very high doping levels and very low temperatures, deviations from the simple Debye law [$C_v \propto (T/\theta)^3$] must be expected. In the case of NTD Ge the effect of the dopants is expected to be very small because the masses of the dopants fall inside the range of the masses of the stable Ge isotopes. No local vibrational modes or broad resonances will be created. We conclude from this that in NTD Ge the effect of dopants on the heat capacity must be much smaller than in a case where dopants of very different mass from the host crystal are introduced via diffusion or ion implantation. This latter case applies, for example, to silicon bolometer material. Careful measurements at very low temperatures will be required to explore this issue.

Acknowledgments

We are indebted to Jon Meese* and John Farmer at the Missouri Research Reactor facility for their great help in providing NTD Ge with excellent reliability. Ernst Kreysa of the Max-Planck-Institute in Bonn provided the measurements shown in Fig. 1 and John Krause of Lake Shore Cryotronics, Inc. made the measurements on three Ge resistors shown in Fig. 2. We are particularly grateful for these measurements as we are not in a position to evaluate samples down to such low temperatures in our laboratory.

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2. See for example: Haller E E, Infrared Physics 25, 257 (1985) and references therein.

3. For reviews of the NTD process, see: Proceedings of the 4th Conference on "Neutron Transmutation Doping of Semiconductor Materials", ed. R.D. Larrabee, Plenum Press, 1984; and earlier Proceedings.

4. See for example: Shklovski B I and Efros A L, Electronic Properties of Doped Semiconductors, Springer Series in Solid State Sciences, 45, 1984.

TABLE I.

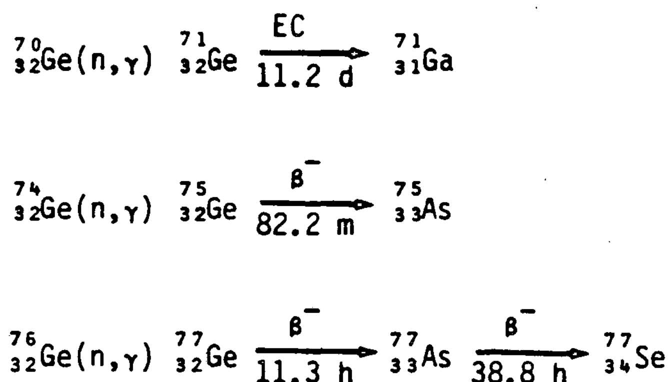

TABLE II.

Sample* No.	Neutron Flux (cm^{-2})	Preexponential Factor c	Exponent Factor Δ
5	7.50×10^{17}	0.50	80.10
6	1.88×10^{18}	0.15	30.84
10	9.25×10^{17}	0.20	72.54
11	1.65×10^{18}	0.20	40.27
12	3.33×10^{18}	0.20	6.25
12**			
Dev. 1			5.48
Dev. 2			5.20
Dev. 3			5.06

*Data from E. Kreysa, MPI, Bonn.

**From the resistance measurements of J. Krause, Lake Shore Cryotronics,, Inc.

TABLE III. SUMMARY OF PUBLISHED CROSS SECTIONS (in barns)

$\sigma_n(^{70}Ge)$	$\sigma_n(^{74}Ge)$	$\sigma_n(^{76}Ge)$	$K = \frac{N_{As} + 2N_{Se}}{N_{Ga}}$	Ref.
3.46	0.62	0.36	0.40	1
3.25	0.52	0.16	0.32	2
3.20	0.50	0.20	0.33	3
3.68 ± 0.8	0.65 ± 0.2	0.20 ± 0.03	0.35	4

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