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Low Temperature Hopping Conduction in Neutron Transmutation Doped Isotopically Enriched 70Ge:Ga Single Crystals

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The temperature dependence of variable range hopping resistivity ρ in neutron transmutation doped (NTD) isotopically enriched ^{70}Ge:Ga samples is reported. Five samples with compensation ratios K less than 0.001 and Ga concentrations between 3×10^{16} and 1.77×10^{17} cm^{-3} were studied. All samples investigated show the $\ln \rho \propto T^{-1/2}$ dependence in the temperature range below 1.5K. As thermistor materials NTD ^{70}Ge:Ga samples are found to have more than factor of two higher sensitivity than commonly used natural NTD Ge in the temperature range between 0.2K and 1K. Our results are compared with theoretical predictions for variable range hopping conduction.

1. INTRODUCTION

Neutron transmutation doped (NTD) germanium with natural isotopic composition (^{nat}Ge) has been widely used for phonon mediated detectors for dark matter searches and neutrino physics [1-3], as thermistors for a wide range of radioastronomical observations [4-7] and for cosmic ray background measurements. [8] Application of the NTD technique to Ge has been the key to successful thermistor fabrication since NTD is known to produce the most homogeneous, perfectly random dopant distribution down to the atomic level.[9] The broken lines labeled "NTD 2~28" in Fig. 1 represent the temperature dependence of the resistivity of a number of ^{nat}Ge samples doped by NTD. Log ρ is plotted against $T^{-1/2}$ in Fig. 1 because the theory of the "variable range hopping conduction" [10], the hole transport mechanism dominant below ~1K, predicts the following temperature dependence of the resistivity ρ for doped Ge:

$$\rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/2} \tag{1}$$

where ρ_0 and T_0 are parameters which depend on the majority dopant concentration N_A and the the compensation ratio K, i.e., the ratio of acceptor and donor concentrations. It is seen in Fig. 1 that the resistivity of all NTD ^{nat}Ge samples obeys the law given in Eq.1. The compensation range 0<K<1 is required for holes to be able to hop from neutral to ionized acceptors using the available thermal energy from the crystal environment.

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A particle (radiation) detector such as a NTD Ge thermistor makes use of the well behaved dependence of the resistivity on temperature described above. The thermistor is maintained at a base temperature T_B by a thermal link connected to a thermal bath. The temperature increase of the thermistor due to energy dissipation of incident particles or radiation is detected by the change in the resistivity. The sensitivity is defined by the temperature coefficient α:

$$\alpha = \frac{1}{R}\left(\frac{\partial R}{\partial T}\right)_{T_B} \qquad (2)$$

where R is the resistance. Electronic noise considerations require an optimum thermistor resistance of 5×10^6 to 5×10^7 Ω. The larger the $\partial R/\partial T$, the larger is the signal for a given ΔT. If one wishes to design $\partial R/\partial T$ for a given T_B, appropriate control of the parameters ρ_0 and T_0 appearing in Eq. 1 is required. As stated above, ρ_0 and T_0 depend on N_A and K. The application of the NTD technique to ^{nat}Ge allows one to control N_A and N_D (by adjusting the amount of neutron irradiation), but the compensation ratio $K(=N_D/N_A)$ remains fixed at 0.32.[9] A control of K can be realized only by changing the isotopic composition of the starting Ge crystals as discussed in Ref. 11.

In this work, 96.3At.% isotopically enriched, chemically pure ^{70}Ge single crystal samples were doped by NTD with Ga via the electron capture reaction $^{70}Ge+n\rightarrow{}^{71}Ge+e\rightarrow{}^{71}Ga$. As a result, homogeneously Ga doped ^{70}Ge samples with extremely small compensation $K<0.001$ were produced (less than 1 out of 1000 Ga sites does not bind a hole !). The low temperature resistivity of these samples was measured in order to understand the effect of small K on ρ_0 and T_0. Results are compared to those of NTD ^{nat}Ge and quantitatively interpreted with hopping conduction theory.

2. EXPERIMENTAL

A single crystal ^{70}Ge with an electrically active impurity concentration $\sim10^{12}$cm^{-3} was grown using the vertical Bridgman method described in Ref. 12. Five 1mm thick wafers cut from the ingot were thermal neutron irradiated at the University of Missouri Research Reactor. Rapid thermal annealing for 10 seconds at 700°C in a N_2 atmosphere was required to remove the fast neutron related defects. A strip about 1mm thick was cut from each wafer and ohmic contacts were formed by the B^+ 3×10^{14}cm^{-2} implantation. 200Å thick Pd and 4000Å Au pads were sputtered on the implanted layer. The strips were annealed again at 300°C for one hour to remove the implantation damage and stress in the metal film. Cu wires were attached to the Au pads. The Cu wires heat sink the samples and provide electrical currents through the ohmic contacts during measurements. The samples were suspended from the contact wires in a Cu box in order to avoid any stress. A two point resistivity measurement was selected because of the high resistance of the five samples measured in this work. An I-V curve of each sample was recorded on a X-Y plotter by slowly changing the bias voltage. The linear (ohmic) part of I-V curve starting from the origin was used to calculate the resistivity of each sample.

3. RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of the resistivity of five NTD ^{70}Ge:Ga and of eight NTD ^{nat}Ge samples. Excellent fits with Eq. 1 are obtained for all resistivity

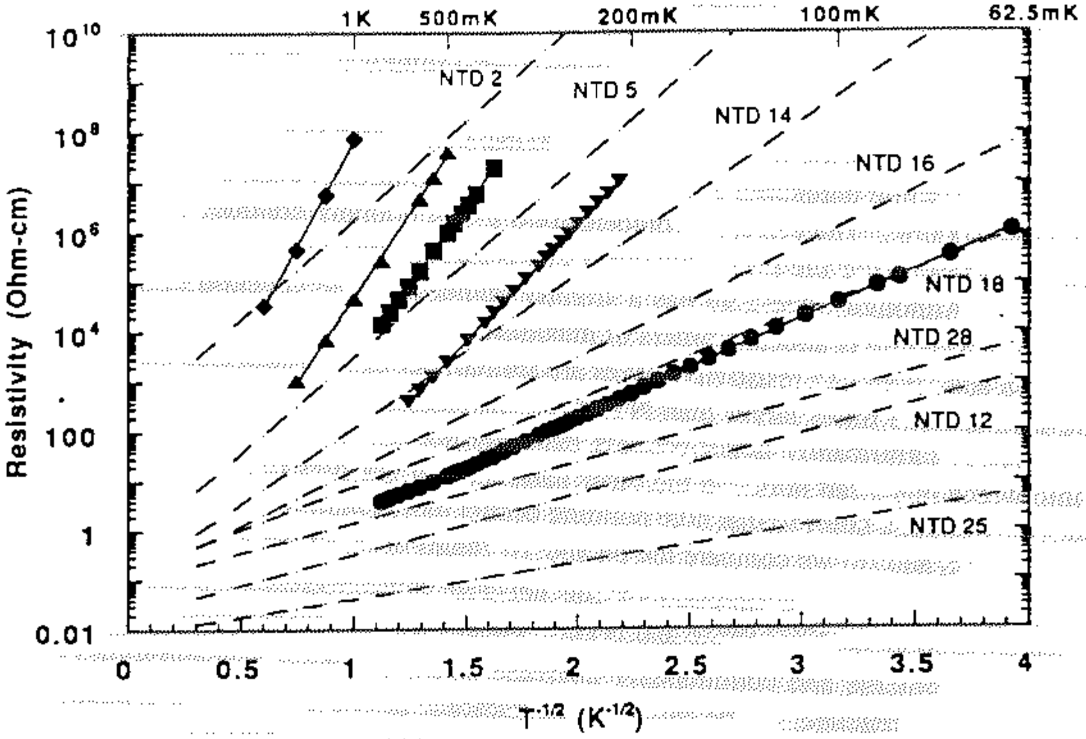

Fig. 1 Temperature dependence of resistivity of various NTD ^{nat}Ge:Ga and NTD ^{70}Ge:Ga samples: ^{70}Ge-3.30 (◆), ^{70}Ge-2.98 (▲), ^{70}Ge-1.90 (■), ^{70}Ge-1.65 (▼), and ^{70}Ge-2.15 (●)

TABLE I

Basic parameters of the NTD Ge samples study in this work

	Concentration ($\times 10^{16}$cm^{-3})						
Sample	[Ga]	[As]	[Se]	Net Hole	K	ρ_0 (Ω cm)	T_0 (K)
NTD 2	0.044	0.013	0.001	0.03	0.32	200	82.9
NTD 5	2.2	0.63	0.041	1.5	0.32	0.47	77.6
NTD 14	3.9	1.1	0.073	2.7	0.32	0.11	49.0
NTD16	6.1	1.7	0.11	4.2	0.32	0.1	26.5
NTD 18	7.7	2.2	0.14	5.3	0.32	0.15	15.9
NTD 28	9.0	2.6	0.17	6.3	0.32	0.09	7.84
NTD 12	9.8	2.8	0.18	6.8	0.32	0.02	7.84
NTD 25	12.3	3.52	0.23	8.6	0.32	0.008	2.74
^{70}Ge-3.30	3.02	<0.003		3.02	<0.001	0.34	364.8
^{70}Ge-2.98	8.00	<0.008		8.00	<0.001	0.0074	247.6
^{70}Ge-1.90	9.36	<0.009		9.36	<0.001	0.0019	201.4
^{70}Ge-1.65	14.5	<0.01		14.5	<0.001	0.0006	100.3
^{70}Ge-2.15	17.7	<0.01		17.7	<0.001	0.0215	20.7

curves. Table I lists basic sample parameters such as [Ga], [As], [Se], and the net-hole concentration (N_A-N_D), compensation ratio K, and the parameters, ρ_0 and T_0, fitted with Eq. 1.

For cosmic ray background [8] and other measurements performed in ^{3}He refrigerators near 300mK, we first note that NTD ^{70}Ge-1.90 is more sensitive than NTD5 for T>300mK by a factor of 2.6. ^{70}Ge-1.90 has a T_0 which is a factor 2.6 larger than T_0 of NTD5 while maintaining the resistivity in the optimum range of $10^5 \sim 10^7 \Omega$ cm at T=300~500mK. The effect of compensation to the hopping conduction can be recognized by comparing the resistivity curves of NTD18 with ^{70}Ge-2.98 and ^{70}Ge-2.15 in Fig. 1. Although ^{70}Ge-2.98 has a slightly higher net-hole concentration than NTD18, ρ of ^{70}Ge-2.98 is almost 4 orders of magnitude larger than ρ of NTD18 around 1K. NTD 18 and ^{70}Ge-2.15 resistivity curves are similar, but the net-hole concentration of ^{70}Ge-2.15 is three times larger than NTD18. The resistivity of ^{70}Ge:Ga samples with K<0.001 is significantly larger because there are not enough empty Ga acceptor states into which holes can hop. On the other hand 32% of Ga sites in NTD ^{nat}Ge are ionized (i.e., without a hole) so that hole hopping occurs more readily.

In Fig. 2 (a) and (b) we compare the ρ_0 and T_0 values of NTD ^{nat}Ge:Ga and NTD ^{70}Ge:Ga, respectively, as a function of the net-hole concentration. Despite the difference in K, ρ_0 of the NTD ^{nat}Ge and NTD ^{70}Ge in Fig. 2 (a) for concentrations up to $\sim 10^{17}$ cm^{-3} coincide and continuously decrease until a net-hole concentration of 1.5×10^{17} cm^{-3} is reached. The higher concentration points of ^{70}Ge rise again. Although a similar dependence was reported for Si:P system [13], confirmation of this increase in ρ_0 requires further investigation. For T_0 significant differences exist between NTD ^{nat}Ge and NTD ^{70}Ge as shown in Fig. 2 (b). For semiconductors with K<<0.1, the value of T_0 approaches zero as the net-hole concentration n_h approaches the metal-semiconductor transition critical concentration n_c with a form: [14]

$$T_0 = A \left(1 - n_h/n_c \right)^{\beta} \qquad (3)$$

where A and β are constants. Using Eq. 3, a good fit to the T_0 of NTD ^{70}Ge (solid line in Fig. 2 (b)) is obtained with:

$$T_0 \, (\text{NTD } ^{70}\text{Ge}) = 437.3 \pm 16 \; \left(1 - n_h / 1.89 \times 10^{17} \text{cm}^{-3} \right)^{1.06 \pm 0.12}, \qquad (4)$$

Eq. 4 allows us to estimate the amount of Ga doping necessary to obtain a specific value of T_0 for our future NTD ^{70}Ge doping. Knowing the value of β also allows us to estimate the other important parameters such as the hole localization length and dielectric constant.[14] However, this will be discussed in a future publication because more T_0 data points are necessary to obtain a truly reliable fit. We also attempted to fit T_0 of NTD ^{nat}Ge with Eq. 3 but were unsuccessful. n_c of NTD ^{nat}Ge must be larger than n_c of NTD ^{70}Ge because NTD ^{nat}Ge has a significantly higher compensation. However, it is impossible to fit T_0 of NTD ^{nat}Ge with n_c larger than 1.89×10^{17}cm^{-3}. In general, much of the theoretical work on the variable range hopping conduction, including Eq. 3, has been developed for the case of nearly uncompensated semiconductors. Further studies are clearly necessary to develop a better understanding of the effect of compensation on hopping conduction.

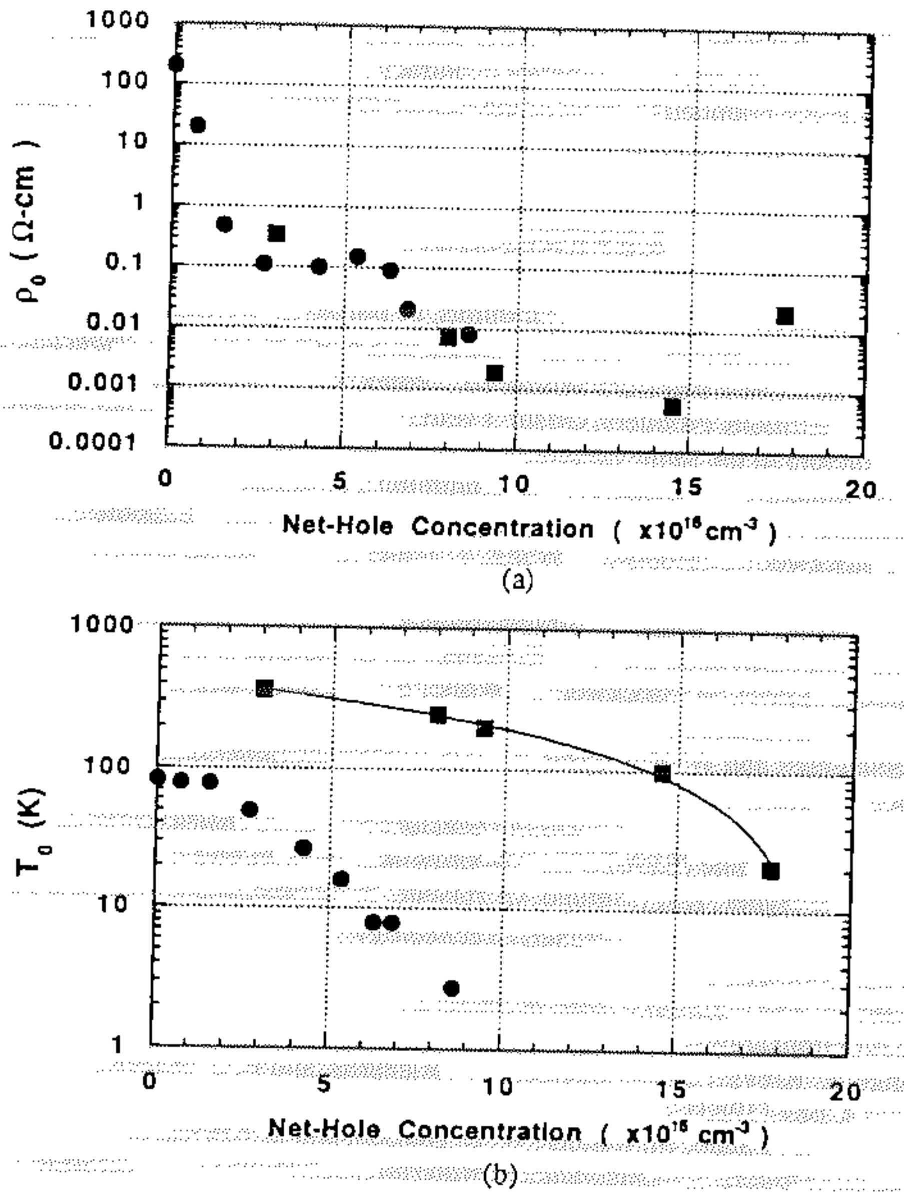

Fig. 2 Net-hole concentration dependence of (a) ρ_0 and (b) T_0 of NTD ^{nat}Ge:Ga (●) and NTD ^{70}Ge:Ga(■)

4. CONCLUSION

The neutron transmutation doping technique was successfully applied to isotopically enriched ^{70}Ge crystals. ^{70}Ge:Ga samples with a range of Ga concentrations with K<0.001 were produced. The temperature dependence of the variable range hopping resistivity of NTD ^{70}Ge:Ga was found to be significantly different from that of NTD ^{nat}Ge due to the difference in the compensation ratio. The NTD ^{70}Ge:Ga thermistors were found to have more than a factor of two higher sensitivity than NTD ^{nat}Ge devices for temperatures T>300mK.

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REFERENCES

[1] B. Sadoulet, T. Shutt, N. Wang, A. Commings, P. Barnes, J. Beeman, J. Emes, Y. Giraud-Heraud, E. E. Haller, A. Lange, J. Rich, and R. Ross, in *Low Temperature Detectors for Neutrinos and Dark Matter III*, edited by L. Brogiato, D. V. Camin and E. Fiorini (Editions Frontiers, Gifsur Yvette, 1990), p. 227, and other papers by various authors in the same volume.

[2] T. Shutt, B. Ellman, P. D. Barnes, Jr., A. Cummings, A. Da Silvia, J. Emes, Y. Giraud-Héraud, E. E. Haller, A. E. Lange, R. R. Ross, J. Rich, B. Sadoulet, G. Smith, W. Stockwell, C. Stubbs, N. Wang, S. White, B. A. Young, and D. Yvon, *Phys. Rev. Lett.* **69**, 3425 (1992).

[3] T. Shutt, N. Wang, B. Ellman, Y. Giraud-Héraud, C. Stubbs, P. D. Barnes, Jr., A. Cummings, A. Da Silvia, J. Emes, E. E. Haller, A. E. Lange, J. Rich, R. R. Ross, B. Sadoulet, G. Smith, W. Stockwell, S. White, B. A. Young, and D. Yvon, *Phys. Rev. Lett.* **69**, 3531 (1992).

[4] C. R. Cunningham and W. K. P. Gear, in *Proc. SPIE: Instrumentation in Astronomy VII* **1235**, 515 (1990).

[5] E. Kreysa, in *Proc. Int. Symp. of Photon Detectors for Space Instrumentation*, edited by T. D. Guyenne (ESA/ESTEC Noordwijk, 1993), in press.

[6] E. Kreysa, E. E. Haller, H.-P. Gmünd, G. Haslam, R. Lemke, and A. Sievers, in *Proc. 4th Intl. Conf. on Space Terahertz Technology*, Univ. California, Los Angels, 3/30-4/1/93

[7] E. E. Haller, in *Proc. 5th Int. Confr. on Infrared Physics, Int. J. IR MM Waves*, accepted for publication.

[8] A. E. Lange, E. Kreysa, S. E. McBride, P. L. Richards, and E. E. Haller, *Int. J. IR MM Waves* **4**, 689 (1983).

[9] E. E. Haller, N. P. Palaio, M. Rodder, W. L. Hansen, and E. Kreysa, in *Neutron Transmutation Doping of Semiconductor Materials*, edited by R. D. Larrabee (Plenum, New York, 1984), p.21.

[10] B. I. Shklovskii and A. L. Efros, in *Electronic Properties of Doped Semiconductors*, Solid State Series Vol. 45 (Springer-Verlag, Berlin Heidelberg, 1984)

[11] K. Itoh, W. L. Hansen, E. E. Haller, J. W. Farmer, and V. I. Ozhogin, in *Proc. 5th Int. Conf. on Shallow Impurities in Semiconductors*, edited by T. Taguchi (Trans Tech, Switzerland, 1993), p. 117.

[12] K. Itoh, W. L Hansen, E. E. Haller, J. W. Farmer, V. I. Ozhogin, A. Rudnev, and A. Tikhomirov, *J. Mater. Res.* **8**, 1341 (1993).

[13] W. N. Shafarman, D. W. Koon, and T. G. Castner, Phys. Rev. B, **40**, 1216(1989).

[14] T. G. Castner, in *Hopping Transport in Solids*, edited by M. Pollak and B. Shklovskii (North-Holland, Amsterdam, 1991), p.1.