RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 45, NUMBER 8 15 FEBRUARY 1992-II

Non-Ohmic hopping conduction in doped germanium at $T < 1$ K

Sabrina M. Grannan and Andrew E. Lange
Department of Physics, University of California, Berkeley, California 94720

Eugene E. Haller
Department of Materials Science, University of California and Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720

Jeffrey W. Beeman
Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720
(Received 8 July 1991)

Measurements of the non-Ohmic behavior of the hopping conductivity of doped germanium between 300 and 700 mK show that the conductivity obeys an electric-field dependence $\sigma(E,T)=\sigma(0,T)\times\exp(eEL/kT)$ at field strengths as low as 0.04 V/cm. This result is in disagreement with theoretical models which predict that the conductivity should obey the relation $\ln\sigma\sim E$ only for field strengths greater than ~ 1 V/cm, below which the conductivity is in an "Ohmic regime." L, the length parameter describing the field dependence, is found to increase with decreasing temperature as $L\sim T^{-1}$ in the variable-range-hopping regime.

I. INTRODUCTION

At very low temperatures the electrical conductivity of doped germanium is dominated by the variable-range-hopping (VRH) mechanism in which electrons hop between impurity sites rather than enter the conduction band. The VRH conductivity obeys the temperature dependence

$$\sigma(T)=\sigma_0\exp[-(T_0/T)^n],\ n=\tfrac{1}{2}\ . \tag{1}$$

The exponent $n=\frac{1}{2}$ is predicted by a model of VRH conduction that accounts for Coulomb interactions between impurity sites, leading to a parabolic density of states near the Fermi level.[1] Previously published results[2,3] show that the conductivity of doped germanium at low bias levels is well described by Eq. (1) at temperatures less than a few degrees kelvin for doping concentrations near 10^{16} cm^{-3}. The present investigation was motivated by the need for further study of non-Ohmic hopping behavior at very low temperatures and bias levels in order to determine the validity of the various theoretical models. Doped germanium is a good candidate for measuring non-Ohmic behavior at ^{3}He temperatures (300–700 mK) because its behavior in the Ohmic limit has been well established.

Theoretical models describing non-Ohmic hopping conduction generally separate non-Ohmic behavior into conduction in low, moderate, high, and very high electric fields. In low fields the conductivity is expected to be nearly independent of the applied field. This is the so-called "Ohmic regime" discussed in the theoretical models of Hill,[4] Pollak and Riess,[5] and Shklovskii.[6] Low fields are defined as fields $E<E_c$, where $E_c=kT/eL$ and L is a length parameter related to R, the maximum hop length between impurity sites. There is some controversy over the dependence of L on R. According to Hill and Pollak and Riess, $L=CR$ where R is the maximum length of a hop between impurity sites and C is a constant of order unity equal to either 0.75 (Hill) or 0.17 (Pollak and Riess). However, Shklovskii found that $L\approx R^2/a$, where a is the radius of the wave function of the impurity states.

Bottger and Bryksin have developed a model for hopping conduction in moderate electric fields.[7,8] They find that for modest electric fields the conductivity will decrease with increasing field before increasing exponentially with the field. This is because some of the electron hops are oriented in the direction opposite to the external field. This effect has been observed experimentally by Zabrodskii and Shlimak,[9] Aleshin and Shlimak,[10] and Aladashvili *et al.*[11]

In high electric fields $E_c<E<kT/ea$, the theoretical models[4-6] predict a conductivity of the form

$$\sigma(E,T)=\sigma(0,T)\exp[e(E-E_c)L/kT]\ . \tag{2}$$

Although these models agree that $\ln\sigma\sim E$, the exact form of $L(R)$ will determine both the field E_c at which non-Ohmic behavior sets in and the strength of this behavior. As L increases, E_c should decrease as L^{-1} and the conductivity should increase as $\ln\sigma\sim L$. The theory of variable range hopping predicts that R, the maximum hop length, is given by $R=(a/2)(T_0/T)^n\sim T^{-n}$ where n is the exponent in Eq. (1).[12] We can therefore discriminate between various theories by measuring the temperature dependence of L.[10] In the models of both Hill and Pollak and Riess $L\sim T^{-n}$, while in the Shklovskii model $L\sim T^{-2n}$. Although these models were developed for the case $n=\frac{1}{4}$, corresponding to a constant density of states near the Fermi level, it has been suggested[10] that the derivations of Eq. (2) should not depend on n. Equation (2) has been verified experimentally for both $n=\frac{1}{4}$ conduction[13] and for $n=\frac{1}{2}$ conduction,[14-16] supporting this claim.

In very high electric fields $E>kT/ea$, theoretical models predict that the conduction becomes "activationless," meaning that the electrons participating in hops acquire

the energy for executing a hop not from thermal activation but from the electric field. In this case the conductivity is independent of temperature and increases with increasing electric field as

$$\sigma(E) \sim \exp(-E_0/E)^m, \tag{3}$$

where the exponent m is equal to the exponent n for the Ohmic conductivity.[17] Activationless hopping conductivity has been observed experimentally, with most authors[14,18-20] finding that for $n=\frac{1}{2}$, $m=\frac{1}{2}$. However, Aleshin and Shlimak[10] found that for $n=\frac{1}{2}$, $m=\frac{1}{4}$. Crandall[21] reports a saturation of the conductivity in extremely high electric fields, for which the conductivity begins to decrease with increasing field as $\ln\sigma \sim 1/E$.

II. EXPERIMENTAL PROCEDURE

Measurements were carried out on neutron-transmutation-doped germanium cubes 0.20 mm on a side. In the neutron-transmutation-doping (NTD) process[22] ultrapure crystalline germanium is exposed to a thermal neutron source. The various stable isotopes capture neutrons and some decay into dopant impurities. NTD is a preferred doping method because the doping is extremely homogeneous and reproducible, and the compensation is fixed by the neutron capture cross sections and the relative abundance of the germanium isotopes to a value of 0.32. To ensure that we were measuring changes in electrical conductivity due to an applied electric field rather than to thermal heating (both of which will increase the conductivity), we glued two samples together with nonconductive epoxy and used the first to measure non-Ohmic conductivity and the second to monitor the system temperature. [In the analysis that follows we have assumed that stress on the samples due to the epoxy bond will not significantly change the form of $L(T)$; this assumption must be verified in future measurements on unstressed samples.]

Electrical contacts were made to each germanium sample with two copper wires 3 mm long and 25 μm in diameter. Only two wires were used for each sample because the contact impedances were typically 4–5 orders of magnitude smaller than the sample impedances. The copper wires were attached to the boron implanted and gold metallized contacts of the samples with conductive epoxy. The other ends of the copper wires were attached to posts which were heat sunk to a temperature-controlled stage thermally linked to a ^{3}He refrigerator with an operating temperature of 300 mK. The stage temperature was held constant to 0.1% by a four-wire calibrated Lakeshore thermometer, a conductance bridge, a negative feedback circuit, and a heater.

The impedances of the germanium samples were measured using an ac square-wave bias at 12 Hz. The ac bias voltage, V_{in}, was applied across the series combination of a room-temperature load resistor and the cold germanium sample under test. The voltage at the germanium chip was amplified by a junction field-effect transistor source follower and demodulated using phase synchronous detection. The ac bias eliminated the effects of thermal emfs and low-frequency noise. The reproducibility of the resistance measured in this manner was on the order of a few parts in ten thousand.

III. EXPERIMENTAL RESULTS

The measured conductivity of two samples of germanium with different doping densities is plotted in Fig. 1. Sample 1 has a doping density $N_A - N_D = 2.6\times10^{16}$ cm^{-3} and sample 2 has a doping density $N_A - N_D = 3.3\times10^{16}$ cm^{-3}. The temperature dependence of both materials is well fit by a law of the form given in (1), with $T_0 = 52.5$ for sample 1 and $T_0 = 42.4$ for sample 2. Uniformity of the doping density was confirmed by measuring several samples of each doping density. The dispersion in T_0 was $\sim 1\%$.

Figure 2 shows the dependence of the electrical conductivity on the applied electric field at several temperatures. We found that for both samples 1 and 2 the conductivity obeyed the relation $\ln\sigma \sim E$ over a range of field strengths 0.04–0.2 V/cm and a range of temperatures from 302 to 707 mK. The upper limit of the field strength is the field at which the conductivity of the second chip began to measurably increase due to thermal heating. L was calculated from the slope of $\ln R$ vs E using the relation $L = (\ln R)kT/eE$, and is plotted against temperature in Fig. 3. Measurements of L were repeated for two samples of each doping density, and variations in L were found to be $\sim 2\%$. For the measured values of L at 300 mK, the Ohmic regime should extend to $E_c = 1.3$ V/cm in sample 1 and to $E_c = 2.0$ V/cm in sample 2. Our results indicate that E_c is significantly smaller than predicted by theoretical models and is smaller than the field strengths in our measurement. Also, we find that $\ln\sigma$ depends linearly on E at values down to $\sigma(E)/\sigma_{Ohm} \approx 1.01$, where σ_{Ohm} is the value of the conductivity in the Ohmic regime. This contradicts a computer simulation by Levin and Shklovskii[12] and the experimental results of Timchenko *et al.*,[14] in which the linear dependence of $\ln\sigma$ on E begins at $\sigma(E)/\sigma_{Ohm} \approx 1.3$.

Since $L \sim T^{-x}$, we can find x from the slope of $\ln L$ vs

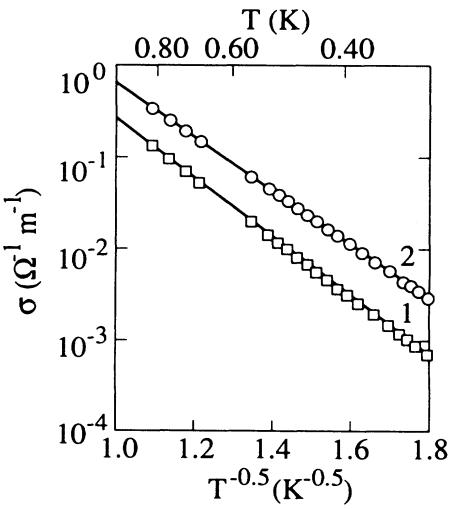

FIG. 1. Temperature dependences of the electrical conductivity of doped germanium samples from 300 to 800 mK. Curves are numbered in the same way as the samples.

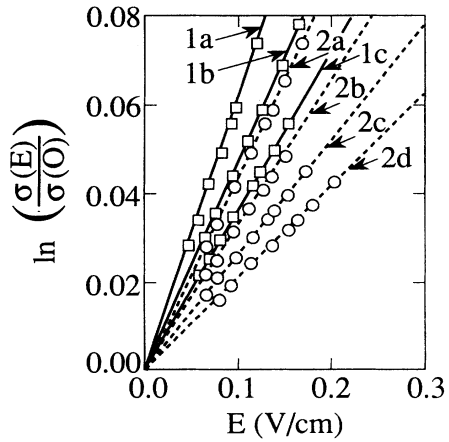

FIG. 2. Field dependences of $\ln[\sigma(E)/\sigma(0)]$ obtained at various temperatures (mK): (a) 317, (b) 362, (c) 422, and (d) 520. Solid lines correspond to sample 1; dashed lines correspond to sample 2.

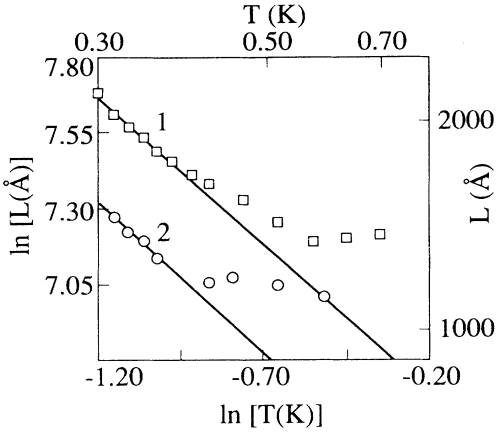

FIG. 3. Temperature dependence of the length parameter L deduced from the field dependences. Best-fit lines are for points at $T < 400$ mK. Curves are labeled in the same way as the samples.

$\ln T$ in Fig. 3. At $T < 400$ mK the best fit to $\ln L$ vs $\ln T$ gives $x = 0.99$ (sample 1) and $x = 1.01$ (sample 2), in agreement with the Shklovskii model predicting that $L \sim T^{-2n} \sim T^{-1}$. However, for $T > 400$ mK, x approaches zero and L becomes nearly temperature independent. This is probably due to a gradual transition between the variable-range hopping regime ($x = 1$) and the nearest-neighbor hopping regime, in which L is temperature independent and determined by the average separation between conduction sites. Measurements of the electrical conductivity over a wider temperature range are necessary to determine whether the samples indeed make a transition to the nearest-neighbor hopping regime, in which $\sigma(T) = \sigma_0 \exp[-(T_0/T)]$. In the literature on $n = \frac{1}{2}$ VRH conduction many different values for x have been reported. Ionov *et al.*[16] obtain a value $x = 0.9$ in crystalline silicon; Aleshin and Shlimak[10] find that $x = 0.8$ and $x = 1.3$ in two samples of amorphous $Ge_{1-x}Cu_x$ films; Timchenko *et al.*[14] measured $L(T)$ in n-type ZnSe crystals and found that $x \sim \frac{1}{2}$; and Rosenbaum, Andres, and Thomas[23] find that L is T independent in Si:P, implying that $x \sim 0$. Perhaps the many values reported for x are due to a difficulty in distinguishing between the VRH and nearest-neighbor regimes. Further study of $L(T)$ over a wider range of temperatures, doping densities, and electric fields is necessary to answer this question.

Using the measured values of T_0 we can calculate R, the maximum hop length, where $R = (a/2)(T_0/T)^{0.5}$ and $a \sim 80$ Å in NTD germanium. In the temperature range studied, for sample 1, we find $R(T)$ lies between 350 and 530 Å with $L(T)$ ranging from 1300 to 2200 Å. For sample 2, $R(T)$ lies between 310 and 480 Å with $L(T)$ ranging from 1000 to 1500 Å. The measured values of L are several times larger than the calculated values of R, again supporting the Shklovskii model but in disagreement with the models of Hill[4] and Pollak and Riess,[5] which predict that $L < R$. In sample 1, L approaches a constant value as R nears 310 Å, which is also the average separation between impurity conduction sites ($N_A - N_D^{-1/3} = 310$ Å). In sample 2, for which the average separation between sites is 340 Å, L approaches a constant value as R nears 350 Å. The asymptotic values of L in both materials are therefore consistent with nearest-neighbor hopping. We note that at a given temperature the value of L for sample 2 is smaller than L for sample 1, which has a lower doping density. This is expected since as the doping density is increased, the average separation between impurity sites decreases. However, among the published results L has not always depended on doping density as expected. Both Kenny *et al.*[24] and Zabrodskii and Shlimak[9] find that L increases with impurity concentration in some samples.

In conclusion, our main results are the following: (i) The dependence of the conductivity on electric field $\ln\sigma \sim E$ begins at fields at least 1 order of magnitude smaller than predicted by theoretical models and is linear down to $\sigma(E)/\sigma_{\text{Ohm}} \approx 1.01$. (ii) In $n = \frac{1}{2}$ VRH conduction the length parameter L varies with temperature as $L \sim T^{-1}$, consistent with the Shklovskii model. As the temperature increases above 400 mK L begins to approach a constant value, which we believe is due to a gradual transition between the variable range and nearest-neighbor hopping regimes.

In the future we would like to test these results by studying the behavior of the electrical conductivity over a wider range of temperatures and applied electric fields. We expect that our results will have an impact on the use of NTD Ge as a thermal sensor and on theories which predict hopping conduction parameters.

[1]B. I. Shklovskii and A. L. Elfros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, Berlin, 1984).
[2]D. Redfield, Phys. Rev. Lett. **30**, 1319 (1973).
[3]A. G. Zabrodskii, Fiz. Tekh. Poluprovodn. **14**, 1130 (1980) [Sov. Phys. Semicond. **14**, 670 (1980)].
[4]R. M. Hill, Philos. Mag. **24**, 1307 (1971).
[5]M. Pollak and I. Riess, J. Phys. C **9**, 2339 (1976).
[6]B. I. Shklovskii, Fiz. Tekh. Poluprovodn. **10**, 1440 (1976) [Sov. Phys. Semicond. **10**, 855 (1976)].
[7]H. Bottger and V. V. Bryksin, Phys. Status Solidi (b) **96**, 219 (1979).
[8]H. Bottger and V. V. Bryksin, Philos. Mag. B **42**, 297 (1980).
[9]A. G. Zabrodskii and I. S. Shlimak, Fiz. Tekh. Poluprovodn. **11**, 736 (1977) [Sov. Phys. Semicond. **11**, 430 (1977)].
[10]A. N. Aleshin and I. S. Shlimak, Fiz. Tekh. Poluprovodn. **21**, 466 (1987) [Sov. Phys. Semicond. **21**, 289 (1987)].
[11]D. I. Aladashvili, Z. A. Adamiya, K. G. Lavdovskii, E. I. Levin, and B. I. Shklovskii, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 390 (1988) [JETP Lett. **47**, 466 (1988)].
[12]E. I. Levin and B. I. Shklovskii, Fiz. Tekh. Poluprovodn. **18**, 856 (1984) [Sov. Phys. Semicond. **18**, 534 (1984)].
[13]R. T. Phillips, A J. Mackintosh, and A. D. Yoffe, J. Phys. (Paris) Colloq. **42**, C4-869 (1981).
[14]I. N. Timchenko, V. A. Kasiyan, D. D. Nedeoglo, and A. V. Simashkevich, Fiz. Tekh. Poluprovodn. **23**, 240 (1989) [Sov. Phys. Semicond. **23**, 148 (1989)].
[15]D. Redfield, Adv. Phys. **24**, 463 (1975).
[16]A. N. Ionov, M. N. Matveev, I. S. Shlimak, and R. Rentch, Pis'ma Zh. Eksp. Teor. Fiz. **45**, 248 (1987) [JETP Lett. **45**, 310 (1987)].
[17]B. I. Shklovskii, Fiz. Tekh. Poluprovodn. **6**, 2235 (1972) [Sov. Phys. Semicond. **6**, 1964 (1972)].
[18]E. I. Savaritskaya, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 231 (1985) [JETP Lett. **41**, 279 (1985)].
[19]A. V. Dvurechenskii, V. A. Dravin, and A. I. Yakimov, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 144 (1988) [JETP Lett. **48**, 155 (1988)].
[20]F. Tremblay, M. Pepper, D. Ritchie, D. Peacock, J. Frost, G. Jones, and G. Hill, Phys. Rev. B **40**, 3387 (1989).
[21]R. S. Crandall, Phys. Rev. B **1**, 730 (1970).
[22]E. E. Haller, Infrared Phys. **25**, 257 (1985).
[23]T. F. Rosenbaum, K. Andres, and G. A. Thomas, Solid State Commun. **35**, 663 (1980).
[24]T. W. Kenny, P. L. Richards, I. S. Park, E. E. Haller, and J. W. Beeman, Phys. Rev. B **39**, 8476 (1989).