Charge Transport along the λ-DNA Double Helix

P. Tran, B. Alavi, and G. Gruner
Department of Physics, University of California at Los Angeles, Los Angeles, California
(Received 28 December 1999)

We have measured the conductivity σ along the lambda phage DNA (λ-DNA) double helix at microwave frequencies using lyophilized DNA in and also without a buffer. The conductivity is strongly temperature dependent around room temperature with a crossover to a weakly temperature dependent conductivity at low temperatures. Removal of the water mantle around the double helix leads to reduced conductivity.

PACS numbers: 87.14.Gg, 72.80.Le

Electronic excitations and motion of electric charges are well known to play a significant role in a wide range of macromolecules of biological interest [1]. Electron transfer involving the DNA double helix is thought to be important in radiation damage and repair and in biosynthesis; the double helix may mediate charge transfer between different metal complexes [2–5]. Recent measurements suggest long-range charge migration [6] with the implication that DNA can be viewed as a one dimensional (1D) well conducting molecular wire. This notion nevertheless has been questioned by recent charge injection experiments conducted at low temperatures on oriented films [7].

Early attempts to measure the conductivity of the DNA double helix were performed on pressed pellets [8], and the results are certainly influenced by charge transport between the DNA strands in close proximity to each other. Two probe resistivity measurements on individual strands have found that DNA is insulating [9] or highly conducting [10]. These experiments were conducted at room temperature only, and there are unresolved questions concerning contact effects and charge injection into the DNA helix. In contrast, semiconducting behavior was observed for short oligomers containing identical base pairs [11].

We have used a configuration which does not require contacts to be attached to the specimen under study and have measured the temperature dependence of the conductivity associated with the DNA double helix at high frequencies. The conductivity was evaluated from the measured loss of highly sensitive resonant cavities operating at 12 and 100 GHz. The technique and the analysis which leads to the evaluation of the conductivity from the measured losses are well established [12]. The material is placed in the high electric field region of the cavity and the resulting change in the quality factor Q of the cavity is measured. Q is inversely proportional to the loss W, and the loss due to the specimen is evaluated from the change (decrease) of Q upon the sample being inserted into the cavity. We treat the DNA strands as thin wires, of 2 nm diameter. For randomly oriented DNA strands placed in a uniform electric field the loss W due to the motion of electric charges along the strands is, to a good approximation, given by [12]

$$W = \frac{1}{3} V \sigma E_0^2 , \tag{1}$$

where V is the volume of the conducting medium (see below), E_0 is the time averaged applied ac field at the position of the sample, the factor of $\frac{1}{3}$ results from a geometrical average of random orientations of the DNA segments with respect to the direction of the applied uniform electric field, and σ refers to the real part of the complex conductivity. Equation (1) was verified by measuring the conductivity of randomly oriented multiwall carbon nanotubes with known dc conductivities.

DNA specimens used in this study are lambda phage DNA (λ-DNA) extracted from *E. coli* and purchased from Sigma-Aldrich and from BioLabs. The "DNA in buffer" samples are DNA lyophilized in buffer [13], and the "dry DNA" samples are purified DNA [14]. In addition, a lyophilized buffer was also prepared and studied to account for the buffer loss. The temperature dependence of the cavity losses due to the dry DNA, DNA in buffer, and buffer alone (at 12 and 100 GHz) are displayed in Fig. 1.

The magnitude of the conductivity of the DNA in buffer was evaluated at 12 GHz in two different ways: (1) by using Eq. (1), and calculating E_0 from the known cavity geometry and the position of the sample, and (2) by comparing the measured loss with the loss measured for a reference material, $Qn(TCNQ)_2$, for which the electrical conductivity is known and proceeds along the direction of a chain structure [12]. We have assumed that the buffer has the density of 1 g/cm^3, while the buoyant density of DNA is 1.7 g/cm^3. The two methods lead to $\sigma = 1.3\ (\Omega\ \mathrm{cm})^{-1}$ and $\sigma = 3.5\ (\Omega\ \mathrm{cm})^{-1}$ with the average, $\sigma = 2.4\ (\Omega\ \mathrm{cm})^{-1}$ at room temperature. Because of geometric constraints and the small sample size we have used, we were able only to estimate the magnitude of the conductivity at 100 GHz, and we have arrived at a value identical, within a factor of 3, to the value quoted above. We conclude therefore that the conductivity, within our measurement accuracy, is independent of the frequency or is only weakly frequency dependent in the spectral range covered by us. Therefore we have normalized the conductivity measured at 100 GHz to the 12 GHz data. In dry DNA the magnitude of

 0031-9007/00/85(7)/1564(4)$15.00

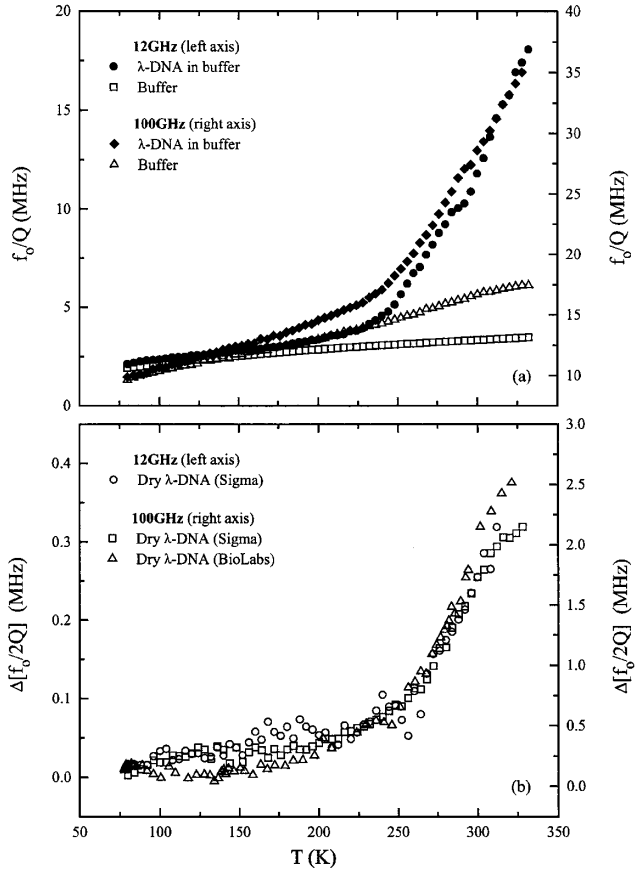

FIG. 1. (a) Temperature dependence of the excess cavity loss for the cavity loaded with the buffer material and the cavity loaded with lyophilized λ-DNA in buffer [13] measured at 12 and at 100 GHz. Buffer materials prepared in slightly different ways all display temperature independent loss, but of somewhat varying magnitude. (b) Temperature dependence of the excess cavity loss for a cavity loaded with dry λ-DNA [14] measured at 12 and at 100 GHz.

the conductivity as evaluated by comparison with the reference material N-Methyl Acridinium $(TCNQ)_2$ [Qn$(TCNQ)_2$] was found to be 0.7 $(\Omega\,\mathrm{cm})^{-1}$ and 0.8 $(\Omega\,\mathrm{cm})^{-1}$ at 12 GHz at room temperature for DNA obtained from both Sigma-Aldrich and from BioLabs, respectively, about 1 order of magnitude smaller than the conductivity found for the DNA in buffer. For these samples the calculated values are 0.4 $(\Omega\,\mathrm{cm})^{-1}$ and 0.46 $(\Omega\,\mathrm{cm})^{-1}$, respectively.

Assuming a helix diameter of $2R = 2$ nm, the effective cross section of a helix is $A = \pi R^2 = 3 \times 10^{-14}$ cm^2 and the conductivity of 1 $(\Omega\,\mathrm{cm})^{-1}$ leads to a resistance of a (hypothetical) 6000 A long helix of approximately $R = 5 \times 10^8$ ohms, about 2 orders of magnitude larger than the estimated (10) dc resistance of a DNA. A 17 μm long λ-DNA strand would have a resistance of 10^{10} ohms, and would appear insulating in a dc measurement of a single strand, in agreement with the findings of Ref. [9].

In Fig. 2 we display the conductivity of λ-DNA, measured at the two different frequencies as the function of inverse temperature, both for the dry DNA products and

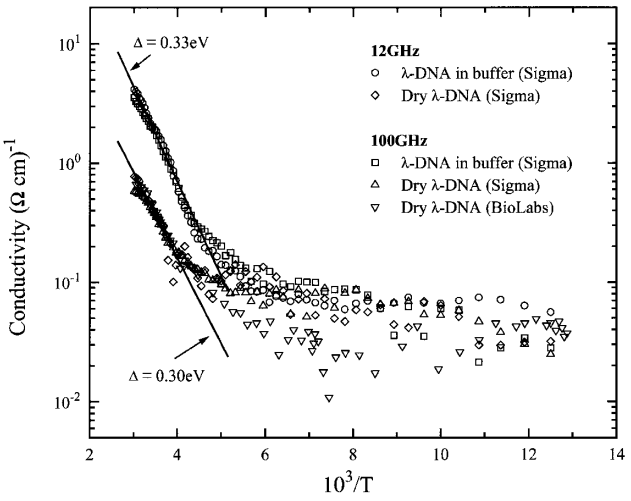

FIG. 2. Conductivity of dry λ-DNA and λ-DNA in buffer versus inverse temperature as measured at 12 and at 100 GHz. The magnitude of the conductivity was determined at 12 GHz, and the 100 GHz data were normalized to the 12 GHz results at room temperature. The full lines are Eq. (2) with Δ values as given in the figure and σ_0 values as given in the text.

for the DNA in buffer. Several aspects of the measured conductivity are of importance. First, as discussed above σ is only weakly frequency dependent over a broad spectral range. Second, the overall temperature dependence is suggestive of two contributions to the transport, a weakly temperature dependent response at low and a strongly temperature dependent contribution at high temperatures. Third, the magnitude of the conductivity at room temperature and above depends on the chemical surroundings of the double helix with a buffer environment leading to larger conductivity.

Several channels may contribute to the charge transport along the DNA double helix; they include electronic conduction along the base pair sequences, ionic conduction associated with the counterions, and loss due to dipole orientation processes in the water mantle surrounding the double helix. While mobile counterions may contribute to the conductivity at low temperatures, where the conductivity is low and is weakly temperature dependent, the absence of buildup of charge polarization upon current flow across the specimens [8] together with the high and strongly temperature dependent conductivity argue for an electronic transport mechanism at and around room temperature. The positions of the water molecules in the layer surrounding the DNA duplex are determined by the electrostatic interactions between the dipoles and the surrounding charges located on the counterions and on the phosphate-sugar backbone. Because of these interactions, the dipole orientations are fixed and losses due to their motion is unlikely. We conjecture therefore that the loss we measure is associated with the motion of electronic charges along the DNA double helix.

Electronic charge transport occurs primarily along one direction in a variety of materials, and in Fig. 3 we compare our findings with the electrical conductivity of

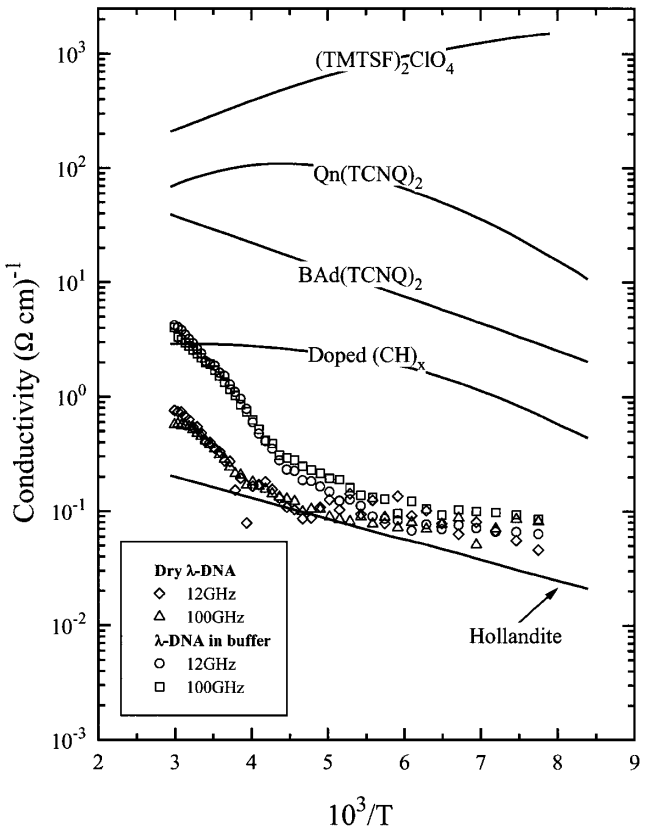

FIG. 3. Conductivity of λ-DNA versus the inverse temperature as measured at 12 and 100 GHz, together with the electrical conductivity of several organic linear chain compounds and an inorganic superionic conductor.

several organic and ionic so-called linear chain compounds where the conduction process occurs along linear stacks of molecules. Tetramethyltetraseleno fulvalene-ClO_4, $(TMTSF)_2ClO_4$, is an organic metal [15] with one of the highest electronic conductivities of any organic conductor along the direction of the stacking axis of the TMTSF molecules. In quinolinium(tetracyanoquinodimethan)$_2$, $Qn(TCNQ)_2$, the conduction process is determined by the randomly positioned counterions which lead to random electrostatic potentials along the TCNQ chains and to an unusual temperature dependence of the conductivity [16]. $NMeAd(TCNQ)_2$ is an organic small band gap semiconductor [17], where the temperature dependence of the electrical conductivity is determined by excitations across a single particle band gap of $\Delta = 0.047$ eV. $(CH)_x$ refers to a highly doped polyacetilene $(CH)_x$ polymer [18] where the conduction is also determined by the dopant carriers and by the random dopant potentials introduced by doping. In all these cases conduction is due to motion of electrons, and in the temperature range displayed the conductivity measured at dc is the same as or close to the conductivity measured at microwave frequencies with little or no frequency dependence observed. Finally, the inorganic compound $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$, called Hollandite, is a superionic conductor where the conductivity is due to motion of highly mobile Li ions in a one-dimensional channel [19]. In this latter case the conductivity is strongly frequency dependent.

The conductivity of λ-DNA at low temperature is comparable to that of a good ionic conductor, and thus, ionic conduction due to counterions may be the primary contribution to the conductivity also in case of the double helix. Such ionic conduction, however, cannot account for a strongly temperature dependent and large conductivity we observe around room temperature and above. As in several other 1D conductors, here we find that the conductivity is well described by the form

$$\sigma = \sigma_0 e^{-(\Delta/2kT)}, \tag{2}$$

which implies temperature driven charge transport processes. A fit to the experimental data, given by the full lines in Fig. 2, lead to $\Delta = 0.33$ eV and $\sigma_0 = 1.2 \times 10^3\ (\Omega\ \mathrm{cm})^{-1}$ for λ-DNA in a buffer environment, and $\Delta = 0.3$ eV and $\sigma_0 = 1.9 \times 10^2\ (\Omega\ \mathrm{cm})^{-1}$ for the dry λ-DNA. The prefactor σ_0 found for DNA in buffer is comparable to what is observed for several organic semiconductors, shown in Fig. 3, where the exponential temperature dependence is due to carrier excitations across single particle gaps or is due to temperature driven hopping transport processes.

Various models have been proposed to describe charge transfer and charge transport along the DNA double helix. First, our findings rule out simple tunneling as the source of charge propagation [20] as tunneling would lead to temperature independent electron transfer rates, and conduction. There are several mechanisms which would lead to strongly temperature dependent electron transport. One possibility is that there is an energy gap for single particle charge excitations which are responsible for the electric current, with the magnitude of the gap determined either by band structure (band semiconductor) or interaction effects [21]. Because of the inherent one dimensionality of the problem, fluctuations are expected to turn a well defined, sharp gap into a smeared, so-called pseudogap [22] but Eq. (2) remains a good approximation at high temperatures. A simple semiconducting gap, however, is unlikely, as the energy scale we find is significantly smaller than the main absorption band of the DNA helix in solution, and smaller than the HOMO-LUMO gap of 6 eV observed in proteins in general. Alternatively, a behavior close to that given by Eq. (2) would occur when phonon assisted polaron hopping [23] or base pair fluctuation limited transport [24] is responsible for the conduction process. Given the soft DNA chain such distortions are likely and the consequences have to be explored in detail. Neither of these models address the issue of the origin of charges responsible for the conductivity, and these models also do not take into account the inherent disorder associated with the random base sequences, and also the random potentials along the DNA double helix arising from the randomly positioned positively charged counterions. Such disorder may have several consequences. First, it may introduce (charged) impurity states into the base pair stacks—these may be responsible for the availability of charges for the

conduction process. Second, it is well established that all electron states are localized by disorder [25] and the conduction under such circumstances proceeds by thermally assisted hopping trough random barriers [26]. At high temperatures hopping occurs between nearest neighbor sites and Eq. (2) is a good approximation [25], with the "gap" reflecting the magnitude of the average of random potentials. Using a model with localized electron states, the charge transport along the DNA helix was calculated recently [27], assuming random transfer integrals along the helix, representing random base pair sequences. While the magnitude calculated is in excellent agreement with the room temperature value we measure, it remains to be seen whether such calculation leads also to the temperature dependence found by us. The different magnitude of the conductivity observed for the DNA in buffer and in a dry environment is in broad agreement with this conjecture. DNA in a buffer is in a water rich environment, while for the dry DNA studied by us, there are approximately five water molecules per base pair [14]. The different water content also leads to different DNA modifications, and also different amounts of disorder along the double helix, with more disorder—and consequently more effective charge localization, and thus smaller conductivity—in a dry environment [28].

Finally, some comments on other measurements of the charge transport are in order. The DNA duplex with random base pair sequences and significant coiling we have investigated is fundamentally different from the short oligomer (built of identical base pairs) studied by Porath *et al.* [11] for which band theory may apply. Second, in view of this disorder the dc conductivity may be orders of magnitude smaller than the transport as measured at high frequencies. In addition to these differences, it is important to recognize that, in view of the one dimensionality of the charge transport, the conductivity is expected to be extremely sensitive to imperfections, and to the local surroundings of the DNA helix. One expects therefore a large variation of the conductivity from different DNA extractions and origins. Experiments involving other DNA helixes, counterion exchange, DNA intercalation, and intentional damage through irradiation are expected to shed further light into the conduction process, and such experiments are underway.

We thank R. Bruinsma, J. Rudnick, and J. Ladik for useful discussions and suggestions. We are grateful to Z. Zettl for providing the nanotube specimens and for communicating his dc results. This research was supported by the National Science Foundation Grant No. DMR-9801816.

[1] A. Szentgyörgyi *et al.,* Proc. Natl. Acad. Sci. U.S.A. **46**, 1444 (1960); D. D. Eley and R. B. Leslie, Nature (London) **197**, 898 (1963).
[2] M. R. Arkin *et al.,* Science **273**, 475 (1996).
[3] C. J. Murphy *et al.,* Science **262**, 1015 (1993).
[4] D. N. Beretan *et al.,* Science **258**, 1740 (1992).
[5] M. D. Purugganan *et al.,* Science **247**, 6548 (1988).
[6] F. D. Lewis *et al.,* Science **277**, 673 (1997); D. B. Hall, R. E. Holmlin, and J. K. Barton, Nature (London) **382**, 731 (1996); P. J. Dondliker, R. E. Holmlin, and J. K. Barton, Science **257**, 1465 (1997); Y. Okahama *et al.,* J. Am. Chem. Soc. **120**, 6165 (1988).
[7] J. Warman, M. de Haas, and A. Rupprecht, Chem. Phys. Lett. **249**, 319 (1996).
[8] R. Pethig, *Dielectric and Electronic Properties of Biological Materials* (Wiley & Sons, New York, 1979), and references cited therein; H. Pohl and W. Kauzman, Rev. Mod. Phys. **36**, 721 (1963).
[9] E. Broun *et al.,* Nature (London) **391**, 775 (1998).
[10] H. W. Fink and C. Schonenberger, Nature (London) **398**, 407 (1999).
[11] D. Porath *et al.,* Nature (London) **403**, 635 (2000).
[12] G. Grüner, in *Millimeter and Submillimeter Wave Spectroscopy of Solids,* edited by G. Grüner, Topics in Applied Physics Vol. 74 (Springer-Verlag, Berlin, 1998), Chap. 4, pp. 111–166; L. I. Buravov and I. F. Shchegolev, Prib. Tekh. Eksp. **2**, 171 (1971). We have neglected depolarization effects in the analysis of the conductivity; such effects most likely do not play a role in random, one dimensional DNA strands. See, for example, M. J. Rice and J. Bernasconi, J. Phys. F **3**, 55 (1973).
[13] Lyophilized from a solution in 1 mM Tris-HCl, pH 7.5, I mM NaCl, 1 mM EDTA, and 330 g/ml DNA, product No. D9768. Lyophilization led to 0.5 mg of DNA (as measured by the intensity of the absorption at 260 nm) in total weight of 4.9 mg. Approximately 80% of the DNA has the full length and approximately 20% are shared, shorter segments.
[14] Purification was performed according to standard procedures. Approximately 85% of the total weight is associated with DNA, and the remaining 15% weight is due to water and residual counterions.
[15] D. Jerome and H. J. Schulz, Adv. Phys. **31**, 229 (1982).
[16] F. Devreux, M. Nechtschein, and G. Grüner, Phys. Rev. Lett. **45**, 53 (1980).
[17] G. Mihály *et al.,* Solid State Commun. **21**, 1115 (1977); K. Holczer *et al.,* J. Phys. C **11**, 4707 (1978).
[18] A. J. Epstein *et al.,* Phys. Rev. Lett. **45**, 1739 (1980); R. Menon *et al.,* Phys. Rev. B **48**, 17 685 (1993).
[19] S. K. Khanna *et al.,* Phys. Rev. Lett. **47**, 255 (1981).
[20] J. J. Hopfield, Proc. Natl. Acad. Sci. U.S.A. **71**, 3640 (1974); J. Jortner, Proc. Natl. Acad. Sci. U.S.A. **95**, 12 759 (1998).
[21] N. F. Mott, *Metal Insulator Transitions* (Taylor and Francis, London, 1990); T. Giamarchi, Physica (Amsterdam) **230B**, 975 (1997).
[22] G. Gruner, *Density Waves in Solids* (Addison-Wesley Publishing Co., Reading, 1994).
[23] P. T. Henderson *et al.,* Proc. Natl. Acad. Sci. U.S.A. **96**, 8353 (1999).
[24] R. Bruinsma *et al.* (unpublished).
[25] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Solids* (Oxford University Press, London, 1971).
[26] K. Holczer *et al.,* Solid State Commun. **31**, 145 (1979); A. N. Bloch, B. R. Weisman, and C. M. Varma, Phys. Rev. Lett. **28**, 753 (1972).
[27] Y. J. Ye *et al.,* Solid State Commun. **112**, 139 (1999).
[28] M. W. Falk, K. A. Kaufman, and R. C. Lord, J. Am. Chem. Soc. **85**, 3843 (1962).