

**Electrical Conduction in Native Deoxyribonucleic Acid: Hole Hopping Transfer Mechanism?**

Zdravko Kutnjak\* and Cene Filipič

*Jožef Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia*

Rudolf Podgornik†

*Department of Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia*

Lars Nordenskiöld and Nikolay Korolev

*Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden*

(Received 21 August 2002; published 3 March 2003)

Measurements of the quasistatic and frequency dependent electric conductivity below 1 MHz were carried out on wet-spun, macroscopically oriented, calf thymus DNA bulk samples, thus effectively extending previous radio frequency data down to quasistatic time scales. The frequency dependence of the electrical conductivity in the frequency range of approximately  $10^{-3}$ – $10^{15}$  Hz agrees well with predictions of the hopping hole mechanism. Temperature dependence of the quasistatic electrical conductivity can be rather well described by the activated Arrhenius law with the activation energy of  $\approx 0.9$  eV; however, based on the quality of the fits, the hopping ansatz cannot be ruled out.

DOI: 10.1103/PhysRevLett.90.098101

PACS numbers: 87.14.Gg, 72.80.Le, 87.15.–v

The conductive properties of DNA have recently attracted substantial interest from both the theoretical as well as the experimental sides [1–4]. Understanding the charge transfer mechanism along a DNA double helix is important in the long-range chemistry of oxidative DNA damage and repair processes, monitoring protein-DNA interactions, and for possible applications in nanoelectronic circuit technology [2,5,6]. However, despite intensive investigations, the nature of the charge transfer mechanism remains a subject of controversy. Various measurements suggest both short- and long-range charge migration [1,2,7,8] with some indication that the DNA duplex can behave similar to a one-dimensional molecular wire [9].

The situation regarding charge transfer mechanisms in DNA became even more confused in view of recent reports on metallic [10], semiconducting [11,12], insulating [13,14], and possibly, at low temperatures, even proximity-induced superconducting [15] behavior of electric conductivity. The dc current-voltage ( $I$ - $V$ ) curves point to a remarkably nonlinear conduction mechanism, apart from classical linear dependence described by Ohm's law.  $I$ - $V$  curves obtained on double stranded  $\lambda$ -DNA show existence of the temperature dependent semiconductive voltage gap [10,12]. It was also shown that, by substituting the imino proton of each base pair with a metal ion, the voltage gap disappears and metallic-like conduction was observed on Zn-DNA [10].

Earlier experiments performed on  $\lambda$ -DNA in the microwave frequency range show large temperature dependent resistivity associated with the DNA duplex and gave evidence for a thermally driven transport process [16]. These experiments together with very recent optical conductivity experiments on native DNA [17] show that the

conductivity in the microwave and optical frequency range is of the order of  $1 \Omega^{-1} \text{m}^{-1}$  at room temperature. Below room temperature, the microwave conductivity is strongly temperature dependent according to the temperature activated ansatz

$$\sigma = \sigma_0 e^{-(U/kT)}, \quad (1)$$

exhibiting a crossover to weakly temperature dependent conductivity at low temperatures [16]. In contrast, it was also shown that temperature dependence of the optical conductivity could be governed by the ansatz

$$\sigma = \sigma_0 e^{-(T_0/T)^\beta}, \quad (2)$$

thus indicating that the variable range hopping could just as well be the dominant conduction mechanism [17]. Nevertheless, various other relaxational and resonant mechanisms such as vibrational and rotational modes could contribute to the imaginary part of the complex dielectric constant, thus influencing the frequency and temperature dependence of the effective electric conductivity at microwave and optical frequencies. Therefore, in order to understand the dc conductivity mechanism, the temperature dependence of the electric conductivity should be extended to low frequencies.

In this Letter, we present quasistatic measurements of the temperature dependent electric conductivity obtained on native wet-spun calf thymus Li-DNA in a dc measuring field and measurements of the frequency dependent conductivity at low frequencies between 20 Hz and 1 MHz. These experiments together with temperature dependent  $I$ - $V$  curves effectively complement previously reported high frequency data, hence extending the frequency range down to quasistatic experimental time

scale. We show that the frequency dependence of the electric conductivity in the frequency range of  $\approx 10^{-3}$ – $10^{15}$  Hz can be well described within the framework of the hopping hole conduction mechanism [4].

Wet-spun oriented samples were prepared from calf thymus Li-DNA (Pharmacia) with a molecular weight of  $10^7$  (corresponding to a contour length of about 5 mm or some  $10^2$  persistence lengths of 50 nm) by wet spinning and then drying [18]. The wet spinning method allows for controlled production of sufficient amounts of highly macroscopically oriented thin films by spooling DNA fibers that are continuously stretched during precipitation into an aqueous alcohol solution. The dried Li-DNA sheets of thickness of about 3–4 mm and surface area between 10 and 20 mm<sup>2</sup> were then cut perpendicularly to the orientational axis of the DNA molecules into bulk samples of  $6.4 \times 4.4 \times 3.4$  mm<sup>3</sup> that were used in conductivity measurements.

Results were checked on various other sample geometries including 20–80  $\mu$ m thick films with typical lateral dimensions of  $5 \times 5$  mm<sup>2</sup>. Electrodes were pressed on both sides of the sample. No difference was observed if gold electrodes were replaced by copper electrodes. Quasistatic resistivity and  $I$ - $V$  curve measurements were performed by the Keithley 617 programmable electrometer on samples kept in 75% relative humidity and on samples dried in vacuum. Frequency dependent conductivity was measured between 20 Hz and 1 MHz via measurements of the imaginary part of the complex dielectric constant by using a HP4284A Precision LCR meter.

Typical  $I$ - $V$  curves for wet-spun Li-DNA samples measured parallel to the DNA orientational axis are shown for three different temperatures in Fig. 1. Wet-spun Li-DNA bulk samples exhibit no visible plateau in the  $I$ - $V$  curve at room temperature, consistent with findings on (Zn)  $\lambda$ -DNA [10]. This indicates that the gap voltage is smaller than the value which can be resolved at room temperature. In fact, taking account of the size of the samples, it was found that the field dependent conductivity  $\sigma_{\parallel}(E)$  of Li-DNA obtained from data in Fig. 1(a) agrees quantitatively with estimates of  $\sigma(E)$  obtained from (Zn)  $\lambda$ -DNA data in Ref. [10]. With decreasing temperature, the electric current at given voltage decreases for about 1 order of magnitude per decrease in temperature of about 20 K [see Figs. 1(a)–1(c)]. This demonstrates the rapid increase of the resistivity with decreasing temperature. Also, the nearly linear region around 0 V becomes steeper with decreasing temperature.

The influence of the electric field on the temperature dependence of  $\sigma_{\parallel}(T, E)$  was verified by measuring the resistivity upon cooling the sample at two different values of the dc voltage. The resistivity of the samples could be followed reliably down to about 220 K, since on further cooling it begins to exceed the electrometer limiting value of  $\approx 10^{16}$   $\Omega$ . Figures 2(a) and 2(b) show tem-

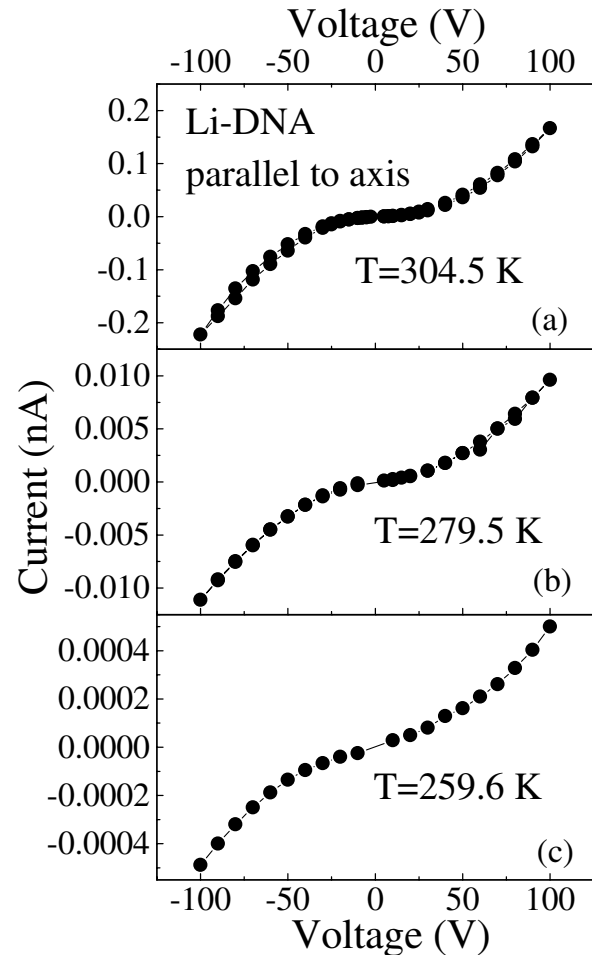


FIG. 1. Current-voltage curves measured at 75% relative humidity at various temperatures on wet-spun Li-DNA. The dc electric field was applied parallel to the duplex axis.

perature dependence of  $\sigma_{\parallel}(T, E)$ , taken at 20 V corresponding to the electric field of 31.25 V/cm, and those taken at 50 V corresponding to 78.13 V/cm. The time scale of the quasistatic experiment determined by both, the data sampling time and the temperature cooling rate, was estimated to be of the order of  $10^{-3}$  Hz. Similar to observations at microwave and optical frequencies [16,17],  $\sigma_{\parallel}(T)$  decreases strongly below room temperature with a crossover to a saturated constant value at temperatures below 230 K. It turned out that this crossover is mainly a consequence of the thermocouple voltage offset in resistance measurements due to the unavoidable temperature gradient in the lead wiring. This offset thermocouple current reflects itself in temperature dependence of  $\sigma$  as a nearly constant background (constant  $B$  in Fig. 2), thus limiting the lowest value of the electric conductivity. The thermal offset current, which is present in the same polarity, was revealed in a separate measurement by the so-called “offset compensation technique” in which the polarity of the measuring voltage is reversed every other reading.

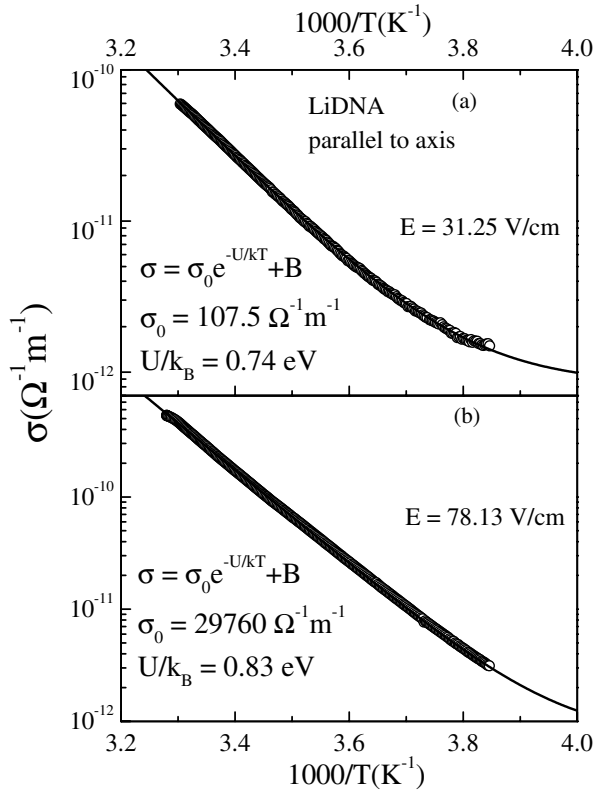


FIG. 2. Temperature dependence of the electric conductivity measured at 75% relative humidity on wet-spun Li-DNA. The dc electric field 31.25 V/cm (a) and 78.13 V/cm (b) was applied parallel to the sample orientational axis.

Taking this experimental effect into account, it was found that the temperature dependence of the conductivity could be well described by a thermally activated Arrhenius ansatz (1) [see Figs. 2(a) and 2(b) for relevant fit parameters] down to about 220 K temperature, at which the resistivity exceeds the value limited by the electrometer. Therefore, our measurements do not support a crossover from a strong temperature to a weak temperature dependence of the quasistatic electric conductivity above 220 K, observed in high frequency data [16,17]. It is still possible that the crossover takes place at lower temperatures as suggested by theoretical calculations [19]; however, it should be noted that in case of microwave and optical measurements [16,17] the above crossover occurs already around 250 K. This difference in the crossover behavior and the difference in the activation energies ( $\approx 0.8$  eV for our quasistatic data and  $\approx 0.3$  eV for high frequency data [16,17]) may indicate that some additional processes may contribute to the electric conductivity at frequencies above 10 GHz.

Data presented in Figs. 1 and 2 reveal that the electric-field dependence of  $\sigma$  is mainly hidden in the field dependence of the prefactor  $\sigma_0$  in Eq. (1). Namely, by increasing the electric field by a factor of 2.5,  $\sigma_0$  increases by more than 2 orders of magnitude, while the

activation energy  $U$  remains practically the same within the experimental error of  $\pm 0.05$  eV. It thus seems that the nonlinear  $I$ - $V$  curves are mainly a consequence of the electric-field induced increase of the charge carrier number. Similar measurements of  $\sigma(T, E)$  were also performed perpendicular to the DNA macroscopic orientational axis. A weak anisotropy of  $\sigma_{\perp}/\sigma_{\parallel} \approx 3$  was found around the room temperature.

Figure 3 shows measurements of  $\sigma(T, E)$  performed on Li-DNA dried in vacuum for more than 24 h at room temperature. A significant decrease in conductivity for almost 1 order of magnitude is in qualitative agreement with recent calculations [20]. Consequently, both  $\sigma_0$  and  $U$  changes are significant. Although  $\sigma_0$  increases for slightly less than 2 orders of magnitude, it seems that increase in  $U$  for about 0.1 eV is the dominant effect in decreasing the conductivity. This supports the idea [17] that, rather than lower carrier number, stronger localization effects due to less regular  $B$  form of DNA may be responsible for lower DNA conductivity in water poor environment.

It should be noted that the temperature dependence of  $\sigma$  presented in Figs. 2 and 3 could also be fitted to the variable range hopping ansatz (2) [see Fig. 3(b) for

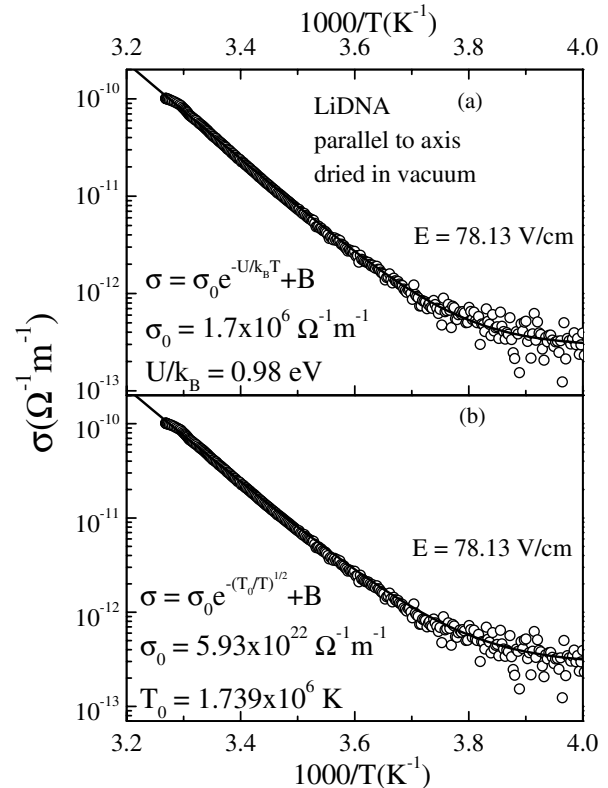


FIG. 3. Temperature dependence of the electric conductivity measured on dried Li-DNA. Shown are fits to an Arrhenius ansatz (a) and to the ansatz describing the variable range hopping (b). Here the electric field was applied parallel to the sample orientational axis.

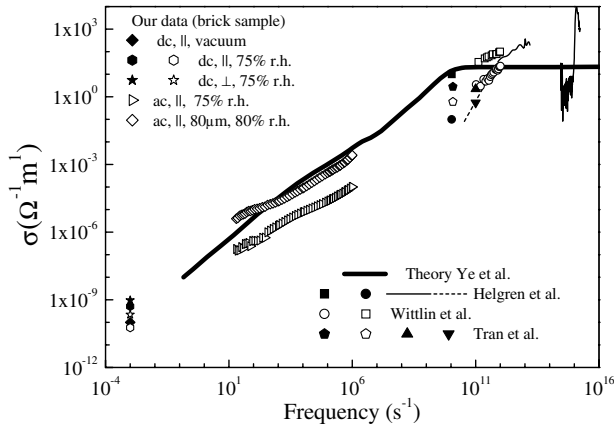


FIG. 4. Frequency dependence of the conductivity obtained with calf thymus wet-spun DNA and  $\lambda$ -DNA. Most of the data scattering is attributed to different relative humidity environments. Model calculations [4] are represented by the thick solid line. Other high frequency data are taken from Refs. [16,17,21]. Orientation of the applied electric field relative to the macroscopic orientational axis of the sample is denoted by  $\parallel$  and  $\perp$ . Data obtained on 80  $\mu\text{m}$  thick calf thymus DNA film are denoted by  $\diamond$ .

relevant fit parameters], with 95% Fisher-Snedecor (F) test confidence level, although with systematically larger  $\chi^2$  values. This means that detailed fits statistically slightly favor the activated mechanism against the variable range hopping mechanism, though the latter cannot be completely ruled out.

Our quasistatic (dc) and low frequency conductivity data combined with previously published microwave and optical conductivity data are displayed in Fig. 4. Here the data between 20 Hz to 1 MHz (denoted by ac) represent effective conductivity  $\sigma(\omega) = \varepsilon''\varepsilon_0\omega$  deduced from measurements of the imaginary part  $\varepsilon''$  of the complex dielectric constant  $\varepsilon^* = \varepsilon' - i\varepsilon''$ . This straightforward deduction was possible since no other relaxational or resonant mechanism was found to contribute to the dielectric spectra below 1 MHz. It seems that the general frequency dependence in this impressive frequency range of more than 18 orders of magnitude agrees qualitatively well with theoretical results assuming the variable range hopping hole conduction mechanism, calculated for aperiodic nucleotide base stacks [4], as well as with recent results of Barton and co-workers [7], who have shown that there is without doubt a hole conduction between DNA base pairs at distances larger than 3.7 nm.

In conclusion,  $I$ - $V$  measurements show that the non-linearity of the  $I$ - $V$  curves could be attributed to the electric-field induced increase of the charge carrier number. In contrast, the dc conductivity data obtained on macroscopically oriented wet-spun Li-DNA samples dried in vacuum suggest that, rather than lower carrier number, it is the stronger localization effects due to less regular  $B$  form of DNA that are responsible for lower

conductivity in a water poor environment. The conductivity measurements extended down to the quasistatic experimental time scale and earlier high frequency data agree qualitatively with theoretical results based on the hopping hole conduction mechanism [4].

This research was supported by the Slovenian Ministry of Education, Science and Sport.

\*URL: <http://www2.ijs.si/~kutnjak>

†Also at Jožef Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia.

- [1] F.D. Lewis, T.F. Wu, Y.F. Zhang, R.L. Letsinger, S.R. Greenfield, and M.R. Wasielewski, *Science* **277**, 673 (1997).
- [2] E.M. Boon and J.K. Barton, *Curr. Opin. Struct. Biol.* **12**, 320 (2002).
- [3] R. Bruinsma, G. Gruner, M.R. D'Orsogna, and J. Rudnick, *Phys. Rev. Lett.* **85**, 4393 (2000).
- [4] Y.-J. Ye, R.-S. Chen, A. Martinez, P. Otto, and J. Ladik, *Solid State Commun.* **112**, 139 (1999).
- [5] M.R. Arkin, E.D.A. Stemp, R.E. Holmlin, J.K. Barton, A. Hormann, E.J.C. Olson, and P.F. Barbara, *Science* **273**, 475 (1996).
- [6] M.D. Purugganan, C.V. Kumar, N.J. Turro, and J.K. Barton, *Science* **241**, 1645 (1988).
- [7] D.B. Hall, R.E. Holmlin, and J.K. Barton, *Nature (London)* **382**, 731 (1996).
- [8] P.T. Henderson, D. Jones, G. Hampikian, Y. Kan, and G.B. Schuster, *Proc. Natl. Acad. Sci. U.S.A.* **96**, 8353 (1999).
- [9] J.M. Warman, M.P. de Haas, and A. Rupprecht, *Chem. Phys. Lett.* **249**, 319 (1996).
- [10] A. Rakitin, P. Aich, C. Papadopoulos, Y. Kobzar, A.S. Vedenev, J.S. Lee, and J.M. Xu, *Phys. Rev. Lett.* **86**, 3670 (2001).
- [11] H.W. Fink and C. Schonenberger, *Nature (London)* **398**, 407 (1999).
- [12] D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, *Nature (London)* **403**, 635 (2000).
- [13] E. Braun, Y. Eichen, U. Sivan, and G. Ben-Yoseph, *Nature (London)* **391**, 775 (1998).
- [14] P.J. de Pablo, F. Moreno-Herrero, J. Colchero, J.G. Herrero, P. Herrero, A.M. Baro, P. Ordejon, J.M. Soler, and E. Artacho, *Phys. Rev. Lett.* **85**, 4992 (2000).
- [15] A.Y. Kasumov, M. Kociak, S. Gueron, B. Reulet, V.T. Volkov, D.V. Klinov, and H. Bouchiat, *Science* **291**, 280 (2001).
- [16] P. Tran, B. Alavi, and G. Gruner, *Phys. Rev. Lett.* **85**, 1564 (2000).
- [17] E. Helgren, A. Omerzu, G. Gruner, D. Mihailovic, R. Podgornik, and H. Grimm, *cond-mat/0111299*.
- [18] A. Rupprecht, *Acta Chem. Scand.* **20**, 494 (1966).
- [19] L. Shen, Y.-J. Ye, and J. Ladik, *Solid State Commun.* **121**, 35 (2002).
- [20] Y.-J. Ye, R.S. Chen, F. Chen, J. Sun, and J. Ladik, *Solid State Commun.* **119**, 175 (2001).
- [21] A. Wittlin, L. Genzel, F. Kremer, S. Haseler, A. Poglitsch, and A. Rupprecht, *Phys. Rev. A* **34**, 493 (1986).