Letter

Heat Conduction through a DNA#Gold Composite

Takashi Kodama, Ankur Jain, and Kenneth E. Goodson

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Heat Conduction through a DNA−Gold Composite

Takashi Kodama,* Ankur Jain, and Kenneth E. Goodson

Department of Mechanical Engineering, Stanford University, Stanford, California 94305

ABSTRACT

This paper reports results from electrical and thermal conduction measurements carried out on the DNA−gold composite for which the overall conduction is shown to be dominated by the DNA rather than the discontinuous gold coatings. The electrical and thermal conductivities of the composite were about 14 S/cm and 150 W/(m K) at room temperature, respectively. The resulting value of 3.6×10^{-4} W Ω/K^2 for the Lorentz number indicates that thermal transport in the DNA is phonon-dominated and that the molecular vibrations play a key role in both electrical and thermal conduction processes of DNA molecules.

The thermal conduction property of nanowires made from, e.g., carbon nanotubes[1] and silicon,[2] is of particular interest in several possible applications of nanotechnology, such as in the design of heat circuits and the development of thermal interface materials. Further, accurate measurement of the thermal conductivity of nanowires will become a significant factor in the development of future nanoelectronic circuits because of the importance of the thermal management among nanoelements. Deoxyribonucleic acid (DNA) is one of foremost nanowire materials due to its surface modification and self-assembly capabilities which makes a wide variety of nanostructures possible. The versatile electrical conductivity of DNA has been extensively studied[3−15] since the first measurements on DNA ropes[3] and on a DNA film.[4] These studies revealed that the electrical conductivity of a DNA molecule depends on its base sequence,[10] length,[11] and ambient conditions, such as the ion density inside the DNA molecule,[12] the properties of the substrate surface,[13] and the humidity.[14] The DNA molecule is considered an insulator for long-range electron transfer (>50 nm).[11] Thus, DNA templated metal nanowires such as those made from gold,[15,16] silver,[17,18] and palladium[19,20] have been developed in order to improve its effective composite electrical conductivity. However, their thermal conduction properties have not been reported. As well as the significance of the several possible applications mentioned above, since solid materials conduct heat via both lattice waves and electron transport, simultaneous measurement of electrical and thermal conductivity is necessary to clarify the conduction mechanism in greater detail, such as to determine the phonon contribution to the conduction process.[21] In this study, a λ-phage DNA was covered with

discontinuous gold layers, suspended across two electrodes (gap size, approximately 2 μm) patterned by standard microfabrication process, and simultaneous electrical and thermal conduction measurements were carried out on the DNA−gold composite using the steady-state Joule heating method.[22,23] Finally, for the first time, the Lorentz number of the DNA molecule was estimated in order to clarify the role of molecular vibration in conduction phenomena.

Parts a and b of Figure 1 show topographic images of DNA and metallized DNA molecules stretched on a mica surface. The DNA molecule was metallized with gold using the procedure described by Gu.[15] In short, a solution of positively charged gold nanoparticles (average diameter = 1.5 nm, Nanoprobes, Inc., Yaphank, NY) was dropped onto the substrate surface. Following incubation for 10 min, the gold nanoparticles were developed by a gold enhancer (Nanoprobes, Inc., Yaphank, NY) for 30 min. Figure 1b shows that the average thickness of the developed metal coating was about 15 nm under these reaction conditions. Furthermore, the images show that a number of nanoscale gaps and a few large gaps existed on the gold surface along the DNA. These discontinuities in the gold coating are due in part to the sparse alignment of seed nanoparticles along the length of the molecule. Figure 1c is a scanning electron microscope (SEM) image of a metallized DNA suspended across gold electrodes and fabricated under the same chemical reaction conditions. The image shows that the single metallized DNA is suspended and has an uneven gold structure on its surface. All conduction measurements were performed using this device under vacuum conditions (<30 mTorr), where convection heat losses were eliminated. All error bars described in the paper represent the margin of analytical error.

* Author to whom correspondence should be addressed: kodama@ stanford.edu.
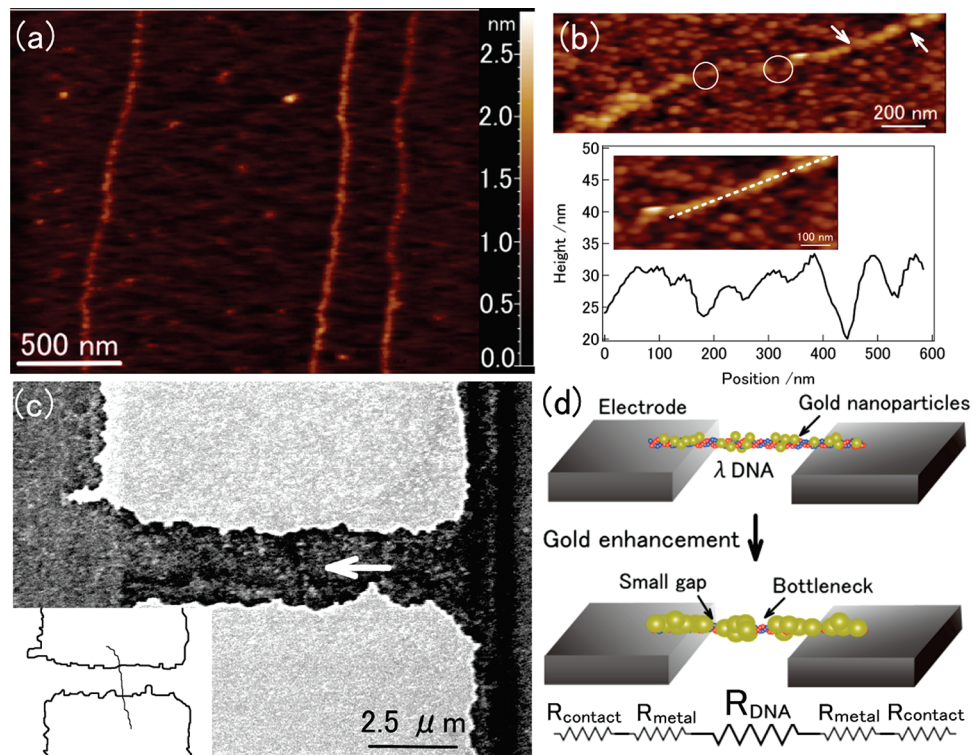
Figure 1. The topographic images of metallized DNA molecuoles. Panels a and b are representative topographic images of DNAs and metallized DNAs on a mica surface measured by atomic force microscopy, respectively. The circles and arrows in (b) represent the large and small gaps on the metallized DNA, respectively. The height profile along the metallized DNA is also shown in (b). Panel c is the scanning electron microscopy image of the suspended metallized DNA. The measurement device was microfabricated by the following procedure. The 100 nm Cr/Au layer was deposited on Si wafer with 500 nm thermal oxide. The gold electrodes were patterned using photolithography. The thiolated oligomer (5′-GGGCGGCGACCT-3′-SH, alphaDNA, Inc., Quebec, Canada) was hybridized with the λ-DNA (Sigma-Aldrich, St. Louis, MO) to introduce a −SH group at its terminus[15] and one terminus of the λ-DNA was attached to the gold surface by chemical bonding (The incubation time is 10 min.) After that, the attached DNA was stretched across the electrode by the application of the compressed air to the droplet along perpendicular direction to the electrodes.[20] Panel d is the schematic view of the conduction mechanism of the metallized DNA.

As seen in Figure 2, the measured electrical resistance is about 2.1 MΩ at room temperature, and the temperature dependence experiments showed that the electrical conductance increases with temperature. Further, the crossover was observed at a temperature T of 225 K, and the electrical conductance has T^{-1} and $T^{-0.25}$ dependence in the high- and low-temperature regions, respectively (see parts d and f of Figure 2, respectively). The results show that conduction is nonmetallic and the conduction behavior is similar to that previously reported for nonmetallized DNA.[8−11]

First, we explored the possibility that the conductivity originated solely from the gold coating. When the metal coating around the DNA is continuous, conduction is dominated by ballistic electron transport in the coating, as in a previous report.[19] However, the conductance increases with T rather than the opposite, and the measured electrical resistance is much larger than that theoretically predicted by the free electron model for the gold coating (see Figure 2a and Supporting Information). Further, when the metal coating is discontinuous, conduction is dominated by electron hopping transport and the electrical conductance depends on the largest gap width and the radius of the metal structure.[24,25] The previous results suggest that the temperature dependence

of the electrical conductivity can be described by a simple Arrhenius-type formula

$$\sigma = \sigma_0 \exp[-E_a/k_B T]$$

where σ_0 is a constant.

$$E_a = \frac{1}{2}e^2[r^{-1} - (r+s)^{-1}]/4\pi\varepsilon\varepsilon_0$$

is the activation energy of the electron hopping transport process, where r is the radius of the metal structure and s is the size of the discontinuity between them (see Supporting Information).[24,25] Parts b and c of Figure 2 show the theoretical temperature dependence of electrical conductivity for discontinuous gold films in which the radius of the metal is 15 and 1.5 nm, respectively. Cleary, the activation energy increases and the electrical conductivity decreases as the gap size increases. However, the conductivity shows single-exponential dependence in this temperature region (see Figure 2, panels b and c). The single-exponential behavior is independent of the gap width and thickness of the metal film and does not agree with the experimental results for the entire temperature region. This disagreement indicates that electrical conduction in the composite is not dominated by the discontinuous gold coating around the DNA molecule.
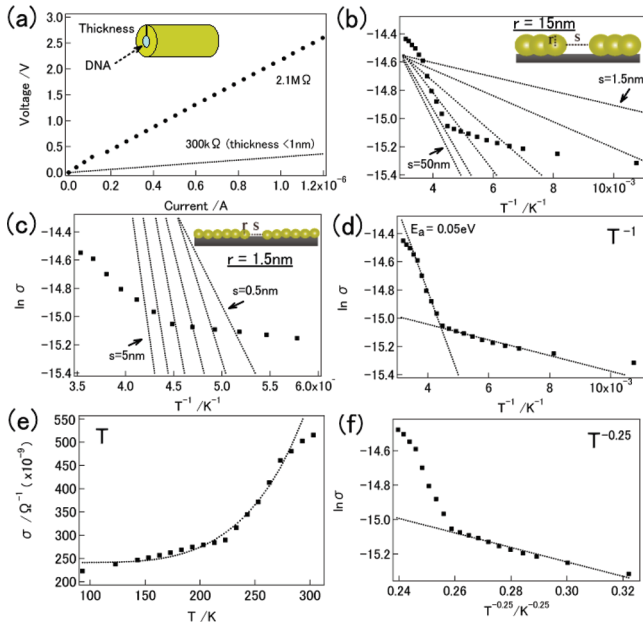
Figure 2. Electrical conduction measurement results of the metallized DNA. (a) The $I-V$ curve of the single metallized DNA measured at $T = 293$ K. The lower dotted line corresponds to the theoretical resistance of a single cylindrical gold nanowire (see Supporting Information). Panels b–f are the temperature dependence of the electrical conductance. The dotted lines in (b) and (c) are temperature dependence of the theoretical electrical conductivity of the discontinuous gold films whose radius of the metal is 15 and 1.5 nm, respectively. The theoretical curves in (b) are generated when the gap size is 1.5, 3, 7.5, 15, 30, and 50 nm (the electrical conductivity decreases as the gap size increases). Further, the curves in (c) are obtained when the gap size is 0.5, 1, 1.5, 3, 5, and 10 nm. On the other hand, the dotted lines in panels d, e, and f are the theoretical curve obtained by the Arrhenius equation, small polaron hopping theory, and Mott variable range hopping theory, respectively.

Next, we explored the possibility that the conductivity originated from the exposed (nonmetallized) DNA segments in the gaps. To allow comparison with the previous results, the present results were accounted for by two types of hopping conduction model. First, the small-polaron hopping model[9,11,26] was used to analyze the experimental data. This theory accounts for phonon assistance to electron hopping, and the electrical conductivity is given by

$$\sigma = \sigma_0 \exp[-E_a/k_B T]$$

where

$$E_a(T) = k_B T \sum_q C_q \tanh(\hbar \omega_q / 4 k_B T)$$

where C_q and ω_q are the coefficient and molecular vibrational frequency, respectively. Figure 2e shows that the small-polaron hopping model agrees well with the experimental data over a wide temperature range. From the data, ω_0 was estimated to be $(3.089 \pm 0.246) \times 10^{14}$ Hz. Next, the electrical conductance in the low-temperature region was analyzed by the Mott variable-range hopping model.[26,27] According to this model

$$\sigma = \sigma_0 \exp(-(T_0/T)^{0.25})$$

where

$$\sigma_0 = e^2 a^2 \nu_{ph} N(E_F)$$

$$T_0 = \lambda \alpha^3 / k_B N(E_F)$$

and e, a, ν_{ph}, $N(E_F)$, α, and λ are the electronic charge, hopping distance, phonon frequency ($=3.089 \times 10^{14}$ Hz), density of localized states at the Fermi level, coefficient of exponential decay of localized states, and dimensional constant, respectively. From the equation, the hopping distance at low temperature

$$a = [9e^{8/3} \nu_{ph}^{4/3} \lambda^{1/3} / 8\pi k_B^{4/3} T_0^{1/3} \sigma_0^{4/3} T]^{3/4}$$

was estimated to be about 20.18 Å at $T = 200$ K. Data from previous experiments on nonmetallized DNA are summarized in Table 1. By comparing of the two cases, we find that the crossover temperature, the temperature dependence at both high and low temperatures (T^{-1} and $T^{-0.25}$, respectively), the molecular vibrational frequency, and the hopping distance at low temperature are close to those of nonmetallized DNA. The three electrical resistances of importance in this experimental setup are the contact resistance ($R_{contact}$), the resistance of the DNA–gold composite (R_{metal}), and that of the nonmetallized DNA strand (R_{DNA}). The electrical resistances are in a series configuration (see Figure 1d). Thus, the overall behavior strongly depends on the conduction property on the part with the largest electrical resistance. The exposed DNA segments in the small gaps of gold film may conduct electrical current but become the conduction bottleneck due to the large short-range electrical resistance (R_{DNA}) as reported elsewhere.[12–14] Therefore, it is concluded that the conductivity of the composite is dominated by that of the nonmetallized DNA strand.

Then the thermal conductivity of the composite was then measured using the steady-state Joule heating method.[22,23] The steady-state one-dimensional heat diffusion equation is as follows

$$\kappa A L \frac{d^2 T}{dx^2} + I^2 R_{T_0}[1 - \alpha(T - T_0)] = 0 \qquad (1)$$

$$T(x = \pm L/2) = T_0 \qquad (2)$$

where κ, A, L, T_0, R_{T_0}, and I are the thermal conductivity, cross-sectional area, length, substrate temperature ($=293$ K), electrical resistance at T_0, and current, respectively. The boundary condition is given by eq 2. The temperature coefficient $\alpha(=dR/dT/R_{T_0})$ was obtained experimentally using a constant-temperature oven. When the governing equations are solved, the temperature $T(x)$ may be derived as

$$T(x) = T_0 - \frac{1}{\alpha}\left(\frac{\exp\left(\frac{I}{L}\sqrt{R_{T_0}\alpha/K}x\right) + \exp\left(-\frac{I}{L}\sqrt{R_{T_0}\alpha/K}x\right)}{\exp\left(\frac{I}{2}\sqrt{R_{T_0}\alpha/K}\right) + \exp\left(-\frac{I}{2}\sqrt{R_{T_0}\alpha/K}\right)} - 1 \right) \qquad (3)$$

where K is the thermal conductance. Integrating the above equation from $-L/2$ to $+L/2$, the averaged temperature, and hence the averaged electrical resistance, is given by

$$\bar{R} = \frac{2R_{T_0}}{I\sqrt{R_{T_0}\alpha/K}} \frac{\exp\left(\frac{I}{2}\sqrt{R_{T_0}\alpha/K}\right) - \exp\left(-\frac{I}{2}\sqrt{R_{T_0}\alpha/K}\right)}{\exp\left(\frac{I}{2}\sqrt{R_{T_0}\alpha/K}\right) + \exp\left(-\frac{I}{2}\sqrt{R_{T_0}\alpha/K}\right)} \qquad (4)$$

where $\bar{R}$ is the averaged electrical resistance, respectively. Figures 3 shows the current dependence of the electrical

Table 1. Summary of the Present Experimental Values and the Previous Results of Nonmetallized DNA

|	this study	previous DNA studies
activation energy E_a (eV) at high temperature	0.05	0.3−0.33,[9] 0.18, 0.12,[10] 0.21[11]
hopping distance (Å) at low temperature	20.1 ($T = 200$ K)	11.2 ($T = 200$ K), 25 ($T > 160$ K)[11]
vibrational frequency ω_0 ($\times 10^{14}$ Hz)	3.089	1.8, 1.3, 0.052,[10] 0.26[11]

resistance change measured at room temperature and the theoretical temperature distribution along the sample. When eq 4 was fit to the experimental data, the thermal conductance was estimated to be 53 ± 2.23 nW/K. The electrical and the thermal conductivity of the DNA−gold composite were calculated to be 14 S/cm and 150 W/mK when the thickness of the gold film and the length were assumed to be 15 nm and 2 μm, respectively. The results show that the electrical conductivity is small compared to that of noble metals, but the thermal conductivity is almost the same.[28]

According to the Wiedemann−Franz law, the Lorentz number of metals, defined as $L_0 = \kappa/\sigma T$ is nearly constant at $L_0 = 2.45 \times 10^{-8}$ W Ω/K^2 except at sufficiently low temperature.[28] This law is frequently used to estimate the phonon contribution to thermal conductivity by subtracting the expected electronic contribution $L_0 \sigma T$ from the measured thermal conductivity. With the thermal and electrical conductance values obtained in this study, which are independent of the geometrical parameters, the Lorentz number L is estimated to be about 3.6×10^{-4} W Ω/K^2. The expected electronic contribution is about 0.01 W/(m K). This suggests that the thermal conductivity of the composite is dominated by phonon transport. These estimated conductivities are not physical parameters for nonmetallized DNA molecules but for the DNA−gold composite. However, the estimated Lorentz number and conduction properties are independent of the geometry and are determined by the property of the conduction bottleneck. Therefore, one can draw a qualitative conclusion about conduction properties of the DNA. As mentioned above, the electrical conductivity of the composite is small compared with that of noble metals, but the thermal conductivity is almost the same. This unique feature originates from the conduction property of DNA. Further, the results show that the thermal conductivity of nonmetallized DNA is phonon-dominated under the present experimental conditions. The low electron transport capability of DNA results in the high electrical resistivity and low electronic contribution to thermal conduction. Further, the temperature dependence of electrical conduction measurements suggests that phonons assist in electron-hopping conduction in the DNA molecule (see Figure 2e). Therefore, molecular vibrations play a key role in both the electrical and thermal conduction processes in DNA molecules.

Supporting Information Available: Theoretical electrical resistivity of a gold cylinder, theoretical electrical resistivity and thermal conductivity of the metal coating around a DNA molecule, and theoretical electron conduction through a disordered metal nanoparticle network. This material is available free of charge via the Internet at http://pubs.acs.org.
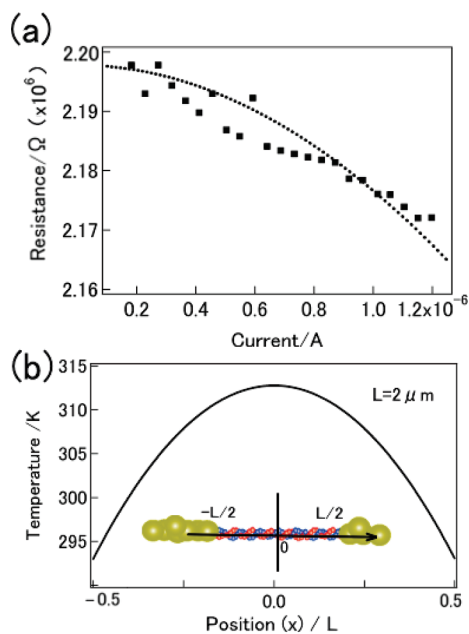
Figure 3. Thermal conduction measurement results of the metallized DNA. (a) The current dependence of the electrical resistance change. The dotted line in the figure is the theoretical curve given by eq 4. (b) The theoretical temperature distribution along the sample by eq 3 ($I = 2$ μA). The schematic view is inserted in the figure.

References

(1) Pop, E.; Mann, D.; Wang, Q.; Goodson, K.; Dai, H. *Nano Lett.* **2006**, *6*, 96.
(2) Li, D.; Wu, Y.; Kim, P.; Shi, Li.; Yang, P.; Majumdar, A. *Appl. Phys. Lett.* **2003**, *83*, 2934.
(3) Fink, H.-W.; Schönenberger, C. *Nature (London)* **1999**, *398*, 407.
(4) Okahata, Y.; Kobayashi, T.; Tanaka, K.; Shimomura, M. *J. Am. Chem. Soc.* **1998**, *120*, 6165.
(5) Porath, D.; Bezryadin, A.; de Vries, S.; Dekker, C. *Nature (London)* **2000**, *403*, 635.
(6) Rakitin, A.; Aich, P.; Papadopoulos, C.; Kobzar, Yu.; Vedeneev, A. S.; Lee, J. S.; Xu, J. M. *Phys. Rev. Lett.* **2001**, *86*, 3670.
(7) Cai, L.; Tabata, H.; Kawai, T. *Appl. Phys. Lett.* **2000**, *77*, 3105.
(8) Yu, Z. G.; Song, X. *Phys. Rev. Lett.* **2001**, *86*, 6018.
(9) Tran, P.; Alavi, B.; Gruner, G. *Phys. Rev. Lett.* **2000**, *85*, 1564.
(10) Yoo, K.-H.; Ha, D. H.; Lee, J.-O.; Park, J. W.; Kim, J.; Kim, J. J.; Lee, H.-Y.; Kawai, T.; Choi, H. Y. *Phys. Rev. Lett.* **2001**, *87*, 198102.
(11) Inomata, A.; Shimomura, T.; Heike, S.; Fujimori, M.; Hashizume, T.; Ito, K. *J. Phys. Soc. J.* **2006**, *75*, 074803.
(12) Zhang, Y.; Austin, R. H.; Kraeft, J.; Cox, E. C.; Ong, N. P. *Phys. Rev. Lett.* **2002**, *89*, 198102.
(13) Storm, A. J.; van Noort, J.; de Vries, S.; Dekker, C. *Appl. Phys. Lett.* **2001**, *79*, 3881.
(14) Kleine-Ostmann, T.; Jordens, C.; Baaske, K.; Weimann, T.; de Angelis, M. H.; Koch, M. *Appl. Phys. Lett.* **2006**, *88*, 102102.
(15) Gu, Q. *DNA-templated assembly of metallic nanowires*; ProQuest Company: Ann Arbor, MI, 2006.
(16) Maubach, G.; Born, D.; Csáki, A.; Fritzsche, W. *Small* **2005**, *1*, 619.
(17) Braun, E.; Eichen, Y.; Sivan, U.; Ben-Yoseph, G. *Nature (London)* **1998**, *391*, 775.
(18) Park, S. H. *Self-assembled DNA nanostructures and DNA-templated silver nanowires*, ProQuest Company: Ann Arbor, MI, 2005.

(19) Richter, J.; Metrig, M.; Pompe, W.; Vinzelberg, H. *Appl. Phys. A: Mater. Sci. Process.* **2002**, *74*, 725.

(20) Lund, J.; Dong, J.; Deng, Z.; Mao, C.; Parviz, B. A. *Nanotechnology* **2006**, *17*, 2752.

(21) Hone, J.; Whitney, M.; Piskoti, C.; Zettl, A. *Phys. Rev. B* **1999**, *59*, R2514.

(22) Goodson, K. E.; Ju, Y. S. *Annu. Rev. Mater. Sci.* **1999**, *29*, 261.

(23) Reifenberg, J.; England, R.; Rao, P.; Schmitt, W.; Yang, Y.; Liu, W.; Sadeghipour, S. M.; Asheghi, M. IMECE2003-42055, ASME International Mechanical Engineering Congress & Exposition, Washington, D.C., Nov 2003.

(24) Abeles, B.; Cheng, P.; Coutts, M. D.; Arie, Y. *Adv. Phys.* **1975**, *24*, 407.

(25) Brust, M.; Bethell, D.; Kiely, C. J.; Schiffrin, D. J. *Langmuir* **1998**, *14*, 5425.

(26) Böttger, H.; Bryksin, V. V. *Hopping conduction in Solids*, Akademie-Verlag: Deerfield Beach, FL, 1985.

(27) Kaynak, A. *Tr. J. Chem.* **1985**, *22*, 81.

(28) Kittel, C. *Introduction to Solid State Physics*, 7th ed.; Wiley: New York, 1998.