Intrinsic Low Temperature Paramagnetism in B-DNA

S. Nakamae,1,2,3 M. Cazayous,1,2 A. Sacuto,1,2 P. Monod,1 and H. Bouchiat3

1Laboratoire de Matériaux et Phénomène Quantiques (UMR 7162), Université Paris 7-Denis Diderot, Paris, France
2Laboratoire de Physique du Solide (UPR 5 CNRS) ESPCI, 10 rue Vauquelin, 75231 Paris, France
3Laboratoire de Physique des Solides, Université Paris-Sud, Bâtiment 510, 91405 Orsay, France

(Received 22 October 2004; published 23 June 2005)

We present an experimental study of magnetization in λ-DNA in conjunction with structural measurements. The results show the surprising interplay between the molecular structures and their magnetic property. In the B-DNA state, λ-DNA exhibits paramagnetic behavior below 20 K that is nonlinear in an applied magnetic field whereas, in the A-DNA state, it remains diamagnetic down to 2 K. We propose orbital paramagnetism as the origin of the observed phenomena and discuss its relation to the existence of long range coherent transport in B-DNA at low temperature.

DOI: 10.1103/PhysRevLett.94.248102 PACS numbers: 87.15.—v, 75.20.Ck, 87.14.Gg

It is now common knowledge that the electrical conduction in DNA is intimately linked to experimental factors such as molecules’ base pair (bp) sequence, type of electrodes, surrounding counterions, and the number of water molecules [1–4]. The experimental accounts to date span a whole spectrum of conduction mechanisms, from insulators, semiconductors, and metals to proximity induced superconductors [5–8]. Magnetization is an alternative, noninvasive mean to probe the intrinsic electronic properties of matter, as the measurements do not require any electrode attachments. Unlike the intensive experimental efforts made in electronic transport in DNA molecules, their magnetization has been scarcely explored due to experimental difficulties such as the overwhelming presence of water. Basic questions about the intrinsic magnetic properties of DNA, such as the magnitude of its magnetic susceptibility, \( \chi \), have remained unclear. It is widely known that DNA is diamagnetic near room temperature, with a sizable anisotropy stemming from the presence of aromatic rings of the base pairs whose magnitude is comparable to that of benzene [9–11]. But how does the overall magnetic state of DNA depend on intrinsic parameters (molecular structure, bp sequence) as well as on extrinsic parameters such as counterion types? Does DNA magnetization depend on these parameters in a way reminiscent to the electrical conduction? And if so, what are the consequences and implications for the usage of DNA as molecular wires? To answer these questions, we have studied the low temperature susceptibility and magnetization of randomly oriented λ-DNA molecules and its relation to their molecular structure (A- and B-DNA) and counterion types (Na\(^+\) and Mg\(^{2+}\)), two parameters known to greatly influence the electronic property of DNA [1]. We find that the magnetization is temperature independent and diamagnetic at high temperatures (100 K and above) regardless of water content in both A- and B-DNA structures. Surprisingly, once the molecules are sufficiently “wet” and thus are found in the B structure, a paramagnetic upturn is observed at lower temperatures that are nonlinear in magnetic field in addition to the atomic diamagnetic component. Collectively, these observations reveal, for the first time, the intrinsic nondiamagnetic state in DNA molecules that is intrinsically related to their molecular structures.

λ-DNA samples (400 \( \mu \)g each) in two counterion types, Na\(^+\) (hereafter called NaDNA) and Mg\(^{2+}\) (MgDNA), were prepared in quartz capillary tubes that served as sample holders for both magnetization (QuantumDesign MPMS-R2 SQUID magnetometer) and structural studies (micro-Raman spectrometer) [12]. λ-DNA (16 \( \mu \)m, 48 502 bp) was chosen specifically because the proximity induced superconductivity and the low temperature negative magnetoresistive behavior were detected previously in these molecules. The molecular structure of DNA changes dramatically with surrounding hydration levels. In an aqueous environment, DNA molecules are in a B-DNA structure where base pairs are stacked parallel to one another with the inter-bp distance of 3.2 \( \text{Å} \) and the helix diameter of 19 \( \text{Å} \). When molecules are dried, the bases become severely tilted off the helix axis and the helical diameter becomes broad (23 \( \text{Å} \)) [13]. The molecular structure of the samples was transformed between the dry A-DNA and the wet, natural B-DNA states by adding or removing water from the samples. In their driest states, NaDNA and MgDNA samples contained <0.1 and ~0.3 \( \mu \)l of H\(_2\)O, respectively. The corresponding values of the sample’s relative humidity (RH) (the weight of H\(_2\)O divided by that of dry DNA) are 0.25 and 0.75. At each stage of rehydration and/or dehydration the quartz capillaries were sealed to maintain a constant water content, and the magnetization and the molecular structure (via micro-Raman spectroscopy) were studied in parallel. Figure 1(a) shows the magnetization (\( M \)) of NaDNA with <0.1, ~0.9 \( \mu \)l (RH = 2.25), and ~1.9 \( \mu \)l (RH = 4.75) of water as a function of temperature (\( T \)) at 5 T. Originally, the sample contained 0.9 \( \mu \)l of H\(_2\)O. Then the water content was increased to 1.9 \( \mu \)l and finally dried down to < 0.1 \( \mu \)l. By subtracting the water contribution from the total magnetization at \( T > 100 \text{ K} \), we have extracted the diamagnetic susceptibility of DNA, \( \chi_{\text{DNA}} = -0.63 \pm 0.1 \times 10^{−6} \text{ EMU} \cdot \text{G}^{-1} \cdot \text{g}^{-1} \). Within the experimental accuracy,
The diamagnetic susceptibility was found to be independent of water content, that is, \( \chi_{\text{NaDNA}} = \chi_{\text{B-DNA}} \). This value, determined from two NaDNA samples, is in fair agreement with the calculated atomic diamagnetic susceptibility of DNA, \( \sim -0.52 \times 10^{-6} \, \text{EMU} \cdot \text{g}^{-1} \). At temperatures below 20 K, the magnetization of NaDNA containing 1.9 and 0.9 \( \mu l \) of H\(_2\)O indicates unexpected paramagnetic upturn that disappeared once the sample was dried to H\(_2\)O < 0.1 \( \mu l \) (RH = 0.25). Figure 1(b), portraying \( M \) (without H\(_2\)O contribution) as a function of magnetic field \( (H) \) at \( T = 2 \, \text{K} \), clearly presents this low temperature paramagnetism. At helium temperature, DNA in an aqueous environment exhibits a crossing over from diamagnetic to paramagnetic magnetization that is nonlinear in magnetic field. The magnitude of this paramagnetic increase, \( \Delta M_{\text{para}} = M_{\text{tot}} - M_{\text{dia}} \), is comparable to that of the diamagnetic contribution of DNA. The corresponding Raman spectra depicting the structural transformation from the A to the B structure in NaDNA are presented in Fig. 2 [15].

Among the large and highly reliable index of Raman bands corresponding to vibrational modes of DNA geometry and conformations [16], we concentrate on two bands representing the backbone vibrations to identify the structural state of our samples, as described in the figure caption. While with <0.1 \( \mu l \) of H\(_2\)O, the sample was found almost purely in the A state, both B-DNA and a small signature of A-DNA were observed with 0.9 \( \mu l \) (RH = 2.25). With a further addition of H\(_2\)O, molecules were found entirely in the B state. By comparing the molecular structure and the magnetization of NaDNA, it appears that B-DNA is a prerequisite condition for the low temperature paramagnetism in DNA. It needs to be noted, however, that the value of RH = 2.25 of our sample, for which the coexistence of A- and B-DNA is observed, exceeds the generally respected value of RH = 0.9 found in the literature, above which DNA is known to exist totally in the B state [17]. This observation indicates that H\(_2\)O is not diffused uniformly due to the sample geometry and the preparation method. The more rigorous investigation of the water content and the structural analysis of NaDNA samples via x-ray diffraction will be reported elsewhere.

In the MgDNA sample, we were unable to remove H\(_2\)O sufficiently to create a predominantly A-DNA state. In fact, the Raman spectra (not shown) of the MgDNA in its driest

---

**FIG. 1.** Evolution of magnetization \( (M) \) of NaDNA with water content. (a) Magnetization of DNA and water as a function of temperature \( (T) \). Above 100 K, the change in \( M \) corresponds to the temperature independent diamagnetic contribution from H\(_2\)O. The numbers in bold letter indicates the order in which the measurements were taken. (b) Magnetization as a function of magnetic field \( (H) \) measured at 2 K without the water contribution \( (\sim 7.2 \times 10^{-10} \, \text{EMU} \cdot \text{G}^{-1} \mu l^{-1}) \). The straight dashed line represents the diamagnetic component of NaDNA measured at 150 K. The dotted curved line superimposed on the data points with H\(_2\)O = 0.9 \( \mu l \) is a guide to the eye. Error bars represent the standard deviation in the measurements. Some error bars on low field data, \( H \leq 1 \, \text{T} \), are removed in order to avoid crowding the graph. A ferromagnetic component originating from impurities in the quartz tube was detected whose magnitude saturates at \( H \sim 7000 \, \text{G} \) \( (M \sim 5 \times 10^{-6} \, \text{EMU} \) for both NaDNA and MgDNA). This component was independent of temperature and of water content and has also been subtracted.

---

**FIG. 2 (color).** Evolution of Raman spectra on NaDNA: The left panel shows the evolution of Raman band corresponding to the complex vibrational mode of the backbone network along the chain \( (5'\text{C-O-P-O-C}3') \). This band shifts from \( 807 \, \text{cm}^{-1} \) in A-DNA to \( 835 \pm 5 \, \text{cm}^{-1} \) in B-DNA. The right panel shows the band associated with the symmetric stretching of the PO\(_2\) moiety mode. This band shifts from \( 1100 \, \text{cm}^{-1} \) in A-DNA to \( 1092 \, \text{cm}^{-1} \) in B-DNA [16].
state (0.3 μl, RH = 0.75) indicated mainly B-DNA bands, and with ~0.5 μl (RH = 1.25) of H2O the molecules were found to be in a purely B-DNA state. This is in marked contrast to NaDNA where the presence of both A- and B-DNA was detected at much higher water content. This observation is consistent with a known property of Mg2+ that prevents the transition from B- to A-DNA more efficiently than Na+ ions [18]. The magnetization measurements on MgDNA with ~0.5 μl of H2O preceded the measurements with 0.3 μl. As can be seen from Fig. 3, a purely diamagnetic behavior at low temperatures was never achieved in MgDNA in line with the observation in NaDNA. In the driest state, only a slight decrease in ΔMpara was detected. Furthermore, the paramagnetic magnetization was found to become independent of water content for H2O values higher than 0.5 μl (measured up to 2.2 μl). The temperature dependence of the magnetization of wet MgDNA follows the Curie law, as shown in the inset. Susceptibility at higher temperatures was determined to be ~0.8 ± 0.1 × 10−6 EMU·G−1·g−1, larger than the value found for the NaDNA sample. This difference (~0.2 × 10−6 EMU·G−1·g−1) corresponds to the diamagnetic susceptibility of the residual buffer ions (MgCl2 and NH4 acetate). It is also noteworthy that the low temperature ΔMpara was found to be ~4 times higher in MgDNA than in NaDNA.

The apparition of paramagnetism in B-DNA at low temperature that is nonlinear in applied field is robust. There are two possible origins for the observed nonlinear paramagnetism: electron spin (s) or orbital magnetism. Assuming the electron spins (magnetic ions or hydroxyl radicals [19], for example) render the observed behavior, we have fit the paramagnetic component of the magnetization, ΔMpara, to the Brillouin and Curie law. The best fits were obtained for s = 1/2–3/2, with the total number of spins of ~10^{15}, or 1-spin/400 bp, for NaDNA and ~4 × 10^{15}, or 1-spin/100 bp, for MgDNA, respectively. Such high concentrations of spins should be detectable by electron paramagnetic resonance (EPR), provided that the signal line width does not exceed 300 G. The examination via EPR [20] revealed no such presence in NaDNA at room temperature. The MgDNA sample was examined between room temperature and 4 K. The only EPR absorption signal was detected at g = 4.28, which can be attributed to Fe3+ (s = 5/2, g = 30/7) in an asymmetric crystal field. The number of these spins was determined to be of the order of 10^{12}, far too small to be responsible for the observed ΔMpara [21]. Furthermore, the magnetization of H2O used to humidify the samples was examined separately using the SQUID magnetometer. ΔMpara (5 T, 2 K) less than 10−6 EMU was found in 2 μl of H2O. Therefore these experiments, as well as the disappearance of paramagnetic component in A-DNA after the drying process, exclude free radicals and magnetic impurities in water and buffer solutions from the possible origins of low temperature paramagnetism, as such impurities cannot be removed from the sample by a simple evaporation of water.

Thus far, the paramagnetism appears to be an intrinsic property unique to B-DNA. An interesting possibility is the existence of persistent current loops along the DNA molecules on a mesoscopic micron scale. The mesoscopic orbital magnetism has been shown theoretically to be paramagnetic and nonlinear when repulsive electron-electron interactions dominate over single particle effects [22,23]. The total magnetization of the system then follows

\[ m(H) = \frac{\chi_L k_F \sqrt{S(T)}}{1 + \left(\frac{H}{\Phi_0 S(T)}\right)^2} \]

where \( \chi_L \) is the Landau susceptibility, and \( k_F \) is the Fermi wave number. The nonlinear magnetization reaches its maximum at \( H_0 = \Phi_0 / S(T) \), where \( \Phi_0 = h/e = 4.14 \times 10^{-7} \text{ G cm}^2 \) is the magnetic flux quantum and \( S(T) \) is the maximum surface area enclosed inside the coherent current loop [Figs. 4(a) and 4(b)]. The orbital magnetism associated with the persistent currents has been already observed in mesoscopic rings and 2D squares and is considered the hallmark of phase coherent transport at low temperatures [24]. In our DNA samples measured at 2 K, the magnitude of the paramagnetic signal is 2–4 times that of the total diamagnetic susceptibility. At lower temperatures the size of orbital paramagnetic susceptibility is expected to grow rapidly. We estimate the electron coherent length, \( L \), using the experimental values from our measurements, \( H_0 = 1 \sim 2 \text{ T} \), via \( S(T) = d \times L(T) \), where \( d \) is the distance between bases of B-DNA molecules. Our calculation yields the electron path on the order of 1 μm along the helical axis of the molecules. Such circulation of electrons enclosing a finite flux can be achieved through the combination of intra- and interstrand (across the hydrogen bonds) transfer of π electrons on bases [Fig. 4(c)]. Hydrogen bond assisted electronic exchange has already been witnessed in some organic molecules [25]. The value of the electron path found here agrees with the coherent length of ~1 μm in A-DNA, determined by Kasumov et al. [3] where prox-

![FIG. 3. M vs H of MgDNA measured at T = 2 K. The data presented here are treated in the same manner as in Fig. 1(b). Inset: M as a function of temperature of wet MgDNA at H = 1 T. Dotted line represents the fit to the Curie law, \( M(T) = C \times H/T \), with C (the Curie constant) = 4.3 ± 0.2 × 10^{-9} \text{ J} \cdot \text{K}/\text{T}^2 \) corresponding to ~10^{15} of 1/2 spins.](248102-3)
imarily induced superconductivity was detected at $T < 1$ K. 
Our observation may also imply a coherent electron transport along the helical length of the molecule at low temperatures, but exclusively in B-DNA, consistent with experimental reports on the DNA electronic conductivity at the midheight of the tube. 

In summary, we have found a low temperature, nonlinear paramagnetic behavior in the B state of λ-DNA molecules. This effect is found in both DNA samples prepared with Na$^+$ and Mg$^{2+}$ counterions. The paramagnetic susceptibility of molecules prepared with Mg$^{2+}$ ions is found larger by a factor of 4 compared to the Na$^+$ counterpart. The present results can be interpreted by the existence of a mesoscopic orbital paramagnetism in B-DNA molecules that may be related to the proximity induced superconductivity observed in these molecules. Magnetization of other types and of aligned DNA molecules should be examined in order to confirm the orbital origin of this paramagnetism.

We thank F. Livolant, A. Bertin, D. Durand, S. Gueron, J. F. Allemand, D. Bensimon, and V. Croquette for stimulating discussions and experimental guidances.