Intrinsic Low Temperature Paramagnetism in B-DNA

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We present experimental study of magnetization in \(\lambda\)-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, \(\lambda\)-DNA exhibits paramagnetic behaviour below 20 K that is non-linear in applied magnetic field whereas in the A-DNA state, 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.

It is now a common knowledge that the electrical conduction in DNA is intimately linked to experimental factors such as molecules’ base-pair sequence, type of electrodes, surrounding counter ions and number of water molecules. The experimental accounts to date span a whole spectrum of conduction mechanism from insulators, semi-conductors, metals to proximity induced superconductors. Magnetization is an alternative, non-invasive mean to probe the intrinsic electronic properties of matter, as the measurements do not require any electrode attachments. Unlike the intensive experimental efforts made on electronic transport in DNA molecules, their magnetization has been scarcely explored due to experimental difficulties such as the overwhelming presence of water. Basic questions on the intrinsic magnetic properties of DNA such as the magnitude of its magnetic susceptibility, \(\chi_g\), 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. But how does the over-all magnetic state of DNA depend on intrinsic parameters (molecular structure, base-pair sequence) as well as extrinsic parameters such as counter ion 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 adorning questions, we have studied the low temperature susceptibility and magnetization of randomly oriented \(\lambda\)-DNA molecules and its relation to their molecular structure (A- and B-DNA) and counter ion types (\(\text{Na}^+\) and \(\text{Mg}^{2+}\)), two parameters known to greatly influence the electronic property of DNA. 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 B-structure, a paramagnetic upturn was observed at lower temperatures that is non-linear 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 intricately related to their molecular structures.

\(\lambda\)-DNA samples (400\(\mu\)g each) in two counter ion types, \(\text{Na}^+\) (hereafter called NaDNA) and \(\text{Mg}^{2+}\) (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). \(\lambda\)-DNA (16\(\mu\)m, 48,502 base-pairs) 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 aqueous environment DNA molecules are in B-DNA structure where base-pairs are stacked parallel to one another with inter-base-pair distance of 3.2 Å and the helix diameter of 19 Å. When molecules are dried, the bases become severely tilted off the helix axis and the helical diameter becomes broad (25 Å). 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. At each stage of rehydration and/or dehydration the quartz capillaries were sealed to maintain the water content constant and the magnetization and the molecular structure (via micro-Raman spectroscopy) were studied in parallel. Figure 1 shows the magnetization (\(M\)) of NaDNA with \(< 0.1, \sim 0.9\) and \(\sim 1.9 \ mu\)l of water as a function of temperature (\(T\)) at 5 Tesla. 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 \(T > 100\) K, we have extracted the diamagnetic susceptibility of DNA, \(\chi_{\text{DNA}} = -0.63 \pm 0.1 \times 10^{-6}\) EMU·G\(^{-1}\)·g\(^{-1}\). Within the experimental accuracy, the diamagnetic susceptibility was found to be independent of water content, that is, \(\chi_{\text{A-DNA}} = \chi_{\text{B-DNA}}\). This value, determined from two NaDNA samples, is in fair agreement with the calculated atomic diamagnetic sus-
ceptibility of DNA, \( \sim -0.52 \times 10^{-6} \) EMU·G\(^{-1}\)g\(^{-1}\). At temperatures below 20 K, the magnetization of NaDNA containing 1.9 and 0.9 \( \mu l \) of H\(_2\)O indicate unexpected paramagnetic up-turn that disappeared once the sample was dried to H\(_2\)O < 0.1 \( \mu l \). Figure 1b portraying \( M \) (without H\(_2\)O contribution) as a function of magnetic field \( (H) \) at \( T = 2 \) K clearly presents this low temperature paramagnetism. At helium temperature, DNA in aqueous environment exhibits a magnetization crossing-over from diamagnetic to paramagnetic that is non linear 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 A- to B structure in NaDNA are presented in Fig. 2. Among the large and highly reliable index of Raman bands corresponding to vibrational modes of DNA geometry and conformations, 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, sample was found almost purely in A-state, with 0.9 \( \mu l \), B-DNA as well as a small signature of A-DNA were observed. With 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 once the relative humidity, \( RH \) (the weight of H\(_2\)O divided by that of dry DNA) exceeds 0.9, the DNA molecules assume B-DNA state. \( RH = 0.9 \) corresponds to 0.36 \( \mu l \) of H\(_2\)O in our sample, far less than the nominal amount of 0.9 \( \mu l \) used here. This observation indicates that H\(_2\)O is not diffused uniformly due to the sample geometry and the preparation method. The more rigorous investigation on the water content and the structural analysis on NaDNA samples via X-ray diffraction will be reported elsewhere.

In MgDNA sample, we were unable to remove H\(_2\)O sufficiently to create predominantly A-DNA state. In fact, the Raman spectra (not shown) of the MgDNA in its driest state (0.3 \( \mu l \)) indicated mainly B-DNA bands, and with \( \sim 0.5 \mu l \) of H\(_2\)O the molecules were found to be in purely B-DNA state. This is in marked contrast with NaDNA where the presence of A- and B-DNA were both detected at much higher water content. This observation is consistent with a known property of Mg\(^{2+}\), \( i.e., \) that prevents the transition from B- to A-DNA more efficiently than Na\(^+\) ions. The magnetization measurements on MgDNA with \( \sim 0.5 \mu l \) of H\(_2\)O preceded the measurements with 0.3 \( \mu l \). As can be seen from Fig. 3, a purely diamagnetic behaviour at low temperatures was never achieved in MgDNA in line with the observation in NaDNA. In the driest state, only a slight decrease in \( \Delta M_{\text{para}} \) was detected. Furthermore, the paramagnetic magnetization was found to become independent of water content for H\(_2\)O values higher than 0.5 \( \mu l \) (measured up to 2.2 \( \mu l \)). 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 \(-0.8 \pm 0.1 \times 10^{-6} \) EMU·G\(^{-1}\)g\(^{-1}\), larger than the value found for NaDNA sample. This difference \( (\sim 0.2 \times 10^{-6} \) EMU·G\(^{-1}\)g\(^{-1}\)) corresponds to the diamagnetic susceptibility of the residual buffer ions (MgCl\(_2\)).
As in Fig. 1b. Inset: K. The data presented here are treated in the same manner. The apparition of paramagnetism in B-DNA at low temperature that is non-linear in applied field is ro-
magnetism. Assuming the electron spins (magnetic ions or hydroxyl radicals [18], for example) to render the ob-
served behaviour, we have fit the paramagnetic component of the magnetization, $\Delta M_{\text{para}}$, to the Brillouin and Curie law. The best fits were obtained for $s = 1/2$–3/2 with the total number of spins of $\sim 10^{15}$ for NaDNA and $\sim 4 \times 10^{15}$ for MgDNA, respectively. Such high concen-
trations of spins should be detectable by Electron Paramagnetic Resonance (EPR) provided that the signal line
width does not exceed 300G. The examination via EPR [19] revealed no such presence in NaDNA at room tem-
perature. 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 Fe$^{3+} (s = 5/2, g = 30/7)$ 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 $\Delta M_{\text{para}}$ [21]. Furthermore, the magnetization of H$_2$O used to humidify the samples was examined sepa-
ately using SQUID magnetometer. 2 $\mu$l of H$_2$O, was found to contain $\Delta M_{\text{para}} (5 T, 2 K)$ less than $10^{-6}$ EMU.
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.

Thus far, the paramagnetism appears to be an intrinsic property unique to B-DNA. An interesting possibil-
ity is the existence of persistent current loops along the DNA molecules on a mesoscopic micron scale. The meso-
scopic orbital magnetism has been shown theoretically to be paramagnetic and non-linear when repulsive electron-
electron interactions dominate over single particle effects [21, 22]. The total magnetization of the system then
follows $m(H) = \frac{\chi L k_F(\sqrt{S(T)}H)}{1+(\frac{\Phi_o}{\sqrt{S(T)}H})^2}$, where $\chi_L$ is the Landau susceptibility, and $k_F$ is the Fermi wave number. The non-linear magnetization reaches its maximum at $H_o = \Phi_o / S(T)$, where $\Phi_o = h/e = 4.14 \times 10^{-7}$ G cm$^2$ is the magnetic flux quantum and $S(T)$ is the maximum surface
area enclosed inside the coherent current loop (Fig. 4(a) and (b)). The orbital magnetism associated to the per-
sistent currents has been already observed in mesoscopic rings and 2-D squares and is considered the hallmark of
phase coherent transport at low temperatures [23]. In our DNA samples measured at 2K, the magnitude of param-
agnetic 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, $H_o = 1 \sim 2$ Tesla, via $S(T) = d \times L(T)$ where $d$ is the distance be-
tween bases of B-DNA molecules. Our calculation yields the electron path on the order of 1 $\mu$m along the heli-
cal axis of the molecules. Such circulation of electrons enclosing a finite flux can be achieved through the com-
bination of intra- and interstrand (across the hydrogen bonds) transfer of $\pi$ electrons on bases (Fig. 4). Hydro-

![Figure 2: 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'C-O-P-O-C3'). This band shifts from 807 cm$^{-1}$ in A-DNA to 835 ± 5 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 cm$^{-1}$ in A-DNA to 1092 cm$^{-1}$ in B-DNA.](image)

![Figure 3: $M$ vs. $H$ of MgDNA sample measured at $T = 2$ K. The data presented here are treated in the same manner as in Fig. 4. Inset: $M$ as a function of temperature of wet MgDNA at $H = 1T$. Dotted line represents the fit to the Curie law, $M(T) = C \times H/T$, with $C$ (the Curie constant) = 4.3 ± 0.2 \times 10^{-9}$ J·K/T$^2$ corresponding to $\sim 10^{15}$ spins of $s = 1/2$.](image)
gen bond assisted electronic exchange has already been witnessed in some organic molecules [24]. The value of the electron path found here agrees with the coherent length of $\sim 1\mu m$ in $\lambda$-DNA determined by Kasumov et al. [3] where proximity 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 that showed higher conductivity in B-DNA, with 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 aligned DNA molecules should be examined in order to confirm the orbital origins of this paramagnetism.

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