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Electronic States of Natural and Metal-ion Doped DNA

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Electronic states of pristine and metal ion doped salmon DNA's are studied with EPR and SQUID. Intrinsically no EPR signal is observed in purified salmon DNA, consistent with a semiconducting nature of the pristine DNA, but inconsistent with a metal or a superconductor as reported previously. Although we obtained successfully the divalent metal ion-DNA complexes with one-dimensional array of ions located in between the bases of a base pair, substantial EPR signal except for the case of 3d transition metal ions is not observed. This leads to the conclusion that divalent metal ions counterbalances two phosphate anions instead of Na counter ions in B-DNA, which contradicts the metallic behavior reported previously (A. Rakitin, et al., PRL 86, 3670 (2001)). A comment will also be given on the recent report: "Intrinsic Low Temperature Paramagnetism in B-DNA" (S. Nakamae et al., PRL 94, 248102 (2005)).

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As a possible candidate of conductive nanowires, the electronic properties of deoxyribonucleic acid (DNA) have attracted much interest in recent years, especially by direct measurements of the electrical conductivity in DNA bundle or even in a single DNA strand.[1–8] Some of them concluded a metallic electrical property[1], in some case, down to 50 mK with a proximity effect of the superconductivity[4] in the pristine DNA (abbreviated B-DNA). Contrary to these, intrinsic semiconducting nature is concluded in a lot of reports[2,7,9,10] including theoretical approaches[11–14] and a recent magnetic study[15]. However, the most recent report on the magnetic property of B-DNA concluded a possible presence of intrinsic paramagnetism assigned to coherent loop currents in macroscopic scales even in the pristine λ-DNA[16].

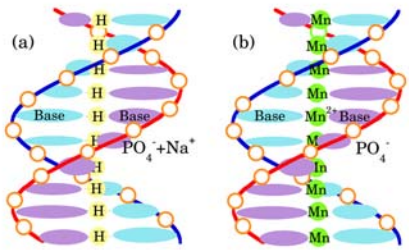

Fig. 1. Schematic structures of B- and Mn-DNA.[15]

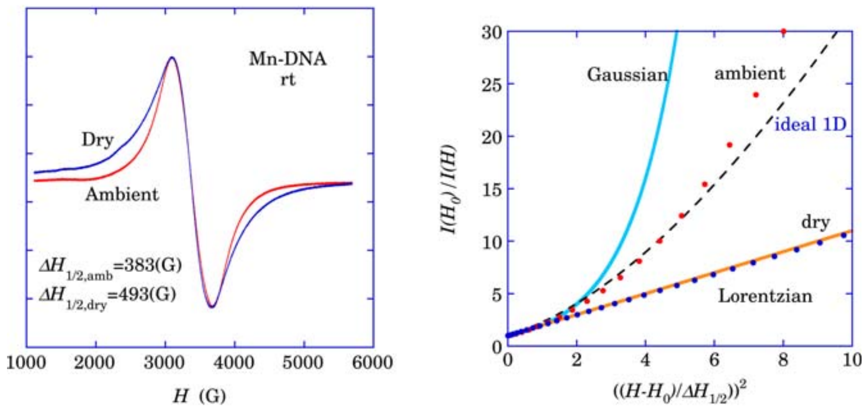

Fig. 2. Left: Comparison of the EPR spectra of the ambient and the dry Mn-DNA. Right: The inverse of the EPR intensity plotted against the square of the magnetic field deviation from the center normalized with the half-width.

In this report, we demonstrate the intrinsic semiconducting nature of B-DNA and divalent-metal ion doped M-DNA's (M=Ca, Mg or Mn) with one-dimensional array structure of ions as shown in Fig. 1[15]. Furthermore, we suggest that the intrinsic paramagnetism[16] is not intrinsic, but possibly a contribution by oxygen to the apparent paramagnetism.

The samples used in this report were prepared following the reported techniques[15,17] with Salmon DNA fiber purchased from Wako Pure Chemical Industries, Ltd. Natural DNA as purchased gives intrinsically no EPR signal, consistent with the semiconducting nature, even in the divalent-ion doped DNA[15].

Figure 2(Left) demonstrates the lineshapes of the ambient Mn-DNA with more than ten water molecules per one base pair and the dry Mn-DNA with about four water molecules. A remarkable difference in the lineshapes

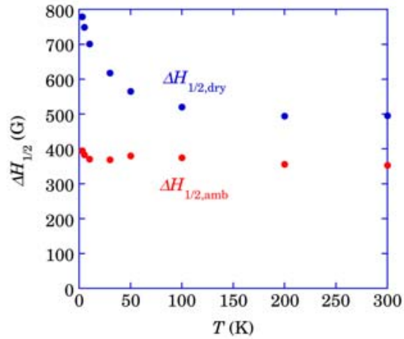

Fig. 3. Temperature dependence of the EPR half-width in the ambient and the dry Mn-DNA. In the dry Mn-DNA, the linewidth increases rapidly below 50 K.

of both Mn-DNA is found, as analysed in Fig. 2(Right). The lineshape of the ambient Mn-DNA is in between Lorentzian and Gaussian and best fitted with one-dimensional lineshape, which is consistent with the linewidth analysis in terms of the electronic dipolar and the exchange interactions between Mn-ions[15]. The lineshape of the dry Mn-DNA is well reproduced with a Lorentzian shape, suggesting a rather random distribution of the Mn ions probably because of the conformational change from the B-form in the usual double helix structure to the A-form that is a stable structure in the moistureless circumstance[18].

Figure 3 suggests a presence of antiferromagnetic ordering only in the dry Mn-DNA that shows the Curie-Weiss temperature of about -2 K, which is compared with -0.8 K in the ambient Mn-DNA[15]. The preliminary data of the specific heat in the dry Mn-DNA demonstrate a peak around 0.4 K, suggesting antiferromagnetic or spin glass ordering of the three-dimensionally distributed Mn S=5/2 spins[19]. The 1D array of the Mn ions in the ambient Mn-DNA is prevented to order three-dimensionally because of weak interhelix interaction with the interion distance of 20 Å or more.

The most recent report on the magnetic property in the pristine DNA has suggested a presence of the intrinsic paramagnetism only in the moisture condition[16], which appears below 20 K similar to the Curie-Weiss behavior with $\Theta \approx$6 K. With removing water molecules from DNA, such paramagnetism almost disappears. The authors claimed that the paramagnetism of B-DNA is due to the long-range coherent charge transport via DNA double helix around 1 μm of transport path. We reconfirmed a similar susceptibility in B-DNA. However, we also found that it is reproducible with a small amount of oxygen gas or air. Then, we have to check the possible contribution of the residual oxygen in sample tubes. It should be extremely careful not to introduce oxygen into a system composed of DNA and water.

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