

## Magnetic study of the electronic states in B-DNA and M-DNA doped with metal ions

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Magnetic properties of pristine and metal ion doped salmon DNAs are investigated with EPR, SQUID and EDS for the first time. Purified salmon DNA gives intrinsically no EPR signal, which is consistent with DNA being a semiconductor, but not with DNA having metallic or superconducting properties as reported previously. Several kinds of divalent ions (Zn, Mn, Ca...) are used as dopants, resulting in no substantial EPR signal except in the case of Mn. This leads to the conclusion that a metal ion 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)).

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From viewpoint of conductive nanowires, the electronic properties of deoxyribonucleic acid (DNA) have been intensively studied in recent years, especially with direct measurement techniques for the electrical conductivity by virtue of recent developments to manipulate DNA bundle or even a single DNA strand.<sup>1-8</sup> However, there is no general consensus about this issue among the reports. On the pristine DNAs (abbreviated B-DNA), Fink and Schenberger have reported ohmic voltage-current characteristics of a few  $\lambda$ -DNA molecules demonstrating efficient charge conduction through the B-DNA bundle.<sup>1</sup> Furthermore, Kasumov and co-workers directly measured the electrical resistivity of double-stranded 16  $\mu\text{m}$ -long  $\lambda$ -DNA with rhenium/carbon (Re/C) bilayer electrodes.<sup>4</sup> They found that DNA was metallic down to 50 mK and reported a proximity effect of the superconductivity of the metallic rhenium. On the other hand, Porath and co-workers have directly measured the electrical conductivity of synthetic DNA (poly(G)-poly(C)) with a length of 10 nm to find a semiconducting behavior with the temperature dependent energy gap of 2-4 eV,<sup>2</sup> which is consistent with the ac-conductivity reported for 17  $\mu\text{m}$ -long  $\lambda$ -DNA by Tran *et al.*<sup>9</sup> In a recent report Zhang *et al.* pointed out the importance of removing salt residue when studying the intrinsic nature of B-DNA with a direct measurement technique.<sup>7</sup> The other issue is an electron-bombardment-induced contaminations discussed by de Pablo *et al.*<sup>10</sup> In this context, it is desirable to investigate the electronic properties of DNA using other experimental techniques, like magnetic and optical studies.

Several theoretical considerations on the conduction mechanisms have been reported.<sup>11-16</sup> They suggest that the electronic states of B-DNA are of semiconducting nature, with hopping conduction between random bases. The mechanism of charge transport in synthetic DNAs with a single base pair would be tunnelling.

By doping DNA with divalent metal ions, Wood and co-workers have synthesized complexes (M-DNA) containing the divalent metal ions  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  and duplex DNA at pH of around 8.5.<sup>17,18</sup> They proposed that the metal dications are substituted for the hydrogen bonds in-between the bases; guanine-cytosine or adenine-thymine as shown in Fig. 1. Charge transport

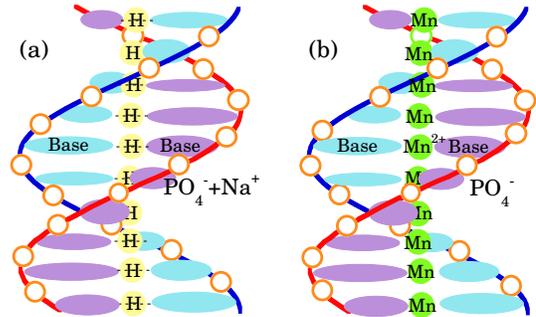


FIG. 1: Schematic structure of (a) B-DNA and (b) Mn-DNA. Two DNA backbones are represented by the sinusoidal curves, made of a repeat of deoxyribose sugar and phosphate ion (open circle). A step of DNA "ladder" is made of a base pair; either guanine-cytosine or adenine-thymine, which is connected by three or two hydrogen bonds, respectively. (a) In B-DNA each phosphate anion is attended by a  $\text{Na}^+$  cation to form a salt. (b) Proposed structure of M-DNA.<sup>5</sup>

of  $\lambda$ -DNA in both forms of B-DNA and M-DNA has been studied with a dc current versus voltage measurement by Rakitin *et al.*<sup>5</sup> They found a finite threshold voltage to excite a sizable current in B-DNA, but no threshold in M-DNA. Thus, they concluded that the electronic states are of semiconducting type with a gap in B-DNA, but of metallic type in M-DNA. However, we will show that this conclusion is questionable.

In this report, we demonstrate the first magnetic study of salmon DNA in both forms of B- and M-DNAs. We use both EPR and SQUID susceptometer, along with Energy Dispersive X-ray fluorescence Spectroscopy (EDS), to unveil the electronic states of DNAs. Special attention is paid to clarify if B-DNA is metallic or not, and whether  $\pi$ -charge injection to the  $\pi$  band of base pairs takes place with the divalent metal ion doping, from a magnetic viewpoint. The important advantages of these techniques are that no electrical contact and no current flow is required, which have been identified as possible errors leading to the controversial interpretations of the electronic states in DNAs.

Two different grades of salmon-DNA (a kind of B-

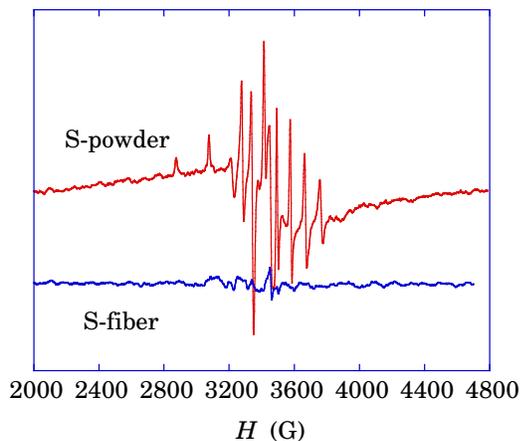


FIG. 2: EPR spectra of S-powder and S-fiber (salmon-DNA). The relative intensities are calibrated relative to each other.

DNA) were purchased from Wako Pure Chemical Industries, Ltd.; DNA powder (S-powder) and DNA fiber (S-fiber). The S-fiber is a purified form of S-powder, thus the fibrous morphology might reflect the rod-like linear structure of the DNA double-helix. Metal ions were inserted in S-fiber by dissolving it in tris-buffer of pH=8.5 with  $\text{ZnCl}_2$ ,  $\text{CaCl}_2$ , or  $\text{MgCl}_2$ , but in purified water with  $\text{MnCl}_2$ , since  $\text{MnCl}_2$  in alkali solution transforms to  $\text{MnO}_x$  having black color. After stirring for 30 min, ethanol at  $-20^\circ\text{C}$  was added to precipitate M-DNA. Finally, the precipitate was washed with pure ethanol to remove unreacted metal ions. The obtained M-DNA film is transparent and colorless, which is typical for semiconducting materials with band gaps larger than the energy of visible light. The doped Mn ion concentration is found both with EPR intensity and SQUID susceptibility to be nearly one  $S=5/2$  spin per base pair.

EPR spectra of S-powder and S-fiber are shown in Fig. 2, where the intensities are calibrated relative to each other. Note that the purified S-fiber DNA gives a negligibly small signal compared with that of the crude S-powder. The calibrated density of  $S=1/2$  spins is  $\approx 2,000$  ppm per base pair for S-powder and  $\approx 50$  ppm for S-fiber, suggesting that most of the observed spins in S-powder come from contaminations of the purchased material. A spin concentration of 50 ppm in S-fiber is low enough to consider the spins to be defects of DNA or other contaminations. If the 50 ppm of spin density were intrinsic to DNA, it would be too small to correspond to Pauli susceptibility of conventional metals as implied by ohmic conduction reported with the direct conductance measurements.<sup>1,4</sup> Assigning the small spin density to defects or contaminations is consistent with the semiconducting gap of several eV between the filled valence and the empty conduction bands, as reported,<sup>2,3,6,7,9-11</sup> which gives no paramagnetic spins/EPR signal.

Another suggested explanation of the conduction in B-DNA is charge transport with spinless charge carriers such as charged solitons and bipolarons, being the mid

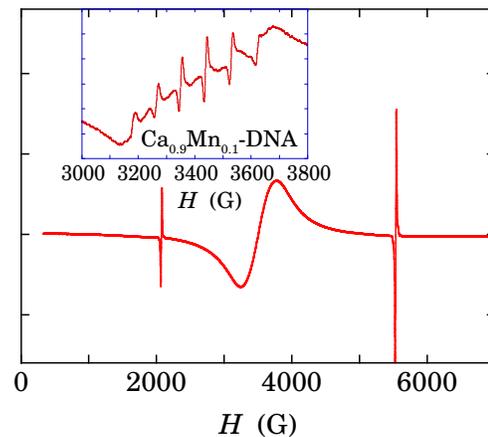


FIG. 3: EPR spectra of Mn-DNA taken at room temperature at X-band. Two sharp peaks above and below the Mn spectrum are the signals from the ruby standard. The inset represents the six hyperfine split peaks in the 10 % Mn doped DNA.

gap states.<sup>19</sup> However, the requirements of ground-state degeneracy for solitons, or strong electron-phonon coupling for bipolarons, should be fulfilled. In addition, it is difficult to find consistency between the band gap and the superconductivity induced by the Cooper pairs in the rhenium metal.<sup>4</sup> Therefore, the present results lead us to the conclusion that B-DNA without charge carrier injections should have semiconducting electronic states with a large energy gap.

EPR spectrum of the Mn-doped M-DNA (Mn-DNA) is shown in Fig. 3, along with the sharp Ruby standard signals. No hyperfine structure is found because of exchange narrowing with the neighboring  $\text{Mn}^{2+}$  ions. In the case of  $\text{Ca}_{0.9}\text{Mn}_{0.1}$ -doped M-DNA in the inset, Mn EPR signals with six peaks corresponding to the hyperfine splitting by Mn nucleus with  $I=5/2$  suggests the presence of isolated  $\text{Mn}^{2+}$  ions. The signal separation and width depend on the direction of nuclear spin; for example, 84.2 G between  $m=5/2$  and  $3/2$  and 94.7 G between  $m=-5/2$  and  $-3/2$ , in contrast to the constant separation of  $\approx 86$  G for  $\text{Mn}^{2+}$  doped into MgO standard sample. Details of this structure will be discussed elsewhere. Note that the center position of the spectrum is near the free electron  $g$ -value,  $\approx 2.00$ , which corresponds to the  $\text{Mn}^{2+}$   $S$ -state ion. This fact along with the absence of Na ions as confirmed by EDS demonstrates that the  $\text{Mn}^{2+}$  ion, instead of two  $\text{Na}^+$  ions, acts as a counterion for the two phosphate anions of DNA double-helix backbone. As a result, charge injection into the base  $\pi$ -band cannot be achieved with the present doping method. Furthermore, the  $\text{Mn}^{2+}$   $S$ -state ion ensures that a simple exchange narrowing model free from the orbital contribution is applicable to the present system.<sup>20</sup>

If we assume a location of each  $\text{Mn}^{2+}$  ion in-between the bases as shown in Fig. 1, forming a linear chain of the ions, as proposed by Rakitin *et al.*,<sup>5</sup> the exchange narrowing successfully accounts for the observed half width

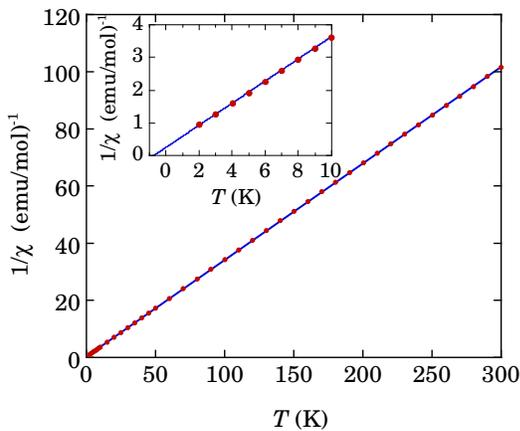


FIG. 4: Magnetic susceptibility of Mn-DNA measured with SQUID susceptometer at 1 T. The estimated spin concentration is about one  $S = 5/2$  spin per base pair. The inset shows the expanded view at low temperatures demonstrating  $\Theta \approx -0.8$  K.

$\Delta H_{1/2} = 380$  G at half maximum. For a powder sample, in general, the angular averaged second moment  $\langle \Delta H^2 \rangle$  and the exchange narrowed width is expressed by<sup>21</sup>

$$\langle \Delta H^2 \rangle = \frac{3}{5} \gamma^2 \hbar^2 S(S+1) \sum \frac{1}{r^6}, \quad (1)$$

$$\Delta H_{1/2,cal} = \frac{\langle \Delta H^2 \rangle}{H_{ex}}, \quad (2)$$

where  $\gamma$  is the gyromagnetic ratio for the electron spins,  $r$  is the nearest neighbor distance between  $\text{Mn}^{2+}$  ions, the summation is taken over the nearest neighbors and the other symbols have their usual meanings. With the average distance of  $\langle r \rangle = 3.44$  Å between ions,  $S = 5/2$  and the exchange field  $H_{ex} = 3k_B |\Theta| / g\mu_B \sqrt{S(S+1)}$  with a Curie-Weiss temperature of  $\Theta = -0.8 \pm 0.1$  K as obtained in Fig. 4,  $\langle \Delta H^2 \rangle = 2.4 \times 10^6$  G<sup>2</sup> and  $\Delta H_{1/2,cal} = 390 \pm 50$  G are obtained. In this estimate of the second moment, only the two nearest-neighbor  $\text{Mn}^{2+}$  ions in the 1D- $\text{Mn}^{2+}$  chain are considered, since the second nearest-neighbor contributes only 1 to 2 %, and the interhelix interaction through the helix diameter of 2 nm contributes less than  $10^{-4}$  of the estimated value. Thus, the good agreement of  $\Delta H_{1/2,cal}$  with  $\Delta H_{1/2} = 380$  G is strong evidence for the linear Mn chain configuration in-between the base pairs, as proposed by Rakitin *et al.*<sup>5</sup> This ion location is also sound because of a highly symmetric configuration for the charge distribution;  $\text{P}^- = \text{Mn}^{2+} = \text{P}^-$ , where the  $\text{P}^-$ s are phosphate ions located in the two polymer backbones of the DNA double-helix. From these observations it is easily imagined that the transport property of Mn-DNA would be similar to that of B-DNA, since no charge carriers are introduced by the Mn-doping, leaving the energy gap in B-DNA unaltered. Therefore, the

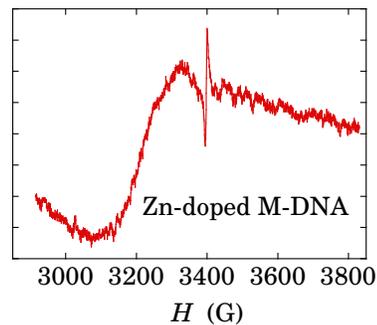


FIG. 5: EPR spectrum of Zn-DNA. The signal intensity is much weaker than that for Mn-DNA, as implied by a low S/N ratio compared with that in Mn-DNA.

present conclusion contradicts the ohmic conduction reported by Rakitin *et al.*<sup>5</sup> As a matter of fact, our attempt to measure the resistivity of the Mn-DNA film resulted in the order of  $10^{10}$  Ω, indicating insulator behavior.

Figure 4 shows the susceptibility of Mn-DNA, demonstrating a fairly small Curie-Weiss temperature  $\Theta$  of  $-0.8$  K. The reason for such weak interaction would be the long average inter-ion distance of 3.44 Å, which is much larger than the Pauling  $3d$  ionic radius of the order of 0.46 Å. This value is compared with  $\sim 0.8$  Å for the  $\pi$ -orbital. It is noteworthy that the transfer energy  $t$  along the 1D-chain of  $\text{Mn}^{2+}$  ions can be estimated to be as small as 2-6 meV with the simple tight binding relation  $J = -2t^2/U$ , where  $J \approx -6 \times 10^{-3}$  meV is the exchange energy obtained by the mean-field relation<sup>22</sup>  $J = 3k_B \Theta / 2zS(S+1)$  with the number of the nearest-neighbors  $z=2$ ,  $S=5/2$ , and  $U$  is the onsite Coulomb energy being of the order of 1-10 eV. With the low  $t$ , the 1D-chain of the metal ions should not be expected to perform as a charge transport channel in M-DNA double-helix.

It is known that Zn ions are located in-between the base pair in Zn-doped M-DNA (Zn-DNA).<sup>5</sup> Figure 5 shows a typical EPR spectrum of Zn-DNA composed of one broad and one sharp signal. In contrast, Ca-doped M-DNA gives no such sharp EPR signal. The broad signal suggests a presence of  $d^9$  electron configuration originating from  $\text{Cu}^{2+}$ , since the  $g$ -value is more than 2 due to the spin-orbit interaction typical of "more than half" filling of the  $d$ -shell.<sup>23</sup> Considering the small spin concentration of less than 2,000 ppm for the broad signal estimated with  $S=1/2$ , it is natural to assign the spins to the  $\text{Cu}^{2+}$  impurity originally contained in the raw material of  $\text{ZnCl}_2$ . The valence of Zn should be +2 because of the absence of EPR signal from Zn ions. On the other hand, the  $g$ -value and the linewidth of the sharp signal are close to the usual  $\pi$ -electron case with  $\approx 2.002$  and several Gauss, respectively, which suggests that a very small amount of Zn, about 20 ppm per base pair, could produce the charge carriers in the base  $\pi$ -band. Interestingly, such a small value is consistent with the existence of accidentally re-oxidized anhydrous  $\text{Zn}^+$  which produces a hole in the base, as proposed theoretically by Kino *et al.*<sup>24</sup> Following this

model, the anhydrous  $\text{Zn}^{2+}$  is assumed to be located near a phosphate anion instead of in-between the two bases of the base pair. This model further predicts that anhydrous Ca does not form a monocation, but rather a dication as the stable species, which is consistent with the present results. However, we failed to observe a definite change of the sharp signal intensity with changing humidity. This should strongly affect the number density of anhydrous monocations, and thus the  $\pi$ -charge carriers. Therefore, the origin of the sharp signal is still an open question. Finally, it should be mentioned that even if the sharp signal comes from the  $\pi$ -carrier, the extremely low number of carriers that should then be localized, cannot account for the ohmic transport in M-DNA reported by Rakitin *et al.*<sup>5</sup> Thus, doping by inserting divalent metal ions in-between the two bases of the base pairs in solution is not an appropriate method for adding charge carriers into the base  $\pi$ -band, since the metal dication simply substitutes the two Na counter ions in B-DNA to form salts with  $\text{PO}_4^-$ . This conclusion is inconsistent with the metallic transport reported by Rakitin *et al.*<sup>5</sup>

In conclusion, the magnetic properties of B-DNA and M-DNA have been investigated with X-band EPR. It is found that the purified form of salmon DNA, S-fiber, does not carry spins, which is consistent with the semiconducting nature of B-DNA as reported theoretically and experimentally, but inconsistent with the metallic nature, especially with the proximity effect of the superconductor. Metal ion doping in solution has been carried out successfully with several species; Mn, Zn, Ca and Mg.

However, with this method of doping by divalent ions  $\pi$ -charge carriers could not be introduced into the base  $\pi$ -band, except for the possibility of accidental doping of anhydrous  $\text{Zn}^{2+}$ . In Mn-doped case, it is confirmed that the  $\text{Mn}^{2+}$  is located in-between the bases, constructing a linear chain of dications. However, the magnetic interaction between the ions as derived from the Curie-Weiss temperature of -0.8 K, is too weak to form a metallic nature of 1D  $\text{Mn}^{2+}$  chain; the transfer energy along the 1D-chain is as small as 2-6 meV estimated with a simple tight binding relation.

To realize conducting wires of DNA, a promising candidate might be trivalent metal ions, such as  $\text{Fe}^{3+}$ , which has the possibility of introducing  $\pi$ -charge carriers into the base  $\pi$ -band. In this case, it is also important to use a single base pair DNA to ensure band conduction.

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