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AF-like Ground State of Mn-DNA and Charge Transfer from Fe to Base-π-Band in Fe-DNA

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The electronic states of M-DNA doped with M = Mg, Ca, Zn, Mn, Fe are investigated mainly with magnetic properties. In the "wet" condition the Mn ions of Mn-DNA form a 1-D chain in the center of a DNA double helix, as evidenced from the formation of the unnatural base pair combination with M, poly(dA)–M–poly(dC), but in the "dry" condition they form a 3-D network with the antiferromagnetic ground state around 0.4 K with the superexchange coupling via water molecules. The valence of 3+ is found only in Fe-DNA, from which the base π-band obtains π charge carriers.

KEYWORDS: DNA, magnetism, ESR, metal ion, charge transfer, antiferromagnetism
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From the viewpoint of conductive nanowire, the electronic properties of deoxyribonucleic acid (DNA) have been intensively studied in recent years.[1–13] These studies have concluded diverse natures of the natural DNA (abbreviated as B-DNA) to be insulating,[8] semiconducting,[3,4,6,7,9,10,12] metallic[2,5,11,13] and induced superconducting.[5] A part of such diversity would originate from possible difficulties of voltage–current (I–V) measurement for a single double helix, avoiding unexpected effects due to salt residues, electron bombardment by an electron microscope, and effective doping.[1] Most of the reports look like consistent with the presence of energy gap in greater or less degree, which is entirely consistent with the diamagnetic nature of the natural DNA.[10] Thus, there seems a consensus that the nature of charge carriers in the natural DNA is different from that of the usual metals with Fermi surface.

As a way to introduce the charge carriers into the base π band of DNA, the insertion of divalent metal ions between the bases of a base pair has been proposed[14] and the linear I–V characteristics with zero-threshold voltage has been found in Zn inserted DNA (Zn-DNA).[6] However, it is also found that the M-DNA with M = Zn, Ca, or Mg is diamagnetic, which suggests the valence of the metal ions to be divalent,[15] meaning that no extra charge injection into the base π band occurs, but M^{2+} takes over for two sodium cations compensating two PO_4^- in these M-DNA compounds.[10] Thus, the interpretation of Ohmic relationship observed in Zn-DNA should not be simple. Recently, Alexandre *et al.* reported the first principles calculation on poly(dC)–M–poly(dG) with metal ions, Zn^{2+}, Co^{2+}, or Fe^{2+}, which substitutes the imino proton to form N–M–N bonds with the bases.[16] They proposed a common stable structure with much narrower band gap consistent with the experimental reports. Thus, the electronic structure of M-DNA is an interesting issue concerned with the conducting nanowire.

In this report, we demonstrate a magnetic study with SQUID, ESR and specific heat at low temperatures to unveil the electronic states of M-DNA with M = Mn or Fe. Both of the systems carry the magnetic moment arising from the 3d electrons, which is not only highly helpful to investigate the electronic states of the M-DNA, but also interesting in their magnetic ground states as magnetic spin arrays. The magnetic nature of Mn-DNA remarkably changes depending on a moisture condition. Under the wet condition, Mn-DNA shows definite one dimensional (1-D) exchange narrowing of ESR spectra, which is consistent with the B-form stable in the lives, providing that the Mn ions form a 1D array, as shown in Fig. 1. Under the dry condition, it is suggested from the Curie–Weiss susceptibility with $\Theta \approx -2$ K and the peak around 0.4 K in the specific heat that the phase transition to antiferromagnetic (AF) like ground state appears below 1 K. It is interesting to know if the divalent metal ions work as a binder for the bases of a base pair or not. Surprisingly, it is possible to make a combination of poly(dA)–M–poly(dC) which never appears in the natural world. Lastly, it is stressed that the charge transfer to the base π band has occurred in the Fe-DNA which is, however, not good conductor probably because of a density wave.

M-DNA was prepared from the 1 mmol/L aqueous solution of DNA (salmon or oligo-DNA), purchased from Wako Pure Chemical and Hokkaido System Science, mixed with the 5 to 10 mmol/L aqueous solution of MCl_2. Here,

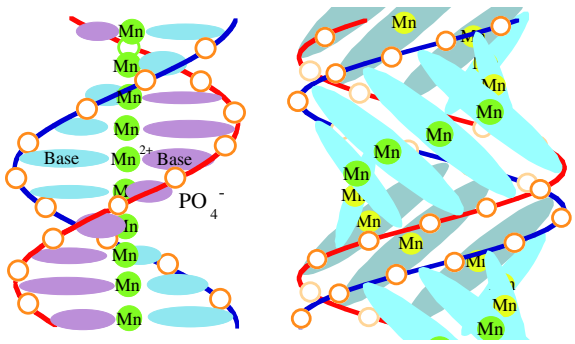

Fig. 1. (Color online) Model structures for the B-form (left) and the A-form (right) of Mn-DNA. Ellipsoids represent bases or base pairs. In the B-form, Mn ions occupy the center axis of the double helix, while they form a coil in the A-form DNA like a rope ladder.

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note that MCl_3 with M^{3+} did not form M-DNA composite. After stirring for 10–30 min, excess cold ethanol at −20 °C is poured into the transparent DNA-MCl_2 solution resulting in transparent precipitate for Mn-DNA and light ocher color for Fe-DNA. The residual MCl_2 is washed out thoroughly from the obtained precipitate in pure ethanol where DNA is insoluble. Thus obtained M-DNA were dried to form a film in the atmosphere. The samples in the "wet" condition were saturated with water molecules at room temperature (RT) and sealed in a quartz tube for SQUID and ESR measurements. The "dry" samples were evacuated for one hour or more before sealed in a quartz sample tube. It was confirmed with ^{1}H NMR that the wet DNA contained about 12 H_2O molecules per each base pair in the double helix of DNA. In the dry state, it contains still about four water molecules. Circular dichroism (CD) spectra are examined to confirm the B-form of the double helix structure of B-DNA and M-DNA solutions. X-ray fluorescence analysis indicated that the molar ratio of phosphorous and metal ion was approximately two to one as expected for the metal ion located in the center of a base pair substituted for two sodium ions compensating two phosphoric anions in DNA backbone.

It is interesting how to assign the position of metal ions in M-DNA. Lee and coworkers have reported the first model that the metal ions occupy the location in-between the bases of each base pair. They concluded from the ^{1}H NMR where the proton signal corresponding to the hydrogen bonding in-between the bases decreases with increasing the metal ion concentration.[14] The support of such a structure in Mn-DNA has also been appeared in the ESR line width analysis which provides the information on the 1D arrangement of the Mn ions.[10] The third experimental support for the 1D chain formation in the center of B-form double helix will be given later, from the analysis of ESR line shapes in Mn-DNA. Furthermore, we found the fourth interesting experimental fact in M-DNA with oligo-double helix. In the natural world, only the combinations of guanine (purine base) with cytosine (pyrimidine base) and adenine (purine) with thymine (pyrimidine) appear with three and two hydrogen bonds, respectively. And then, the guanine never makes a bond with the thymine, and the adenine does not with the cytosine. This natural rule guarantees the duplication of genes and the self-organization. If the metal ion makes a bond between the pyrimidine and the purine without hydrogen bonds as proposed by Lee and coworkers,[14] it is expected that the metal ion could join any pyrimidine with any purine, such as the guanine with the thymine, and the adenine with the cytosine. With synthesized oligomers, we have succeeded in confirming such a reaction in the combination of poly(adenine)$_{10}$ and poly(cytosine)$_{10}$ with excess $MnCl_2$. The obtained oligomeric Mn-DNA shows the same magnetic behavior as the salmon Mn-DNA. This observation strongly suggests not only that the Mn^{2+} ions are located at the center of the adenine and the cytosine base pair, but also that the divalent metal ions could disturb the gene duplication in heredity. An X-ray study on M-DNA is undertaken to obtain more direct structural evidence.

It is found that ESR line shape remarkably changes depending on the humidity condition in Mn-DNA, as shown in Fig. 2. In the wet condition, the ESR spectrum has shorter tails than that with minimum water molecules in the dry condition. To analyze more quantitatively, the inverse of intensity is plotted in Fig. 3. The line shape in the wet condition is consistent with the 1D exchange narrowing case.[17] In contrast, the dry Mn-DNA gives a good Lorentzian shape as demonstrated in Fig. 3. This humidity dependence can be ascribed to the isomeric transformation from the B-form stable in the lives to the A-form (Fig. 1) realized in the dry circumstance with decreasing the humidity.

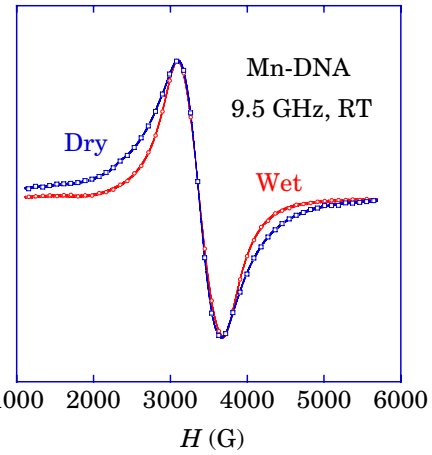

Fig. 2. (Color online) The humidity dependence of the ESR line shape in Mn-DNA. In the wet condition, the ESR line shape is intermediate of Gaussian and Lorentzian. In contrast, the line shape changes to the almost perfect Lorentzian in the dry condition.

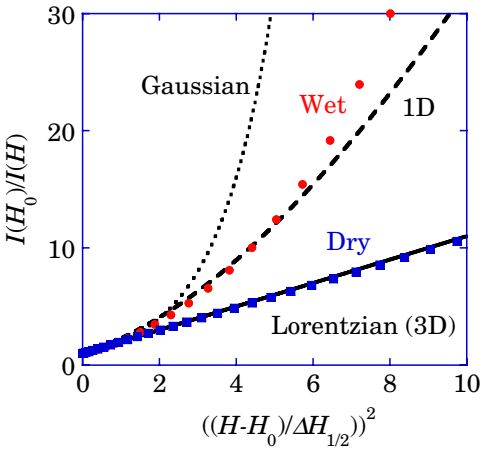

Fig. 3. (Color online) The inverse of the normalized intensity $I(H_0)/I(H)$ is plotted against the square of the normalized magnetic field deviation from the resonance center, $[(H - H_0)/\Delta H_{1/2}]^2$. In this plot, the Gaussian line shape is represented by a exponential and the Lorentzian by a straight line.

It is known that the hydrogen bonds in-between the bases of a base pair are approximately located near the center axis of the B-form DNA of which structure is similar to a twisted ladder (Fig. 1, left). Then, the metal ions are expected to form a 1D chain along the center axis of double helix. The observed 1D exchange narrowing of the line shape in Figs. 2 and 3 is consistent with such a 1D formation of the Mn ions in the B-like-form of Mn-DNA. Thus, the distance of the neighboring Mn ions in the intra- and the inter-double helicies is strongly anisotropic; the distance ratio reaches

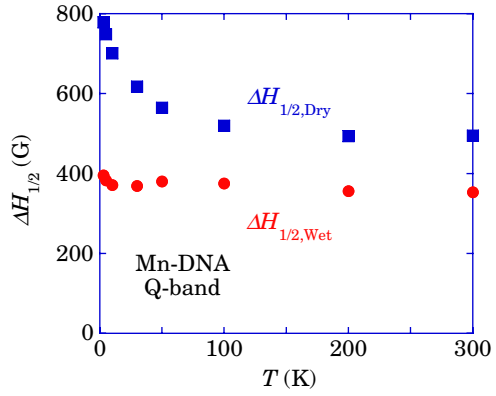

Fig. 4. (Color online) The temperature dependence of ESR line width for Mn-DNA in the wet (circles) and the dry (squares) conditions. The line width is dominantly governed by the electronic dipolar interaction between Mn ions at RT.[10] Note the low temperature increase of the line width in the dry condition, typical of antiferromagnetic interaction.

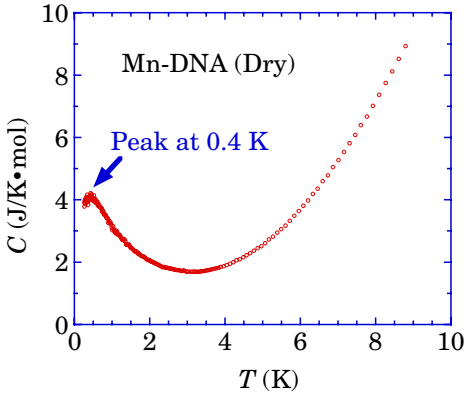

Fig. 5. (Color online) The low temperature specific heat of Mn-DNA in the dry condition (A-form). A peak is found at 0.4 K below the disappearance of the phonon contribution. It is suggested that the peak originates from some AF-like magnetic ordering of Mn ions, which corresponds to the Curie–Weiss temperature of ≈ -2 K.

nearly six and the ratio of the corresponding dipolar interactions up to 200. On the other hand, the structure of A-form is similar to a solenoid coil wound by a ladder around a cylinder, where the metal ions also form a solenoid (Fig. 1, right). As a result, the Mn ion interacts with the other Mn ions not only within the double helix but also over the neighboring double helices surrounding three dimensionally. Thus, the expected ESR line shape becomes Lorentzian in the A-form of Mn-DNA. Finally, the ESR line shapes in Fig. 3 suggest that the metal-inserted M-DNA also has the A-like-form under vacuum as in the natural DNA.

The Curie–Weiss temperature of the dry Mn-DNA is $\Theta \approx -2$ K which is twice of ≈ -1 K of the wet Mn-DNA.[10] Figure 4 shows the temperature dependence of the ESR line width which demonstrates a difference of the dimensionality of magnetic interactions, that is, 1D for the wet and 3D for the dry Mn-DNA. In the dry system, the ESR line width rapidly broadens below 50 K. The specific heat has been measured to confirm the origin of the line broadening. Figure 5 demonstrates the temperature dependence of the specific heat below 10 K with the peak around 0.4 K, being ascribed to some antiferromagnetic-like long-range ordering. Thus, the line broadening below 50 K is also interpreted not with the motional narrowing, but with the development of the antiferromagnetic correlation between Mn magnetic moments. Note that even with $\Theta \approx -1$ K in the B-like-form of Mn-DNA, a half of the A-like-form, no remarkable increase of the line width has been observed, which suggests that the 3D magnetic couplings among Mn ions are too weak for the long-range order to develop.

The nature of the magnetic ground state in the A-like-form is not clear now, but there are two possibilities; One is a long-range antiferromagnetism and the other is a spin glass type ground states. Since the A-like-form of Mn-DNA prepared with the salmon DNA has random sequences of the base pairs and the complicated 3D structure, the magnetic ground state would not be simple. Furthermore, providing that the average separation of Mn ions within the double helix of the A-form is larger than that of the B-form, the larger Θ of the dry than the wet Mn-DNA suggests the complicated superexchange mechanism via water molecules; for example, the higher number of water molecules as in the B-form of the wet condition might suppress the total exchange coupling between the neighboring Mn ions. Thus, further investigations of the ground state should be encouraged to unveil the magnetic systems with super-hierarchal Mn-DNA structures.

All the M-DNA synthesized so far carry the metal ions with the valence of 2+ which suggests that the net charge transfer from the metal to the base π band does not occur.[6,10,15] Here, we report the first example in which the net charge transfer from Fe to the base π band actually occurs. It is known that the color of Fe^{2+}, such as $FeCl_2$, is light green but, in contrast, Fe^{3+} shows ocher color. Actually, the color of the mixture of salmon DNA and $FeCl_2$ is almost transparent or very lightly greenish. However, the collected Fe-DNA as the precipitate with excess ethanol turns to ocher color indicating the transformation of Fe^{2+} to Fe^{3+} accompanied with charge doping to the base π band. This conclusion is consistent with the fact that the number of Fe atoms is approximately a half of the number of P atoms estimated from the X-ray fluorescence analysis. In contrast, the number of Na is negligibly smaller than that of Fe, suggesting almost perfect ion exchange from Na to Fe. It is also confirmed with CD spectra that the double helix structure in B-DNA is also held in both Mn-DNA and Fe-DNA, as demonstrated in Fig. 6.

Another evidence for Fe^{3+} in Fe-DNA is found in the resonance position of ESR. As demonstrated in Fig. 7, the ESR spectrum appears almost at the free electron g-factor, as in Mn-DNA.[10] This situation can be realized only if $S = 1/2$ or $5/2$, corresponding to the π-electron spin and the low spin state of Fe^{3+} or the high spin state of Fe^{3+}, respectively. In these cases, the total orbital angular momentum which could cause the g-shift through the spin–orbit interaction is zero. Both of the ESR spectrum and the magnetization curve taken at 2 K are consistently accounted for as superposition of multiple spin sources with $S = 1/2$ and $5/2$. The narrowest spectrum corresponding to the susceptibility with $\Theta \approx -40$ K could be assigned to the π spins in the base π-band. The detailed analysis will appear elsewhere.

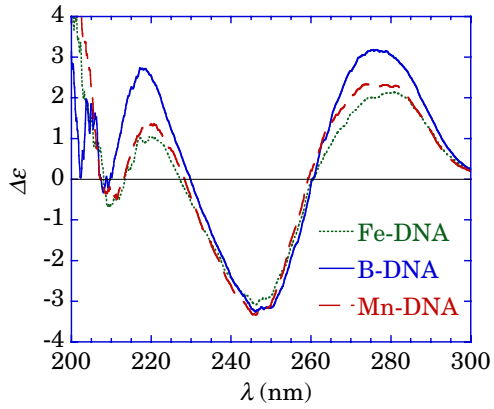

Fig. 6. (Color online) The spectra of circular dichroism (CD) in aqueous solution of B-DNA (solid line), Mn-DNA (dashed) and Fe-DNA (dotted). All the three spectra represent typical of double helix DNA with the large positive values at 200 nm, in contrast with that around zero for denatured, single stranded DNA.

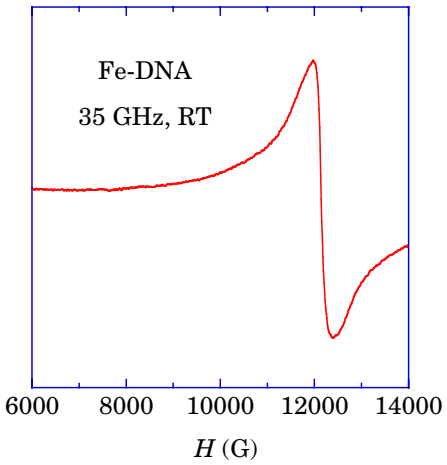

Fig. 7. (Color online) ESR spectrum of the wet Fe-DNA taken at 300 K and Q-band. Note that the magnetic field corresponding to $g = 2$ is around 1.21 T.

Concluding remarks: It is confirmed that the M-DNA also shows the isomeric transformation from the B-form stable in the lives to the A-form in the dry condition. A kind of antiferromagnetic ground state has been found only in the dry Mn-DNA with 3D magnetic interactions. The charge transfer from the metal ions to the base π-band has been achieved in the Fe-DNA system. Interestingly, it is found that the unnatural pairing such as A–C and G–T could occur with the divalent metal ions as a binder of the purine and the pyrimidine bases. This fact suggests that the divalent metal ions could disturb a correct duplication of DNA, which is important observation on the effect of the divalent metal ions to genes.

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1) R. G. Endres, D. L. Cox, and R. R. P. Singh: Rev. Mod. Phys. **76** (2004) 195.
2) H.-W. Fink and C. Schenenberger: Nature **398** (1999) 407.
3) D. Porath, A. Bezryadin, S. d. Vries, and C. Dekker: Nature **403** (2000) 635.
4) B. Giese, J. Amaudrut, A.-K. Kohler, M. Spormann, and S. Wessely: Nature **412** (2001) 318.
5) A. Y. Kasumov, M. Kociak, S. Gueron, B. Reulet, V. T. Volkov, D. V. Klinov, and H. Bouchiat: Science **291** (2001) 280.
6) A. Rakitin, P. Aich, C. Papadopoulos, Y. Kobzar, A. S. Vedeneev, J. S. Lee, and J. M. Xu: Phys. Rev. Lett. **86** (2001) 3670.
7) K.-H. Yoo, D. H. Ha, J.-O. Lee, J. W. Park, J. Kim, J. J. Kim, H.-Y. Lee, T. Kawai, and H. Y. Choi: Phys. Rev. Lett. **87** (2001) 198102.
8) Y. Zhang, R. H. Austin, J. Kraeft, E. C. Cox, and N. P. Ong: Phys. Rev. Lett. **89** (2002) 198102.
9) Z. Kutnjak, C. Filipic, R. Podgornik, L. Nordenskiold, and N. Korolev: Phys. Rev. Lett. **90** (2003) 098101.
10) K. Mizoguchi, S. Tanaka, T. Ogawa, N. Shiobara, and H. Sakamoto: Phys. Rev. B **72** (2005) 033106.
11) S. Nakamae, M. Cazayous, A. Sacuto, P. Monod, and H. Bouchiat: Phys. Rev. Lett. **94** (2005) 248102.
12) K. Mizoguchi, S. Tanaka, and H. Sakamoto: Phys. Rev. Lett. **96** (2006) 089801.
13) S. Nakamae, M. Cazayous, A. Sacuto, P. Monod, and H. Bouchiat: Phys. Rev. Lett. **96** (2006) 089802.
14) J. S. Lee, L. J. P. Latimer, and R. S. Reid: Biochem. Cell Biol. **71** (1993) 162.
15) J. B. MacNaughton, E. Z. Kurmaev, L. D. Finkelstein, J. S. Lee, S. D. Wettig, and A. Moewes: Phys. Rev. B **73** (2006) 205114.
16) S. S. Alexandre, J. M. Soler, L. Seijo, and F. Zamora: Phys. Rev. B **73** (2006) 205112.
17) M. J. Hennessy, C. D. McElwee, and P. M. Richards: Phys. Rev. B **7** (1973) 930.