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Physical properties of natural DNA and metal ion inserted M-DNA

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ABSTRACT

DNA has attracted much interest as a material for nano science and technology. We have studied DNA both in natural forms and modified forms M-DNA by insertion of a variety of metal ions. On the ground of basic science, we tried to unveil the intrinsic physical properties, especially magnetic properties of natural DNA and a possibility of charge carrier doping by the metal ion insertion. Diamagnetic nature of natural DNA and a variety of features in M-DNA will be presented.

Keywords: DNA, charge transfer, metal ion, magnetic susceptibility, ESR

1. INTRODUCTION

As a vehicle of the life information, a lot of researches on deoxyribonucleic acid (DNA) have been reported, so far, since the double helix structure was found in 1953 by Watson, Click, Wilkins and Franklin.[1–4] Recently, the physical properties, such as electrical and magnetic properties of pristine DNA (abbreviated as B-DNA) has attracted our attention as one of the prospective materials of the nanotechnologies for nano-wires, nano-architectures, *etc*,[5–16] because of excellent ability of DNA in self-organisation and designing, based on the complementation of the base pairing. Unfortunately, the diverse conclusions were reported in the electrical properties about 2000; metallic,[5] semiconducting,[6,8] vicinity effect of the Cooper pair in superconductor,[10] insulating.[11] The possible origins of these discrepancies with direct measurements of DNA double helix or DNA bundles would be due to salt residue, effective doping, for example, caused by electron bombardment of TEM, interaction with substrates and so on. At least in B-DNA a consensus has been reached on this issue that B-DNA is of semiconducting with the energy gap around 4 eV on the basis of transport, optical, magnetic and theoretical investigations.[7–9,11,17–19]

Thus, charge carrier doping is required from the viewpoint of nanotechnological application of DNA. Lee and coworkers reported a cooperative conformational change of DNA with divalent metal ions, which were located in-between the bases of a base pair,[20] and Rakitin and coworkers suggested that DNA incorporated with Zn^{2+} could show a metallic transport nature.[15,21] Alexandre and coworkers[22] theoretically suggested the electronic states with the reduced energy gaps strongly dependent on the metal ion species for Zn^{2+}, Co^{2+} and Fe^{2+}. The magnetic studies on M-DNA with divalent metal ions, M=Ca, Mg, Mn, Co, Ni, Zn reported absence of the charge transfer from M to DNA bases, which suggests the energy gap keeps alive, irrespective of 4 eV or less.[18,23–25] Very interestingly, Fe^{2+} ion incorporated into DNA transforms to Fe^{3+}, as evidenced by the ESR g-shift around the free electron g-value, the magnetization curves and the color change from weak greenish to light ocher, suggesting the electron transfer from Fe to bases.[23]

In this report, the magnetic studies with mainly ESR and SQUID techniques will be reviewed on pristine salmon DNA (B-DNA) and DNA incorporated with divalent metal ions (M-DNA), to unveil the intrinsic nature of B-DNA and M-DNA based on the reported works in Refs.[18,23–25]

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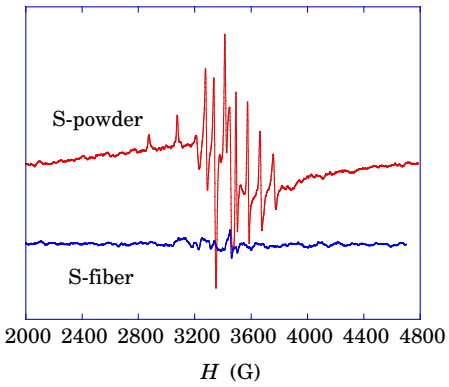

Figure 1. (After Ref.[18]) ESR spectra of the S-powder and the S-fiber which is a purified form of the S-powder. Note that the purification dramatically reduced the ESR intensity down to ≈50 ppm/bp of $S = 1/2$ spins. This small number of spins might be understood to be impurity contribution.

2. EXPERIMENTAL

Two different grades of salmon-DNA (a kind of B-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 rodlike linear structure of the DNA double helix.

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 (M = Mg, Ca, Mn, Fe, Co, Ni, Zn). Here, 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 M-DNA, except for light ocher color for Fe-DNA. The residual MCl_2 is washed out thoroughly from the obtained precipitate in pure ethanol where DNA and M-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.

3. NATURAL DNA

It has been controversial if natural DNA possesses intrinsic magnetic spins or not. The conclusion of this report is that the probable reason of this issue might be due to impurities contaminated or remained in the extraction processes of DNA and/or sample tube, adsorbed oxygen molecules, defects caused by irradiation, *etc.*

3.1 Electron Spin Resonance

Figure 1 shows ESR spectra of the S-powder and the S-fiber taken at X-band around 9.4 GHz. The double integrated intensity for these spectra corresponds to ≈ 2000 ppm/bp of $S = 1/2$ spins for the S-powder and ≈ 50 ppm/bp for the S-fiber. The broad contribution for the S-powder would come from $3d$-transition metal impurities and the structured sharp spectra from defects of DNA and residual proteins. The S-fiber, purified form of the S-powder demonstrates remarkable suppression of the ESR intensity which is a strong suggestion that this spectra would be resulted from residual contaminations in the purification processes of these DNA samples. Thus, the present ESR result is consistent with the semiconducting electronic states with the 4 eV energy gap, which predicts simple diamagnetic susceptibility.

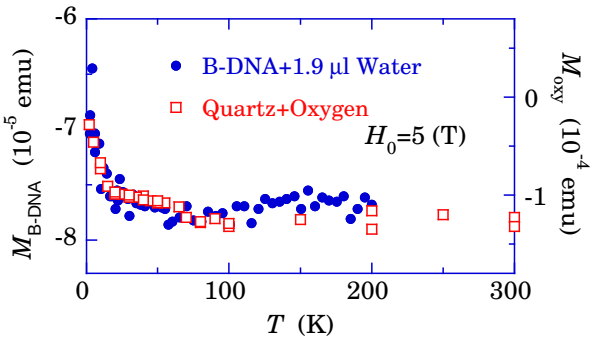

Figure 2. (After Ref.[27]) The temperature dependences of the magnetization for the reported data of B-DNA+1.9 μl water[19] and of the quartz wool+oxygen molecules.[27] Note a similar behavior of those not only in the temperature dependence, but also in the magnetization curve.[27]

Lee and coworkers reported that A-form DNA extracted from Salmon sperm shows the broad signal around 500 G together with the relatively narrow signals around 3000 G.[26] They interpreted them by coexistence of an applied magnetic field-induced mesoscopic orbital magnetism associated with a long-range coherent transport in well ordered regions and a Pauli paramagnetism arisen from an incoherent hopping transport in disordered regions.[26] This experimental results and the interpretation are in some meaning, very interesting, but should be taken with great care, because their magnetic susceptibility shows large Curie contribution in addition to the diamagnetic one which suggests the presence of Curie spin impurities in the specimen and the Pauli paramagnetism could not be expected in the semiconducting electronic states. Furthermore, the mesoscopic orbital magnetism is incredible idea for the natural DNA and should be checked with care.

3.2 Effect of Oxygen

Following the conclusion of Sec. 3.1, it is natural to expect that the magnetic susceptibility of B-DNA would be purely diamagnetic. Actually, $\chi \approx$ -4×10^{-4} (emu/mol-bp) has been observed, consistent with the reported value in Ref.[19] The observed χ is almost independent of temperature, but frequently shows very weak hump below 50 K and Curie-Weiss like behavior below 20 K, independent of samples, λ- and Salmon DNA.[19,27,28] It is a well known fact that the oxygen molecules provide the hump of magnetic susceptibility around 50 K, which would come from the antiferromagnetic ordering of the 3D oxygen solid. Finally, we also found the Curie-Weiss behavior for oxygen molecules, might be 2D layer of oxygen molecules, with the Curie-Weiss temperature of $\approx$ -6 K,[27] as demonstrated in Fig. 2 where only the quartz wool as oxygen adsorbent gives a qualitatively similar temperature dependence to the reported DNA data. Although physically interesting interpretations have been proposed so far,[19,26] this observation for oxygen molecules suggests that careful subtraction of the oxygen molecular contribution from the magnetic susceptibility should be done to make such interpretations meaningful.

4. DIVALENT METAL ION INSERTION

Several types of investigations to inject charge carriers into the natural DNA have been reported, so far. One is an effect of oxygen molecules. It was experimentally found that the electrical conductivity could be controlled by the oxygen concentration.[29] Starikov has theoretically proposed the hole carrier doping mechanism with oxygen molecules.[30,31] It was also reported that iodine molecules could supply hole carriers into the bases of DNA.[32,33] It is noteworthy that these hole injections could occur site-selectively, particularly in G-C unit. In the present report we will not discuss further on these points, but we concentrate on the divalent metal ion insertion to DNA.

Lee and coworkers have reported that the divalent metal ions, such as Zn^{2+}, Co^{2+} and Ni^{2+}, could be inserted in-between the bases of a base pair and made DNA conducting, useful for nanotechnological applications.[15,20,21] They reported that the incorporation of divalent metal ions, Zn^{2+}, Co^{2+} and Ni^{2+}, to DNA could be controlled by pH of solution with ethidium bromide (EB). We started our study with the procedure as reported, however,

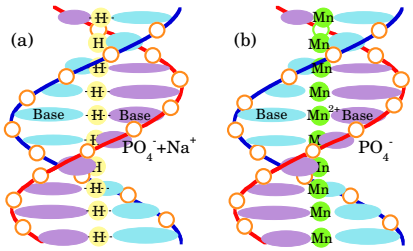

Figure 3. The schematic double helix structure of B-form DNA and Mn^{2+} ion inserted Mn-DNA. Lee and coworkers have proposed that metal ions are incorporated in-between the bases of a base pair, instead of the hydrogen bonds.[20]

it is not applicable to Mn^{2+}, particularly useful for ESR technique to study the electronic states of M-DNA. Thus, we developed the simple, but powerful new procedure to form M-DNA with a wide variety of divalent metal ions, as describe in Sec. 2, which makes us possible to study the magnetic properties of M-DNA and the electronic states through them.[18,23–25]

4.1 Structure

Fig. 3 shows the schematic structures of DNA of B-form and M-DNA proposed by Lee et. al.[15,20,21] The divalent metal ions locate in the center of DNA double helix structure, instead of hydrogen bonds. They confirmed this model directly with the reduction and disappearance of ^{1}H NMR intensity assigned to the hydrogen bonds.[20] We also found other facts which support this model, as follows.

1) ESR line width of Mn-DNA could be well accounted for by the electronic dipolar interaction with one-dimensional Mn chain separated by ≈ 3.4 Å.[18]

2) ESR lineshape definitely changes following the hydration conditions; the wet and the dry, as will be discussed in Sec. 4.2.2.[23]

3) Mn ions could be incorporated not only into A-T and G-C pairs, but also into A-C and G-T pairs, which could never been joined by hydrogen bonds.[23]

4) If once Mn-DNA is dried enough, with a probable structure of A-form, similar to the hydrogen bonded natural DNA, Mn-DNA never return to the B-form, even with excess H_2O, making Mn-DNA gel-form. B-form comes back from A-form, only after complete dissolution in water.

5) Fe-DNA film could not be dissolved in water. If Fe ions locate outside of DNA, they could be hydrated and soluble.[23]

All these features support the proposed structure depicted in Fig. 3. The ratio of the number of divalent metal ions to phosphor was estimated with X-ray fluorescence analysis to be ≈ 0.5 and Na ions were not observed. On Mg-DNA and Ca-DNA, unfortunately, we have not direct structural evidence if Mg locates a similar position to the Mn and Zn cases, as shown in Fig. 3.

4.2 Magnetic and Electronic Properties

If we have been successful to induce the charge carriers by the incorporation of divalent metal ions into the base pairs of DNA, we could expect the corresponding ESR spectra of electrons, such as π-electrons on the base pair. In this meaning, ESR is a useful technique to check the charge injection by doping. We will discuss details of the metal ion insertion to DNA.

4.2.1 Ca-, Mg-, and Zn-DNA

Kino and coworkers have proposed a possible charge injection mechanism to DNA on the basis of density functional theory (DFT) calculation for the metal ions of Ca, Mg, and Zn doped DNA.[34] They suggested that the hydrated metal ions located near the phosphate anions of the DNA backbone are stabilized as M^{2+}. However, in the anhydrous conditions, missing the hybridization of metal ion with the oxygen $2p$-orbitals of H_2O molecule, Zn and Mg ions become mono-cation, giving rise to hole doping to guanine base, but Ca ion does not.[34] Fig.

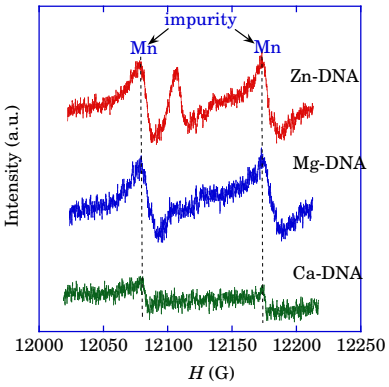

Figure 4. ESR derivative spectra in the dry state of Zn-DNA, Mg-DNA and Ca-DNA taken at Q-band (≈ 35 GHz) in the limited magnetic field range. Two signals around 12,080 G and 12,180 G might be the hyperfine structure of Mn ESR with the nuclear spin $I = 5/2$, originated from $MnCl_2$ impurity contained in the chemicals used to prepare M-DNA. Note the signals around 12,110 G with almost free electron g-value, prominent in Zn-DNA, only a trace in Mg-DNA and nothing in Ca-DNA.[18] This tendency is consistent with the proposed theoretical model,[34] but not with the humidity dependence of these signals.[18]

4 demonstrates ESR spectra for the dry state of M-DNA with M = Zn, Mg, and Ca, which is consistent with this theoretical suggestion; Zn and Mg doping seems to successfully induce new ESR signal, but Ca doping does not. However, we finally concluded these small ESR signals around g ≈ 2 are impurities in origin, since the ESR intensities did not affected with any change of humidity, that is, any change of hydration.

Thus, the electronic states of M-DNA with Ca, Mg and Zn were interpreted to be semiconducting even with the divalent metal ion insertions, keeping the energy gap unchanged as observed in optical spectra.[35] The only effect in the divalent metal ion insertion is an ion exchange from two monocations, $2Na^+$, to single divalent cation, M^{2+}, to compensate two anions, $2PO_4^-$, in the DNA backbone. This conclusion contradicts the Ohmic charge transport observed in Zn-DNA.[18,21]

When one observes ESR spectra in the wider magnetic field range, one frequently finds weak but broad ESR signals with larger g-factors than the free electron value $g \approx 2$ in M-DNA.[23] However, since it has been confirmed with the X-ray fluorescence analysis that the insertion rate of the divalent metal ions into DNA was nearly 100 %, the ESR intensity for Zn-DNA was still enough weak compared with the expected ESR intensity, less than 1%.[23] However, there still remains a possibility that the strong electron-electron correlation effect might suppresses the induced susceptibility by the charge modification of the bases caused by the insertion of the divalent metal ions into DNA. Therefore, anyway, we have to conclude that the formation of metallic DNA would not be realized with the divalent metal ion insertion with Zn, Mg and Ca.

4.2.2 Mn-DNA

Mn-DNA with $S = 5/2$ and $L = 0$ is a useful system for ESR study. As demonstrated in Fig. 5, the single ESR spectrum at $g = 2.0$ is observed. Here, note the strong hydration effect to the ESR lineshape; sharp cutoff for the wet condition, and long tail for the dry. It is well known that DNA transforms its double helix structure from B-form, as shown schematically for Mn-DNA in the left of Fig. 6 familiar in the living cells, to A-form, the right of Fig. 6 stable in anhydrous circumstance.[4] If Mn-DNA shows a similar phase transformation to the natural DNA as in Fig. 6, the hydration change in Fig. 5 would be consistent with the proposed M-DNA structure of Fig. 6 where the divalent metal ions locate in-between the bases of a base pair, instead of the imino hydrogen bond.[20]

Fig. 5 (right) provides an easy way to analyze visually the ESR lineshape. When the lineshape is Lorentzian, typical of the 3D networked spin systems,

$$I(H) = \frac{I(H_0)}{1 + ((H - H_0)/\Delta H_{1/2})^2}, \tag{1}$$

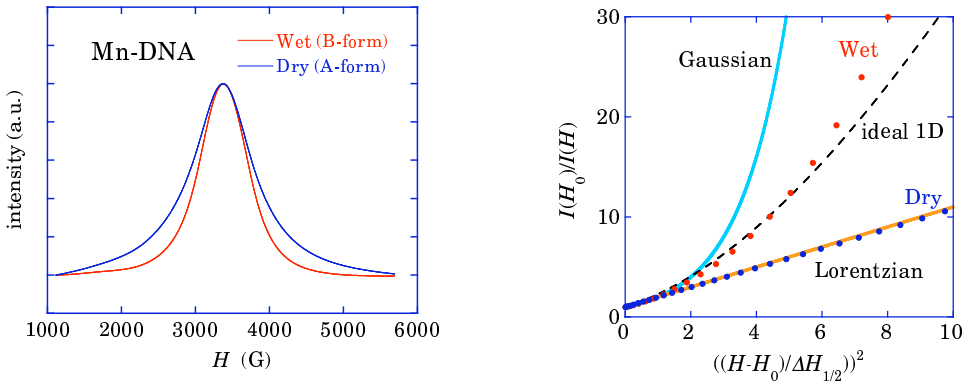

Figure 5. (After Ref.[23]) (Left) The ESR absorption spectra of Mn-DNA both in the wet and the dry conditions taken at X-band around 9.4 GHz. Note the definite difference in lineshape caused by the hydration conditions. (Right) The characteristic plot for ESR lineshape analysis. The abscissa is a square of the magnetic field deviation from the resonance field H_0 normalized by the half width at half height $\Delta H_{1/2}$ of the absorption spectrum. The ordinate is the inverse signal intensity $I(H)$ normalized by the center height $I(H_0)$. The wide spectrum for the dry condition is reproduced well with the Lorentzian lineshape, but that for the wet condition with the characteristic lineshape for the 1D exchange narrowing case.[23,36] See the text in detail.

the inverse of the normalized intensity, $I(H_0)/I(H)$ corresponds to a straight line against the square of the field deviation, $((H - H_0)/\Delta H_{1/2})^2$, as in the lowermost line assigned to "dry" in Fig. 5 (right). In contrast, we have the intermediate lineshape between Lorentzian and Gaussian for the exchange narrowed spectrum in the 1D arrayed spin systems,[23,36] corresponding to "ideal 1D" in Fig. 5 (right). These features ideally correspond to the structural transformation caused by the hydration. The wet Mn-DNA with the B-form, equivalently 1D array of $S = 5/2$ spins, shows almost "ideal 1D" lineshape. In contrast, the dry Mn-DNA with the A-form or a helical structure of spins gives Lorentzian lineshape. In the crystal of the dry Mn-DNA the helical spin chains could form a 3D network of spins, while the 1D spin chains of the wet Mn-DNA are isolated by more than 20 Å from the neighboring chains.

Mn-DNA shows the Curie-Weiss behavior with $\Theta \approx$ -1 K for the wet and $\approx$ -2 K for the dry. The increase of interaction in the dry Mn-DNA would be consistent with the increase in the number of neighboring Mn spins because of the helical spin structure. As expected in the 3D coupled spin system, we observed a peak of the specific heat around 0.4 K, which would correspond to antiferromagnetic long-range ordering of the Mn ions.[23]

We have tried to form Mn-DNA with unnatural pairing of synthesized oligo-DNA, poly{dA}-poly{dC} with $MnCl_2$. The magnetic properties of Mn-poly{dA}-poly{dC} have been confirmed to reproduce all of the Mn-DNA results as reported here, including the hydration effect in Fig. 5, which strongly suggests that Mn ions actually work as the binder for any bases to form base pairs.[23] This is one of the reasons for the heavy metal ions to disturb heredity information.

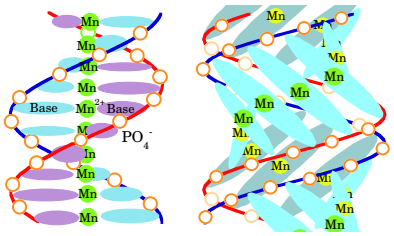

Figure 6. The schematic structures for M-DNA in the wet (B-form, Left) and the dry (A-form, Right) conditions, assuming similar structures to that of the natural DNA.[4] In the B-form, Mn ions form a 1D array of $S = 5/2$ spins, in contarst, they form a spiral structure in the A-form.

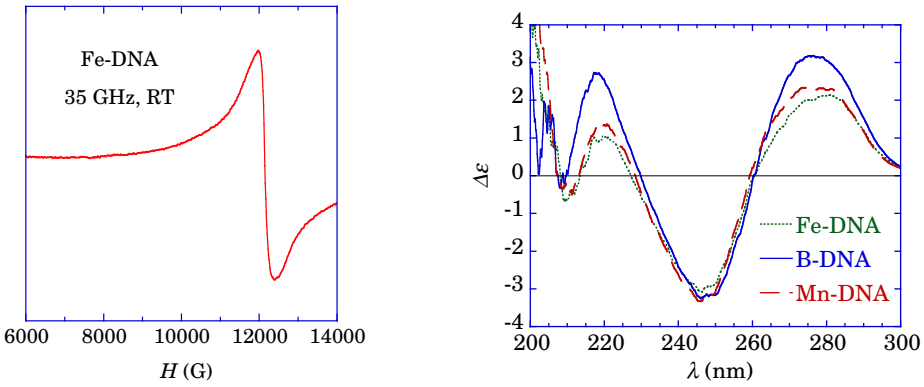

Figure 7. (After Ref.[23]) (Left) The ESR spectrum of Fe-DNA taken at Q-band ($\approx$ 35 GHz, corresponding to 12,500 G for $g = 2$). From g-factor nearly equal to 2, the electronic states of Fe ion are suggested to be Fe^{3+} with $S = 5/2$ for high spin state, as same as Mn^{2+} ion, and $S = 1/2$ for low spin state, which depends on the crystalline field. (Right) The circular dichroism spectra for B-DNA, Mn-DNA, and Fe-DNA. The finite change around 220 nm has found in M-DNAs from B-DNA, suggesting some difference of B-form structure in M-DNA from B-DNA.

4.2.3 Fe-DNA

All the M-DNAs discussed in the former sections have never shown any traces of charge injection from the divalent metal ions to the DNA bases or backbones. Thus, no essential change in the electronic structures of M-DNA can be expected, keeping the energy gap unchanged, as confirmed in the optical absorption of Zn-DNA.[35] Very interestingly, we found one exception to this category, Fe-DNA. Fe-DNA was prepared with the same procedure as the others: solution of DNA is mixed with $FeCl_2$ solution. The solution is transparent and very light greenish in color. However, the solution changes color to ocher typical of Fe^{3+} ions, with time or with pouring cold alcohol to precipitate the sample. Actually, other physical properties also suggested that Fe^{2+} ions in the solution were converted into Fe^{3+} ions in the dried Fe-DNA film.[23]

Figure 7 (left) demonstrates one of the evidences for the charge transfer from Fe^{2+} to DNA. Since Fe^{2+} has six d-electrons, $S = 2$ and $L = 2$ are expected for the high spin state. Non-zero orbital angular momentum could provide zero-field splitting, even in the zero external magnetic field through the spin-orbit interaction. Thus, for Fe^{2+} ions, it is expected that the resonance field usually deviates largely from $g = 2$, the free electron value. Therefore, the observed signal at $g \approx 2$ in Fig. 7 (left) is a strong evidence for the Fe^{3+} in Fe-DNA. The presence of Fe^{3+} is also confirmed with the Mössbauer effect of Fe.

From the CD spectra in Fig. 7 (right), it is confirmed that the double helix structure in M-DNA is still maintained. We do not have definite evidence for the location where the electron transferred from Fe^{2+}. One possible candidate is the base pair. In this case, ESR from π-electron might be observed around $g \approx 2$. The observed ESR signal in Fig. 7 (left) suggests that the lineshape is not simply reproduced by a single Lorentzian, but composed of 2 to 3 components to reproduce the spectra successfully.[23] On the other hand, the electrical conductivity did not show any enhancement over B-DNA, which suggests the presence of the strong electron-electron correlation effect in the baes π-electron band. Recently, we confirmed the presence of the intragap absorption around 3 eV which would imply the π-charge contribution. Details of this issue will be published elsewhere in near future.

5. SUMMARY

Magnetic study has been applied to investigate the electronic states of B-DNA and M-DNAs incorporated with the divalent metal ions. The conclusion on B-DNA is that the electronic states are semiconducting with the energy gap of nearly 5 eV. The controversial interpretations on the direct electrical transport measurements of single DNA or bundles reported so far might be due to several aritificial effects, that would be common thinking on this issue.

Almost all M-DNAs, inserted with the divalent metal ions, have still large energy gap comparable with B-DNA. The first effect of the divalent ion insertion might be ion exchange from $2Na^+$ to one M^{2+}, keeping the electronic states less modified. Only the exception, Fe-DNA was found, where the charge transfer from Fe^{2+} to e^-+Fe^{3+} has occurred. Unfortunately, the location of the transferred electrons from Fe^{2+} has been still open question. Further investigation on the electronic states of M-DNA and other charge transfer doping mechanism will be proceeded with magnetic, electronic, and optical techniques in future.

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