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Abstract

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ON FERROMAGNETISM OF ORGANIC STRUCTURES

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In 1958, in our laboratory, the appearance of broad lines of electron magnetic resonance in preparations of nucleic acids and nucleoproteids was discovered (^1). These lines resembled the corresponding properties of samples with collective spin interaction (ferromagnets and antiferromagnets). Later analogous effects were found in some synthetic polymers with conjugated bonds (^2). To estimate the intensity of this effect we used a comparison of the integral intensity of these lines with the EPR lines of ordinary paramagnetic standards. However, after it had been found (^3,4) that preparations giving broad magnetic-resonance lines are also characterized by saturation of the static magnetic susceptibility in comparatively weak magnetic fields, it became clear that this was not a matter of paramagnetism and paramagnetic resonance, but of a phenomenon similar to ferromagnetism and ferromagnetic resonance. Therefore the numbers of unpaired electrons given in our works and in the works of other authors who used the same method should be understood as the number of unpaired electrons of an ordinary paramagnet that can give an EPR line of the same integral intensity as the samples under study. As we have repeatedly emphasized earlier, the intensity estimates obtained in this way can serve only for a comparative characterization of the magnitude of the effect and are of a purely conventional nature. The true number of unpaired electrons in the presence of collective spin interaction may be three to four orders of magnitude smaller. In works carried out in our and other laboratories (^5-7), numerous data have been obtained indicating a connection between the observed magnetic properties and the structure of biological and synthetic polymers, with their other physical properties, and also changes in magnetic characteristics during the development of unicellular structures.

In works (^8-10) attempts were made to give a theory of the phenomenon discovered as a property of organic highly ordered structures of definite construction. At the same time, the ferromagnetic nature of the effect makes it quite probable that it can be explained by the presence of a comparatively small quantity of ferromagnetic impurities. Analysis of the available experimental material and

consideration of possible interpretations of the observed magnetic properties were carried out earlier (^11). Aleksandrov, Gavrilov, and others (^12) gave data in favor of attributing the effect observed in the case of nucleic acids to external ferromagnetic contaminants. Dorfman (^13) showed that almost all the detected magnetic properties of biological and synthetic polymers can be explained by the presence of ferrite colloidal inclusions of the type of iron oxides and hydroxides. Shulman and co-workers ([14,]15), studying the ferromagnetism of nucleic acids, came to the conclusion that the observed effects may be due to ferromagnetic colloidal particles of composition Fe_3O_4, formed from iron ions inside the cell.

The aim of the present work was an attempt to establish directly the possibility of reducing the observed ferromagnetism of organic structures to trivial ferromagnetic contaminants. By the latter are meant ferromagnetic inclusions forming a separate inorganic phase, regardless of whether they entered the sample from outside or formed in it from paramagnetic particles during isolation and treatment. For this purpose, preparations of DNA were isolated under the cleanest possible conditions and several types of polymers with conjugated bonds were synthesized; their magnetic-resonance spectra were measured, magnetization curves were taken, and analyses were carried out for the content of iron and other metals. The results of the analysis were compared with the magnetic properties according to the values of the magnetization per unit weight of the sample at saturation, since the magnetic-resonance curves gave, as a rule, overestimated values of the integral intensity, apparently as a result of an admixture of dispersion. In all cases, the sample subjected to analysis was the one whose magnetic properties were measured. Measurement of the static magnetism was carried out by the Faraday method. The magnetic balance was repeatedly calibrated against a paramagnetic standard before and after the measurements. The accuracy of the magnetization measurements was not worse than 5%. Analysis for iron was carried out by the orthophenanthroline method; the most interesting samples were analyzed by emission spectroscopy for Fe, Co, Ni, Cr, Mn, and some other metals. The accuracy of spectral determination was 5–10%, depending on the content. All the preparations investigated were homogeneous both with respect to magnetic properties and with respect to metal content. In all, several dozen preparations of nucleic acids and synthetic polymers were investigated.

The ferromagnetic-resonance curves of all biological and synthetic polymers with anomalous magnetic properties investigated by us and in other laboratories have the following principal characteristics: the g-factor of the signal center is 2.2–3.0; the line width between the points of maximum slope is 600–1500 oersted; when the temperature is lowered the curve broadens and shifts toward larger values of the g-factor. Among the most widespread ferromagnets, iron oxides of the type Fe_3O_4 (magnetite), γ-Fe_3O_2, and certain other ferrites have analogous characteristics, of which magnetite has the largest saturation magnetization. Metallic iron gives ferromagnetic-resonance lines 150–200 oersted wide, g-factor 2.0, narrowing and shifting toward smaller values of the g-factor when the temperature

is lowered. In the critical articles mentioned above, ferrite iron oxides are cited as the most probable contaminants. Therefore, we made the comparison of the magnetic properties with the results of analysis on the assumption that all the iron present in the sample is in the form of a piece of magnetite of large dimensions, i.e., can give a saturation magnetization of 127 gauss calculated per 1 g of iron. All other ferrite iron oxides have a smaller magnetic moment. In [11] it was shown that the observed magnetic properties may be produced by colloidal ferromagnetic particles containing 10^3–10^4 iron atoms. In work [16] the magnetic characteristics of colloidal ferrite particles were investigated, and it was shown that Fe_3O_4 particles containing on average $6 \cdot 10^4$ iron atoms have a saturation magnetization of 56 gauss calculated per 1 g of iron.

Iron ions not included in the ferromagnetic phase cannot contribute to the ferromagnetic characteristics under investigation. Wacker and Vallee [17] showed that nucleic acids contain firmly bound iron in an amount of $2\text{–}8 \cdot 10^{-2}$%, which is practically all present in the form of chelate-bound isolated Fe^{2+} ions. The nucleic-acid preparations obtained by us with special precautions contained from $6 \cdot 10^{-3}$ to $2 \cdot 10^{-2}$% iron. We succeeded in showing qualitatively that at least a substantial part of it is in the form of isolated

of Fe^{2+} ions, but it was not possible to carry out precise quantitative determinations. Therefore we did not introduce a correction for iron in ionic form. Table 1 gives some of the results we obtained. The contents of Co, Ni, Cr, and other metals were, as a rule, 1–3 orders of magnitude lower than the iron content and therefore could be disregarded.

Table 1

No.	Preparation	Magnetization at saturation I, G · cm^3/g	Iron content, %	Amount of iron (%), required to obtain the observed value of I: as $(Fe_3O_4)_\infty$	Amount of iron (%), required to obtain the observed value of I: as $(Fe_3O_4)_{coll}$	Amount of iron (%), required to obtain the observed value of I: as $CuOFe_2O_3$, $MgO \cdot Fe_2O_3$
1	Calf thymus DNA	$2.4 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$	–

No.	Preparation	Magnetization at saturation I, G · cm^3/g	Iron content, %	Amount of iron (%), required to obtain the observed value of I: as $(Fe_3O_4)_\infty$	Amount of iron (%), required to obtain the observed value of I: as $(Fe_3O_4)_{coll}$	Amount of iron (%), required to obtain the observed value of I: as $CuOFe_2O_3$, $MgO \cdot Fe_2O_3$
2	DNA from phage T_2 [1]	$3.9 \cdot 10^{-3}$	$3.3 \cdot 10^{-2}$	$3.1 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	–
3	DNA preparation 2 [1]	$1.6 \cdot 10^{-2}$	$1.0 \cdot 10^{-1}$	$1.3 \cdot 10^{-2}$	$2.9 \cdot 10^{-2}$	–
4	Product of dehydration of xanthan cellulose, preparation 1	$1.7 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$
5	Product of dehydration of xanthan cellulose, preparation 2	$4.9 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	$3.82 \cdot 10^{-2}$	$8.8 \cdot 10^{-2}$	$8.2 \cdot 10^{-2}$

No.	Preparation	Magnetization at saturation I, G · cm^3/g	Iron content, %	Amount of iron (%), required to obtain the observed value of I: as $(Fe_3O_4)_\infty$	Amount of iron (%), required to obtain the observed value of I: as $(Fe_3O_4)_{coll}$	Amount of iron (%), required to obtain the observed value of I: as $CuOFe_2O_3$, $MgO \cdot Fe_2O_3$
6	Product of dehydration of xanthan cellulose, preparation 3	$7.2 \cdot 10^{-2}$	$9.2 \cdot 10^{-2}$	$5.65 \cdot 10^{-2}$	$1.29 \cdot 10^{-1}$	$1.2 \cdot 10^{-1}$
7	Polytetracyanoethylene magnesium	$8.9 \cdot 10^{-2}$	$3.1 \cdot 10^{-2}$	$7.0 \cdot 10^{-2}$	—	$1.5 \cdot 10^{-1}$
8	Polydiethynylbenzene, preparation 4	Diamagnetic	$5.5 \cdot 10^{-3}$	—	$1.6 \cdot 10^{-1}$	—
9	Polydiethynylbenzene, preparation 1	$1.0 \cdot 10^{-2}$	$6.0 \cdot 10^{-3}$	$7.9 \cdot 10^{-3}$	$1.8 \cdot 10^{-2}$	—
10	Polydiethynylbenzene, preparation 2	$1.4 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$	$1.1 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	—
11	Polydiethynylbenzene, preparation 3	$6.8 \cdot 10^{-2}$	$5.1 \cdot 10^{-2}$	$5.4 \cdot 10^{-2}$	$1.2 \cdot 10^{-1}$	—
12	Polydiethynyldiphenoxide	$7.0 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$5.5 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$	—

No.	Preparation	Magnetization at saturation I, G · cm^3/g	Iron content, %	Amount of iron (%), required to obtain the observed value of I: as $(Fe_3O_4)_\infty$	Amount of iron (%), required to obtain the observed value of I: as $(Fe_3O_4)_{coll}$	Amount of iron (%), required to obtain the observed value of I: as $CuOFe_2O_3$, $MgO \cdot Fe_2O_3$
13	Polymer of methyl-β-chlorovinyl ketone	$1.1 \cdot 10^{-1}$	$5.0 \cdot 10^{-2}$	$8.8 \cdot 10^{-2}$	$2.0 \cdot 10^{-1}$	–
14	Polyphenylacetylene[4], preparation 1	$1.5 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	–
15	Polyphenylacetylene, preparation 2	$5.3 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$	$4.1 \cdot 10^{-3}$	$9.4 \cdot 10^{-3}$	–
16	Polyphenylacetylene, preparation 3	$9.1 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$	$7.2 \cdot 10^{-3}$	$8.3 \cdot 10^{-3}$	–

[1] Preparations of phage DNA were isolated without special precautions and, as a rule, contained considerably more iron.

[2] Preparation nos. 4, 5, 6 contained copper in an amount of about 10^{-2}%. Therefore, in the last column the figures are given that correspond to ferrite of composition $CuO \cdot Fe_2O_3$.

[3] Preparation no. 7 contained ~15% Mg. Therefore, in the last column the value is given that corresponds to ferrite of composition $MgO \cdot Fe_2O_3$.

[4] Different preparations of polydiethynylbenzene and polyphenylacetylene differed in the conditions of thermal treatment.

From the data in the table it is evident that, in a number of samples, the iron content is insufficient to explain the observed ferromagnetism, even if all of it is present in the form of large pieces of magnetite, and it is still more

insufficient if it forms colloidal ferromagnetic particles. It should be noted that, in accordance with the chemical nature of the preparations studied, the bulk of the metal impurity must be in the form of isolated ions, which cannot contribute to ferromagnetism.

It is necessary to emphasize one experimental fact, verified by us on dozens of samples. Polymers with conjugated bonds, consisting only of C and H atoms and showing ferromagnetism according to static magnetic measurements (for example, samples of polydiethynylbenzene and polyphenylacetylene), never exhibit the broad ferromagnetic-resonance lines that are always observed in systems containing heteroatoms in the conjugation chain. The impossibility of detecting a resonance signal in ferromagnetic samples may be explained, for example, by the fact that in these systems, owing to weak spin–orbit coupling, the spin–lattice relaxation time is very long and the sample is saturated by microwave power. Whatever the explanation of this effect, it is necessary to postulate that the ferromagnetic regions and their properties are closely connected with the basic organic structure.

The experimental data presented make the attribution of the effect to trivial contaminants practically incredible, but they do not contradict the possibility that the source of the unpaired electrons forming ferromagnetic domains may be iron atoms. Theoretically, if all five $3d$-electrons of each Fe^{3+} ion participate in the construction of a domain, the saturation magnetization per 1 g of iron may reach 460 gauss. Then, in all the cases we studied, the amount of iron present is sufficient to ensure the observed ferromagnetism. But this would mean that iron forms, with the basic organic structure, ferrites of a new type, and that one is dealing with a single magnetic system rather than with inorganic magnetic impurities. In order to resolve the question of the possibility of collective magnetic effects in pure organic structures, it would be necessary to obtain preparations considerably freer of iron than was achieved in the present work. This task is not insoluble, but it is extremely difficult, since all organic systems that exhibit anomalous magnetic properties avidly bind heavy-metal ions.

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Note: Figure translations are in progress. See original paper for figures.