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Abstract

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PHYSICS

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ON THE QUESTION OF THE NATURE OF UNUSUAL MAGNETIC PHENOMENA DISCOVERED IN SOME ORGANIC SUBSTANCES

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L. A. Blumenfeld and co-workers $^{(1-8)}$, as well as Müller, Gotz, and Zimmer $^{(9)}$, described unusual magnetic properties discovered in a wide variety of organic objects of both synthetic and natural origin, which had hitherto been regarded as classical diamagnetics. These unusual properties consist of: 1) anomalously broad radio-frequency absorption signals extending from the field $H = 0$ to a field of several thousand oersteds; 2) a positive sign of the magnetic susceptibility and magnetization up to saturation at $H \cong 10^2 \sim 10^3$ oersteds. These properties do not change upon heating to 100° C. In most of the samples described in $^{(1-8)}$, the anomalous properties disappear upon cooling to 80° K, which, however, was not found in the samples in $^{(9)}$.

L. A. Blumenfeld and V. A. Benderskii $^{(8)}$ interpret the totality of these properties as a new class of magnetic phenomena, which they have called "pseudoferromagnetism." They suppose that these properties are due to a special macromolecular structure in which unpaired spins, present in amounts from 10^{18} to 10^{21} per 1 g of substance, interact with one another through organic chains of conjugated bonds. V. L. Ginzburg and V. M. Fain $^{(10)}$ incline toward the same theory.

This interpretation of the observed properties is, in our opinion, erroneous. Let us first consider the number of unpaired spins. The authors $^{(1-9)}$ sometimes call the numbers they give "conditional." However, they nowhere indicate any other numbers and in practice use the "conditional" ones as unconditional. These numbers N' were obtained by simple comparison of the integral intensities of the radio-frequency absorption of the sample and of a standard (diphenylpicrylhydrazyl).

Since the absorption intensities must be proportional to the magnetizations of the sample σ and of the standard σ_0, the authors take $N'/N_0 = \sigma/\sigma_0$ (where N_0 is the known number of spins in the standard), basing themselves on the “conditional” assumption that both substances are paramagnetic and obey Curie' s law, i.e.

$$\sigma_0 = \frac{N_0\mu^2 H}{3kT} \quad \text{and} \quad \sigma = \frac{N'\mu^2 H}{3kT}$$

(μ is the magnetic moment of the spin, T the absolute temperature, k Boltzmann' s constant). But this “conditional” assumption does not correspond to reality and, consequently, N' has no physical meaning. In fact, in the fields used, all the samples, in contrast to the standard, are magnetized to saturation and do not obey Curie' s law. Hence one must take $\sigma \cong N\mu$ (where N is the true number of spins in the sample). Thus,

$$N/N' \cong \mu H/3kT \cong 10^{-3} - 10^{-4}$$

(for $H \cong 10^3$ and $T \cong 3 \cdot 10^2$).

Thus, the true numbers of spins N turn out to be 3-4 orders of magnitude lower than the fictitious N' and amount to only 10^{14}—10^{18} per 1 g. Exactly the same values of N follow from experimental data on the magnetization of the samples.

How, then, are these spins distributed in the samples? The presence of radio-frequency absorption at $H \cong 0$, at the same frequency as at $H \cong 10^3$ oersteds, indicates the presence in the samples of residual internal magnetic fields H_i of the order of 10^3 oersteds, created by the spins themselves. Since the field

of a magnetic dipole is inversely proportional to the cube of the distance, it is easy to see that under these conditions the distances between spins cannot exceed 3—$4 \cdot 10^{-8}$ cm. Thus, these 10^{14}—10^{18} spins are by no means dispersed throughout the specimen but, on the contrary, are gathered into dense clumps or crystallites embedded in the organic mass. The fact that they are readily magnetized to saturation makes it possible to recognize them as ferromagnetic.

The authors ($^{1-9}$) did not find residual magnetization in the specimens, which is, however, not surprising, since it could not have exceeded 10^{-2}—10^{-3} CGSM per 1 g. The ferromagnetism of the embedded particles is clearly indicated by the form of the radio-frequency absorption curves, which practically does not differ from the form of typical ferromagnetic-resonance curves (see (^{12})). As is to be expected, the magnetization of a specimen falls sharply when the organic mass is dissolved in liquids (^{6}), which is explained by the Brownian motion of the suspended ferromagnetic particles.

Apparently, the particles may consist of Fe_3O_4, γFe_2O_3, hydroxides, and their mutual mixtures and solid solutions. The disappearance or sharp decrease of the anomalous properties of some specimens at 80° K ($^{1-8}$) is readily explained by the well-known transition of Fe_3O_4 into a strongly anisotropic modification.

Heating in the presence of air increases the concentration of Fe_2O_3, but upon prolonged heating with water γFe_2O_3 irreversibly passes into nonferromagnetic αFe_2O_3, which was observed, for example, in (^{6}). On the other hand, in the work (^{9}) the particles apparently consisted of pure and dry γFe_2O_3, as a result of which cooling had no effect, whereas heating in vacuum to 250° C irreversibly converted γFe_2O_3 into αFe_2O_3, as follows from (^{14}).

Thus, the extensive experience of magnetochemistry (^{13,14}) shows that the entire set of unusual magnetic phenomena ($^{1-9}$) can be fully explained by the presence of an Fe impurity in an amount from 10^{-2} to 10^{-6}% (by weight of the specimen), without resorting to special hypotheses about the structure of the organic mass.

The fact that the aforementioned authors operated with enormous fictitious numbers N' of spins (instead of N) led them to the erroneous conclusion that the magnetic properties they observed could have been attributed to Fe only on the condition that its impurity amounted to 2%! They therefore contented themselves with establishing the absence of such enormous contaminations. And since, in this way, in none of the works ($^{1-9}$) was the possibility of an Fe impurity of 10^{-2}—10^{-3}%, quite sufficient for reproducing all the "unusual" properties, excluded, L. A. Blumenfeld' s hypothesis on the existence of "pseudoferromagnetism" of highly ordered macromolecular structures cannot be regarded as at all substantiated.

All the more hasty are the various far-reaching conclusions drawn from this hypothesis for biology (^{11}).

Note added in proof. During the printing of the present note, an experimental study was published (^{15}) confirming our conclusion.

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

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