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Corresponding Member of the Academy of Sciences of the USSR V. L. GINZBURG and V. M. FAIN

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Abstract

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ON POSSIBLE ANOMALOUS MAGNETIC PROPERTIES OF MACROMOLECULES*

Recently it has been discovered ([1−3]) that strong lines of electron paramagnetic resonance appear and that anomalous magnetic properties exist in a whole series of macromolecules (polymers). It is essential here that the initial links of the chain (monomers) and short chains have no unpaired electrons, i.e., are diamagnetic. Thus, what is involved is a transition, as the chain is lengthened, from a diamagnetic state to a state of the para- or ferromagnetic type. This interesting effect has not yet been explained, and we therefore wish to indicate one possibility that presents itself here. Namely, let us suppose that a finite, but not too short and not too long, chain of monomers is antiferromagnetic. This means that the electrons under consideration (for simplicity we shall assume that each monomer is similar to the molecule H_2 and has two paired electrons) form, as it were, two antiparallel sublattices, whose direction is fixed by some weak "effective magnetic anisotropy field" H_A (see, for example, ([4−6])).** The fact that an antiferromagnetic state can be the lowest state of a system is proved by the very existence of macroscopic three-dimensional antiferromagnets. We do not at present see grounds for doubting an analogous possibility for finite one-dimensional and two-dimensional systems. Moreover, intuitively it appears that precisely such a state should be the lowest in a chain of monovalent atoms with exchange interaction

$$H_{ex} = -\frac{1}{2}\sum_{lm} 2J_{lm}S_{lS}m$$

(S_l is the spin operator in units of $\hbar$) for $J_{lm} < 0$, which corresponds to a negative exchange integral. Indeed, with interaction only between nearest neighbors, the lowest state would seem to be the state illustrated in Fig. 1 I. The same could also occur for $J_{21} > 0$ (Fig. 1 II; the distances 12 and 21 in Fig. 1 are proportional to $1/|J_{12}|$ and $1/|J_{21}|$). Of course, even if in the case most favorable to us, $J_{12} \sim J_{21}$, the antiferromagnetic state is realized, it probably becomes less and less favorable as $|J_{21}| < |J_{12}|$ decreases. On the other hand, with a small number of monomers antiferromagnetism certainly does not arise, since the directions of the sublattices are not fixed in space and too large an anisotropy field H_A is required for an antiferromagnetic state to exist. However,

Fig. 1

Figure 1: Fig. 1

when the chain is lengthened, antiferromagnetism can in principle already be realized at small anisotropy fields. In this case, if

Fig. 1

* Reported at the theoretical seminar of the P. N. Lebedev Physical Institute of the Academy of Sciences of the USSR on 22 December 1959.

** In the case under consideration, the monomers are held together by side bonds, the nature of which we disregard here.

if antiferromagnetism occurs in the chain, it can be detected by a magnetic method, by antiferromagnetic resonance absorption, by a neutronographic method, and by the method of nuclear magnetic resonance*.

In what follows we shall assume that the ground state of a not too short chain is antiferromagnetic. Of course, this assumption has not been proved and is a hypothesis, since, in any sufficiently rigorous formulation, the question of the character of the ground state as a function of J_{12}, J_{21}, the number of links in the chain N, and the field H_A, as far as we know, remains completely unclear ([6–10]).

For the lowest excited states of an antiferromagnet, as in the case of ferromagnets, the approximation of spin waves carrying a magnetic moment $\pm\mu$ usually proves to be good. The excitation energy of an antiferromagnet is equal to the sum of such independent waves with energies $n_k^\pm \varepsilon_k^\pm$, $n_k^\pm = 1, 2, ...$, where ([4,5,11,12])

$$\varepsilon_k^\pm = \varepsilon_k \pm \mu H; \qquad \varepsilon_k = \sqrt{(\mu H_A + 2J)^2 - 4J^2 \cos^2 ak}, \tag{1}$$

where $\mu = ge\hbar/2mc$ is the magnetic moment of the excitation (in our case the spin $s = 1/2$ and $g = 2$); H is the external magnetic field, collinear with H_A; $k = \pi l/Na$ ($l = 0, \pm1, \pm2, \ldots, \pm N/2$) is the wave vector; a is the lattice parameter (see Fig. 1), and J depends on J_{12} and J_{21}. It can be shown that $J = \sqrt{J_{21}J_{12}}$ for the chain of Fig. 1 I and $J = \sqrt{|J_{12}|J_{21}}\sqrt{|J_{12}|/(|J_{12}| + J_{21})}$ for Fig. 1 II. For $|J_{21}| \ll |J_{12}|$ the spin-wave approximation itself may prove to have only limited validity (one may think that this approximation at $T = 0$ is valid if $J/N \ll |J_{21}|$)**. The ends of the chain are here considered to be free, and therefore the derivative of the magnetization at the ends must vanish (from this we find the possible values of k).

As follows from (1), for the lower levels:

$$\varepsilon_k^{\pm} \simeq \sqrt{4J\mu H_A + \frac{4\pi^2 l^2 J^2}{N^2}} \pm \mu H, \qquad \varepsilon_{k=0}^{\pm} \equiv \varepsilon_{\min}^{\pm} \simeq \sqrt{4J\mu H_A} \pm \mu H \equiv \mu(H_c \pm H) \tag{2}$$

(where $\sin ak = ak = \pi l/N$ and $\mu H_A \ll 2J$ have been put).

As N increases, the levels (2) are lowered and, even without the field H, tend to zero as $N \to \infty$ and $H_A \to 0$. Therefore, also owing to the character of the distribution of levels in the one-dimensional case, a sufficiently long antiferromagnetic chain is unstable. On the basis of works ([9,10]) it may be assumed that with a more exact account of the anisotropy (the introduction of the field H_A is a very crude device) an infinite chain is unstable (in the sense of the existence of long-range antiferromagnetic order) even for nonzero, but perhaps not too large, anisotropy. For us this still unresolved point*** is immaterial. We note that, as N increases, the excitation energy falls, which has a clear physical meaning: in flipping neighboring spins an energy $\sim J$ is needed, whereas a gradual rotation of a spin through the angle π over the entire length of the chain requires only an energy $\sim J/N$, so long as the anisotropy energy is negligible. The magnetic susceptibility of an antiferromagnet is determined by the formula (see, for example, ([11])):

$$\chi = \frac{dM}{dH} = \frac{\mu^2}{4\varkappa T} \sum_{k \geq 0} \left(\frac{1}{\operatorname{sh}^2(\varepsilon_k^+/2\varkappa T)} + \frac{1}{\operatorname{sh}^2(\varepsilon_k^-/2\varkappa T)} \right) \simeq$$

* In ([2]) a report is made of work by American authors ([14]) (which remained inaccessible to us) who found internal magnetic fields in nucleic acids. This is just what should be expected in the presence of antiferromagnetism.

** Formula (1) is fully valid for $J_{12} = J_{21} = -J < 0$. The values of J given in the text for $J_{12} \neq J_{21}$ refer only to the lower case of interest to us, when in (1) one may put $ak \ll 1$. In addition, for the case shown in Fig. 1 II, N must be understood as the number of monomers divided by 2.

*** From the fact that phases cannot exist in one-dimensional systems ([13]), it apparently also follows that long-range order is impossible; with any anisotropy it would be destroyed at some temperature (the Ising model, in which the anisotropy is infinite, is in this respect not very indicative).

$$\simeq \frac{\mu^2 N a}{8\pi\varkappa T} \int_0^{k_{\max}} \left(\frac{1}{\operatorname{sh}^2(\varepsilon_k^+/2\varkappa T)} + \frac{1}{\operatorname{sh}^2(\varepsilon_k^-/2\varkappa T)} \right) dk, \tag{3}$$

where the last expression refers to a linear chain (level density $Na\,dk/2\pi$) in the case when one may pass from the sum to the integral.

From (2) and (3) it is clear that the value of χ for a chain is determined by the lower levels; the same, but less sharply, holds for a two-dimensional system. In the three-dimensional case, however, where the level density is proportional to k^2dk, the lower levels play a role only for microscopic systems. In view of what has been said, in a rough estimate of χ for a chain one may restrict oneself to taking into account a single lower level with $k = 0$, provided only that this level is not too close to the ground state. The mean number of spin waves at a given level is $\bar{n}_k^{\pm} = (e^{\varepsilon_k^{\pm}/\varkappa T} - 1)^{-1}$, and for the lower level $k = 0$ (M_0 is the mean magnetic moment of the lower level)

$$\bar{n}_0^{\pm} = \{\exp[\mu(H_c \pm H)/\varkappa T] - 1\}^{-1}, \quad M_0 = \mu(\bar{n}_0^- - \bar{n}_0^+), \quad \chi_0 = dM_0/dH,$$
$$\mu H_c = \sqrt{4J\mu H_A}. \tag{4}$$

Obviously, in a weak field

$$H \ll H_c = \sqrt{4\mu J H_A}/\mu, \tag{5}$$

the susceptibility $\chi \sim \chi_0$ is exponentially small for $\mu H_c \gg \varkappa T$, while for $\mu H_c \sim \varkappa T$ already $\chi \sim \mu^2/\varkappa T$. If, however,

$$\mu H_c \ll \varkappa T, \tag{6}$$

then

$$\bar{n}_0^{\pm} = \frac{\varkappa T}{\mu(H_c \pm H)}, \quad M_0 = \frac{2\varkappa T H}{H_c^2 - H^2}, \quad \chi_0(H \ll H_c) = \frac{2\varkappa T}{H_c^2} = \frac{2\mu^2}{\varkappa T}\left(\frac{\varkappa T}{\mu H_c}\right)^2. \tag{7}$$

In attempting to compare these formulas with the data(1−3), one must assume* $|2J_{12}| \sim 3$ eV, $|2J_{21}| \sim 0.03$ eV and, consequently, $2J \sim 0.3$ eV $\sim 5 \cdot 10^{-13}$ CGSE $\sim 3000^\circ$. Then, in the anisotropy field $H_A \sim 1$ oersted, at $T \sim 200^\circ$K,

$$H_c = \sqrt{4JH_A/\mu} \sim 7 \cdot 10^3\sqrt{H_A} \sim 10^4, \quad \chi_0 \sim 10^{-21}, \quad \bar{n}_0^{\pm}(H \ll H_c) \sim 10^2. \tag{8}$$

The susceptibility of a classical paramagnet containing N free moments μ is equal to $\chi_p = \mu^2 N/3\varkappa T$, and, thus, $\chi_0 = \chi_p$ for $N = N_p = 6(\varkappa T/\mu H_c)^2 \sim 10^5$. This means that, in recalculating the susceptibility of chains to the paramagnetic one(1−3), one may draw the conclusion (for $N \ll N_p$) about the "unpairing" of all external electrons in the monomers. The approximation used can be valid only so long as $\bar{n}_0^{\pm} \ll N$. In a weak field (see (5)) this requirement, for $T \lesssim 3 \cdot 10^2$

and $H_c \gtrsim 10^3 \div 10^4$, is fulfilled if $N \gg 10^2 \div 10^3$. An estimate of the field H_A for the magnetic interaction gives $H_A \sim \mu/d^3 \sim 1$ oersted for the distance between moments $d \sim 20$ Å. The susceptibility χ begins to depend on the external field H if it is comparable with H_c. Thus, the rather widespread opinion that, when $\mu H/\varkappa T \ll 1$, the field H can strongly affect magnetic properties only in the case of ferromagnets is completely erroneous. Of course, our molecule may also be called ferromagnetic, but this is not expedient, since the moment M vanishes as $T \to 0$. If $H \to H_c$, the initial state of the chain becomes unstable, as is well known also for ordinary antiferromagnets when $H \to \sqrt{H_A(H_A + 4J/\mu)}$(4,5). As a result of the instability, the spins rotate and χ drops sharply. We cannot now indicate the dependence of χ on H for $H \sim H_c$. However, the analogy with ferromagnets already permits one to expect that on the average (for

* The authors are grateful to L. A. Blumenfeld and V. A. Benderskii for communicating these figures and for discussion.

aggregate of differently oriented chains, in somewhat different conditions) a saturation effect will be observed. Absorption of electromagnetic waves in the samples should be observed at frequencies $\nu_0 = \mu(H_c + H)/2\pi\hbar$; for $H_c \sim 10^4$ and $H \ll H_c$ the frequency is $\nu_0 \sim 3 \cdot 10^{10}$ ($\lambda_0 = c/\nu_0 \sim 1$ cm). Thus, for a "polycrystal," at a fixed frequency ν absorption will be observed not at a definite value of H, but over a broad interval of these values (moreover, the frequency ν_0 indicated above refers only to the case when the fields H and H_A are parallel to the magnetization of the sublattices, and the field of the wave H' is perpendicular to this direction; it must be borne in mind that the field H_A depends on temperature.

The discussion above concerned a one-dimensional system (a chain). However, the lower levels play the basic role also for two- and three-dimensional systems of sufficiently small size (see formulas (1)–(3), with the meaning of the quantity J changing somewhat ([4])). In the three-dimensional case the antiferromagnetic state arises, generally speaking, more readily than in the one-dimensional case ([6]). Therefore the "lateral" bonds cementing the chains into a three-dimensional formation will play a stabilizing role.

The estimates given, despite their crudeness, are in themselves very favorable from the point of view of explaining the effects ([1–3]). The critical question, therefore, is precisely that of the very possibility of the emergence of an antiferromagnetic ground state.*

An important experiment that should be carried out consists in determining the temperature dependence of the moment of the samples M—in the absence of ferromagnetism this moment should tend to zero as $H \to 0$. However, the presence of a small residual ferromagnetic moment M may also be closely connected with antiferromagnetism, as occurs in the case of ferrites and of "weak" (relativistic) ferromagnetism of antiferromagnets ([15,16]). For axially nonsymmetric and helical antiferromagnetic chains the appearance of such an effect would seem quite natural (in the three-dimensional case the moment M of "weak" ferromagnets amounts to fractions of a percent or to percents of the moment of the sublattices).

In conclusion let us note that, if the proposed explanation is relevant to the phenomena ([1–3]), then in biology a large role may possibly be played by spin waves propagating along macromolecules with a velocity $v \simeq Ja/\hbar \sim 10^7$ cm/sec. This remark, however, probably remains valid also if the effects ([1–3]) are connected with the emergence of some ferromagnetism not related to our model.

P. N. Lebedev Physical Institute
Academy of Sciences of the USSR

Scientific-Research Radiophysical Institute
at N. I. Lobachevsky Gorky State University

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* Low excited states with a magnetic moment different from zero, and therefore with greater susceptibility, may also be possessed by systems in which the ground state is not antiferromagnetic in the usual sense of the word. However, in this aspect the problem under discussion has not yet been considered by us.

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