SOVIET PHYSICS JETP VOLUME 15, NUMBER 1 JULY, 1962

ON THE MAGNETIC PROPERTIES OF PARAMAGNETIC "FLUIDS" OF THE MOLECULAR CHAIN TYPE

V. L. GINZBURG and V. M. FAĬN

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.; Radiophysics Institute, Gor'kii State University

Submitted to JETP editor July 4, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **42**, 183-190 (January, 1962)

The magnetic susceptibility of molecular chains of a certain type is discussed. Arguments are given to show that the susceptibility of a chain which is not too long, and in which the interaction is antiferromagnetic, increases exponentially with increase in the number of links. Chains of spins may be considered to form a certain type of paramagnetic "fluid." When the interaction is antiferromagnetic, the susceptibility of such a "fluid" is weakly dependent on the temperature T, providing that $T \lesssim J/k$ (J is the energy of the exchange interaction between adjacent links; the number of spins is assumed to be large).

THE magnetic properties of chains of spins have been a topic of interest for a long time, primarily because of the relative simplicity of this case in comparison with two- and three-dimensional systems. In addition, a chain of spins may serve in a certain approximation as a model for long molecules (molecular chains). The interest in such molecules is continuing to grow at present, both as a result of the development of polymer physics and because of extremely important applications in biology (especially as regards the nucleic acids).

One of the most interesting problems dealing with the magnetic properties of chains is that of determining their dependence on the chain length. In particular, it is important to establish whether it is possible for a molecular chain consisting of diamagnetic links (monomers) to exhibit a large paramagnetic susceptibility. The present authors have discussed this problem[1,2] in connection with [3] and [4], but we shall discuss it here on a somewhat different level.

Naturally, the problem of the nature of the variation in the susceptibility of a chain as the number of links increases is closely related to the magnetic properties of an infinitely long chain of spins. For interactions more complex than in the Ising model, the latter problem has not yet been solved rigorously and is very difficult. We shall therefore consider only some approximate calculations and the qualitative aspect of the subject.

In studying the magnetic properties of chains and certain other objects, it is convenient to use the concept of "paramagnetic fluids," or systems of spins interacting rather strongly, but not in a "solid" or ordered state, i.e., not ferro- or antiferromagnetic.[2] Of course, the paramagnetic fluids include all ferro- and antiferromagnetic materials at temperatures T above but comparable with the Curie temperature Θ. In this region, to a certain approximation, the susceptibility $\chi = \text{const}/(T \pm \Theta)$, whereas for a paramagnetic "gas" $\chi = \text{const}/T$. If we limit our consideration to the magnetic "states of aggregation" existing within a single phase in the ordinary sense (i.e., we rule out atomic rearrangements), we are concerned with continuous transitions between paramagnetic "fluids" and "gases."

Paramagnetic fluids of the second type comprise the degenerate ideal Fermi gas and the real systems (liquid He^3 and electrons in metals) which behave analogously (Fermi fluids). In this case, $\chi = \text{const}$ over the temperature range from $T = 0$ to a temperature determined by the degeneracy energy and the exchange interaction between the spins.[5]

The third type of paramagnetic fluids, in which we shall be solely interested here, comprises the systems for which the Curie temperature Θ is anomalously low or zero for some reason or another. This type, in particular, comprises the chains, as well as planar and finely-dispersed structures.[2] For sufficiently large three-dimensional systems, $\Theta \sim \Theta_0 \sim J/k$, where J is the exchange-interaction energy of the spins. However, for infinite chains, $\Theta = 0$, while in certain other cases, $\Theta \ll \Theta_0$. Throughout the interval $\Theta \leq T \sim \Theta_0$ such spin systems are "fluid."*

1. Let us consider a large molecule (or polymer) consisting of N links (monomers), in which each link has an even number of valence electrons and a singlet ground state (of energy E_1). In the simplest case, the first excited state of the monomer is a triplet state with energy E_3, with $E_3 - E_1 \sim J_0$, where J_0 is the exchange-interaction energy for the monomer. When $J_0 \gg kT$, the monomer will be diamagnetic. However, we shall be interested in the relation of the magnetic susceptibility χ of the polymer to N and T. Obviously, χ may become positive and large only when the triplet levels of the system (or other levels having non-zero magnetic moment) fall considerably and their statistical weight increases sufficiently as the number of links increases.

Such a lowering of the levels as N increases is not only possible in principle, but is precisely a characteristic peculiarity of spin systems having the exchange interaction

$$\mathcal{H}_{ex} = \frac{1}{2} \sum_{l,m} 2J_{lm} s_l s_m \tag{1}$$

(where s_l is the spin operator in units of $\hbar$; J_{lm} is the exchange integral with sign chosen such that $J_{lm} > 0$ in the antiferromagnetic case).

If the system is large and in the antiferromagnetic state, its lower excited levels, as we know well from the spin-wave theory, will be separated from the ground state by a distance $\Delta E_{\min} \sim J/N$ (neglecting the anisotropy energy). Besides, in chains it is precisely the lower levels which determine the value of χ. Hence, the susceptibility of an antiferromagnetic chain which is not too long should, roughly speaking, have the form

$$\chi \sim (\mu^2/kT) \exp(-\xi J/kTN), \quad \xi \sim 1 \tag{2}$$

[cf. Eq. (4) in [1] with substitution of $\xi J/2N$ for H_c].

However, long-range order cannot exist in an infinite chain at $T \neq 0$. That is, such a chain cannot be antiferromagnetic in the ordinary sense of the word. Thus, we also cannot use the ordinary spin-wave approximation. For a finite but long chain, we can no longer strictly speak of long-range order, and the assumption that there exists a certain quasi-antiferromagnetic state maintained by the anisotropy field (see [1]) is not inconsistent. Nevertheless, such an assumption is clearly artificial and ungrounded (in any case, as applied to molecular chains). Thus the possibility noted in [1] may be criticized. The fundamental moment, as we wish to emphasize here (see also the last footnote in [1]), arises from the fact that we need not assume antiferromagnetic ordering of the ordinary type in deriving a formula such as Eq. (2). The point is that the validity of the law $\Delta E_{\min} \sim J/N$ (or the more general relation $\Delta E_{\min} \to 0$ as $N \to \infty$) does not necessarily depend on the existence of antiferromagnetic order, such that the mean spins of the sublattices $\langle S_z^{(1)} \rangle$ and $\langle S_z^{(2)} \rangle$ differ from zero. Such a conclusion is favored, first, by the fact that the chain energy is insensitive to the degree of long-range order (for details see [6] and [7]). Second, approximate calculations of the susceptibility of an infinite chain (see below), as well as certain more general considerations, indicate the existence of levels having non-zero spin which may approach arbitrarily closely to the spinless ground state. Third, the simplest and most convincing argument arises from a numerical calculation of Orbach[8] for a chain described by a very simple Hamiltonian similar to Eq. (1), that is,

$$\mathcal{H}_{ex} = 2J \sum_{l=1}^{N} \left(s_l s_{l+1} - \frac{1}{4} \right), \quad s_{lz} = \pm \frac{1}{2}. \tag{3}$$

Namely, this calculation gave a law $\Delta E_{\min} \sim J/N$. Actually, in the antiferromagnetic case (i.e., when $J > 0$), the energy difference between the ground state and the first excited state (with spins of zero and unity, respectively), for chains of 4, 6, 8, and 10 spins is

$$\Delta E_{min} = \mathrm{const} \cdot J/N. \tag{4}$$

The Hamiltonian of Eq. (3) and the more general Hamiltonian

$$\mathcal{H} = 2J(1-\alpha) \sum_{l=1}^{N} s_l s_{l+1} + 2J\alpha \sum_{l=1}^{N} s_{lz} s_{l+1,z} \tag{5}$$

commute with the projection of the total spin of the system $S_z = \Sigma s_{lz}$. Hence, if we know the levels $E(n, S_z)$ of the system [i.e., the eigenvalues of the operator (5)], we can find directly the mean magnetic moment in a field **H** in the direction of the z axis:

$$M_z = \frac{\sum_{n, S_z} \mu S_z \exp\{-(E(n, S_z) - \mu S_z H)/kT\}}{\sum_{n, S_z} \exp\{-(E(n, S_z) - \mu S_z H)/kT\},}, \qquad \mu = \frac{e\hbar}{mc}. \tag{6}$$

---

*The term "paramagnetic fluid" may not be the best, of course. However, in applying the term "fluid," we consider it useful to emphasize the distinction between the properties of disordered spin systems having strong and weak interactions. The fact that this difference is ordinarily only quantitative is also true to a considerable degree of the difference between real gases and liquids.

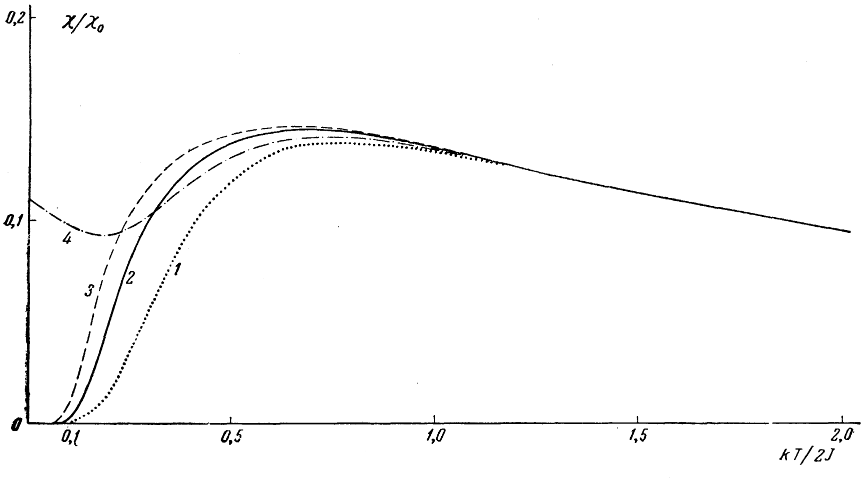

FIG. 1. The susceptibility of an antiferromagnetic chain as a function of the temperature for the case $\alpha = 0$. Curve 1: $N = 4$; curve 2: $N = 6$; curve 3: $N = 8$; curve 4: $N = \infty$ (Bethe method).

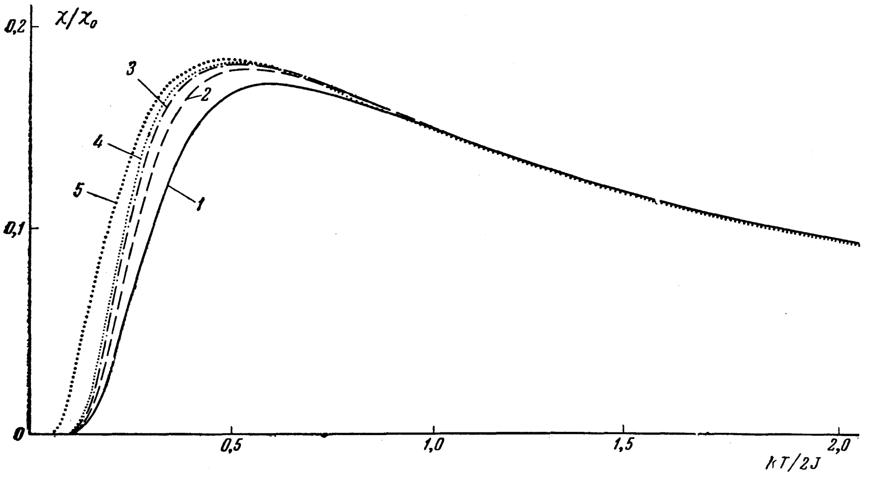

FIG. 2. Values for $\alpha = 1$ (the Ising model). Curve 1: $N = 4$; curve 2: $N = 6$; curve 3: $N = 8$; curve 4: $N = 10$; curve 5: $N = \infty$ (exact solution).

Hence, as the field $H \rightarrow 0$,

$$\chi = \frac{dM_z}{dH} = \frac{\mu^2}{kT} \sum_{S_z} S_z^2 g_{S_z} \Big/ \sum_{S_z} g_{S_z},$$

$$g_{S_z} = \sum_n \exp\{-E(n, S_z)/kT\}. \qquad (7)$$

Of course, we must also include in the denominator here the ground state with $S_z = 0$.

The results of a numerical calculation* of the values of $\chi(T)/\chi_0 = 2J\chi(T)/\mu^2 N$ for antiferromagnetic chains for various values of N, for $\alpha = 0$ and $\alpha = 1$ (the Ising model) are given in Figs. 1 and 2 (the levels calculated by Orbach[8] are used for $\alpha = 0$; the results discussed below for $N \rightarrow \infty$ are also given in the diagrams).

We may see from the calculations for $\alpha = 0$, and directly from Eqs. (4) and (7), that an expression for χ similar to Eq. (2) is valid when the interaction is antiferromagnetic. When $N \ll J/kT$, the paramagnetic susceptibility χ is very small, but increases exponentially as N increases. When $N \sim J/kT$, it attains a value of

$$\chi \sim \mu^2 N/J. \qquad (8)$$

When $N > J/kT$, the higher levels begin to participate, and χ ceases to increase further with increasing N or decreasing T [owing to the coefficient μ^2/kT of the exponential term in Eq. (2)]. The latter is obvious from the results for an infinite chain having an antiferromagnetic interaction (see Fig. 1). We note that an exact solution for $\chi(T, H)$ is known for $N \rightarrow \infty$ and $\alpha = 1$, namely[9]

$$\chi(T, H = 0) = (\mu^2 N/4kT)\exp(-J/kT). \qquad (9)$$

In this case, $\chi \sim \mu^2 N/J$ only at $\sim kT$. This is due to the fact that, in distinction from the exchange model with an Ising interaction, $\Delta E_{\min} = 2j$, and is independent of N.

2. Taking into account all that has been said, let us assume, for a chain having an antiferromagnetic interaction and $\alpha \ll 1$, that formulas of the type of Eqs. (2), (4), and (8) are indeed valid over a broad range of values of N. Then the problem still arises of the relation between the properties of a simple chain of spins (Fig. 3a) and the be-

---

*These calculations were performed in the computation department of the Radiophysics Institute, Gor'kii State University, under the direction of G. M. Zhislin.

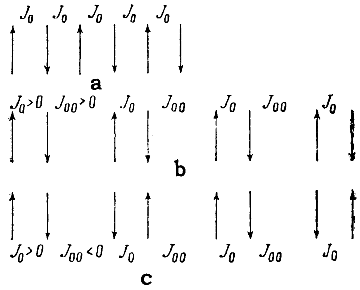

FIG. 3.

havior of real molecular chains. On this level, we must note first of all that, within a certain range of values of the parameters J_0 and J_{00}, the qualitative picture characteristic of a simple chain should be maintained in the more complex chains, such as are schematically portrayed in Figs. 3b and c. Thus, in the spin-wave approximation, as was stated in reference 1, we may derive the same result by using the Hamiltonian of Eq. (1) for such chains as for the chains in Fig. 3a, but we must replace J by $J_{eff} = \sqrt{J_0 J_{00}}$; or when $J_{00} < 0$ (ferromagnetic interaction), we then replace J by

$$J_{eff} = \sqrt{J_0 \cdot |J_{00}|}\sqrt{J_0/(J_0 + |J_{00}|)}.$$

In the qualitative sense, it is also obvious that when $J_{00} \neq J_0$, the spins may undergo gradual rotation; this involves the lowering of the levels as N increases and the broadening of the Bloch transition layers.*

Chains of mixed type, obviously, are more closely related to polymers (with an exchange interaction J_{00} between monomers, and J_0 within the bounds of one monomer unit). As for the use of the Hamiltonian of Eq. (1) to find the energy levels of the polymer, this is a well-known method insofar as only homopolar bonds are taken into account. It was recently shown[10] that the Hamiltonian of Eq. (1) may indeed be applied within certain limits even in the case in which the polar states play an essential role (here J_{ik} in Eq. (1) is no longer an exchange integral but a different sort of quantity which can be either positive or negative).

Thus, we have grounds for assuming that, in a linear molecular chain with an interaction of the exchange type (in the sense that the Hamiltonian of Eq. (1) may be used), the excited levels (with non-zero spin) will be lowered as the number N of links increases. Hence, and also in view of the nature of the distribution of levels in a linear system, within a certain range of values of N, the paramagnetic susceptibility of a chain of this type will increase exponentially as the chain is lengthened, up to a value $\chi \sim \mu^2 N/J_{eff}$. As N increases further, the susceptibility will vary rather slowly; for a given N, it will reach a gentle maximum at $T \sim J/kN$, and will then decrease with increasing T (for $T \gg J/kN$, $\chi \sim 1/T$). For a paramagnetic "gas," the susceptibility becomes field-dependent only when $\mu H \sim kT$. However, in a chain of strongly-interacting spins (and in general among paramagnetic fluids), there are other energy parameters characterizing the energy spectrum of the system in the absence of a field. Under such conditions, χ can depend on the field even when $\mu H \ll kT$. For example, if χ is due to a single lower excited level $E_3 \sim J/N$, χ will be independent of H only when $\mu H \ll J/N$.

When $J \gg kT$, the paramagnetic effect discussed here will appear only at relatively large values of N. Let us consider the other case, in which the molecular levels shift appreciably even when the number of links is small, so that polar states arise. This is just what takes place in the formation of the so-called charge-transfer complexes.[4] The formation of such complexes may be due to a classical Coulombic interaction. The cases in which we take into account only the Coulomb interaction or only the generalized exchange interaction obviously are limiting cases of the more general problem in which we must take into account both types of interaction. Hence it is possible to observe experimentally highly differing dependences on N, in addition to those of the types of Eqs. (2) and (4).

We should also note that above we have basically considered the case of chains having an antiferromagnetic interaction, since this is the case of interest in discussing the relation of χ to N in molecular chains. For chains having a ferromagnetic interaction (which form paramagnetic fluids of the ferromagnetic type), a lowering of the lowest excited level with increasing N also occurs (in this case, $\Delta E \sim J/N^2$), and has been rigorously demonstrated for states having a single reversible spin.

3. For an arbitrary finite chain, or in general for a finite aggregate of spins, we can hardly obtain quantitative results by any method other than numerical calculation. Hence, let us consider an

---

*On the other hand, there are no numerical results for complex chains. Also, as $J_{00} \to 0$, the chain practically disintegrates, and the lowering of the levels with increasing N cannot, of course, take place. Thus it is clear that the case $J_{00} \neq J_0$ (especially when $J_{00} \ll J_0$) shows qualitative peculiarities, and the problem of whether relations of the type of Eq. (4) are valid for complex chains undoubtedly requires especial study. We shall proceed here on the assumption that in a certain range of values of J_0 and J_{00}, the spacing $\Delta E_{min} = f(J_0, J_{00})/N$, or at least that $\Delta E_{min} \to 0$ as $N \to \infty$.

infinite chain of spins, i.e., for practical purposes, the case of quite large values of N. We have already pointed out the single known rigorous solution for this case (for the Ising interaction).

Let us consider now some approximate results.

The self-consistent spin-wave theory which we have developed[2] makes it possible to study the properties of ferro- and antiferromagnetic materials over the entire temperature range from $T = 0$ to the Curie point Θ. For an infinite chain, $\Theta = 0$, but we can obtain the value $\chi(\Theta) = \chi(0)$ even in this case from the formulas derived in reference 2 by limiting approximation as $\Theta \rightarrow 0$. Besides, here we need not even carry out any calculations, since the value of $\chi(\Theta)$ in [2] [see Eq. (45)] is actually independent of Θ, and for a linear antiferromagnetic chain without anisotropy,

$$\chi(0) = \chi(\Theta) = \mu^2 N/8J. \tag{10}$$

By using the self-consistent method of Bethe,[9,11] we can exactly take into account the interaction of a given spin with its nearest neighbors, while the role of more distant spins may be taken into account by introducing some sort of effective field. For a chain with the Hamiltonian of Eq. (5), the corresponding calculations have been performed by one of the present authors.[12] For $\alpha \ll 1$ for the chain in Fig. 3a,

$$\chi(0) = (\mu^2 N/18J)\left(1 - \tfrac{1}{3}\alpha\right), \quad \chi(T \gg J/k) = \mu^2 N/4kT. \tag{11}$$

The variation of $\chi(T)$ throughout the temperature range (for the case $\alpha = 0$) is clear from Fig. 1.

However, if $(1 - \alpha) \ll 1$,

$$\chi(0) = \mu^2 (1 - \alpha)^2 N/4J, \quad \chi(T \gg J/k) = \mu^2 N/4kT. \tag{12}$$

For the Ising case ($\alpha = 1$), the corresponding function $\chi(T)$ obtained by the Bethe method is shown in Fig. 4. This diagram shows clearly how close the approximate solution is to the exact solution.

For the chain of Fig. 3b, for $(1 - \alpha) \ll 1$, we have

$$\chi(0) = \mu^2 (1 - \alpha)^2 J_0^2 J_{00}^2 N/2(J_0^5 + J_{00}^5),$$
$$\chi(T \gg J/k) = \mu^2 N/4kT. \tag{13}$$

The very important qualitative result, as is clear from Eqs. (10) — (13), is that $\chi(0) \neq 0$ when $\alpha < 1$. As regards the Ising case, $\chi(0) = 0$, owing to the absence of excited levels with energy $E < 2J$. However, if $\alpha < 1$, such levels exist, for otherwise the susceptibility χ at $T = 0$ would be zero. The numerical calculations also demonstrate that the maximum of the χ curve approaches the axis of ordinates as the number N of links increases. According to the Nernst theorem, $d\chi/dT = 0$ at $T = 0$, but the value $\chi(0) \neq 0$ is permissible, of course [$\chi(0) \neq 0$ for Fermi fluids as well]. We note that the Bethe method gives a value $(d\chi/dT)_{T=0} \neq 0$ for the antiferromagnetic case with $\alpha < 1$. Of course, this shows that the region of applicability of the Bethe method is limited. However, as we suppose, this does not affect the conclusion that $\chi(0) \neq 0$.

Thus, we can assume that a paramagnetic fluid of the chain type having an antiferromagnetic interaction exhibits a non-zero susceptibility at $T = 0$. From that point on, χ varies weakly, but begins to decline according to a law approximately as $1/(T + \Theta_0)$ for $T > \Theta_0 \sim J/k$. Analogous behavior is shown also by a polycrystalline antiferromagnetic material[13] having $\chi = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$, since $\chi_{\parallel}(0) = 0$, and $\chi_{\perp}(0) = \mu^2 N/24J$.

For a ferromagnetic interaction in the Ising case, Eq. (9) is valid for $J < 0$. In this case, $\chi(0) = \infty$. A calculation by the Bethe method (with $\alpha = 0$) gives the function $\chi(T)$ shown in Fig. 5 (the Nernst theorem cannot be directly applied in this case, owing to the presence of degeneracy). It is clear from Fig. 5 that paramag-

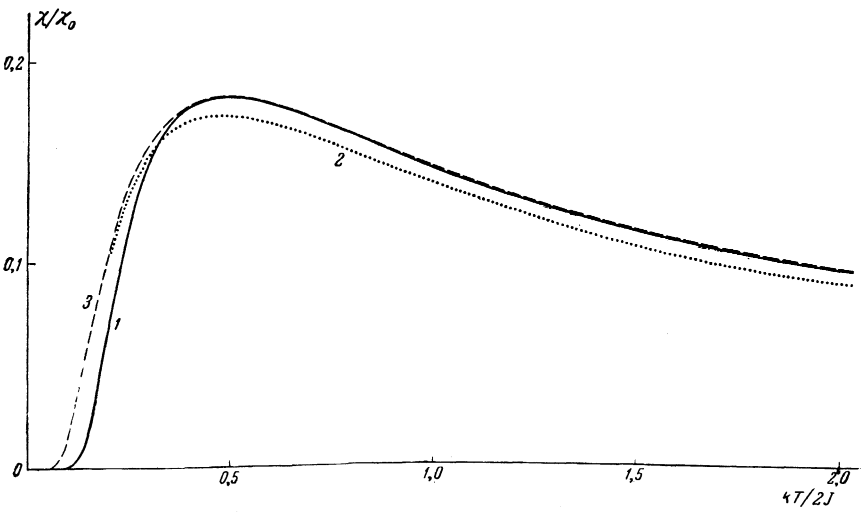

FIG. 4. The susceptibility of an antiferromagnetic chain as a function of the temperature for the case $\alpha = 1$. Curve 1: $N = 10$; curve 2: $N = \infty$ (Bethe method); curve 3: $N = \infty$ (exact solution).

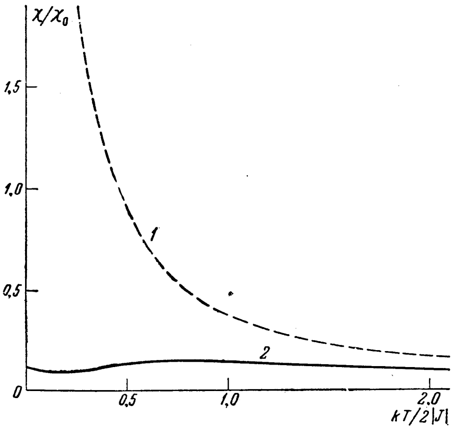

FIG. 5. The susceptibility given by the Bethe method for $\alpha = 0$, $N = \infty$, $\chi_0 = \mu^2 N/2|J|$. Curve 1: the ferromagnetic case; curve 2: the antiferromagnetic case.

netic fluids of the molecular-chain type with ferro- and antiferromagnetic interactions are essentially different in their magnetic properties in the temperature range $T < J/k$.

In conclusion, the authors wish to thank G. A. Semenov for drawing the diagrams.

---

[1] V. L. Ginzburg and V. M. Faĭn, DAN SSSR **131**, 785 (1960), Soviet Phys.-Doklady 5, 328 (1960).

[2] V. L. Ginzburg and V. M. Faĭn, JETP **39**, 1323 (1960), Soviet Phys. JETP **12**, 923 (1960).

[3] L. A. Blyumenfel'd, Biofizika **4**, 515 (1959), Biophysics **4**, No. 5, 3 (1959).

[4] L. A. Blyumenfel'd and V. A. Benderskiĭ, DAN SSSR **133**, 1451 (1960), Soviet Phys.-Doklady 5, 919 (1961).

[5] A. A. Abrikosov and I. M. Khalatnikov, Usp. Fiz. Nauk **66**, 177 (1958), Soviet Phys.-Uspekhi **1**, 68 (1958).

[6] R. Orbach, Phys. Rev. **112**, 309 (1958).

[7] T. W. Ruijgrok and S. Rodriguez, Phys. Rev. **119**, 596 (1960).

[8] R. Orbach, Phys. Rev. **115**, 1181 (1959).

[9] C. Domb, Adv. in Physics 9, 150 (1960).

[10] D. I. Paul, Phys. Rev. **118**, 92 (1960); **120**, 463 (1960); L. F. Mattheiss, Phys. Rev. **123**, 1209 (1961).

[11] P. R. Weiss, Phys. Rev. **74**, 1493 (1948).

[12] V. M. Faĭn, FMM (Phys. of Met. and Metallogr.) in press.

[13] J. Ziman, Proc. Phys. Soc. **A65**, 548 (1952).

Translated by M. V. King
30