1442 (1972) [Sov. Phys. JETP 35, 758 (1972)].
[7] E. A. Turov, in Ferromagnitnyĭ rezonans (Ferromagnetic Resonance), Fizmatgiz, 1961, Chap. 5.
[8] R. F. Soohoo, Magnetic Thin Films, Harper and Row, 1965 (Russ. transl., Mir, 1967).
[9] I. M. Lifshitz, M. Ya. Azbel', and M. I. Kagnov, Elektronnaya teoriya metallov (Electron Theory of Metals), Nauka, 1971 (translation, Plenum Publishing Corp., 1973).
[10] J. Callaway, Energy Band Theory, Academic Press, 1964 (Russ. transl., Mir, 1969).
[11] R. C. Wayne and R. L. Edwards, Colloq. Int. CNRS 188, 369 (1970).
[12] Yu. F. Komnik and E. I. Bukhshtab, Zh. Eksp. Teor. Fiz. 54, 63 (1968) [Sov. Phys. JETP 27, 34 (1968)]; Yu. F. Komnik, E. I. Bukhshtab, Yu. V. Nikitin, and F. I. Chuprinin, Thin Solid Films 11, 43 (1972).

Translated by W. F. Brown, Jr.

Phase diagram of an excitonic ferromagnet at finite temperatures

B. A. Volkov, A. I. Rusinov, and R. Kh. Timerov

P. N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted October 21, 1975)
Zh. Eksp. Teor. Fiz. 70, 1130–1141 (March 1976)

The phase diagram of an excitonic ferromagnet is investigated at finite temperatures. It is shown that near the ferromagnetic-transition temperature, the Curie law holds for the static magnetic susceptibility. The conditions under which a nondegenerate electron system can go over into the ferromagnetic state are determined. The possible existence of two Curie temperatures, outside of which the substance is paramagnetic, is observed. The character of the phase transition is investigated using the two-parameter Landau expansion. Certain experimental data are discussed qualitatively on the basis of the results.

PACS numbers: 75.30.Jy, 75.30.La

1. INTRODUCTION

This is a continuation of our investigation of excitonic ferromagnets.[1] We investigate here the behavior of excitonic ferromagnets at finite temperatures.

We obtain first an expression for the longitudinal static magnetic susceptibility χ of the excitonic-insulator phase at $T\neq 0$. This expression is used to determine the limits of the region of the instability of the dielectric phase with respect to its transition to the ferromagnetic state at different values of the singlet (g_s) and triplet (g_t) coupling constants. We show that near the instability region the susceptibility χ obeys the Curie law $\chi^{-1}\sim T-T_c$. We then obtain analytic expressions for the phase-transition line in the low-temperature region. It turns out that at low concentrations $2n$ of the excess electrons, the dielectric phase, in which the chemical potential μ of the electrons lies inside the dielectric gap $2\Delta_s(\Delta_s>\mu)$, exhibits ferromagnetic instability. Inasmuch as at close values of the singlet and triplet coupling constants the temperatures T_s and T_c of the dielectric and ferromagnetic transitions are close to each other in a considerable region on the (n, T) plane, it becomes possible to construct in this region a two-parameter Landau expansion for the free energy F in powers of the singlet (Δ_s) and triplet (Δ_t) order parameters. An investigation of this expansion shows that the ferromagnetic transformation proceeds always (except for the case $g_s=g_t$) by a second-order phase transition. At strictly equal constants, there exists a section where the entropy S and the order parameters change jumpwise.

In conclusion, we present results of numerical computer calculations, in the self-consistent field approximation, of the complete phase diagram of an excitonic ferromagnet and its susceptibility in the paramagnetic region.

2. FUNDAMENTAL EQUATIONS

A model for an excitonic ferromagnet was proposed in[2] and was considered in detail for $T=0$ in[1] in the high-density approximation ($e^2/\hbar v_F\ll 1$, where e is the electron charge and v_F is its Fermi velocity). In this paper we investigate an excitonic ferromagnet at finite temperatures in the same approximation, using the Hamiltonian and the notation of[1], i.e., we consider a semimetal having one electron and one hole Fermi surface, the centers of which are either at one point of the Brillouin zone, or are shifted relative to each other by one-half the reciprocal lattice vector, the electron density being larger than the hole density by an amount $2n$ (for example, owing to doping). We retain in the interaction Hamiltonian only the terms that determine the instability of the semimetal with respect to formation of charge density and spin-density waves (CDW and SDW, respectively). These instabilities correspond to singlet (g_s) and triplet (g_t) coupling constants, expressions for which in terms of the initial interaction constants are given in[1] (see (1–21)[1)]). The development of these instabilities is accompanied by appearance of a singlet Δ_s (CDW) and triplet Δ_t (SDW) order parameters.

To obtain a self-consistent system of equations in the high-density approximation we use the method of temperature Green's functions[3] defined by the formulas

$$\hat{G}=\{G_{\alpha\beta}(\mathbf{r},\mathbf{r}',\tau)\}=\{-\langle T_\tau\psi_\alpha(\mathbf{r},\tau)\psi_\beta^+(\mathbf{r}',0)\rangle\},\tag{1}$$

where

$$\psi_\alpha(\mathbf{r},\tau)=\exp[\tau(\hat{H}-\mu\hat{N})]\psi_\alpha(\mathbf{r})\exp[-\tau(\hat{H}-\mu\hat{N})].$$

Here, in contrast to (1–6), T_τ is the operator of ordering in the reciprocal temperature τ, which ranges from $-T^{-1}$ to T^{-1} and the expressions for $\psi_\alpha(\mathbf{r})$, $\hat{H}$, etc. are the same as in[1].

As always, it is convenient to change over in the equations for the functions $\hat{G}$ from the coordination representation to a representation in the Block functions (1–7) and to carry out a Fourier transformation in τ, introducing the discrete frequency $\omega=\pi T(2n+1)$, where $n=0, \pm1, \ldots$.[3] Then the system of equations for the operator Green's function (1) in an external magnetic field H takes the form

$$\begin{gathered}(i\omega-\hbar^2k^2/2m^*-{}^1/_2\varepsilon_g+m\boldsymbol{\sigma}\mathbf{H}+\mu)\hat{G}_{11}+\hat{\Delta}\hat{G}_{21}=1,\\ \hat{\Delta}\hat{G}_{11}+(i\omega+\hbar^2k^2/2m^*+{}^1/_2\varepsilon_g+m\boldsymbol{\sigma}\mathbf{H}+\mu)\hat{G}_{21}=0,\end{gathered}\tag{2}$$

where m is the Bohr magneton, $\hat{\Delta}=\Delta_s+\boldsymbol{\Delta}_t\,\sigma$(1 and 2 band indices), and in accordance with[1] both order parameters Δ_s and $\boldsymbol{\Delta}_t$ are chosen to be real.

The conditions for the self-consistency of this system of equations are analogous to conditions (1–20) and can be written in the form

$$\Delta_s={}^1/_2g_sT\sum_{\mathbf{k},\omega}\operatorname{Sp}\hat{G}_{21},\quad \boldsymbol{\Delta}_t={}^1/_2g_tT\sum_{\mathbf{k},\omega}\operatorname{Sp}\sigma\hat{G}_{21}.\tag{3}$$

Since we are interested in the longitudinal susceptibility, it follows that, using the isotropy of the problem, we can assume that H and $\boldsymbol{\Delta}_t$ are directed along the same axis, for example z. Then, solving (2) with respect to G_{21}, we can substitute the obtained expressions in (3) and change over in the usual manner[3] from summation over $\mathbf{k}$ to integration with respect to the energy ε near the Fermi surface. We obtain

$$\begin{gathered}2\Delta_s\ln\frac{T_{s0}}{T}+\Delta_s[I(\Delta_+,\mu_+)+I(\Delta_-,\mu_-)]+\Delta_t[I(\Delta_+,\mu_+)-I(\Delta_-,\mu_-)]=0,\\ 2\Delta_t\ln\frac{T_{t0}}{T}+\Delta_t[I(\Delta_+,\mu_+)+I(\Delta_-,\mu_-)]+\Delta_s[I(\Delta_+,\mu_+)-I(\Delta_-,\mu_-)]=0,\end{gathered}\tag{4}$$

where $\Delta_\pm=\Delta_s\pm\Delta_t$, $\mu_\pm=\mu\pm mH$, and T_{s0} are the temperatures of the phase transitions of the undoped semimetal in the state of an excitonic insulator with CDW ($\Delta_s\neq0$, $\Delta_t=0$) or SDW ($\Delta_t\neq0$, $\Delta_s=0$), respectively. These temperatures are determined by the formulas

$$T_{s0}=\gamma\pi^{-1}\Delta_{s0},\quad T_{t0}=\gamma\pi^{-1}\Delta_{t0},\quad \gamma\cong1.78,$$

where Δ_{s0} and Δ_{t0} are the equilibrium values of the order parameters at μ, $n=0$ and $T=0$ (see (1–23) and (1–24)). The function $I(\Delta,\mu)$ can be written in the form

$$I(\Delta,\mu)=\int_0^\infty d\varepsilon\left\{\frac{n(-E-\mu)-n(E-\mu)}{E}+\frac{n(\varepsilon)-n(-\varepsilon)}{\varepsilon}\right\}.\tag{5}$$

Here $E=(\varepsilon^2+\Delta^2)^{1/2}$, and $n(x)$ is the usual Fermi distribution:

$$n(x)=T\sum_\omega\frac{e^{i\omega\tau}}{i\omega-x}\Bigg|_{\tau\to+0}=\frac{1}{2}\left\{1-\operatorname{th}\frac{x}{2T}\right\}.\tag{6}$$

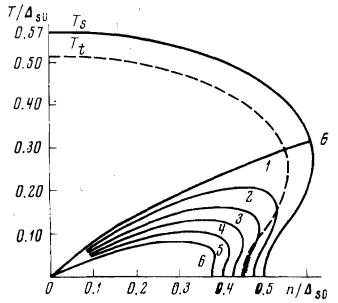

FIG. 1. Dependence of the Curie temperatures T_c of the ferromagnetic transition on the concentration n for the following values of the ratio Δ_{t0}/Δ_{s0}: 1—1.0, 2—0.9, 3—0.8, 4—0.7, 5—0.6, 6—0.5, and the temperatures T_s and T_t of dielectric transition ($\Delta_{t0}/\Delta_{s0}=0.9$).

Since we are considering a system with a fixed number of particles (there are no other partially-filled bands and there are no bound states in which an electron can land as a result of the phases transition), Eqs. (4) must be supplemented by the requirement of conservation of the total electron density, which obviously takes the form

$$2n=\int_0^\infty d\varepsilon\,[n(E_+-\mu_+)+n(-E_+-\mu_+)+n(E_--\mu_-)+n(-E_--\mu_-)].\tag{7}$$

where $2n$ is the density expressed in energy units: $N=4N(0)n$, N is simply the concentration of the "excess" electrons, and $N(0)$ is the level density at the Fermi level in one band per spin. In the limit as $T\to0$, Eqs. (4) and (7) go over into (1–22) and (1–28), if account is taken of the fact that ([3], p. 376 of the Russian edition)

$$\int_0^{\tilde{\omega}}\frac{d\varepsilon}{\varepsilon}\operatorname{th}\frac{\varepsilon}{2T}=\ln\frac{\tilde{\omega}\gamma}{\pi T}.$$

3. PARAMAGNETIC SUSCEPTIBILITY OF PARAMAGNETIC PHASE AT $T\neq0$

In a zero magnetic field, Eqs. (4) and (7) admit of a solution with only one nonzero order parameter. If, for example, $g_s>g_t$, then as the temperature is lowered a solution is realized with $\Delta_s\neq0$ and $\Delta_t=0$. The critical temperature T_s, as a function of the concentration n at which the phase transition into a CDW state takes place, is determined from the condition for the appearance of a nontrivial solution for Δ_s of the system (4) at $\Delta_t=0$:

$$\ln(T_{s0}/T)+I(0,n)=0.\tag{8}$$

We have used here the equality $\mu=n$, which can usually be obtained by direct integration of (7) at $\Delta_\pm=0$ and $H=0$. A plot of $T_s(n)$ is shown in Fig. 1 and marked T_s. The curve has a region where it is doubly-valued, but as shown in[4], a second-order transition takes place everywhere on this line, and the phase with the disturbed symmetry is always to the left of this line.

We calculate now the ferromagnetic susceptibility of this phase (the excitonic insulator phase). To this end it is necessary to find, in the approximation linear in the external field H, a solution of the system (4) with condition (7), and to calculate with the aid of the obtained expressions the induced magnetic moment **M**, which is defined as the difference between the concentrations of the electrons with opposite spins:

$$\mathbf{M}=2mN(0)\int_0^\infty d\varepsilon\,[n(E_+-\mu_+)+n(-E_+-\mu_+)-n(E_--\mu_-)-n(-E_--\mu_-)]. \tag{9}$$

Here $N(0)$ is the density of states on the Fermi surface

Recognizing that the magnetic field H can induce a triplet gap against the background of the singlet gap that exists in the paramagnetic phase of the excitonic insulator, it follows from (4), at the required accuracy, that

$$\begin{gathered}\ln(T_{s0}/T)+I(\Delta_s,\mu)=0,\\ \Delta_t\left[\ln\frac{T_{t0}}{T}+I(\Delta_s,\mu)+2\Delta_s^2\frac{\partial I(\Delta_s,\mu)}{\partial\Delta_s^2}\right]+\Delta_s\frac{\partial I(\Delta_s,\mu)}{\partial\mu}mH=0.\end{gathered} \tag{10}$$

In the same approximation, regarding the concentration n in (7) as a function of two independent variables $\mu(\mu=\mu_\pm)$ and $\Delta_s^2(\Delta_s=\Delta_\pm)$, we obtain for the moment M:

$$M=4mN(0)\left\{mH\frac{\partial n}{\partial\mu}+2\Delta_s\Delta_t\frac{\partial n}{\partial\Delta_s^2}\right\}. \tag{11}$$

In the derivation of (10) and (11) we took into account the fact that, according to (7), the expression for the chemical potential does not contain expansion terms linear in Δ_t and H.

By direct differentiation in (5) and (7) we can show that

$$\frac{\partial I(\Delta,\mu)}{\partial\mu}=2\frac{\partial n}{\partial\Delta_s^2}. \tag{12}$$

Determining now Δ_t from (10), substituting the result in (11), and taking (12) into account, we easily see that the susceptibility χ of the dielectric phase is

$$\chi=\frac{M}{H}\Big|_{H\to0}=4m^2N(0)\left\{\frac{\partial n}{\partial\mu}+\Delta_s^2\left(\frac{\partial I}{\partial\mu}\right)^2\left(\ln\delta^2-2\Delta_s^2\frac{\partial I}{\partial\Delta_s^2}\right)^{-1}\right\}. \tag{13}$$

Here $\delta^2=\Delta_{s0}/\Delta_{t0}$, and the derivatives are calculated at equilibrium values of Δ_s and μ corresponding to the paramagnetic phase ($\Delta_t=0$). The first term in (13) is connected with the well known Pauli paramagnetism of the free electrons, and the second differs from zero only if the triplet coupling constant $g_t\neq0$. At the Curie temperature T_c defined by the equality

$$\ln\delta=\Delta_s^2\frac{\partial I}{\partial\Delta_s^2}, \tag{14}$$

this term in (13) becomes infinite, indicating that $T=T_c$ the paramagnetic phase is stable to spontaneous formation of the triplet order parameter Δ_t at $H=0$. Consequently, in accordance with (9), a spontaneous magnetic moment M also appears. Obviously, if we expand (13) the denominator near T_c in powers of $\tau=(T-T_c)/T_c$, we obtain the usual Curie law for the susceptibility of a ferromagnet in the paramagnetic region.

Thus, to find the line of the phase transitions into the ferromagnetic state on the (n, T) plane it is necessary first to find for all n and T the solution of the problem of the excitonic insulator, i.e., to solve (4) and (7) at $H=0$ and $\Delta_t=0$, and then substitute this solution in relation (14) and solve it with respect to T (or n). This can not be done analytically at arbitrary values of the temperature and the coupling constant g_s. We therefore consider some particular cases.

4. LOW TEMPERATURES

At low temperatures $T_c\ll T_s$ (where T_s is defined by formula (8)), it is necessary to investigate two limiting cases, depending on whether the $2n$ excess electrons in the paramagnetic phase are degenerate or not.

Nondegenerate case. We obtain first the solution of (4) and (7) for the paramagnetic phase ($\Delta_t=0$), which at $\Delta_t=0$ can be written with the aid of (6) in the form

$$\begin{gathered}\ln(T_{s0}/T)+I(\Delta_s,\mu)=0,\\ 2n=\int_0^\infty d\varepsilon\left[\operatorname{th}\frac{E+\mu}{2T}-\operatorname{th}\frac{E-\mu}{2T}\right],\end{gathered} \tag{15}$$

where

$$I(\Delta_s,\mu)=\int_0^\infty d\varepsilon\left[\frac{1}{2E}\left(\operatorname{th}\frac{E+\mu}{2T}+\operatorname{th}\frac{E-\mu}{2T}\right)-\frac{1}{\varepsilon}\operatorname{th}\frac{\varepsilon}{2T}\right]. \tag{16}$$

In this case, at the limit of small T, we shall assume that the following inequalities hold:

$$T\ll\Delta_s-\mu,\quad T\ll\mu. \tag{17}$$

Then the argument of the hyperbolic tangents in (15) and (16) is large, so that we can use their asymptotic expansion $\tanh x\approx1-2e^{-2x}$ and confine ourselves to the first order in the parameter $\exp(-\Delta_s/T)$. Substituting the asymptotic expansion of the hyperbolic tangent in the integrals (15) and (16), we readily note that, with the degree of accuracy required by us, the main contribution to the integrals is made by the region near the lower integration limit. We can therefore make approximately the substitution $E\to\Delta_s+(2\Delta_s)^{-1}\varepsilon^2$ under the integral sign, after which all the integrals become Gaussian and can be easily calculated. Thus, from the second equation of (15) we obtain

$$\frac{\Delta_s-\mu}{T}\approx\frac{1}{2}\ln\frac{\pi T\Delta_s}{2n^2}\gg1. \tag{18}$$

This expression enables us to introduce the Fermi degeneracy temperature $T_F\sim n^2\Delta_s^{-1}$. Obviously, the considered case (17) corresponds to high temperatures $T\gg T_F$. Hence, taking (17) into account, we obtain $\Delta_s\gg T_F$ or $\Delta_s\gg n$, i.e., our analysis is valid only at concentrations that are small in comparison with the critical concentration n_c of the doping of the excitonic insulator $n\ll n_{cr}=\Delta_{s0}/2$ (see (1–30)).

With the same accuracy, it follows from (16) that

$$I(\Delta_s,\mu)\approx-\ln\left(\frac{\gamma\Delta_s}{\pi T}\right)-\left(\frac{\pi T}{2\Delta_s}\right)^{1/2}\exp\left\{\frac{\mu-\Delta_s}{T}\right\}, \tag{19}$$

hence, taking (18) into account, we obtain

$$\partial I/\partial\Delta_s \approx \Delta_s^{-1}(nT^{-1}-1).$$

Substituting the last expression (14), we find that in the case of the phase-transition line the nondegenerate paramagnetic phase of the excitonic insulator, in the region of small concentrations of excess carriers, undergoes a phase transition into the ferromagnetic state at the Curie temperature T_c defined by the formula

$$T_c = n[1+\ln(\Delta_{s0}/\Delta_{t0})]^{-1}. \tag{20}$$

Thus, in the nondegenerate case the Curie temperature increases linearly with increasing carrier density, with a slope that depends linearly on the difference $g_s^{-1} - g_t^{-1}$ between the reciprocal coupling constants (see formulas (1-23) and (1-24)). We note that the assumption (17) made at the beginning of this section concerning the nondegeneracy of the electrons in the region of the ferromagnetic transition is justified at small values of n, since $T_c \sim n$ and the degeneracy temperature $T_F \sim n^2$. It should also be noted that, accurate to $\exp(-\Delta_s/T)$, the singlet gap Δ_s does not depend on the temperature in the paramagnetic phase and has the same form as at $T=0$. This can be usually verified with the aid of Eqs. (15), (18), and (19).

Degenerate case. In this case the chemical potential μ is in the conduction band. At low temperatures $T \ll \mu - \Delta_s$, the hyperbolic tangent of the summary argument can be set equal to unity in (15) and (16). On the other hand, in the same region, the hyperbolic tangent of the difference argument represents a steep step. This makes it possible to integrate the integrals containing this hyperbolic tangent by parts, by changing over to integration with respect to the quasiparticle energy E. The subsequent calculations are standard[5] and are based on the expansion of the slowly varying part of the integrand in powers of $E-\mu$. As a result we obtain the approximate expression for the integrals in the form of a series in even powers of T. Thus, accurate to T^2 we can readily obtain from (15) and (16)

$$n = (\mu^2-\Delta_s^2)^{1/2} - {}^1/_6\pi^2\Delta_s^2T^2(\mu^2-\Delta_s^2)^{-3/2},$$
$$I(\Delta_s,\mu) = \ln\frac{\pi T/\gamma}{\mu+(\mu^2-\Delta_s^2)^{1/2}} + \frac{\pi^2}{6}\frac{\mu T^2}{(\mu^2-\Delta_s^2)^{3/2}}, \tag{21}$$

whence

$$\frac{\partial I}{\partial\Delta_s^2} = \frac{(\mu^2-\Delta_s^2)^{-1/2}/2}{\mu+(\mu^2-\Delta_s^2)^{1/2}} + \frac{\pi^2}{4}\frac{\mu T^2}{(\mu^2-\Delta_s^2)^{5/2}}. \tag{22}$$

The temperature increments in these expressions must be expressed in terms of the values of Δ_s and μ at $T=0$:

$$\Delta_s^2 = \Delta_{s0}(\Delta_{s0}-2n), \quad \mu = \Delta_{s0}-n. \tag{23}$$

With the aid of (15), (21), (29), and (23) we obtain accurate to T^2,

$$\Delta_s^2 = \Delta_{s0}(\Delta_{s0}-2n) + (3n)^{-1}\pi^2\Delta_{s0}T^2, \tag{24}$$
$$\mu = \Delta_{s0} - n + (6n^2)^{-1}\pi^2\Delta_{s0}T^2.$$

According to these formulas, the dielectric gap Δ_s for the degenerate paramagnetic phase at low T increases with increasing T. Therefore the temperature of the dielectric transition also increases with increasing electron density n. This, in turn, leads to the appearance of ambiguity on the $T_s(n)$ curve at $n > n_{\text{cr}}$ $(2n_{\text{cr}} = \Delta_{s0})$ (see Fig. 1, curve T_s). This circumstance was first noted in[4].

To find the dependence of the Curie temperature of the ferromagnetic transition on the concentration of the excess electrons in the degenerate paramagnetic phase of an excitonic insulator, it is necessary to substitute expressions (22) and (24) in (14) and solve the obtained equation with respect to T_c. We ultimately obtain

$$T_c^2 = \frac{30}{\pi^2}\frac{n_c^3(n-n_c)}{\Delta_{s0}^2+(5n_c-3\Delta_{s0})^2}, \tag{25}$$

for the quantity

$$n_c = 2^{-1}\Delta_{s0}(1+\ln\delta)^{-1} \tag{26}$$

determines the critical concentration of the ferromagnetic transition at $T=0$, above which no paramagnetism is observed.

It follows from (25) that near the critical concentration n_c the Curie temperature increases with increasing doping level like $T_c \propto (n-n_c)^{1/2}$. If the singlet (g_s) and triplet (g_t) coupling constants are equal, then it follows from (26) that $n_c = n_{\text{cr}}$ and $T_c = T_s$, i.e., at $g_s = g_t$ and at low temperatures a degenerate semimetal goes over at directly to the ferromagnetic state, bypassing the paramagnetic dielectric phase. For $T=0$, this follows from the calculation of the free energy F of the two phases, which is carried out in[1], and for finite T we shall verify this by constructing the Landau expansion for F.

5. TWO-PARAMETER LANDAU EXPANSION

We have just verified that at equal values of the coupling constants the temperatures T_s and T_c of the dielectric and magnetic transformations coincide, at least in the low-temperature region. We can therefore expect at close values of these constants near the $T_s(n)$ and $T_c(n)$ lines both order parameters Δ_s and Δ_t to be small. We can then expand the self-consistency and electric-neutrality equations (4) and (7) in powers of these parameters, confining ourselves to a finite number of terms of this expansion.

Equations (4) can be regarded here as definitions of the extremum of the free-energy functional $F(\Delta_s, \Delta_t)$ under the additional condition (7). Integrating the self-consistency equations with respect to Δ_s and Δ_t, which are regarded as independent variables, we can reconstruct the form of the functional F accurate to a certain factor. The unknown factor can be obtained from a comparison of the formula obtained here for F with its exact expression, which is known at $T=0$.[1]

It is thus easy to obtain the following expression for F near the line $T_s(n)$, accurate to Δ_s^4 and Δ_t^4:

$$F = -\alpha_1\Delta_s^2 - \alpha_2\Delta_t^2 + {}^1/_2\beta_1(\Delta_s^4+\Delta_t^4) + \beta_2\Delta_s^2\Delta_t^2, \tag{27}$$

where all the coefficients $\alpha_{1,2}$ and $\beta_{1,2}$ are calculated in the vicinity of the point $(n_s = n(T_s), T_s)$ accurate to the first nonvanishing term in τ and ν. Here

$$\tau = (T-T_s)/T_s, \quad \nu = (n-n_s)/n_s. \tag{28}$$

Equations (4), together with (7), which minimize the functional (22), take this approximation the form

$$\Delta_s\alpha_1=\beta_1\Delta_s^3+\beta_2\Delta_t^2\Delta_s,\quad \Delta_t\alpha_2=\beta_1\Delta_t^3+\beta_2\Delta_s^2\Delta_t. \tag{29}$$

The expressions for the coefficients $\alpha_{1,2}$ and $\beta_{1,2}$ in the form of sums in the odd frequencies can be obtained by integrating in (5) with respect to the energy ε, and substituting there n (6) in the form of a series. We then obtain at $H=0$

$$\begin{gathered}\alpha_1\equiv\alpha=n_s^2(\tau-\nu)\varphi_2-\tau,\quad \alpha_2=\alpha-\ln\delta^2,\\ \beta_1=0.5n_s^2\varphi_2^2-n_s^2\varphi_3+0.25\varphi_2,\quad \beta_2=0.5n_s^2\varphi_2^2-3n_s^2\varphi_3+0.75\varphi_2,\\ \varphi_m=4\pi T\sum_{\omega>0}\frac{\omega}{(\omega^2+n^2)^m}\end{gathered} \tag{30}$$

This representation of the coefficients (30) is convenient at high temperatures, for in this case the series converge rapidly and the first few terms suffice for estimating purposes. If we know the form of the function $T_s(n)$ (8), then we can express all the functions φ_m in terms of derivatives of $T_s(n)$ with respect to n, because

$$\partial\varphi_m/\partial n_s^2=-m\varphi_{m+1},$$

and $\alpha=0$ on the $T_s(n)$ line, i.e., we have on this line

$$\varphi_2=n_s^{-2}\left(1-\frac{\nu}{\tau}\right)^{-1}=n_s^{-2}\left(1-\frac{\Delta n}{\Delta T}\frac{T_s}{n_s}\right)^{-1}=n_s^{-2}\left(1-\frac{T_s}{n_s}\frac{\partial n_s}{\partial T_s}\right)^{-1}.$$

From this it follows, incidentally, that

$$\alpha=\left(1-\frac{T_s}{n_s}\frac{\partial n_s}{\partial T_s}\right)(\tau-\nu)-\tau. \tag{31}$$

Expressions of this type for the coefficients may turn out to be convenient in the experimental reduction of the results.

We consider now the possible solutions of (29). It is obvious that three types of solutions are formally admissible (in addition to the trivial solution):

$$\begin{aligned}&1)\ \Delta_t=0,\quad \Delta_s^2=\alpha/\beta_1>0,\\ &2)\ \Delta_s=0,\quad \Delta_t=(\alpha-\ln\delta^2)/\beta_1>0,\\ &3)\ \Delta_s^2=\frac{\alpha}{\beta_1}-\frac{\beta_2}{\beta_1}\Delta_t^2,\quad \Delta_t^2=\frac{\alpha}{\beta_1+\beta_2}-\frac{\beta_1\ln\delta^2}{\beta_1^2-\beta_2^2}.\end{aligned} \tag{32}$$

Solutions (1) and (2) are paramagnetic with CDW and SDW, respectively. Solution (3) is ferromagnetic.

All these solutions determine in the physical region ($\Delta_s^2\geqslant 0$, $\Delta_t^2\geqslant 0$) a certain minimum of the functional of the free energy F(27), since $\beta_1>0$ on the line $T_s(n)$ (8). The latter can be verified by numerical computer calculations, which agree with the results of Kopaev.[4] It follows from (32) that the limits of the regions of the paramagnetic singlet $T_s(n)$ and triplet $T_t(n)$ phases, and also of the ferromagnetic phase $T_c(n)$ are defined by the equation

$$\begin{gathered}T_s(n)\to\alpha=0,\quad T_t(n)\to\alpha=\ln\delta^2,\\ T_c(n)\to\alpha=\frac{\beta_1}{\beta_1-\beta_2}\ln\delta^2.\end{gathered} \tag{33}$$

Since it follows from the definition (30) that the coefficient α increases with decreasing ν, physically admissible (Δ_s, $\Delta_t>0$) solutions of (32) can be realized in the (n, T) plane only to the left of their limits (33) (see Fig. 1, curves T_s; T_t; 1, 2, ...). With the aid of (31) and (32), calculating the functional F(27), we can show that at $\Delta_{s0}>\Delta_{t0}$ ($\ln\delta>0$), from energy considerations, the solution of the triplet type is not realized at all. And when the concentration ν is decreased or when the temperature τ is changed, a paramagnetic dielectric phase is generated via a second-order phase transition on the $T_s(n)$ line, after which ferromagnetism sets in on the $T_c(n)$ line also via a second-order phase transition.

It should also be noted that the $T_c(n)$ curve lies between the $T_s(n)$ and $T_t(n)$ curves if $\beta_2<0$, and to the left of them if $\beta_2>0$. As follows from the third formula of (32), the parameter Δ_s, and with it also the CDW amplitude, increases with increasing SDW amplitude (Δ_t) if $\beta_2<0$ and decreases if $\beta_2>0$. Numerical computer calculations show that β_2 vanishes at the point $n=0.53\,\Delta_{s0}$, $T_s(n)=0.17\,\Delta_{s0}$ on the (n, T) plane, with β_2 increasing with increasing T.

All the foregoing results are valid if $\beta_2-\beta_1\gg\alpha$. At $\beta_2-\beta_1\sim\alpha$ the expansion (27) is insufficient, because at $\beta_1=\beta_2$ an unphysical divergence appears in the third formula of (32). Mathematically this is connected with the fact that in our approximation the Jacobian of the system (29) vanishes at $\beta_1=\beta_2$. With the aid of a direct calculation or by comparing the expression for $T_c(n)$ (33) with the definition of $T_c(n)$ in terms of the susceptibility (13), we can note that the condition $\beta_1=\beta_2$ corresponds to the vanishing of the quantity $\partial I/\partial\Delta_s^2$ in the formula for the susceptibility (13) at $\Delta_s=0$. Consequently, in the vicinity of the point θ, the coordinates of which are determined by the equations $\alpha=0$ and $\beta_1=\beta_2$, it is necessary to retain in the Landau expansion for the free energy the terms of the order parameter raised to the sixth power, and take into account the dependence of the difference $\beta_1-\beta_2$ on τ and ν accurate to terms linear in τ and ν.

It follows from considerations of the invariance of the functional F and the symmetry of Eqs. (4) that in the vicinity of θ it is necessary to add to the functional (22) a term in the form

$$\tfrac{1}{3}\gamma_1(\Delta_s^6+\Delta_t^6)+\gamma_2(\Delta_s^4\Delta_t^2+\Delta_t^4\Delta_s^2). \tag{34}$$

We shall not write out here the explicit expressions for the coefficients γ_1 and γ_2, and merely note the following. In the case of equal coupling constants ($\ln\delta=0$) we easily find from the equations for the minimization of the functional of the free energy with allowance for (34) in the vicinity of the point θ that, accurate to terms cubic in α and $\beta_1-\beta_2$, the energy gain accompanying the transition of the paramagnet into the ferromagnetic state is equal to

$$\delta F=F_c-F_s\approx-\frac{1}{4}\left(\frac{\alpha}{\beta_1}\right)^2\left\{\beta_1-\beta_2+\frac{\alpha}{\beta_1}(\gamma_1-\gamma_2)\right\}, \tag{35}$$

where F_c is the energy of the ferromagnetic phase, and F_s the energy of the paramagnetic phase. Naturally, any of the phases, both the singlet (in the CDW) and the ferromagnetic, can exist only if $\alpha\geqslant 0$. Therefore, at equal coupling constants, the reason of existence of the ferromagnetic phase near the point θ is bounded by the

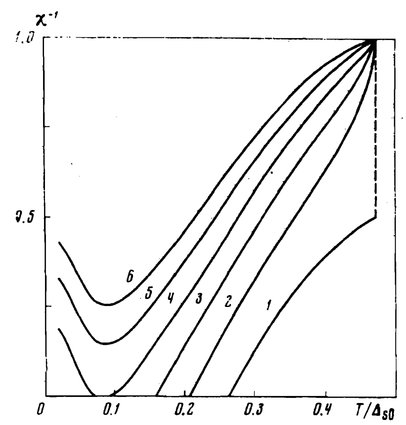

FIG. 2. Dependence of the reciprocal susceptibility χ^{-1} (normalized to the susceptibility of the normal semimetallic phase) on the temperature T at $n = 0.45$ for the following values of the parameter Δ_{t0}/Δ_{s0}: 1—1.0, 2—0.9, 3—0.8, 4—0.7, 5—0.6, 6—0.5.

straight line $\alpha = 0$ and by the straight line

$$\beta_1(\beta_1-\beta_2)+\alpha(\gamma_1-\gamma_2)=0, \tag{36}$$

which intersect at the point θ. If no account is taken near θ of the contribution made to the free energy by the sixth-ordered terms in (34), then we obtain in place of (36) the incorrect result $\beta_1 - \beta_2 = 0$.

From formula (35) for the energy gain δF it follows that at equal coupling constants the phase transition on the line (36) is of first order, since at $\alpha > 0$ the energy gain is a linear function of $T - T_c$, and consequently the entropy experiences at T_c a jump proportional to α^2. At the same time, the triplet order parameter Δ_t appears jumpwise, a fact that follows directly from the equations for the minimization of the free energy (at $\Delta_{s0} = \Delta_{t0}$ we always have $\Delta_s = \Delta_t$ in the ferromagnetic phase). This fact is not surprising in the sense that at $T = 0$ and at equal coupling constants the first derivative of the energy with respect to the coupling constant Δ_{s0} also changes jumpwise at the phase-transition point (see (1–51)). Consequently, the pressure also changes jumpwise, and this also leads to a first-order transition.

Near the point θ we can determine the phase-transition line also at different coupling constants ($\ln\delta \neq 0$). For this purpose it is necessary to substitute in the total equations for the minimization of the functional of the free energy, which takes into account the increment (34), their solution for the pure singlet phase ($\Delta_s \neq 0$ $\Delta_t = 0$), and then find the conditions under which the obtained system of equations is compatible as $\Delta_t \to +0$. It is these conditions which determine the line $T_c(n)$. The final equation for $T_c(n)$ takes the form

$$\beta_1^2 \ln\delta^2=\alpha[\beta_1(\beta_1-\beta_2)-\alpha(\gamma_1-\gamma_2)]. \tag{37}$$

Comparing with (36), we see that in the (n, T) plane, near the point θ, the line T_c takes in the general case the form of a hyperbola with asymptotes defined by equations (36) and $\alpha = 0$.

6. RESULTS OF NUMERICAL CALCULATIONS

To construct the complete phase diagram of an excitonic ferromagnet, we have performed numerical computer calculations of the curves $T_s(n)$ and $T_c(n)$ using Eqs. (14) and (15) at different values of the ratio Δ_{s0}/Δ_{t0}. Figure 1 shows the phase-transition line in the state of the excitonic insulator T_s and the ferromagnetic transformation lines (curves 1–6) at Δ_{t0}/Δ_{s0} equal to 1.0, 0.9, 0.8, 0.7, 0.6, and 0.5. We see that these results agree with the limiting cases investigated in Secs. 4 and 5: for example, the behavior of T_c near the triple point θ (the coordinates of which in the (n, T) plane are $n \approx 0.609\,\Delta_{s0}$ and $T_s(n) \approx 0.318\,\Delta_{s0}$), and the ambiguity of the line T_c in the region of large concentrations. Thus, at $n > n_c$ (26), with decreasing temperature, we first land in the region of the excitonic insulator, then in the ferromagnetic region, from which we go over with further decrease of T again to the paramagnetism region, i.e., two Curie temperatures can be observed.

According to formula (13) for the paramagnetic susceptibility χ, in the paramagnetic region, where only one of the order parameters (Δ_s or Δ_t) differs from zero, the system has a large exchange gain. The results of numerical calculations of χ are shown in Fig. 2. We see that near T_c the reciprocal susceptibility tends linearly to zero at $T \to T_c$, as is indeed required by the Curie law. If the concentration of the excess electrons exceeds the concentration which the transition to the ferromagnetic state takes place, then the maximum of the susceptibility is reached at a finite temperature. Taking this into account, and also the fact that at $n > n_c$ there exist two Curie temperatures, we should expect the spontaneous magnetic moment M in the ferromagnetic phase also to reach its maximum finite temperatures at $H = 0$ (11), and then decrease again as $T \to 0$. This obviously will take place when the concentration n is high enough, at least larger than the concentration at which strong ferromagnetism is observed at $T = 0$ (1–44). It is precisely this behavior of the magnetization which can explain the results of the work by Ivanov-Omskiĭ and co-workers.[6]

---

1) References to the formulas of [1] will henceforth be designated (1–21) etc.

1B. A. Volkov, Yu. V. Kopaev, and A. I. Rusinov, Zh. Eksp. Teor. Fiz. 68, 1899 (1975) [Sov. Phys. JETP 41, 952 (1975)].

2B. A. Volkov and Yu. V. Kopaev, Pis'ma Zh. Eksp. Teor. Fiz. 19, 168 (1973) [JETP Lett. 19, 104 (1973)].

3A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statistecheskoĭ fizike (Quantum Field Theoretical Methods in Statistical Physics) Fizmatgiz, 1962 [Pergamon, 1965].

4Yu. V. Kopaev, Fiz. Tverd. Tela 12, 3 (1970) [Sov. Phys. Solid State 12, 1 (1970)].

5R. Peierls, Quantum Theory of Solids, Oxford, 1964 (Russ. transl., IIL, 1956, p. 112).

6V. I. Ivanov-Omskiĭ, B. T. Kolomiets, V. M. Mel'nik, V. K. Ogorodnikov, and K. D. Tovstyuk, Fiz. Tekh. Poluprovodn. 2, 904 (1968); 4, 690 (1970) [Fiz. Tekh. Poluprovodn. 2, 757 (1968); 4, 584 (1970)].

Translated by J. G. Adashko