# Magnetic susceptibility of a ferromagnet with a structural transformation

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The temperature dependence of the magnetic susceptibility in a system in which charge- and spin-density waves coexist (excitonic ferromagnet) is investigated. The analysis is within the framework of the Landau two-parameter expansion of the free energy. The results of the present paper are therefore taken to be more general than the "excitonic" ferromagnetism model itself. It is shown that above the structural transition temperature $T_s$ the magnetic susceptibility $\chi$ contains only a fluctuating component with a square-root singularity at $T_s$. The susceptibility calculated in the mean-field approximation is equal to zero at $T_s$ and diverges in accordance with the Curie-Weiss law at $T_C$ (the Curie temperature). The fluctuation contribution to $\chi$ at $T_C$ turns out again to be finite with a square-root singularity. A qualitative comparison is made of the calculation results with the results of magnetic measurements in $ZrZn_2$ and $GaMo_5S_6$.

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## 1. INTRODUCTION

We shall investigate the temperature dependence of the magnetic susceptibility of a ferromagnet in which the magnetic transition is connected with its structural instability. We determine the collective-excitation spectrum of such a ferromagnet. The entire analysis is within the framework of the Landau two-parameter expansion of the free energy. The concrete microscopic model that leads to this functional is the previously proposed[1] excitonic-ferromagnet scheme.

It is known that the singularities of the single-electron spectrum can lead, when account is taken of the interactions between the electrons, to formation in the system of either a charge-density wave (CDW) and the ensuing structural distortions, or a spin-density wave (SDW) (band antiferromagnetism). States other than those mentioned above are also possible in principle.[2,3] The coexistence of CDS and SDW leads to ferromagnetic ordering of the band electrons[1,4,5] (excitonic ferromagnet). A characteristic feature of the excitonic-ferromagnet model is the presence of two phase transitions, first a structural one (appearance of CDS),[1)] and then, at lower temperature, a ferromagnetic one. Below the structural-transformation temperature there appears in the system a singlet order parameter $\Delta_s$, and at the Curie point there appears a triplet order parameter $\Delta_t$. The coexistence of two order parameters $\Delta_s$ and $\Delta_t$ leads to ferromagnetic ordering, with the magnetic moment proportional to $\Delta_s\Delta_t$.

The necessary presence of two parameters should cause the temperature dependence of the magnetic susceptibility to be different from that in other models. The present paper is devoted to a clarification of this question.

## 2. CALCULATION OF THE MAGNETIC SUSCEPTIBILITY

We investigate in this section the temperature dependence of the magnetic susceptibility. At sufficiently high temperatures of the structural and the magnetic transitions (this is the only case considered below) it is convenient to use a phenomenological approach. In this situation it is permissible to expand the free energy in terms of both order parameters $\Delta_s$ and $\Delta_t$. The free-energy functional of an excitonic ferromagnet in the absence of an external magnetic field is of the form

$$\mathcal{F}=\int dr\{g_s(\nabla\Delta_s)^2+\alpha_s\Delta_s^2+{}^1/_2\beta_s\Delta_s^4+\beta_2\Delta_s^2\Delta_t^2+g_t(\nabla\Delta_t)^2+\alpha_t\Delta_t^2+{}^1/_2\beta_t\Delta_t^4\}, \tag{1}$$

where $\alpha_{s,t}=a(T-T_{s,t})$; $T_s$ and $T_t$ are the temperatures of the structural and antiferromagnetic transitions with their mutual influence neglected.

It can be deduced from the microscopic theory that within the framework of the isotropic band scheme we have $\beta_s=\beta_t=\beta_1$ and $g_s=g_t=g$ (Ref. 6). These relations will henceforth be regarded as satisfied. As shown earlier,[6] in an external magnetic field H the expression for the free energy acquires a term $\gamma\Delta_s\Delta_t\cdot H$. It describes the interaction of the magnetic moment in the system with the external field. We consider below the case when the structural-transition point lies above the Curie point (this is precisely the situation in the compound $GaMo_5S_6$, $T_s\approx 50$ K, $T_C\approx 19$ K, which is apparently closest to the considered model).

2. We proceed to calculate the susceptibility. We ascertain first the behavior of $\chi$ at $T>T_s$. To find the fluctuating component of $\chi$ we follow the method of the effective Hamiltonian in the region of Gaussian fluctuations.[7] Above the temperature of the structural transition, the free energy is given by

$$\exp\left(-\frac{\mathcal{F}}{T}\right)=\exp\left(-\frac{\mathcal{F}_0}{T}\right)\int\exp\left(-\frac{H_{\text{eff}}}{T}\right)d\{\eta_s\}d\{\eta_t\}; \tag{2}$$

$$H_{\text{eff}}=\int dr\{g(\nabla\eta_s)^2+\alpha_s\eta_s^2+g(\nabla\eta_t)^2+\alpha_t\eta_t^2-\gamma\eta_s\eta_t\mathrm{H}\}, \tag{3}$$

$$\mathcal{F}_0=V(\alpha_s\Delta_s^2+\alpha_t\Delta_t^2-\gamma\Delta_s\Delta_t\mathrm{H}), \tag{4}$$

where $\mathcal{F}_0$ is the free energy in the mean-field approach.

The susceptibility is defined within the framework of the self-consistent field framework as

$$\chi_{SC}=-\frac{1}{V}\frac{\partial^2\mathcal{F}_0}{\partial H^2}, \tag{5}$$

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where the order parameters $\Delta_s$ and $\Delta_t$ in (5) satisfy the self-consistency equations

$$\alpha_s\Delta_s={}^1/_2\gamma\Delta_t H, \quad \alpha_t\Delta_t={}^1/_2\gamma\Delta_s H. \tag{6}$$

The system (6) has at $T>T_s(T_s>T_t)$ only the trivial solution $\Delta_s=\Delta_t=0$, so that according to (5) $\chi_{SC}\equiv 0$. Thus, the susceptibility at $T>T_s$ turns out to be zero in the mean-field approximation.

We calculate now the fluctuation part of the susceptibility. Expanding the order parameters $\eta_s$ and $\eta_t$ in Fourier series, we have

$$\eta_s(\mathbf{r})=\frac{1}{V^{1/2}}\sum_{\mathbf{k}}\eta_{s\mathbf{k}}e^{i\mathbf{k}\mathbf{r}},$$
$$\eta_t(\mathbf{r})=\frac{1}{V^{1/2}}\sum_{\mathbf{k}}\eta_{t\mathbf{k}}e^{i\mathbf{k}\mathbf{r}}.$$

The effective Hamiltonian (3) then takes the form

$$H_{\text{eff}}=\sum_{\mathbf{k}}\{(g\mathbf{k}^2+\alpha_s)|\eta_{s\mathbf{k}}|^2+(g\mathbf{k}^2+\alpha_t)|\eta_{t\mathbf{k}}|^2-\gamma\mathbf{H}(\eta_{s\mathbf{k}}\eta_{t-\mathbf{k}}+\eta_{s-\mathbf{k}}\eta_{t\mathbf{k}})\}; \tag{7}$$

$H_{\text{eff}}$ in (7) is diagonalized by the transformation

$$\eta_{s\mathbf{k}}=u_{\mathbf{k}}\eta_{s\mathbf{k}}'+v_{\mathbf{k}}\eta_{t-\mathbf{k}}', \quad \eta_{t\mathbf{k}}=u_{\mathbf{k}}\eta_{t\mathbf{k}}'-v_{\mathbf{k}}\eta_{s-\mathbf{k}}', \tag{8}$$

where

$$u_{\mathbf{k}}^2,\ v_{\mathbf{k}}^2={}^1/_2(1\pm\Omega_-/(\Omega_-^2+\gamma^2H^2)^{1/2}), \quad \Omega_-=\alpha_s-\alpha_t.$$

The fluctuation contribution to the free energy is defined by the relation

$$\mathcal{F}=-TV\ln\left\{\int\exp\left(-\frac{H_{\text{eff}}'}{T}\right)D\left(\frac{\eta_s,\eta_t}{\eta_s',\eta_t'}\right)d\{\eta_{s\mathbf{k}}'\}d\{\eta_{t\mathbf{k}}'\}\right\}, \tag{9}$$

where $D$ is the Jacobian of the transition from the old variables $\eta_{s\mathbf{k}}$ and $\eta_{t\mathbf{k}}$ to the new ones $\eta_{s\mathbf{k}}'$ and $\eta_{t\mathbf{k}}'$, and

$$H_{\text{eff}}'=\sum_{\mathbf{k}}\{\Omega_s^2(\mathbf{k})|\eta_{s\mathbf{k}}'|^2+\Omega_t^2(\mathbf{k})|\eta_{t\mathbf{k}}'|^2\},$$
$$\Omega_{s,t}(\mathbf{k})=g\mathbf{k}^2+{}^1/_2(\alpha_s+\alpha_t)\pm{}^1/_2(\Omega_-^2+\gamma^2H^2)^{1/2}. \tag{10}$$

Carrying out a continual integration in (9), we get

$$\mathcal{F}=-TV\sum_{\mathbf{k}}\ln\frac{\pi T}{[(g\mathbf{k}^2+\alpha_s)(g\mathbf{k}^2+\alpha_t)-\gamma^2H^2/4]^{1/2}}. \tag{11}$$

As a result we obtain the fluctuating susceptibility per unit volume

$$\chi_{fl}=-\frac{1}{V}\frac{\partial^2\mathcal{F}}{\partial H^2}=\frac{T\gamma^2}{4}\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{1}{(g\mathbf{k}^2+\alpha_s)(g\mathbf{k}^2+\alpha_t)}. \tag{12}$$

We ultimately have

$$\chi_{fl}=\frac{T\gamma^2}{16\pi(g^3a)^{1/2}}\frac{1}{(T-T_s)^{1/2}+(T-T_t)^{1/2}}. \tag{13}$$

It is seen from this expression that when $T_s$ is approached from above the fluctuation susceptibility has a square-root growth, but remains finite at $T_s$. The growth of $\chi_{fl}$ is due to the fact that the fluctuations of the singlet order parameters increase near the temperature of the structural transition. This fluctuation by itself does not lead to an increase of $\chi_{fl}$, since the parameter $\Delta_s$ is not conjugate to the field H. It is the connection between the fluctuations of $\Delta_s$ and the fluctuations of $\Delta_t$ ($\Delta_t$ is conjugate to the field H), however, which lead to the increase of $\chi_{fl}$.

It if of interest to estimate the restrictions on the coefficients of the free-energy functional in (1) that make the contribution from the unaccounted-for terms of fourth order in $\Delta_s$ and $\Delta_t$ small. We obtain the estimate by perturbation theory.

We have the following correction to the free energy:

$$\delta\mathcal{F}=V\left\{\int\exp\left(-\frac{H_{\text{eff}}}{T}\right)\left\{\frac{\beta_1}{2}\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0}(\eta_{s\mathbf{k}_1}\eta_{s\mathbf{k}_2}\eta_{s\mathbf{k}_3}\eta_{s\mathbf{k}_4}\right.\right.$$
$$+(\eta_{t\mathbf{k}_1}\eta_{t\mathbf{k}_2})(\eta_{t\mathbf{k}_3}\eta_{t\mathbf{k}_4}))+\beta_2\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0}\eta_{s\mathbf{k}_1}\eta_{s\mathbf{k}_2}\eta_{t\mathbf{k}_3}\eta_{t\mathbf{k}_4}\Big\}$$
$$\left.\times d\{\eta_{s\mathbf{k}}\}d\{\eta_{t\mathbf{k}}\}\right\}\left\{\int\exp\left(-\frac{H_{\text{eff}}}{T}\right)d\{\eta_{s\mathbf{k}}\}d\{\eta_{t\mathbf{k}}\}\right\}^{-1}. \tag{14}$$

It is convenient to use in the calculations the formula

$$\int\exp\left(-\frac{H_{\text{eff}}}{T}\right)\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0}\eta_{s\mathbf{k}_1}\eta_{s\mathbf{k}_2}\eta_{s\mathbf{k}_3}\eta_{s\mathbf{k}_4}=T^4\frac{\partial}{\partial\lambda_{\mathbf{k}_1}}\frac{\partial}{\partial\lambda_{\mathbf{k}_2}}\frac{\partial}{\partial\lambda_{\mathbf{k}_3}}\frac{\partial}{\partial\lambda_{\mathbf{k}_4}}$$
$$\times\int\exp\left\{-\frac{1}{T}\left(H_{\text{eff}}+\sum_{\mathbf{k}}\lambda_{\mathbf{k}}\eta_{s\mathbf{k}}\right)\right\}d\{\eta_{s\mathbf{k}}\}d\{\eta_{t\mathbf{k}}\}, \tag{15}$$

and put in the final formulas $\lambda_{\mathbf{k}_i}=0$. We proceed analogously also with the other terms of (14). After some calculations we obtain the susceptibility correction obtained above in the Gaussian approximation:

$$\delta\chi_{fl}=-\frac{1}{V}\frac{\partial^2\delta\mathcal{F}}{\partial H^2}=-\frac{\beta_2T^2\gamma^2}{(16\pi)^2g^3a}\left(\frac{1}{(T-T_s)^{1/2}+(T-T_t)^{1/2}}\right)^2. \tag{16}$$

The requirement that $\delta\chi_{fl}$ be small compared with $\chi_{fl}$ ($\delta\chi_{fl}\ll\chi_{fl}$) yields

$$(T_s-T_t)/T_s\gg\beta_2^2T_s/(16\pi)^2g^3a, \tag{17}$$

i.e., the temperatures $T_s$ and $T_t$ must note be too close. We shall use hereafter the Landau expansion in $\Delta_s$ and $\Delta_t$ also below the Curie point, so that we must stipulate $(T_s-T_t)/T_s\ll 1$. This calls for satisfaction of the following condition:

$$\beta_2^2T_s/(16\pi)^2g^3a\ll 1. \tag{18}$$

We call attention to the fact that at $\beta_2>0$ the correction $\delta\chi_{fl}$ is diamagnetic. The reason is that at $\beta_2>0$ the Curie point, at which the parameter $\Delta_t$ arises and with it the ferromagnetism, is shifted by the structural transition towards lower temperatures[6] $T_C>T_t$. Therefore the fluctuations of the triplet order parameter are somewhat suppressed by their interaction with the fluctuations of $\Delta_s$ (this interaction is described by the term $\beta_2\Delta_s^2\Delta_t^2$). At $\beta_2<0$ the Curie temperature $T_C$ in the presence of CDW is higher than $T_t$, i.e., the fluctuations of $\Delta_s$ and $\Delta_t$ enhance rather than suppress each other. At $\beta_2<0$ the correction $\Delta\chi_{fl}$ has therefore the same sign as $\chi_{fl}$.

We proceed now to calculate the susceptibility in the temperature interval $T_C<T<T_s$. We obtain first the susceptibility in the mean-field approach. To this end we must calculate the following integral by the saddle-point method:

$$\exp(-\mathcal{F}/T)=\int\exp\{-\mathcal{F}(\Delta_s,\Delta_t,\mathbf{H})/T\}. \tag{19}$$

Calculating the integral (19) by the saddle-point method near the equilibrium values of $\Delta_s$ and $\Delta_t$ in an external field, we get

$$\exp(-\mathcal{F}/T)=\exp(-\mathcal{F}_0/T)\int\exp(-H_{\text{eff}}/T)d\{\eta_s\}d\{\eta_t\}, \tag{20}$$

where the contribution to the free energy is, within the mean-field framework,

$$\mathcal{F}_0=V(-|\alpha_s|\Delta_s^2+{}^1/_2\beta_1\Delta_s^4+\beta_2\Delta_s^2\Delta_t^2+\alpha_t\Delta_t^2-\gamma\Delta_s\Delta_t H), \quad (21)$$

with $\Delta_s$ and $\Delta_t$ in (20) satisfying the following self-consistency equations that determine the saddle point from the order parameters $\Delta_s$ and $\Delta_t$:

$$-|\alpha_s|\Delta_s+\beta_1\Delta_s^3={}^1/_2\gamma\Delta_t H, \quad \alpha_t\Delta_t+\beta_2\Delta_s^2\Delta_t={}^1/_2\gamma\Delta_s H. \quad (22)$$

Taking (20) and (21) into account, we obtain the magnetic susceptibility in the self-consistent-field approximation:

$$\chi_{SC}=-\frac{1}{V}\frac{\partial^2\mathcal{F}_0}{\partial H^2}=\frac{\gamma^2}{2}\frac{\Delta_{s0}^2}{\alpha_t+\beta_2\Delta_{s0}^2}. \quad (23)$$

Recognizing that $\Delta_{s0}^2=|\alpha_s|/\beta_1$, we get

$$\chi_{SC}=\frac{\gamma^2}{2(\beta_1-\beta_2)}\frac{T_s-T}{T-T_C}, \quad (24)$$

and the Curie temperature is defined by the condition

$$\bar{\alpha}_t=\alpha_t+\beta_2\Delta_{s0}^2=0. \quad (25)$$

It is seen from (24) that $\chi_{SC}$ vanishes at $T=T_s$. This is easily understood if it is recognized that at $T_C<T<T_s$ the system feels the magnetic field to the extent that $\Delta_s$ and $\Delta_t$ differ simultaneously from zero, and the triplet order parameter appears in the system only because it is induced by the field against the background of $\Delta_s$. At $\Delta_s=0$ the triplet order parameter therefore vanishes, and with it also the susceptibility $\chi_{SC}$. At the Curie point, $\chi_{SC}$ diverges in accord with the Curie-Weiss law. We note that the Curie-Weiss behavior of the susceptibility appears only below the structural-transition temperature. It is precisely this behavior that is observed experimentally[8] in the compound $GaMo_5S_6$.

We obtain now the fluctuation correction to the susceptibility $\chi_{SC}$. To this end we must calculate the integral in (20), which contains the following effective Hamiltonian:

$$H_{\text{eff}}=\int d\mathbf{r}\{g(\nabla\eta_s)^2-|\alpha_s|\eta_s^2+3\beta_1\Delta_s^2\eta_s^2+\beta_2\Delta_t^2\eta_s^2+g(\nabla\eta_t)^2+\alpha_t\eta_t^2+\beta_2\Delta_s^2\eta_t^2+4\beta_2\Delta_s\Delta_t\eta_s\eta_t-\gamma\eta_s\eta_t H\}, \quad (26)$$

where $\Delta_s$ and $\Delta_t$ in $H_{\text{eff}}$ satisfy Eqs. (22) that define the saddle point with respect to $\Delta_s$ and $\Delta_t$ in an external field. The quantities $\eta_s$ and $\eta_t$ in (26) are the deviations from the mean values of the order parameters $\Delta_s$ and $\Delta_t$. After calculating the integral in (20) we obtain the fluctuation contribution to the free energy, and by differentiating twice we then obtain

$$\chi_{\text{fl}}=\frac{T\gamma^2}{4}\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{1}{(g\mathbf{k}^2+2|\alpha_s|)(g\mathbf{k}^2+\bar{\alpha}_t)}. \quad (27)$$

We note that when the fluctuation increment to the free energy is differentiated with respect to H the dependence of $\Delta_s$ and $\Delta_t$ on the field need not be taken into account, inasmuch as in the Gaussian approximation this would be an exaggeration of the accuracy of the calculation of the fluctuation corrections. We ultimately have

$$\chi_{\text{fl}}=\frac{T\gamma^2}{16\pi(g^3a)^{1/2}}\left[(2(T_s-T))^{1/2}+(T-T_C)^{1/2}\left(\frac{\beta_1-\beta_2}{\beta_1}\right)^{1/2}\right]^{-1}. \quad (28)$$

At the structural transition point, the total susceptibility is a continuous function of the temperature. However, as follows from (13), (24), (25), and (38), at $T=T_s$ the susceptibility has a break. At the Curie temperature, $\chi_{fl}$ is also finite, therefore near $T_C$ the susceptibility obtained in the mean-field approximation always exceeds $\chi_{fl}$. Near the structural transition, owing to the vanishing of $\chi_{SC}$, this is no longer the case.

We determine now the criteria for the smallness of the corrections to the susceptibility $\chi_{SC}$ near $T_s$. The condition

$$\chi_{\text{fl}}\gg\chi_{\text{fl}} \quad (29)$$

yields, with allowance for (24) and (38),

$$\frac{T_s-T}{T_s}\gg\frac{1}{8\pi}\left(\frac{T_s\beta_1^2}{g^3a}\right)^{1/2}\left(\frac{T_s-T_t}{T_s}\right)^{1/2}. \quad (30)$$

In the region where the Landau expansion is valid, we have the inequality derived by Levanyuk and Ginzburg[9]:

$$T_s\beta_1^2/g^3a\ll 1. \quad (31)$$

Thus, as follows from (30), the fluctuation corrections to the susceptibility are small if the temperature is not too close to $T_s$. We call attention also to one circumstance. In the scheme were the order parameter is the magnetization M and the expansion of the free energy takes the form $\mathcal{F}=\alpha\mathbf{M}^2-\mathbf{MH}$ (at $T>T_C$), it is easy to verify that the fluctuation component of the susceptibility is zero in the Gaussian approximation. The self-consistent part is not equal to zero and $\chi_{fl}\sim 1/(T-T_C)$.

4. We proceed now to calculate the susceptibility at $T<T_C$. After calculating the integral in (19) by the saddle-point method we obtain

$$\exp(-\mathcal{F}/T)=\exp(-\mathcal{F}_0/T)\int\exp(-H_{\text{eff}}/T)\,d\{\eta_s\}\,d\{\eta_t\}, \quad (32)$$

where

$$\mathcal{F}_0=V(-|\alpha_s|\Delta_s^2+{}^1/_2\beta_1\Delta_s^4+\beta_2\Delta_s^2\Delta_t^2-|\alpha_t|\Delta_t^2+{}^1/_2\beta_1\Delta_t^4-\gamma\Delta_s\Delta_t H). \quad (33)$$

The saddle point with respect to $\Delta_s$ and $\Delta_t$ is determined by the self-consistency conditions

$$\begin{aligned}&-|\alpha_s|\Delta_s+\beta_1\Delta_s^3+\beta_2\Delta_t^2\Delta_s={}^1/_2\gamma\Delta_t H,\\ &-|\alpha_t|\Delta_t+\beta_1\Delta_t^3\Delta_t+\beta_2\Delta_s^2\Delta_t={}^1/_2\gamma\Delta_s H.\end{aligned} \quad (34)$$

We assume here that $\mathbf{H}\parallel\Delta_t$. In this case it is more convenient to determine the susceptibility from the relation

$$\chi_{SC}=\partial\mathbf{M}/\partial\mathbf{H}, \quad (35)$$

where $\mathbf{M}=\gamma\Delta_s\Delta_t$. In weak fields we have

$$\chi_{SC}=\gamma\left\{\left(\frac{d\Delta_s}{dH}\right)_{H=0}\Delta_t+\left(\frac{d\Delta_t}{dH}\right)_{H=0}\Delta_s\right\}. \quad (36)$$

Differentiating the self-consistency equations (34) with respect to H, we obtain $d\Delta_t/d\mathbf{H}$ and $d\Delta_t/d\mathbf{H}$. Substituting the result in (36) we have

$$\chi_{SC}=\frac{\gamma^2}{4}\left\{\frac{\beta_1\Delta_{t0}^2-\beta_2\Delta_{s0}^2}{\Delta_{s0}^2}+\frac{\beta_1\Delta_{s0}^2-\beta_2\Delta_{t0}^2}{\Delta_{t0}^2}\right\}\Big/(\beta_1^2-\beta_2^2). \quad (37)$$

The equilibrium values of the order parameter in the absence of a field and at $T<T_C$ are given by

$$\Delta_{s0}^2=|\alpha_s|/\beta_1-\beta_2\Delta_{t0}^2/\beta_1,$$
$$\Delta_{t0}^2=(|\alpha_t|\beta_1-|\alpha_s|\beta_2)/(\beta_1^2-\beta_2^2),$$

with $\Delta_{t0}^2\sim(T_C-T)$, near the Curie point, while $\Delta_{s0}^2$ has at $T=T_C$ a finite nonzero value.

Separating the divergent part of $\chi_{SC}$, we have

$$\chi_{SC}=\frac{\gamma^2\beta_1\Delta_{s0}^2\Delta_{t0}^{-2}}{4(\beta_1^2-\beta_2^2)}=\frac{\gamma^2}{4(\beta_1-\beta_2)}\frac{T_s-T_C}{T_C-T}, \tag{40}$$

i.e., $\chi_{SC}$ diverges in accord with the Curie-Weiss law. We note that $\chi_{SC}>0$ at $\beta_1>\beta_2$ ($\beta_1$ is always positive). It is precisely this condition which is necessary for the expansion of the free energy in (1) to be valid. At $\beta_1 \approx \beta_2$ it is necessary to retain in (1) the terms of next order in $\Delta_s$ and $\Delta_t$. From a comparison (24) and (40) it follows that the "rule of two" for the susceptibility, which holds within the framework of the functional $\mathcal{F}=\alpha\mathbf{M}^2+\frac{1}{2}\beta\mathbf{M}^4-\mathbf{MH}$, is valid here, too.

We stipulate one circumstance. Strictly speaking, below $T_s$ we can in principle express the free energy in terms of the magnetization $\mathbf{M}=\gamma\Delta_s\Delta_t$ but in this form the expression for the free energy is more complicated and less convenient for the calculations. In addition, the coefficients of such a functional (if $T_s$ and $T_C$ are close) are irregular functions of the temperature. Above $T_s$, on the other hand, the free-energy functional can in principle not be expressed in terms of the magnetization parameter. Therefore the expression for the free energy would take a different form above and below $T_s$. On the other hand, the free-energy functional in the form (1) is valid in the entire temperature interval of interest to us. In essence it is precisely this fact which is kept in mind when it is stated that the magnetization is not a true order parameter.

To determine the fluctuation correction to the susceptibility it is necessary to calculate the integral in (32) with the following effective Hamiltonian:

$$H_{\text{eff}}=\int dr\{g(\nabla\eta_s)^2-|\alpha_s|\eta_s^2+3\beta_1\Delta_{s0}^2\eta_s^2+\beta_2\Delta_{t0}^2\eta_s^2$$
$$+4\beta_2\Delta_{s0}\Delta_{t0}\eta_t\eta_s+g(\nabla\eta_t)^2-|\alpha_t|\eta_t^2+3\beta_1\Delta_{t0}^2\eta_t^2+\beta_2\Delta_{s0}^2\eta_t^2-\gamma\eta_s\eta_t\mathbf{H}\}. \tag{41}$$

As already mentioned, the dependence of the equilibrium values on $\Delta_s$ and $\Delta_t$ on the field need not be taken into account in $H_{eff}$. Taking into account the self-consistency equations at $\mathbf{H}=0$

$$-|\alpha_s|+\beta_1\Delta_{s0}^2+\beta_2\Delta_{t0}^2=0, \quad -|\alpha_t|+\beta_1\Delta_{t0}^2+\beta_2\Delta_{s0}^2=0, \tag{42}$$

$H_{eff}$ takes the form

$$H_{\text{eff}}=\int dr\{g(\nabla\eta_s)^2+2\tilde{\alpha}_s\eta_s^2+g(\nabla\eta_t)^2+2\tilde{\alpha}_t\eta_t^2+4\beta_2\Delta_{s0}\Delta_{t0}\eta_t\eta_s-\gamma\eta_s\eta_t\mathbf{H}\}, \tag{43}$$

where $2\tilde{\alpha}_{s,t}=2\beta_1\Delta_{s,t0}^2$. As a result we obtain the fluctuation correction to the susceptibility

$$\chi_n=\frac{T\gamma^2}{16\pi g^{3/2}}\frac{1}{(2\tilde{\alpha}_s)^{1/2}+(2\tilde{\alpha}_t)^{1/2}}+\frac{T\gamma^2\beta_1^2\Delta_{s0}^2\Delta_{t0}^2}{16\pi g^{3/2}\lambda}\left(\frac{1}{\alpha_+}+\frac{1}{\alpha_-}\right); \tag{44}$$

we have introduced here the notation

$$\alpha_\pm=\{\tilde{\alpha}_s+\tilde{\alpha}_t\pm[(\tilde{\alpha}_s+\tilde{\alpha}_t)^2-4\beta_2^2\Delta_{s0}^2\Delta_{t0}^2]^{1/2}\}^{1/2},$$
$$\lambda=(\tilde{\alpha}_s+\tilde{\alpha}_t)^2-4\beta_2^2\Delta_{s0}^2\Delta_{t0}^2.$$

We note that the condition $\beta_1>\beta_2$ again ensures that is real. The second term of (44) vanishes at $T=T_C$; at the Curie point we have

$$\chi_n=\frac{T_C\gamma^2}{16\pi(g^3a)^{1/2}}\frac{1}{\{2(T_s-T_C)\}^{1/2}}; \tag{45}$$

the fluctuation component is thus finite and continuous at the Curie point. The continuity follows from (28) and (45).[2)]

The qualitative form of the temperature dependence of the magnetic susceptibility $\chi$ is shown in Fig. 1. The total susceptibility is shown by the solid line. The dash-dot line shows the susceptibility in the self-consistent field approximation, and the dashed line shows the fluctuation component.

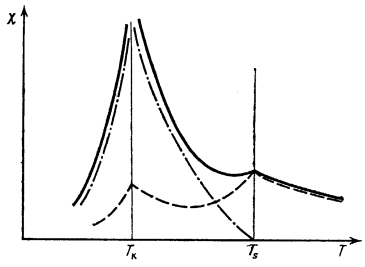


FIG. 1. Temperature dependence of the magnetic susceptibility.

We note here that at the structural-transition point the susceptibility has a break.

## 3. COLLECTIVE-EXCITATION SPECTRUM

1. We consider now the collective excitations in an excitonic ferromagnet. In fact, it is the fluctuations of these mode which contribute to the fluctuation susceptibility. We calculate first the collective-excitation spectrum below the Curie point. At $T<T_C$ the magnetic moment can oscillate with constant amplitude. Such a motion is described by the Bloch equations[10]

$$\partial\mathbf{M}/\partial t=[\Omega\times\mathbf{M}]. \tag{46}$$

We determine the value of $\Omega$ by a known method.[10] This calls for finding the change of the free energy following a small change of the order parameters:

$$\delta\mathcal{F}=-\int H_1\delta\Delta_s dr-\int\mathbf{H}_2\delta\Delta_t dr. \tag{47}$$

At large wavelengths and low temperatures, the energy dissipation in collective motions with conservation of the magnetic moment is small and can be neglected.

The energy dissipation as the magnetization varies with time is given by

$$Q=T\frac{\partial S}{\partial t}=-\frac{\partial\delta\mathcal{F}}{\partial t}, \tag{48}$$

where $S$ is the entropy of the system. Recognizing that $\mathbf{M}=\gamma\Delta_s\Delta_t$ and using (46)–(48) we get

$$Q=T\frac{\partial S}{\partial t}=\int\left(\frac{H_1\Delta_s-\mathbf{H}_2\Delta_t}{\Delta_s}\right)\frac{\partial\Delta_s}{\partial t}dr+\int\mathbf{H}_2[\Omega\times\Delta_t]dr. \tag{49}$$

The condition $\partial S/\partial t=0$ that there be no dissipation leads to the relations

$$\partial\Delta_s/\partial t=0, \quad \overline{\Omega}=\text{const}\,\mathbf{H}_2. \tag{50}$$

To determine the effective field $\mathbf{H}_2$ we calculate the variation of the free energy (1) with respect to $\Delta_t$ and, omitting terms parallel to $\Delta_t$ in $\mathbf{H}_2$ (since they drop out of the equation (46) on account of the vector product with $\Delta_t$), we get

$$\mathbf{H}_2=2g\nabla^2\Delta_t+\gamma\Delta_{s0}\mathbf{H}. \tag{51}$$

Taking (46) and (49)–(51) into account we have

$$\partial\mathbf{M}/\partial t=\text{const}\,\gamma\Delta_{s0}[2g\nabla^2\Delta_t+\gamma\Delta_{s0}\mathbf{H},\Delta_t]. \tag{52}$$

If account is taken of only exchange interactions that are independent of the direction of the magnetic moment, the equation of motion (52) for a uniformly magnetized body should reduce to the equation of motion of a freely precessing moment[10]:

$$\frac{\partial \mathbf{M}}{\partial t}=\frac{|e|}{mc}[\mathbf{H}\times\mathbf{M}]. \tag{53}$$

From a comparison of relations (52) (at $\nabla^2\Delta_t=0$) and (53) we obtain the constant coefficient in (53):

$$\text{const}=|e|/mc\gamma\Delta_{s0}; \tag{54}$$

here $\Delta_{s0}$ is the equilibrium value of the singlet order parameter. The final equation of motion (at $H=0$) takes the form

$$\frac{\partial \Delta_t}{\partial t}=\frac{2|e|g}{mc\gamma\Delta_{s0}}[\nabla^2\Delta_t\times\Delta_t]. \tag{55}$$

We seek the solution of (55) in the form $\Delta_t=\Delta_{t0}+\mathbf{m}e^{i(\mathbf{kr}-\omega t)}$ (with $|\mathbf{m}|\ll\Delta_{t0}$ and $\Delta_{t0}\parallel Z$). We obtain

$$\begin{aligned} i\omega m_x&=\frac{2|e|g\Delta_{t0}}{mc\gamma\Delta_{s0}}\mathbf{k}^2m_y,\\ i\omega m_y&=-\frac{2|e|g\Delta_{t0}}{mc\gamma\Delta_{s0}}\mathbf{k}^2m_x. \end{aligned} \tag{56}$$

The condition for the existence of a solution of (56) determines the magnon spectrum: we have

$$\omega=\frac{2|e|g\Delta_{t0}}{mc\gamma\Delta_{s0}}\mathbf{k}^2. \tag{57}$$

The magnon spectrum turns out to be quadratic in the momentum, just as in an ordinary ferromagnet.[10] The magnetization rotates in this case in the $(x, y)$ plane. We note that the temperature dependence of the frequency is given by

$$\omega\sim\left(\frac{T_C-T}{T_s-T}\right)^{1/2}$$

[since $\Delta_{s0}\sim(T_s-T)^{1/2}$, $\Delta_{t0}\sim(T_C-T)^{1/2}$], whereas in an ordinary ferromagnet $\omega\sim(T_C-T)^{1/2}$. At the given collective motion, no changes take place in the singlet order parameter, i.e., there is no change in the electron density and hence in the lattice deformation.

2. We determine now the spectrum of the collective modes that lead to changes of the electron density and of the magnetic moment.[3)] When calculating the spectrum of the collective motion it is necessary to solve the equations for the order parameter, with the free-energy functional serving as the potential energy. In the case of small deviations of the order parameter from the equilibrium values it suffices to use the expansion of the free energy at the extremum point, accurate to the quadratic terms.

Taking (1) into account, we have the equations of motion for the moduli of the order parameters (more accurately, for deviations from the equilibrium values at $T<T_C$):

$$\begin{aligned} M_s(\mathbf{k})\ddot{\eta}_s+V(4\beta_1\Delta_{s0}^2\eta_s+2g\mathbf{k}^2\eta_s+4\beta_2\Delta_{s0}\Delta_{t0}\eta_t)=0,\\ M_t\ddot{\eta}_t+V(4\beta_1\Delta_{t0}^2\eta_t+2g\mathbf{k}^2\eta_t+4\beta_2\Delta_{s0}\Delta_{t0}\eta_s)=0. \end{aligned} \tag{58}$$

Here $V$ is the volume of the system, $M_s(\mathbf{k})$ and $M_t$ are certain effective masses, and $\Delta_{s0}$ and $\Delta_{t0}$ are the equilibrium values of the order parameters from (38) and (39).

We make one remark concerning the masses $M_s(\mathbf{k})$ and $M_t$. The mass $M$ is in fact the mass of the triplet exciton. The situation with the mass $M_s(\mathbf{k})$ is more complicated. Since the dispersion curve of the spectrum of the excitations of the singlet exciton crosses the optical-phonon branch, entanglement of the spectrum of the excitations of the singlet exciton and of the phonon of the unstable mode take place. As a result static distortions $\langle u\rangle$ of the lattice arise[12] in proportion to $\Delta_s$ ($\langle u\rangle\sim g_{ph}^2\Delta_s$, $\langle u\rangle$ is the static deformation of the lattice, and $g_{ph}$ is the electron-phonon interaction constant). The term crossings cause also the effective mass $M_s(\mathbf{k})$ to become dependent on k. If, for example, the decay of the phonon mode occurs at $\mathbf{k}=0$, then $M_s(\mathbf{k})$ at small k becomes approximately equal to the mass of the singlet exciton, and at large k (on the order of the reciprocal-lattice vector) $M_s(\mathbf{k})$ almost coincides with the ion mass. Since we are interested in small $k$, we put henceforth $M_s(\mathbf{k})\cong M_s$ ($M_s$ is the mass of the singlet exciton).[4)]

From the system (58) we obtain the spectrum of the collective-mode excitations:

$$\begin{aligned} \omega_{s,t}(\mathbf{k})=(2V)^{1/2}\Big\{&\frac{g\mathbf{k}^2}{2M_+}+\beta_1\left(\frac{\Delta_{s0}^2}{M_s}+\frac{\Delta_{t0}^2}{M_t}\right)\\ &\pm\left[\left(\frac{g\mathbf{k}^2}{2M_+}+\beta_1\left(\frac{\Delta_{s0}^2}{M_s}+\frac{\Delta_{t0}^2}{M_t}\right)\right)^2-4\frac{\beta_2^2\Delta_{s0}^2\Delta_{t0}^2}{M_sM_t}\right]^{1/2}\Big\}^{1/2}; \end{aligned} \tag{59}$$

here $1/M_+=1/M_s+1/M_t$. The condition $\beta_1>\beta_2$ discussed above ensures that the frequencies of the collective excitations are real.

At temperatures $T_C<T<T_s$ we have

$$\begin{aligned} \omega_s(\mathbf{k})&=2V^{1/2}\left(\frac{a(T_s-T)}{M_s}+\frac{g\mathbf{k}^2}{2M_s}\right)^{1/2},\\ \omega_t(\mathbf{k})&=V^{1/2}\left(\frac{a(T-T_C)}{M_t}+\frac{g\mathbf{k}^2}{2M_t}\right)^{1/2}. \end{aligned} \tag{60}$$

Finally, at $T>T$ and $T>T_C$ we get

$$\begin{aligned} \omega_s(\mathbf{k})&=V^{1/2}\left(\frac{a(T-T_s)}{M_s}+\frac{g\mathbf{k}^2}{2M_s}\right)^{1/2},\\ \omega_t(\mathbf{k})&=V^{1/2}\left(\frac{a(T-T_t)}{M_t}+\frac{g\mathbf{k}^2}{2M_t}\right)^{1/2}. \end{aligned} \tag{61}$$

To obtain the excitation spectrum in the temperature intervals $T>T_{s,C}$ and $T_C<T<T_s$ we must solve equations similar to (58), where the potential energy is replaced by the expansion of the free energy in the corresponding temperature regions.

Thus, there are two more longitudinal collective-excitation modes. One of them, $\omega_s(\mathbf{k})$ (at $T>T_C$) has the meaning of the excitation energy of the singlet exciton, i.e., of the oscillation of the electron density. Connected with the oscillations of the electron density are the oscillations of the phonon subsystem, since $\langle u\rangle\sim g_{ph}^2\Delta_s\sim\omega_s$. The frequency $\omega(\mathbf{k})$ pertains (at $T>T_C$) to the excitation spectrum of the triplet exciton, i.e., to the oscillations of the electron spin (this is not accompanied by lattice deformation). Below the Curie point, the changes of the electron subsystems (and the associated lattice vibrations) and the oscillations of the magnetization turn out to be related. The connection between the phonon and magnetic subsystems do not have a relativistic small quantity in this model. We note also that the triplet order parameter $\Delta_t$ is a vec-

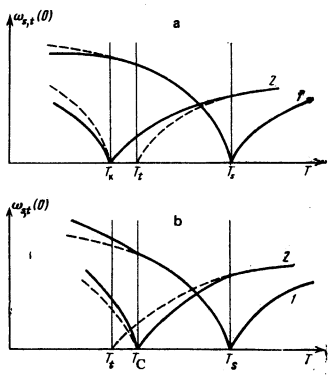


FIG. 2. Temperature dependences of the collective excitation frequencies: a) $\beta_2 > 0$, b) $\beta_2 < 0$.

tor spin quantity, so that three oscillations modes are possible with different orientations of the spin of the triplet exciton.

Figure 2 shows the temperature dependences of the frequencies of the collective modes at $k=0$ for the cases $\beta_2 > 0$ and $\beta_2 < 0$. Curves 1 and 2 at $T > T_C$ pertain to the excitation spectrum of the singlet and triplet excitons, respectively. At $T < T_C$, as already mentioned there are two coupled electron-magnon (phonon-magnon) modes. The excitation spectrum, as seen from Fig. 2, becomes acoustic only at the point of the structural transition, and for the triplet exciton at the Curie point. At the temperatures of the structural and ferromagnetic transitions the temperature dependences of the collective modes have breaks. The dashed lines show the plots of the frequencies for the independent excitation modes of the singlet and triplet excitons.

## 4. DISCUSSION OF THE RESULTS

We now compare qualitatively our results with the experimental data. The closest to the considered model are the compounds $ZrZn_2$ and $GaMo_5S_8$. Dublon and Weger[13] discuss in their paper the experimental data obtained for $ZrZn_2$ in the paramagnetic region. They conclude from the measurements of the sound velocity, of the electric resistance,[14] and NMR[15] that CDW (i.e., structural transitions) are produced in $ZrZn_2$ at ~50 K. At $T_C \approx 28$ K (Ref. 15), $ZrZn_2$ becomes a ferromagnet with band type ferromagnetism and with a small spontaneous moment, ~0.2 Bohr magneton per cell. It appears that this compound is an example of an excitonic ferromagnet.

It follows from the measurement of the spectra of the NMR at the $^{91}Zr$ nuclei (Ref. 15) that a strong broadening of the NMR lines takes place at ~50 K. On the other hand the NMR frequency shift (the change of the effective field at the nucleus) occurs below 50 K. According to the excitonic ferromagnetism model, the NMR line broadening at $T > T_s$ can be explained in the following manner. The growth of the fluctuations of the magnetic moment at the nucleus is proportional to $\langle M^2 \rangle^{1/2} \sim \chi_{ph}$. The singularity of the fluctuation susceptibility at $T \sim T_s$ should lead to a strong broadening of the NMR line. In this model, a nonzero average magnetic moment at the nucleus (it is this moment which determines the NMR frequency shift) occurs only below $T_s$ and is proportional to $M_{av} \sim \chi_{SC} H$, therefore a change of the NMR frequency should take place only below $T_s$, in qualitative agreement with the experimental data.

Measurements of the magnetic susceptibility of $GaMo_5S_8$, performed by Alekseevskii's group,[8] show that the magnetic susceptibility has a kink at the structural transition point $T_s$ and a Curie-Weiss behavior appears only below $T_s$. These data are also in qualitative agreement with the results obtained for the reported model.

[1)] To be specific, we consider the case when the temperature at which the CDW occur is higher than that of the onset of the SDW, although the converse can also take place.

[2)] Actually, the expressions obtained for $\chi_{fl}$ in the Gaussian approximation are, of course, not valid in a narrow region near $T_s$ and $T_C$. It appears, however, that the qualitative shapes of the curves remains the same also in this region, therefore the plots of $\chi_{fl}$ are shown in Fig. 1 to be continuous in $T_s$ and $T_C$.

[3)] Within the framework of the microscopic scheme, the spectrum of the collective excitations in an excitonic ferromagnet was considered by Fetisov and Khmelinin.[11]

[4)] In Ref. 11 no account was taken of the coupling of the phonon and exciton subsystems.


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