Magnetic properties of structurally transforming ferromagnets

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A phenomenological theory of ferromagnets that undergo coupled structural and magnetic transitions is constructed which takes account of the presence of a mixed third-order invariant. It is significant that in this case the ferromagnetic properties are not connected with the critical behavior of the coefficient attached to the square of the homogeneous magnetization in the functional. The singularities that arise in the temperature dependence of the magnetic susceptibility at the structural and magnetic transition points are explained within the framework of the present theory. The dependence of the structural transition temperature on the magnetic field is predicted. A scheme describing the structural distortion and the magnetic order in the defective spinels is proposed.

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It is well known[1,2] that the defective spinels Mo_4S_8Me and Mo_4Se_8Me (where Me is the third-group element Ga or Al) undergo a ferromagnetic phase transition at low (~20 K) temperatures. Prior to this, at a higher temperature (~50 K) these materials are found to undergo a structural phase transition. Especially noteworthy is the fact that the paramagnetic susceptibility of such compounds obeys the Curie-Weiss law ($\chi^{-1} \propto T - T_{cr}$, where T_{cr} is the critical temperature of the ferromagnetic transition) only at temperatures below the structural transition temperature T_S. At higher temperatures the behavior of the paramagnetic susceptibility is not singular. It conforms to the Curie ($\chi^{-1} \propto T$), or even the Néel ($\chi^{-1} \propto T + T_C$, $T_C > 0$), law.[1-3]

If we attempt to explain why this change occurs in the law governing the temperature variation of the paramagnetic susceptibility at the structural phase transition point within the framework of models like the Heisenberg or the Stoner model,[4] then we have to make the extremely artificial assumption that the sign of the exchange interaction changes at the second-order structural phase transition point T_S.

In the exciton-ferromagnet model,[5,6] such behavior of the susceptibility finds a natural explanation, which is that the appearance of a charge density wave (CDW) at T_S leads to the decompensation of the possible fluctuations in the spin angular momentum at the various crystal-lattice sites, since these sites become nonequivalent below T_S as a result of the presence of the CDW. The ferromagnetic properties in the exciton-ferromagnet model are due to the appearance below the Curie temperature T_{cr} of a spin density wave (SDW) in phase with the CDW. As a result, the ferromagnetic order in the system of magnetic moments decompensated on account of the presence of the CDW (the magnetic moments of the nonequivalent sites are different) gives rise to a homogeneous magnetization M.

Unfortunately, the direct application of the microscopic exciton-ferromagnet model to materials of the defective-spinel type is quite questionable. This model is suitable for metals with congruent Fermi surfaces, but, judging from the experimental data,[1] the magnetic defective spinels are dielectrics. Furthermore, in the simple exciton-ferromagnet model the paramagnetic susceptibility at high temperatures has a metallic character ($\chi \sim$ const, i.e., a Pauli-type susceptibility). Experimentally, however, the Curie law ($\chi^{-1} \propto T$) is observed.

The foregoing necessitates the construction of a phenomenological model for the description of systems that undergo coupled structural and magnetic phase transitions, to which the microscopic exciton-ferromagnet model is not directly applicable. The appearance of ferromagnetism in this model has the same causes, and is due to the coexistence of SDW and CDW. The exciton ferromagnet should be regarded as a particular case of this more general phenomenological model.

Let us assume that there can arise in the system a charge-density wave $\rho(\mathbf{r})$, a spin-density wave $\mathbf{S}(\mathbf{r})$, and a homogeneous magnetization M. Then if the irreducible representation of the crystal space group according to which $\rho(\mathbf{r})$ transforms coincides with the irreducible representation according to which the scalar product $\mathbf{M} \cdot \mathbf{S}(\mathbf{r})$ transforms, it is possible to construct a mixed third-order invariant:

$$\rho(\mathbf{r})\mathbf{M}\mathbf{S}(\mathbf{r}). \tag{1}$$

This invariant should enter into the Landau functional describing the phase transition in a system that is unstable against the formation of CDW $\{\rho(\mathbf{r})\}$ and SDW $\{\mathbf{S}(\mathbf{r})\}$. The existence of such an invariant shows that the magnetic and structural transformations in the system are coupled.

Since, normally, the formation of CDW leads to structural distortions, which can be characterized by an order parameter η describing the atomic displacements, while the formation of SDW leads to the antiferromagnetic ordering of the sublattices with magnetic moment **l**, the invariant (1) can be rewritten as:

$$\eta\mathbf{M}\mathbf{l}. \tag{2}$$

Then the Landau functional assumes the form

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$$F=\alpha_s\eta^2+\alpha_l l^2+aM^2-MB-\gamma\eta Ml+F^{(4)}, \quad (3)$$

where $F^{(4)}$ denotes all the possible fourth-order invariants. Here, as usual, $\alpha_s \propto T-T_s$, $\alpha_t \propto T-T_t$, $a \propto T+T_C$ and $T_s \propto T_t \gg T_C$; the remaining coefficients are constants. The external magnetic field B is included in the functional (3) in a natural manner as the product $\mathbf{M}\cdot\mathbf{B}$. It is not difficult to notice that the two-parameter functional of the exciton ferromagnet[6] is a consequence of the three-parameter functional (3) if we eliminate from the latter the homogeneous-magnetization parameter M by minimizing F with respect to M.

From the form of the functional (3) it immediately follows that, because of the presence in it of the mixed invariant (2), the appearance in the system of CDW and SDW together leads to once to the magnetization of the system ($M\neq 0$ at $B=0$ and η, $l\neq 0$):

$$M=\frac{B}{2(a+\beta_4\eta^2)}-\frac{\beta_3(Bl)l}{2(a+\beta_4\eta^2)(a+\beta_3 l^2+\beta_4\eta^2)}+\frac{\gamma l}{2(a+\beta_3 l^2+\beta_4\eta^2)}. \quad (4)$$

This formula is obtainable from the condition, $\delta F/\delta \mathbf{M}=0$, for equilibrium when the fourth-order invariants are chosen in the simplest form:

$$F^{(4)}=\tfrac{1}{2}\beta_1(l^4+\eta^4)+\beta_2 l^2\eta^2+\beta_3(Ml)^2+\beta_4 M^2\eta^2.$$

Minimizing the function F, (3), with respect to the order parameters η and l, and using the formula (4), we easily obtain expressions for the paramagnetic susceptibility $\chi=M/B$ in different temperature regions. Thus, at temperatures above the structural and antiferromagnetic transition temperatures, T_S and T_t respectively, in the unreconstructed phase (in which $\eta=l=0$), the susceptibility

$$\chi^{-1}=2a\propto T+T_c \quad (5)$$

obeys the Curie law. If the antiferromagnet transition temperature $T_t>T_S$, and these transitions are not coupled (i.e., $\gamma=0$, $\beta_2=0$) then from the minimization conditions for the functional F we obtain the normal longitudinal ($\chi_\parallel$) and transverse ($\chi_\perp$) susceptibilities of an antiferromagnet when $T<T_t$:

$$\chi_\parallel^{-1}=2(a-\beta_3\alpha_t/\beta_1), \quad \chi_\perp^{-1}=2a. \quad (6)$$

If the structural transformation occurs earlier (i.e., if $T_S>T_t$), but the CDW and SDW are, as before, not coupled ($\gamma=0$, $\beta_2=0$), then at $T<T_s$ we have the susceptibility of a structurally distorted system:

$$\chi^{-1}=2(a-\beta_4\alpha_S/\beta_1). \quad (7)$$

Of greatest interest is the case in which the structural and antiferromagnetic transitions are coupled (i.e., in which $\gamma\neq 0$, $\beta_2\neq 0$). Let the structural-transition temperature T_S be higher than T_t. Then, in the absence of the external magnetic field B, there exist in the system in the temperature range $T_S>T>T_{cr}$ CDW with equilibrium order-parameter value given by the relation

$$\eta_0^2=-\alpha_S/\beta_1. \quad (8)$$

On account of the presence in the functional (3) of the mixed third-order invariant (2), the switching on of the magnetic field B leads immediately to the appearance in the system of a SDW (l) induced by this field. Minimizing F with respect to l in the presence of B, we easily find that

$$l=\gamma\eta B/[4a(\alpha_t+\beta_2\eta_0^2)-\gamma^2\eta_0^2]. \quad (9)$$

Therefore, according to the formulas (4) and (9), the temperature behavior of the magnetic susceptibility in the temperature range between T_S and T_{cr} is described by the expression

$$\chi=\frac{1}{2(a+\beta_4\eta_0^2)}\left[1+\frac{\gamma^2\eta_0^2}{4a(\alpha_t+\beta_2\eta_0^2)-\gamma^2\eta_0^2}\right]. \quad (10)$$

The first term in (10) is the nonsingular part of the susceptibility, while the second term diverges in paramagnetic fashion according to the Curie-Weiss law ($\chi^{-1}\propto T-T_{cr}$) at the temperature

$$T_{cr}=T_t\left[1-\left(\beta_2-\frac{\gamma^2}{2a}\right)\frac{\eta_0^2}{\alpha}\right]. \quad (11)$$

Here we have used the fact that $\alpha_t=\alpha(T-T_t)$. Thus, in the three-parameter-Landau-functional model (3), the interaction between the spin subsystem and the lattice leads to a ferromagnetic transition.

Finally, for temperatures below the Curie temperature (11) the expressions for the longitudinal and transverse susceptibilities have the form

$$\chi_\parallel=\frac{1}{2(a+\beta_3 l_0^2+\beta_4\eta_0^2)}\left[1+\frac{\gamma^2\eta_0^2}{4a(\alpha_t+\beta_2\eta_0^2)-\gamma^2\eta_0^2}+\frac{\gamma^2 l_0^2}{4a(\alpha_S+\beta_2 l_0^2)-\gamma^2 l_0^2}\right],$$
$$\chi_\perp=1/2(a+\beta_4\eta_0^2), \quad (12)$$

where η_0 and l_0 are the equilibrium values of the order parameters in the absence of the field B:

$$\eta_0^2=\frac{\alpha_S\beta_1-\alpha_t(\beta_2-\gamma^2/4a)}{\beta_1^2-(\beta_2-\gamma^2/4a)^2},$$
$$l_0^2=\frac{\alpha_t\beta_1-\alpha_S(\beta_2-\gamma^2/4a)}{\beta_1^2-(\beta_2-\gamma^2/4a)^2}. \quad (13)$$

Figure 1 shows the behavior of the inverse longitudinal susceptibility $\chi_\parallel^{-1}$ for a structurally-transforming magnetic system in the entire temperature range [the formulas (5), (10), and (12)]. It can be seen that the susceptibility obeys the Curie-Weiss law at temperatures below the structural-transition point and the law of "two" at temperatures below the Curie point. It is precisely such behavior of the paramagnetic susceptibility that has been observed in the defective spinels Mo_4S_8Me and Mo_4Se_8Me (Refs. 1 and 2).

As to the other anomalies in the behavior of systems described by the three-parameter functional (3), we must first of all note among them the dependence, re-

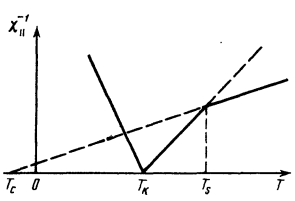

FIG. 1.

sulting from the F-minimization equations, of the structural transition temperature on the external magnetic field B. This field dependence $T_S(B)$ is given up to terms quadratic in B by the equation

$$\alpha_s\alpha_t=\gamma^2B^2/16a^2 \quad (\beta_3,\ \beta_4\ll\gamma), \tag{14}$$

whence [if $\alpha_s=\alpha(T-T_s)$, $\alpha_t=\alpha(T-T_t)$]

$$T_s(B)=T_s-\frac{T_s-T_t}{2}+\left[\frac{(T_s-T_t)^2}{4}+\frac{\gamma^2B^2}{16\alpha^2a^2}\right]^{1/2}\approx T_s+\frac{\gamma^2B^2}{16\alpha^2a^2(T_s-T_t)}. \tag{15}$$

Thus, the magnetic field should raise the structural transition temperature.

In order to use the three-parameter Landau functional (3) to describe the magnetic properties of the defective spinels, we must have information about the crystal structure of these materials in the high-temperature phase. Such information is contained in Refs. 2 and 7. In the high-temperature phase, the defective spinel Mo_4S_8Me has the cubic symmetry group T_d^2. Its unit cell contains 13 atoms and one vacancy. Experimentally, the most thoroughly studied of all such compounds is the system Mo_4S_8Ga. The structural transition at $T_S=48$ K and the ferromagnetic transition at $T_{cr}=19$ K are indicated by anomalies in the temperature dependence of the susceptibility χ and the specific heat,[3] the specific heat having at $T>T_S$ the characteristic phonon behavior ($\sim T^3$) and at $T<T_{cr}$ the characteristic magnon behavior ($\sim T^{3/2}$). A structural transition from the cubic phase into a rhombohedral phase has been identified on the basis of x-ray structural analysis data.[2] The relative nearness of the structural and magnetic transition temperatures, T_S and T_{cr}, indicates that these phase transitions are coupled.

The principal structural element of the compound Mo_4S_8Ga is the tetrahedron formed by the four Mo atoms, at the center of which is a vacancy, to which the Mo atoms are slightly displaced. This tetrahedron is a carrier of a magnetic moment whose magnitude is equal to $1.8m_B$ (m_B is the Bohr magneton) at $T>T_S$. We should expect the structural unit Mo_4 to play the decisive role in the structural and ferromagnetic transitions. Therefore, in the discussion below the remaining constituents of the compound Mo_4S_8Ga will not be considered: it is possible to separate out a sublattice whose sites are occupied by the Mo_4 groups. This sublattice is a face-centered lattice with the symmetry group T_d^2. It is convenient to represent it in the form of "atomic" layers disposed perpendicularly to the body diagonal of the cube. Within each layer, the "atoms" (the Mo_4 groups) are packed in a triangular lattice. These layers are shown in Fig. 2. It is important that all the layers in the high-temperature phase are equivalent, but that there is no center of symmetry in each of them.

Let the cause of the structural transition be the softening of the longitudinal phonon at the L point of the Brillouin zone. If the layers possessed a center of symmetry, then such a phonon would belong to the even-parity representation of the D_{3d} group at the L point. The vibrations corresponding to an unstable phonon that transforms according to an even-parity

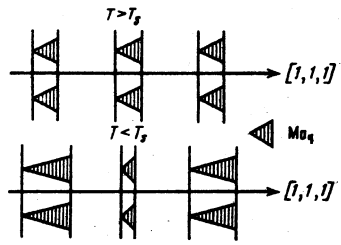

FIG. 2.

representation correspond to alternating compressions and extensions in the system of layers (if one layer is compressed, then the two nearest to it are extended). It is clear that, if the layers did not possess a finite thickness (i.e., if they were made of real atoms instead of the Mo_4 group), then there would be no even-parity phonon mode in such a system. The instability of the longitudinal phonon at the L point leads during the structural transition to a doubling in the system of layers in the [111] direction, i.e., to a transition into a rhombohedral phase with symmetry C_{3v}. The doubling in the system of layers, which corresponds to the compression of one layer and the extension of the neighboring one, makes these layers nonequivalent (see Fig. 2). Because of this, there occurs an increase in the magnetic moment of one layer and a decrease in the moment of the neighboring one: There arises an imbalance in the moments. Now the antiferromagnetic ordering of a system of such layers with the L-point wave vector at T_{cr} will result in the appearance of a homogeneous magnetization (i.e., of ferromagnetism).

In terms of the functional (3), this corresponds to the assertion that the appearance in the system of a parameter η describing a structural distortion of the lattice, and transforming according to the representation A_1 of the C_{3v} group, results in an imbalance in the magnetic moments of the layers because of the presence of the mixed invariant (2). The existence of this invariant is guaranteed by the fact that the quantity $\mathbf{M}\cdot\mathbf{l}$ also transforms according to the representation A_1 of the C_{3v} group.

The fact that the effective magnetic moment of the structural unit Mo_4 is equal to $1.8m_B$ at temperatures above T_S (Refs. 1 and 7), but is two and a half times smaller (i.e., is equal to $0.7m_B$) at $T\ll T_{cr}$ (Ref. 1) also finds a natural explanation within the framework of the expounded model. The latter quantity ($0.7m_B$) should be regarded as the difference between the moments of the two layers that results from the imbalance arising in the structural phase transition. After the structural transition the moment of one layer (e.g., the extended layer) turns out to be equal to $(1.8+0.7/2)m_B$, while the moment of the other layer (the compressed one) turns out to be equal to $(1.8-0.7/2)m_B$.

Finally, the antiferromagnetic behavior of the paramagnetic susceptibility observed in Mo_4S_8Al at temperatures above the structural transition point can also be explained naturally if the dependence $a(T)$ in the formula (5) has the form $a\propto T+T_C$ with $T_C>0$.

The symmetry-related predictions presented in the this paper are based essentially on the idea that the magnetic moment is associated with the Mo_4 clusters. This undoubtedly needs to be experimentally verified. One of such experiments could be the measurement of the local effective magnetic field acting on the molybdenum nuclei. Above T_s this field is the same for all the clusters, after the structural transition there arise two types of nonequivalent clusters and, consequently, two different effective fields, and below T_{cr} these fields begin to differ in sign. If it turns out that the magnetism is not connected with the Mo_4 cluster, other phonon modes that give rise to a structural transition into a phase with symmetry C_{3v}, and guarantee the existence of the mixed invariant (1), should be investigated.

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