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PHENOMENOLOGICAL THEORY OF THE STRUCTURAL AND MAGNETIC PHASE TRANSITIONS IN $KMnF_3$-CRYSTAL

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1. INTRODUCTION

Experimental work up to date indicates that $KMnF_3$ undergoes a series of structural and magnetic phase transitions. At room temperature $KMnF_3$ is a paramagnet with the cubic, perovskite structure; the space group is $Pm3m(O_h^1)$. At T = 186,6K it undergoes the structural phase transition to the tetragonal structure D_{4h}^{18} (I4/mcm)[1] and at T = 91.5K another structural phase transition occurs to the tetragonal structure D_{4h}^5 (P 4/mbm)[2]. At T = 88.5K $KMnF_3$ becomes antiferromagnetic with the sublattice magnetization parallel to the z-axis, and around the Curie temperature $T_C = 81.5K$ another magnetic phase transition takes place to the weak ferromagnetic phase in the plane perpendicular to the z-axis[3].

The mutual interrelation of the magnetic and structural phase transitions is evident. For instance, weak ferromagnetism is not possible in the crystal with the cubic symmetry. Although the nature of this correlation has not yet been clarified.

The phenomenological approach to this problem is presented by Izyumov et al.[4], however these authors investigate the influence of the first structural phase transition only on the magnetic one.

The microscopic model describing a complete sequence of the phase transitions observed in $KMnF_3$ is presented in [5-8].

The purpose of this paper is to re-examine the problem concerning the relation between both of the structural and magnetic phase transitions on the basis of the Landau theory.

The paper is organized as follows. In Sec.2 we construct the Landau free-energy functional for the crystal. In Sec.3 we shall discuss the occurrence and stability of the structural and magnetic phases. Further we compare some results of this paper with those obtained in [5-8].

2. FREE-ENERGY FUNCTIONAL

According to Minkiewicz et al.[1] and Hidaka[2] the structural phase transitions exhibited by $KMnF_3$ at 186.6K and 91.5K are mainly due to rotations of the Mn-F octahedra. The former phase transition is accompanied by a softening and the condensation of the $M2^+$ lattice mode (troughout this paper, the irreducible representations will be labelled in accordance with [9], and a K-site was used as the origin).

The atomic displacements are schematically illustrated in Fig.1: (a) shows one component of $R5^-$ and (b) $M2^+$ representation. The transition at 186.6K brings the F-ions to the positions shown by the arrows. The resulting tiltings of the neighbouring octahedra have the same magnitude but are in the opposite direction. In the case of the lower structural transition the tiltings of the octahedra appear in the same direction around the z-axis.

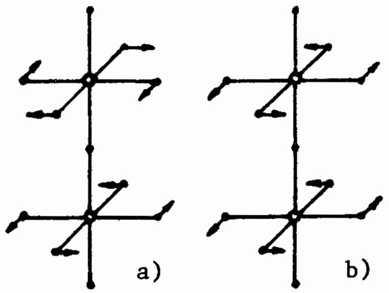


Fig.1. Directions of shifts of F-ions on MnF_6 octahedra: a) a component of $R5^-$-mode b) $M2^+$-mode.

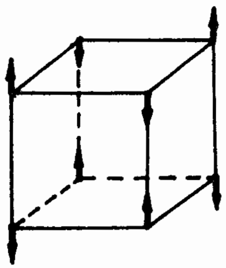


Fig.2. Spin arrangement in the antiferromagnetic region.

The magnetic structure below the transition temperature $T_N = 88K$ is of the G-type and is schematically presented in Fig.2. It belongs to the three-dimensional irreducible representation $R5^-$ of the Pm3m group.

Examining all possible second- and fourth-order invariants, which may be constructed with the use of the basis functions of the above representations, we obtain the following Landau free-energy functional

$$
\begin{aligned}
F = F_0 &+ \alpha_1\Big(\sum_{i=1}^{3} r_i^2\Big) + \beta_1\Big(\sum_{i=1}^{3} r_i^4\Big) + \gamma_1\Big(\sum_{i\neq j} r_i^2 r_j^2\Big) + \\
&+ \alpha_2\Big(\sum_{i=1}^{3} m_i^2\Big) + \beta_2\Big(\sum_{i=1}^{3} m_i^4\Big) + \gamma_2\Big(\sum_{i\neq j} m_i^2 m_j^2\Big) + \\
&+ \alpha_s\Big(\sum_{i=1}^{3} s_i^2\Big) + \beta_s\Big(\sum_{i=1}^{3} s_i^4\Big) + \gamma_s\Big(\sum_{i\neq j} s_i^2 s_j^2\Big) + \\
&+ A_1\Big(\sum_{i=1}^{3} r_i^2\Big)\Big(\sum_{i=1}^{3} m_i^2\Big) + A_2\Big(\sum_{i=1}^{3} r_i^2 m_i^2\Big) +
\end{aligned}
\qquad (1)
$$

$$+ B_1\left(\sum_{i=1}^{3} r_i^2\right)\left(\sum_{i=1}^{3} s_i^2\right) + B_2\sum_{i=1}^{3}(r_i s_i)^2 + B_3\left(\sum_{i=1}^{3} r_i^2 s_i^2\right) +$$

$$+ C_1\left(\sum_{i=1}^{3} s_i^2\right)\left(\sum_{i=1}^{3} m_i^2\right) + C_2\left(\sum_{i=1}^{3} s_i^2 m_i^2\right).$$

The $n=3$ vector structural and magnetic order parameters (r_1, r_2, r_3), (m_1, m_2, m_3), (s_1, s_2, s_3) transform according to the R5$^-$, M2$^+$, R5$^-$ representations, respectively.

It is assumed that only temperature dependent coefficients are α_1, α_2, α_s and

$$\alpha_1 = \alpha_1^\circ(T - T_R^\circ);\quad \alpha_2 = \alpha_2^\circ(T - T_M^\circ);\quad \alpha_s = \alpha_s^\circ(T - T_N^\circ),$$

where T_R°, T_M°, T_N° are respectively the critical temperatures of (r_1, r_2, r_3), (m_1, m_2, m_3) and (s_1, s_2, s_3) separately.

3. THERMODYNAMICAL BEHAVIOUR AND STABILITY OF POSSIBLE PHASES

In this section we shall discuss the critical behaviour of $KMnF_3$ in the Landau-theory approximation.

According to experimental data [1-3], we shall restrict our consideration to the phases which are characterized by the following values of the $n=9$ component order parameter

$\{(r_1, r_2, r_3), (m_1, m_2, m_3), (s_1, s_2, s_3)\}$:

R: $\{(0, 0, r_3), (0, 0, 0), (0,0,0)\}$; R – M: $\{(0, 0, r_3), (0, 0, m_3), (0, 0, 0)\}$;

R–M–S$_3$: $\{(0,0,r_3), (0,0,m_3), (0,0,s_3)\}$; R–M–S$_1$: $\{(0,0,r_3), (0,0,m_3), (s_1,0,0)\}$.

Let us consider the stability conditions and values of the order parameters for the above-mentioned phases. R-phase: An algebraic discussion of the minima of the potential (1) shows that the R-phase is stable if the following conditions are fulfilled

$$\alpha_1 < 0, \tag{2a}$$

$$\gamma_1/2\beta_1 > 1, \tag{2b}$$

$$\alpha_2 + A r_3^2 > 0, \tag{2c}$$

$$\alpha_2 + A_1 r_3^2 > 0, \tag{2d}$$

$$\alpha_s + B_1 r_3^2 > 0, \tag{2e}$$

$$\alpha_s + B r_3^2 > 0, \tag{2f}$$

where $A = A_1 + A_2$ and $B = B_1 + B_2 + B_3$. The corresponding value of the structural order parameter is

$$r_3^2 = -\frac{\alpha_1}{2\beta_1}. \tag{3}$$

R–M phase: The stability of R–M phase requires

$$\alpha_1 + \gamma_1 r_3^2 + A_1 m_3^2 > 0, \tag{4a}$$

$$\beta_1 > 0, \tag{4b}$$

$$4\beta_1\beta_2 - A^2 > 0, \tag{4c}$$

$$\alpha_2 + \gamma_2 m_3^2 + A_1 r_3^2 > 0, \tag{4d}$$

$$\alpha_s + B_1 r_3^2 + C_1 m_3^2 > 0, \tag{4e}$$

$$\alpha_s + B r_3^2 + C m_3^2 > 0;\qquad C = C_1 + C_2 \tag{4f}$$

and the order parameter of this phase is

$$r_3^2 = \frac{-2\alpha_1\beta_2 + A\alpha_2}{4\beta_1\beta_2 - A^2}, \tag{5a}$$

$$m_3^2 = \frac{-2\alpha_2\beta_1 + A\alpha_1}{4\beta_1\beta_2 - A^2}. \tag{5b}$$

R–M–S$_3$ phase: As has been mentioned above, at T_N $KMnF_3$ undergoes a transition to an antiferromagnetic phase with the sublattice magnetization along z-axis. The examination of the minimum of the form (1) shows that

$$r_3^2 = [-\alpha_1(4\beta_2\beta_s - C^2) - \alpha_2(BC - 2A\beta_s) - \alpha_s(AC - 2B\beta_2)]/||M||, \tag{6a}$$

$$m_3^2 = [-\alpha_1(BC - 2A\beta_s) - \alpha_2(4\beta_1\beta_s - B^2) - \alpha_s(AB - 2C\beta_1)]/||M||, \tag{6b}$$

$$s_3^2 = [-\alpha_1(AC - 2B\beta_2) - \alpha_2(AB - 2C\beta_1) - \alpha_s(4\beta_1\beta_s - A^2)]/||M||, \tag{6c}$$

where

$$||M|| = 8\beta_1\beta_2\beta_s - 2A^2\beta_s - 2C^2\beta_1 - 2B^2\beta_2 + 2ABC \tag{7}$$

and stability conditions read

$$||M|| > 0, \tag{8a}$$

$$\beta_1 > 0, \tag{8b}$$

$$4\beta_1\beta_2 - A^2 > 0, \tag{8c}$$

$$\alpha_1 + \gamma_1 r_3^2 + A_1 m_3^2 + B_1 s_3^2 > 0, \tag{8d}$$

$$\alpha_2 + \gamma_2 m_3^2 + A_1 r_3^2 + C_1 s_3^2 > 0, \tag{8e}$$

$$\alpha_s + \gamma_s s_3^2 + B_1 r_3^2 + C_1 m_3^2 > 0. \tag{8f}$$

R-M-S_1-phase: At $T_C = 81.5$K another phase transition to the magnetically ordered phase is observed. In this new phase the magnetic moments are directed along the x (or y)-axis. Similarly as for R-M-S_3-phase, we obtain

$$r_3^2 = [-\alpha_1(4\beta_2\beta_s - C_1^2) - \alpha_2(B_1C_1 - 2A\beta_s) - \alpha_s(AC_1 - 2B_1\beta_2)]/||M_1||, \tag{9a}$$

$$m_3^2 = [-\alpha_1(B_1C_1 - 2A\beta_s) - \alpha_2(4\beta_1\beta_s - B_1^2) - \alpha_s(AB_1 - 2C_1\beta_1)]/||M_1||, \tag{9b}$$

$$s_1^2 = [-\alpha_1(AC_1 - 2B_1\beta_2) - \alpha_2(AB_1 - 2C_1\beta_1) - \alpha_s(4\beta_1\beta_2 - A^2)]/||M_1||, \tag{9c}$$

where

$$||M_1|| = 8\beta_1\beta_2\beta_s - 2A^2\beta_s - 2C_1^2\beta_1 - 2B_1^2\beta_2 + 2AB_1C_1. \tag{10}$$

Comparing the free energies of the neighbouring phases we obtain the following expressions for the critical temperatures

$$T_R = T_R^\circ, \tag{11a}$$

$$T_M = T_M^\circ + \frac{A\alpha_1^\circ}{A\alpha_1^\circ - 2\beta_1\alpha_2^\circ}(T_R^\circ - T_M^\circ), \tag{11b}$$

$$T_N = T_N^\circ + \frac{[\alpha_1^\circ(AC - 2B\beta_2)(T_R^\circ - T_N^\circ) + \alpha_2^\circ(AB - 2C\beta_1)(T_M^\circ - T_N^\circ)]}{[\alpha_1^\circ(AC - 2B\beta_2) + \alpha_2^\circ(AB - 2C\beta_1) + \alpha_s^\circ(4\beta_1\beta_2 - A^2)]}. \tag{11c}$$

The transition temperature T_C can be found from the condition

$$\begin{aligned}
&[\alpha_1^2(\tfrac{1}{2}C^2 - 2\beta_2\beta_s) + \alpha_2^2(\tfrac{1}{2}B^2 - 2\beta_1\beta_s) + \alpha_s^2(\tfrac{1}{2}A^2 - 2\beta_1\beta_2) + \\
&+ \alpha_1\alpha_s(2B\beta_2 - AC) + \alpha_1\alpha_2(2A\beta_s - BC) + \alpha_2\alpha_s(2C\beta_1 - AB)]/||M|| = \\
&= [\alpha_1^2(\tfrac{1}{2}C_1^2 - 2\beta_2\beta_s) + \alpha_2^2(\tfrac{1}{2}B_1^2 - 2\beta_1\beta_s) + \alpha_s^2(\tfrac{1}{2}A^2 - 2\beta_1\beta_s) + \\
&+ \alpha_1\alpha_s(2B_1\beta_2 - AC_1) + \alpha_1\alpha_2(2A\beta_s - B_1C_1) + \alpha_2\alpha_s(2C_1\beta_1 - AB_1)]/||M_1||.
\end{aligned} \tag{12}$$

One can easily check that the squares of the order parameters r_3^2, m_3^2, s_3^2 vanish for the temperatures T_R, T_M, T_N, respectively. So, the transitions to the R-M- and R-M-S_3-phases are of the second order.

On the other hand, from the condition (12) it follows that at $T = T_C$ the order parameter s_1^2 is nonvanishing, hence this transition is of the first order.

The temperature dependence of the structural order parameters r_3 and m_3 is schematically presented in Fig.3 (a,b). For $T_M < T < T_R$ (the phase R) we have

$$r_3^2(T) = -\frac{\alpha_1^\circ(T - T_R^\circ)}{2\beta_1}. \tag{13}$$

In the region $T_N < T < T_M$ (the R-M-phase)

$$r_3^2(T) = \frac{2\alpha_1^\circ\beta_2 - A\alpha_2^\circ}{4\beta_1\beta_2 - A^2}[T_R^\circ + \frac{A\alpha_2^\circ}{2\alpha_1^\circ\beta_2 - A\alpha_2^\circ}(T_R^\circ - T_M^\circ) - T], \tag{14a}$$

$$m_3^2(T) = \frac{2\alpha_2^\circ\beta_1 - A\alpha_1^\circ}{4\beta_1\beta_2 - A^2}[T_M^\circ + \frac{A\alpha_1^\circ}{A\alpha_1^\circ - 2\beta_1\alpha_2^\circ}(T_R^\circ - T_M^\circ) - T]. \tag{14b}$$

Similarly as for the R-M-phase, we have for $T_C < T < T_N$

$$r_3^2(T) = r[T_R^\circ + \frac{1}{r||M||}(\alpha_2^\circ(BC - 2A\beta_s)(T_M^\circ - T_R^\circ) + \alpha_s^\circ(AC - 2B\beta_2)(T_N^\circ - T_R^\circ)) - T], \tag{15a}$$

$$m_3^2(T) = m[T_M^\circ + \frac{1}{m||M||}(\alpha_1^\circ(BC - 2A\beta_s)(T_R^\circ - T_M^\circ) + \alpha_s^\circ(AB - 2C\beta_1)(T_N^\circ - T_M^\circ)) - T], \tag{15b}$$

where

$$r = [\alpha_1^\circ(4\beta_2\beta_s - C^2) + \alpha_2^\circ(BC - 2A\beta_s) + \alpha_s^\circ(AC - 2B\beta_2)]/||M||, \tag{16a}$$

$$m = [\alpha_1^\circ(BC - 2A\beta_s) + \alpha_2^\circ(4\beta_1\beta_s - B^2) + \alpha_s^\circ(AB - 2C\beta_1)]/||M||. \tag{16b}$$

It should be also noted, that the comparison of the stability condition of the R- and R-M-phases at the temperature T_M yields the additional condition

$$A_2 < 0. \tag{17}$$

Besides, if we compare the stability conditions of the R-M-S_3 and R-M-S_1-phases with those for the R-M-phase (Eqs. (4e,f)), we find that for the R-M-S_3-phase

$$(B - B_1)r_3^2 + (C - C_1)m_3^2 < 0 \tag{18a}$$

and for the R-M-S_1-phase

$$(B - B_1)r_3^2 + (C - C_1)m_3^2 > 0. \tag{18b}$$

So, one can see that for $(B - B_1) < 0$ and $(C - C_1) > 0$ the increase in the m_3 order parameter, caused by the temperature, makes the transition to the R-M-S_1-phase more easy. At this

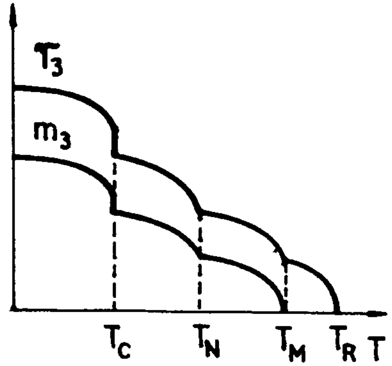


Fig.3. A schematic temperature dependence of the structural order parameters.

point we shall note that according to Izyumov et al. [4], it is enough to account for the R-point phase transition alone to obtain the proper sequence of magnetic phase transitions. Our results indicate that the influence of the M-point phase transition is also important.

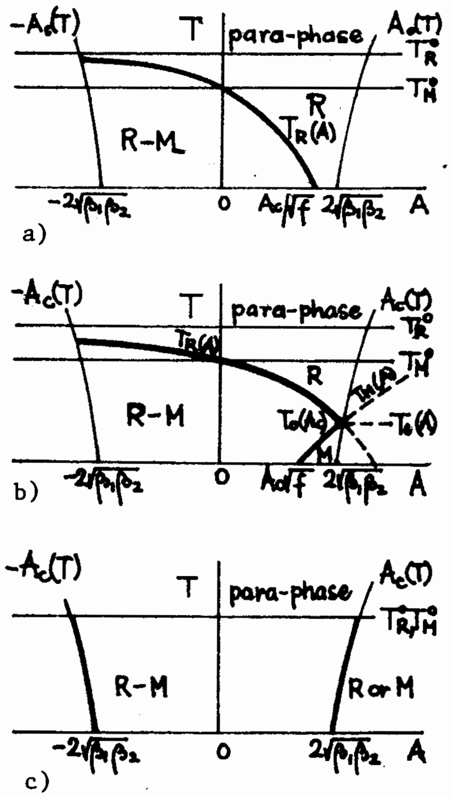
Secondly, the supposed by these authors the Dzialoshinskii-Moriya mechanism must have the smaller effect on the phase transition to the weak-ferromagnetic phase because Mn^{2+}- is in the S-state.

Now we shall present the phase diagrams obtained for our model. We confine ourselves to the first two structural transitions only. The phase diagrams for a full sequence of phase transitions discussed above are quite complicated and will not be discussed here.

In order to analyze the phase diagrams, it is convenient to define, as it has been done in [10], some additional parameters:

1) The ratio of the free-energy densities of the separate order parameters at $T=0$, $f = F_R(0)/F_M(0)$, where

$$F_{R,M}(0) = \frac{(T^{\circ}_{R,M}a^{\circ}_{1,2})^2}{\beta_{1,2}}. \qquad (19)$$



2) The strength of the coupling $A=A_1+A_2$, a convenient measure for which is A/A_c, A_c being equal to $2\sqrt{\beta_1\beta_2}$. We shall refer, as in [10], to the coupling as weak or strong according to whether $A/A_c<1$ or $A/A_c>1$, respectively. First, consider the case $T^{\circ}_R > T^{\circ}_M$.

a) $F_R(0) > F_M(0)$ (see Fig.4a). For $T>T^{\circ}_R$ the system is in disordered state (para-phase). For T just below T°_R the R-phase appears. It exists until the

Fig.4. Phase diagrams in the A-T-plane for: a) $F_R(0) > F_M(0)$, $T^{\circ}_R > T^{\circ}_M$, b) $F_R(0) < F_M(0)$, $T^{\circ}_R > T^{\circ}_M$, c) $F_R(0) = F_M(0)$, $T^{\circ}_R = T^{\circ}_M$. The full thick lines are second-order phase transition lines. The broken thick lines are limits of stability. The $T_0(A)$ line is a first order transition line.

temperature becomes equal to $T_R(A)$ given by the solution of equation

$$A = 2\beta_1 a_2/a_1. \qquad (20)$$

The low-temperature phase (under the $T_R(A)$-line) is the R-M-phase. For this case the curve $T_R(A)$ is characterized by the following relations:

$$T_R(0) = T^{\circ}_M; \quad T^{\circ}_M < T_R(-A_c) < T^{\circ}_R; \quad T_R(A_c/\sqrt{f}) = 0. \qquad (21)$$

b) $F_R(0) < F_M(0)$. For $T>T^{\circ}_R$ we deal with the para-phase. For T just below T°_R the situation dependens on the strength of coupling. For the weak coupling we have the R-phase up to the line given by Eq. (20). Then the R-M-phase appears. When the temperature is lowered further, T crosses $T_M(A)$ given by the equation

$$A = 2\beta_2 a_1/a_2 \qquad (22)$$

and we have M-phase in which m_3 has a nonvanishing value. For $T_M(A)$ we obtain

$$T_M(A_c\sqrt{f}) = 0; \; T_M(A) < T_R(A); \; T_M(A_c) = T_R(A_c). \qquad (23)$$

In the case of strong coupling $T_R(A)$ and $T_M(A)$ are defined by the same equations as above. $T_0(A)$ is a first-order transition line where M replaces R as the absolute minimum.

c) $F_R(0) = F_M(0)$, $T^{\circ}_R = T^{\circ}_M$. For $T>T^{\circ}_R$ we have, as in the previous cases, para-phase. For $T<T^{\circ}_R$ we have R-M-phase for the weak coupling and the phase equilibrium between R or M-ordering for the strong coupling. In this case the $T_R(A)$-line coincides with $A_c(T)$.

Finally, we want to compare the above results with those obtained on the basis of the microscopic theory [7]. In particular, we shall limit ourselves to the discussion of the problem which of the possible phases occurs below the M-point. In order to do that we have to determine the parameters in the free energy expansion (1). It can be shown that they are connected with those proposed by Konwent and Plakida [7] by means of

$$\gamma_1 = \gamma_2 = \Gamma_2; \quad A_1 = \Gamma_2; \quad A_2 = 3\Gamma_1 - \Gamma_2; \; \beta_1 = \beta_2 = \frac{1}{2}\Gamma_1. \qquad (24)$$

Additionally we have $a^{\circ}_1 \sim a^{\circ}_2$.

Now it is easy to check that for such values of the parameters the stability conditions for the R-M-phase are not fulfilled. Moreover, since these values correspond to our c-case for the strong coupling, the first-order phase transition from the R- to M-phase does not exist. On the other hand, the experimental data indicate the existence of the R-M-phase. The authors of paper [7] suggest that the interactions of the R- and M-modes with the displacements of K-ions could provide such phase. This possibility has been studied in the other paper [11].

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Подольска-Стрыхарска А. E17-82-888
Феноменологическая теория структурных и магнитных фазовых переходов в кристалле $KMnF_3$

Дано термодинамическое описание структурных и магнитных фазовых переходов в перовскитном кристалле $KMnF_3$. В частности, рассмотрено влияние структурного фазового перехода в точке M на последовательность магнитных фазовых переходов. Проводится сравнение с результатами микроскопической теории.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1982

Podolska-Strycharska A. E17-82-888
Phenomenological Theory of the Structural and Magnetic Phase Transitions in $KMnF_3$-Crystal

Thermodynamical description of the structural and magnetic phase transitions in the perovskite-type crystal $KMnF_3$ is presented. In particular, the influence of the structural phase transition at the M-point on the sequence of magnetic phase transitions is discussed. The comparison with the results of the microscopic theory is performed.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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