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THE THEORY
OF A NONCOLLINEAR FERROMAGNETISM
OF THE $U_3 X_4$ COMPOUNDS

ЛАБОРАТОРИЯ ТЕОРЕТИЧЕСКОЙ ФИЗИКИ

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THE THEORY
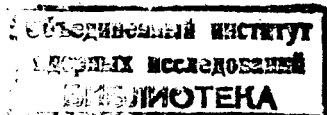# OF A NONCOLLINEAR FERROMAGNETISM
OF THE $U_3 X_4$ COMPOUNDS

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1. Introduction

In recent years much attention has been drawn to the magnetic properties of uranium compounds of Th_3P_4 type, especially to U_3P_4 and U_3As_4 . Investigations done on powder samples showed /1,2,3,4/ that U_3P_4 becomes ferromagnetic below $T_c = 138°K$ (there is, however, some disagreement in this value) and in the neutron diffraction measurements /5/ it appeared that magnetic structure of U_3P_4 is really ferromagnetic. The authors of /5/ con - cluded that we deal in this case with a simple collinear ferromagnetism. The same meaning is expressed in /3/ on the ground of unpublished susceptibility data.

Another point of view has been proposed since magnetic measurements on the monocrystalline samples became available. From the magnetization data /6/ it became clear that U_3P_4 and U_3As_4 are highly anisotropic with resulting magnetic moment along [111] direction and it was

suggested that due to the three-axial character of the crystal field anisotropy a noncollinear structure should appear in these compounds.

Quite recent measurements of the magnetostriction and magnetization of U_3P_4 [7] confirmed the data of [6] and showed that the anisotropy of U_3P_4 is extremely high: there is no saturation reached at fields as big as 200kOe and it may be estimated that the anisotropy is of an order $10^6 - 10^7$ Oe.

The possibility of appearing of a noncollinear structure in these compounds was also established by the symmetry considerations: it was shown in [8] with the help of Landau's theory of the 2-nd order phase transitions that at the ferromagnetic phase transition the paramagnetic cubic symmetry of U_3P_4 $(I\bar{4}3d\,1')$ should be changed to the rhombohedral $R3c'$ symmetry, which admits a noncollinear structure. As it was demonstrated in [9] the neutron diffraction data of [5] do not contradict this statement.

Noncollinear ordering of magnetic moments in U_3P_4 is also suggested in [10] basing on the consideration of the symmetry and magnitude of the crystal field. Recent resistivity measurements [11] seem also to confirm this assumption.

Thus, as we may see, a noncollinearity of ferromagnetism of U_3P_4 is now widely accepted in spite of the fact that there is no direct proof of this and a precise neutron diffraction analysis of these compounds is badly

needed. There is also lack of any theoretical model in framework of which we could discuss the physical properties of these structures.

It is just our purpose to construct such a model basing on the symmetry considerations of the problem and to describe the behaviour of the system in the external magnetic field.

This article is organized as follows: In Sec. 2 we describe the supposed magnetic structure of $U_3 P_4$ in terms of magnetic symmetry groups /12/ and with the help of basis functions of an irreducible representation of the space group /13/. In Sec. 3 we propose a microscopic Hamiltonian, invariant with respect to the symmetry operations of $R3c'$ group, which contains the three-axial crystal field anisotropy, the uniaxial exchange anisotropy and usual exchange isotropic interaction. Exchange interactions are restricted to the nearest neighbours. Then the ground state configuration is considered and it is shown to be of a three-axial nature. In Sec. 4 we discuss the behaviour of the system at the external magnetic field directed along[111] axis. Furthemore, in Sec. 5, we consider the asymptotic behaviour of the magnetization at the fields tending to infinity and, in Sec. 6, the initial susceptibility. The formula for the Curie temperature is derived in Sec. 7 in a simplest molecular field approximation. Finally, in Sec. 8, we provide some numerical estimations of the considered quantities, and in Sec. 9 we summarize the results.

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II. <u>Description of the Magnetic Structure of</u> U_3P_4

U_3X_4 compounds belong to the cubic symmetry group $\bar{I}43d$. For the generators of this group we may choose the following set of the symmetry operations (see, e.g. [14]):

$$C_{2z}: (\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z); \qquad C_{2x}: (\frac{1}{2} + x, \frac{1}{2} - y, \bar{z});$$

$$C_3: (z, x, y); \qquad \sigma_{xy}: (\frac{1}{4} + y, \frac{1}{4} + x, \frac{1}{4} + z) \qquad (2.1)$$

adding all translations of the b.c.c. lattice. In U_3P_4 magnetic ions occupy the following equivalent positions:

$$p_1 = (3/8, 0, 1/4); \quad p_2 = (1/8, 0, 3/4); \quad p_3 = (1/4, 3/8, 0); \qquad (2.2)$$

$$p_4 = (3/4, 1/8, 0); \quad p_5 = (0, 1/4, 3/8); \quad p_6 = (0, 3/4, 1/8).$$

and form, in such a way, 6 equivalent Bravais' sublattices. In the paramagnetic region we have to add to the symmetry elements of $\bar{I}43d$ also time-reversal operator $-\Theta$.

As it has been shown in [8], if we account for the fact that in the ferromagnetic region resulting magnetic moment is directed along [111] then, at the phase transition of the second order, the symmetry should be changed to $R3c'$ The generators of this group are: a threefold axis [111] $-C_3$, a glid plane $(\Theta \sigma_{xy} | \vec{\tau})$ and the corresponding group of the primitive lattice translations. Rotational part of $R3c'$ consists of the following symmetry elements:

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$$\{E\}, \ \{C_3, C_3^2\}, \ \{\theta\sigma_{xy}, \ \theta\sigma_{xy} C_3, \ \theta\sigma_{xy} C_3^2\}. \qquad (2.3)$$

The most general magnetic structure, invariant with res-
pect to the symmetry operations of $R3c'$ in positions
(2.2), is the following one[8]:

$$\vec{S}_1 = \begin{pmatrix} u \\ v \\ w \end{pmatrix}, \qquad \vec{S}_2 = \begin{pmatrix} u \\ w \\ v \end{pmatrix}, \qquad \vec{S}_3 = \begin{pmatrix} w \\ u \\ v \end{pmatrix}, \qquad (2.4)$$

$$\vec{S}_4 = \begin{pmatrix} v \\ u \\ w \end{pmatrix}, \qquad \vec{S}_5 = \begin{pmatrix} v \\ w \\ u \end{pmatrix}, \qquad \vec{S}_6 = \begin{pmatrix} w \\ v \\ u \end{pmatrix}.$$

An alternative description of this structure may be
given, following Bertaut[13,15] by means of the basis
functions of the irreducible representations of the
crystallographic space groups. To do this we observe,
first of all, that at the phase transition the unit cell
of $U_3 P_4$ does not change, hence, it is enough to consi-
der only irreducible representations with $\vec{k} = 0$.

In the case of $R3c$ group the problem is quite simple:
we have only 3 different irreducible representations
associated with $k = 0$ and they are given in the character
Table 1:

<div align="center">Table 1</div>

	$\{E\}$	$\{C_3, C_3^2\}$	$\{\sigma_{xy}, \sigma_{xy} C, \sigma_{xy} C_3^2\}$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	1	0

Since the structure (2.4) is invariant with respect to $R3c'$ thus it belongs to a one-dimensional representation of $R3c$, in this case to Γ_2. Starting, successively, from the spin-vector components S_1^x, S_1^y, S_1^z, we construct, in the usual manner, the following basis functions of Γ_2 :

$$\Psi^x \equiv S_1^x + S_2^x + S_3^y + S_4^y + S_5^z + S_6^z ,$$

$$\Psi^+ \equiv S_4^x + S_5^x + S_1^y + S_6^y + S_2^z + S_3^z , \qquad (2.5)$$

$$\Psi^- \equiv S_3^x + S_6^x + S_2^y + S_5^y + S_1^z + S_4^z .$$

The following combination of the functions (2.5)

$$\Psi = u\,\Psi^x + v\,\Psi^+ + w\,\Psi^- \qquad (2.6)$$

gives the structure (2.4).

Any bilinear combination of the basis functions (2.5) gives an invariant contribution to the thermodynamic potential of the considered phase.

We will demonstrate, however, that out structure may be described also by means of the basis functions of an irreducible representation of $I43d$ – i.e. the symmetry group of the paramagnetic phase.

All the irreducible representations of any space group, including magnetic groups, are already tabulated[14] and we provide here only character table (Table II) for the representations with $k = 0$.

By means of projective operators technique we may project the functions (2.5) onto the basis vectors of different irreducible representations of $\overline{I43}\,d$ Projective operators are defined as usual:

$$\hat{P}_{ll}\,(\Gamma^{a}) \equiv \sum_{g \in G} \Gamma^{a}_{ll}\,(g) \cdot g \,. \qquad (2.7)$$

<center>Table II</center>

	{E}	{8C_3}	{3C_2}	{6S_4}	{6σ_d}
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	2	1	2	0	0
Γ_4	3	0	-1	-1	1
Γ_5	3	0	-1	1	-1

where summation is taken over the group **G** and $\Gamma^{a}_{ll}\,(g)$ is a matrix element of g in an irreducible representation Γ^{a} .

It may be easily verified that the functions (2.5) have non-zero components only on the basis of Γ_4 . These are the following:

$$\vec{F} \equiv \hat{P}_{ll}\,(\Gamma_4)\,\Psi^{x} = 8 \begin{pmatrix} S^{x}_1 + S^{x}_2 \\ S^{y}_3 + S^{y}_4 \\ S^{z}_5 + S^{z}_6 \end{pmatrix}, \qquad (2.8)$$

$$\vec{B}^{\pm} \equiv \hat{P}_{11}(\Gamma_4)\,\Psi^{\pm} = 4 \begin{pmatrix} S_3^x + S_4^x + S_5^x + S_6^x \pm (S_3^z - S_4^z - S_5^y + S_6^y) \\[4pt] S_1^y + S_2^y + S_5^y + S_6^y \pm (S_5^x - S_6^x + S_2^z - S_1^z) \\[4pt] S_1^z + S_2^z + S_3^z + S_4^z \pm (S_4^x - S_3^x + S_1^y - S_2^y) \end{pmatrix} \qquad (2.9)$$

Since all of these basis vectors belong to the same (three-dimensional) irreducible representation Γ_4 -any scalar product of these vectors gives to the thermodynamic potential a contribution invariant with respect to $\bar{I}43\,d$ group. And it is noteworthy that thermodynamic potential of the second order should be sufficient to describe our structure[15].

We are not going, however, to discuss the behaviour of our system in this language, but in the next Section we will construct a microscopic Hamiltonian which will serve as a basis of our further considerations.

III. The Effective Hamiltonian and Semiclassical Ground State Configuration

For the description of our system we propose the following effective Hamiltonian:

$$\mathcal{H} = -\mu_B\,\vec{H}\sum_{\vec{i}} \vec{S}_i - \frac{1}{2}J\sum_{\vec{i}}\sum_{\vec{\delta}} \vec{S}_i\,\vec{S}_{i+\delta} +$$

$$- K \sum_{\vec{i}} \sum_{\vec{\delta}} \left[S^x_{\vec{i}} (S^y_{\vec{i}+\vec{\delta}} + S^z_{\vec{i}+\vec{\delta}}) + S^y_{\vec{i}} S^z_{\vec{i}+\vec{\delta}} \right] +$$

$$(3.1)$$

$$- D \left[\sum_{\vec{i}} \,_{1,2} (S^x_{\vec{i}})^2 + \sum_{\vec{i}} \,_{3,4} (S^y_{\vec{i}})^2 + \sum_{\vec{i}} \,_{5,6} (S^z_{\vec{i}})^2 \right],$$

where $\vec{S}_{\vec{i}}$ denotes the respective angular momentum spin operator of the ion at the site $\vec{i}$; $\vec{\delta}$ a vector which separates the nearest neighbours; μ_B Bohr's magneton; $\vec{H}$ the external magnetic field. Vectorial indices 1, 2, 3, 4, 5, and 6 mean that summation runs over $\vec{i}$ belonging to the 1st , 2nd etc. sublattices, respectively.

This Hamiltonian is apparently invariant with respect to the symmetry operations of $R 3c'$ group, but unaxial exchange term, K breaks the cubic symmetry.

Thus, accounting only for interactions between the nearest neighbouring ions, we consider here isotropic exchange *(J)* unaxial exchange-type anisotropy *(K)* and three-axial crystal field anisotropy *(D)* .

We will discuss, first of all, the problem of the ground state configuration in a semiclassical approach. For this purpose we have to replace in (3.1) the spin operators $\hat{\vec{S}}$ by classical axial vectors $\vec{S}$ and to discuss the conditions under which corresponding classical energy has a minimum. Because we are interested in the spontaneous magnetization we put $H = 0$. Since there are six magnetic ions in the unit cell we have to solve, in general, a system of 18 non-linear equations with 18 un-

known . Therefore, to simplify the problem, we will only look for the solutions of the type (2.4), i.e. we apply the result of the symmetry considerations. Thus we substitute (2.4) for the spin vectors of different sublattices to the form (3.1). In such a way we reduce the problem to finding minimum of the function

$$F = -J(v+w)(4u+v+w) - K[4u^2 + 4u(v+w) + 3(v+w)^2] - Du^2 \quad (3.2)$$

at the additional condition

$$u^2 + v^2 + w^2 = 1 . \quad (3.3)$$

Not going to the detailed discussion at this moment, we would like to point out an important result: if we are interested only in the ferromagnetic solutions then we get that

$$v = w . \quad (3.4)$$

Thus we arrive at the conclusion that Hamiltonian (3.1) describes a ferromagnetic structure which is three-axial with resulting magnetic moment along[111] direction. This structure has the property that ions within positions P_1 and P_2 belong to the first sublattice, P_3 and P_4 to the second, and P_5 and P_6 to the third. We will describe this structure by assigning to each sublattice magnetization a unit vector of the form

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$$\vec{M}_{\vec{i}} = \sqrt{3}\, v\, \vec{e}_{111} + \rho\, \vec{e}_{i}^{\,f}\ , \qquad (3.5)$$

where i is the sublattice number, and

$$\vec{e}_{111} = \frac{1}{\sqrt{3}}\,(1,1,1)\ , \qquad \vec{e}_{i} = (\delta_{i1}, \delta_{i2}, \delta_{i3})\ , \qquad v + \rho = u\ . \qquad (3.6)$$

Each magnetic ion has $z = 8$ nearest neighbours, all belonging to other sublattices, i.e. no direct interaction inside a given sublattice.

To solve our problem completely it will be convenient to rewrite our Hamiltonian (3.1) in slightly different form:

$$\mathcal{H} = -\mu_B \vec{H} \sum_{R_n} \vec{S}(\vec{R}_n) - \frac{1}{2} \sum_{R_n} \sum_{R'_m} \wp^{\alpha\beta}(\vec{R}_n - \vec{R}'_m)\, S^{\alpha}(\vec{R}_n)\, S^{\beta}(\vec{R}'_m) \qquad (3.7)$$

with

$$\vec{R}_n = \vec{R} + \vec{\rho}_n\ .$$

where $\vec{R}$ denotes a primitive translation of the lattice, and $\vec{\rho}_n$ is a vector describing the position of an ion belonging to the sublattice n inside the unit cell.

$$\wp^{\alpha\beta}(\vec{R}_n - \vec{R}'_m) \equiv \Delta(\vec{R}_n - \vec{R}'_m)\, J^{\alpha\beta} + 2D\, e_n^{\alpha}\, e_m^{\beta}\, \delta(\vec{R}_n - \vec{R}'_m)\ , \qquad (3.8)$$

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$$\Delta(\vec{R}_n - \vec{R}'_m) \equiv \begin{cases} 1 & \text{if} \quad |\vec{R}_n - \vec{R}'_m| = \text{n.n. distance} \\ \\ 0 & \text{otherwise} \end{cases} \quad (3.9)$$

$$\hat{J} \equiv \begin{Bmatrix} J & K & K \\ K & J & K \\ K & K & J \end{Bmatrix} \quad (3.10)$$

$$\delta(\vec{R}_n - \vec{R}'_m) \qquad -\text{usual} \quad \delta - \text{function,} \qquad (3.11)$$

e_n^{α}, e_m^{β} - the components of the unit vectors $\vec{e}_i$.
In the case of such a Hamiltonian various methods
(see /16,17/) lead to the same aquations for the magne-
tization directions

$$\lambda'(\vec{R}_n)\,\vec{\sigma}(\vec{R}_n) = \mu_B \vec{H} + \sum_{R'_m} \hat{\mathcal{P}}(\vec{R}_n - \vec{R}'_m)\,\vec{\sigma}(\vec{R}'_m), \qquad (3.12)$$

where

$$\vec{\sigma}(\vec{R}_n) \equiv \langle \vec{S}(\vec{R}_n) \rangle. \qquad (3.13)$$

Further we will assume

$$\vec{\sigma}(\vec{R}_n) = \sigma \cdot \vec{M}_n \qquad (3.14)$$

with $\vec{M}_n$ being a unit vector in the direction of $\vec{\sigma}(\vec{R}_n)$
and for $T = 0°K$ we will put $\sigma = S$. It must be noted
that in the derivation of Eqs. (3.12) we linearized the
crystal field term formally in the same manner as the
exchange terms. We think that it is not especially wrong
since we are interested primarily in the zero-temperature
behaviour.

Using now the fact that we are dealing only with three ferromagnetic sublattices we rewrite (3.12) in slightly more explicit form:

$$\lambda_i \, \vec{M}_i = \mu_B \vec{H} + 2S \vec{\Gamma}_i \, , \qquad (3.15)$$

where

$$\vec{\Gamma}_i \equiv 2\hat{J} (\vec{M} - \vec{M}_i) + D \vec{e}_i (\vec{M}_i \, \vec{e}_i) \qquad (3.16)$$

$i = 1, 2, 3;$ $\vec{M}_i$ – is the unit vector defined above and $\vec{M} \equiv \sum\limits_{i=1}^{3} \vec{M}_i$.

From (3.15) we have the expression for λ_i :

$$\lambda_i = \mu \vec{H} \vec{M}_i + 2S \vec{\Gamma}_i \vec{M}_i \qquad (3.17)$$

and if we substitute here (3.5) we will get, for $H = 0$:

$$\lambda = 2S \vec{\Gamma}_i \vec{M}_i = 2S [4v(3v + 2\rho)(J + 2K) + 4\rho^2 K + D(v + \rho)^2] \qquad (3.18)$$

which does not depend on i .

Unfortunately, it is still difficult to get general solution of the system (3.15) at an arbitrary magnetic field. Therefore we will solve these equations, in the next section, for the case of H being parallel to [111] but for other directions we will discuss only the asymptotic behaviour.

IV. Ground State Configuration and the Behaviour at the Field Parallel to the Symmetry Axis

From Hamiltonians (3.1) or (3.7), knowing that we are dealing with a three-sublattice structure, we obtain the following expression for the ground state energy:

$$E_0 = -2SN \left\{ \mu_B \vec{H}\vec{M} + 2S \sum_{i=1}^{3} \vec{M}_i \hat{J}(\vec{M}-\vec{M}_i) + SD \sum_{i=1}^{3} (\vec{M}_i \vec{e}_i)^2 \right\}, \tag{4.1}$$

where N denotes the number of magnetic ions in one sublattice, and $\vec{M} = \Sigma \vec{M}_i$. In this Section we consider only the case

$$\vec{H} = H\vec{e}_{111} \tag{4.2}$$

Substituting (4.2) and (3.5) to (4.1) we get

$$E_0 = -2SN \left\{ \sqrt{3}\,\mu_B H(u + 2v) + 3S[4Jv(2u + v) + \right.$$

$$\left. + 4K(u^2 + 2uv + 3v^2) + Du^2] \right\}. \tag{4.3}$$

It will be convenient to introduce spherical coordinates taking [111] - axis as the polar axis - Z. Thus we have the transformation:

$$u' = \frac{1}{\sqrt{2}}(u - v) = \sin\theta \cos\phi$$

$$v' = \frac{1}{\sqrt{6}}(u - v) = \sin\theta \sin\phi \tag{4.4}$$

$$w' = \frac{1}{\sqrt{3}}(u + 2v) = \cos\theta$$

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from where it follows that

$$tg\, \phi \; = \; \frac{v'}{u'} \; = \; \frac{\sqrt{3}}{3}\; , \quad sin\, \phi \; = \; \pm\, \frac{1}{2}\; , \quad cos\, \phi = \pm\, \frac{\sqrt{3}}{2}\; . \tag{4.5}$$

Substituting (4.4) and (4.5) to (4.3) we get

$$E_0 = -2SN\{3\mu_B H\, cos\, \theta + S[D + 12(J + K) +$$

$$+ (D - 18(J + K))\, sin^2\, \theta \; \underline{\pm}\; \sqrt{2}\, D\, sin\, 2\theta]\} \tag{4.6}$$

and

$$\frac{dE_0}{d\theta} = -2SN\{-3\mu_B H\, sin\, \theta + S[(D - 18(J + K))\, sin\, 2\theta \pm$$

$$\pm\, 2\sqrt{2}\, D\, cos\, 2\theta]\} = 0\, . \tag{4.7}$$

Thus, for $H = 0$, we obtain the formula

$$tg\, 2\theta \; = \; \mp\, \frac{2\sqrt{2}\, D}{D - 18(J + K)} \tag{4.8}$$

and stability condition

$$\frac{d^2 E_0}{d\theta^2}\bigg|_0 = -4S^2 N[D - 18(J + K)]\, cos\, 2\theta_0\, (1 + tg^2\, 2\theta_0) > 0\, . \tag{4.9}$$

From this condition sign"-"has to be taken in (4.8) for $0 < \theta_0 < 90°$ and "+"for $90° < \theta_0 < 180°$. The following conclusions may be derived from (4.8):

1°. Collinear structure is incompatible with $D \neq 0$.

2^O. The structure with sublattice magnetization along different fourfold axes (x, y, z), which was suggested in $/6,10/$, needs $(J + K)/D = 0$. For $H \neq 0$ we get from (4.7) the following equation:

$$\sin 2(\theta - \theta) - \kappa \sin \theta = 0, \tag{4.10}$$

where

$$\kappa \equiv \frac{3 \mu_B H \cos 2\theta_0}{S[D - 18(J + K)]}. \tag{4.11}$$

If the condition (4.9) is fulfilled then $\kappa < 0$ and the solutions of (4.10) are automatically stable for $0 < \theta < 90°$.

Eqs. (4.10) is already well known in magnetism (see $/18/$). It is rather impossible to solve it analytically but it may be easily tabulated. We may, however, solve it asymptotically in the limited high fields and get

$$\sigma(H) = \sigma(\infty) \cos \theta(H) \rightarrow \sigma(\infty)(1 - \frac{4}{9} \frac{S^2 D^2}{\mu_B^2 H^2}). \tag{4.12}$$

Because

$$\vec{\sigma} = S \sum_{i=1}^{3} \vec{M} = 3S \cos \theta \, \vec{e}_{111} = \sigma(H) \, \vec{e}_{111} \tag{4.13}$$

we have

$$\sigma(\infty) = 3S. \tag{4.14}$$

On the other hand, in the limit $H \to 0$, we may write

$$\sigma(H) = \sigma(0) + \frac{d\sigma(H)}{dH}\Big|_0 H = \sigma(0) + \chi H . \qquad (4.15)$$

Differentiating (4.10) with respect to H we have

$$\frac{d\theta}{dH}\Big|_0 = - \sin\theta \ \frac{d\kappa}{dH}\Big|_0 \qquad (4.16)$$

and we finally get

$$\chi_{[111]} = -\frac{9}{2} \ \frac{\mu_B \sin^2\theta_0 \cos^2\theta_0}{D - 18(J + K)} . \qquad (4.17)$$

V. The Behaviour of the Magnetization in the Limited High Fields

If the external field is applied in an arbitrary direction then the symmetry is broken and to solve Eqs. (3.15) we cannot use the assumption (3.5). Thus we have to solve the system of 9 nonlinear algebraic equations (or of 6 trigonometrical equations) and it becomes a fairly complicated problem. But even not solving these equations we may note that the collinear solution cannot be reached at any finite magnetic field. Obviously, this is a consequence of the noncommutativity of the Hamiltonian with the full - spin operator of the system.

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In this Section we derive the expression similar to (4.12) for different crystallographic directions. For this purpose we will solve Eqs. (3.15) by means of the iteration procedure.

Thus we may rewrite (3.15) as follows:

$$\vec{M}_i = (\vec{M}_i \cdot \vec{H}_i^{\,eff})^{-1} \vec{H}_i^{\,eff} \quad . \tag{5.1}$$

We take as a zero-order solution

$$\vec{M}_\partial^{(0)} = \vec{h} \ , \tag{5.2}$$

where $\vec{h}$ denotes the unit vector in the magnetic field direction. Substituting (5.2) to the right-hand side of (5.1) we get

$$M_i^{(1)} = \frac{\vec{h} + x\,\vec{\gamma}_i}{1 + x(\vec{h}\,\vec{\gamma}_i)} \ , \tag{5.3}$$

where

$$x \equiv (\mu_B H)^{-1}$$

and

$$\vec{\gamma}_i = 2S[\,4\hat{J}\vec{h} + D(\vec{e}_i,\vec{h})\,\vec{e}_i\,] \ . \tag{5.4}$$

Expanding (5.3) over x and taking $'$

$$\cos \theta = \frac{\vec{h} \, \vec{M}_i^{(1)}}{\{ \vec{M}_i^{(1)} \vec{M}_i^{(1)} \}^{1/2}} \tag{5.5}$$

we obtain

$$\sigma_i(H) = \sigma_i(\infty)\left(1 - \frac{1}{2} \frac{\gamma_i^2 - (\vec{\gamma}_i \, \vec{h})^2}{\mu_B^2 H^2}\right). \tag{5.6}$$

Let us consider a few cases:

$$\vec{h} = \vec{e}_{111} \tag{5.7}$$

hence

$$\sigma_i(111) = \sigma_i(\infty)\left(1 - \frac{4}{9} \frac{S^2 D^2}{\mu_B^2 H^2}\right) \tag{5.8}$$

which is just the same as (4.12).

For other directions we will get e.g.:

$$\sigma_i(e_i) = \sigma_i(\infty)\left(1 - 64 \frac{S \, K}{\mu_B^2 H^2}\right) \qquad h = e_i \tag{5.9}$$

$$\sigma_{1,2}(h_\perp) = \sigma_{1,2}(\infty)(1 - \frac{1}{2} \frac{S^2 D^2}{\mu_B^2 H^2})$$

$$h_\perp = \frac{1}{\sqrt{2}}(1,\bar{1},0) \qquad (5.10)$$

$$\sigma_3(h_\perp) = \sigma_3(\infty)$$

VI. The Initial Susceptibility at $T = 0°K$

For the zero-temperature limit we may define the initial susceptibility tensor in the following way

$$\chi^{\alpha\beta} = \frac{\partial}{\partial H^\beta} \sum_{i=1}^{3} M_i^\alpha \Big|_{H=0} = \sum_{i=1}^{3} \frac{\partial M_i^\alpha}{\partial H^\beta} \Big|_0 = \sum_{i=1}^{3} \chi_i^{\alpha\beta}, \qquad (6.1)$$

where M_i^α are solutions of (3.15).
If we substitute here

$$M_i^\alpha = \lambda_i^{-1}(\mu H^\alpha + 2S\Gamma_i^\alpha) \qquad (6.2)$$

and differentiate, we will obtain, after some tedious but straightforward calculations, the following system of linear equations:

$$\sum_{\nu=1}^{3} \{d_i^{\alpha\nu} \chi_i^{\nu\beta} - \sum_{i \neq j} B_i^{\alpha\nu} \chi_i^{\nu\beta}\} = A_i^{\alpha\beta}, \quad i,j,\alpha,\beta = 1,2,3, \qquad (6.3)$$

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$$d\,_i^{\,a\nu} \equiv \delta^{\,a\nu} - 2S\lambda^{-1}\{\delta_{ai}\,\delta_{\nu i}\,D - 2S\lambda^{-1}\Gamma_i^{\,a}\,[\Gamma_i^{\,\nu} + e_i^{\,\nu}\,D(\vec{e}_i\,,\vec{M}_i\,)]\}, \quad (6.4)$$

$$B\,_i^{\,a\nu} \equiv 4S\lambda^{-1}[J^{\,a\nu} - 2S\lambda^{-1}\Gamma_i^{\,a}\sum_{\mu=1}^{3} M_i^{\,\mu}\,J_i^{\,\mu\nu}\,], \quad (6.5)$$

$$A\,_i^{\,a\beta} \equiv \mu_B\lambda^{-1}(\delta^{\,a\beta} - 2S\lambda^{-1}\Gamma_i^{\,a}\,M_i^{\,\beta}) \quad (6.6)$$

with all the symbols as defined in Sec. 3 and $\vec{\Gamma}_i$, $\vec{M}_i$ taken at $\vec{H} = 0$.

It will be more convenient to write (6.3) in a different form:

$$\begin{pmatrix} \hat{d}_1 & -\hat{B}_1 & -\hat{B}_1 \\ -\hat{B}_2 & \hat{d}_2 & -\hat{B}_2 \\ -\hat{B}_3 & -\hat{B}_3 & \hat{d}_3 \end{pmatrix} \begin{pmatrix} \vec{\chi}_1^{\,\beta} \\ \vec{\chi}_2^{\,\beta} \\ \vec{\chi}_3^{\,\beta} \end{pmatrix} = \begin{pmatrix} \vec{A}_1^{\,\beta} \\ \vec{A}_2^{\,\beta} \\ \vec{A}_3^{\,\beta} \end{pmatrix} \quad (6.7)$$

where $\vec{\chi}_i^{\,\beta}$ and $\vec{A}_i^{\,\beta}$, denote vectors with components $(\chi_i^{\,1\beta}, \chi_i^{\,2\beta}, \chi_i^{\,3\beta})$ and $(A_i^{\,1\beta}, A_i^{\,2\beta}, A_i^{\,3\beta})$ respectively. $\hat{d}_i$ and $\hat{B}_i$ denote three-dimensional matrices with elements defined by (6.4-6.5).

If all the parameters in (6.7) are known we may solve these equations numerically. Then summing

$$\sum_{i=1}^{3} \chi_i^{\,a\beta} = \chi^{\,a\beta} \quad (6.8)$$

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we will obtain the initial susceptibility tensor. If we denote the matrix in the l.h.s. of (6.7) by $\hat{P}$, and its inverse by P^{-1} , and 9-component vectors in the r.h.s of (6.7) by $\vec{a}_i^{(\beta)}$ $i = 1, 2, \ldots, 9$ then we may write the result of (6.8) formally as follows

$$\chi^{\alpha\beta} = \sum_{i=1}^{9} a_i^{(\beta)} \sum_{n=0}^{2} (\hat{P}^{-1})_{\beta \, \alpha + 3n, \, i} \tag{6.9}$$

with $\alpha, \beta = 1,2,3$.

Because it seems rather difficult to calculate (6.9) without a computer we propose, in order to make some rough estimation of $\hat{\chi}$, an approximate solution of the problem. Namely, we will apply the same iteration procedure as in deriving (5.6) with the difference, that instead of (5.2) we will use (3.5) (since we are dealing now with the limit $H \to 0$). Thus, substituting (3.5) to the r.h.s. of (5.1) we obtain

$$\vec{M}^{(1)} = \vec{M}^{(0)} + \delta\vec{M} = \sum_{i=1}^{3} \frac{\vec{H}_i^{\,eff}}{\vec{M}_i \, \vec{H}_i^{\,eff}} \quad , \tag{6.10}$$

where

$$\vec{H}_i^{\,eff} = \mu_B \vec{H} + 2S\vec{\Gamma}_i \tag{6.11}$$

and $\vec{M}_i$, $\vec{\Gamma}_i$ taken again at $H = 0$.

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If we expand the r.h.s. of (6.10) over H and define

$$(\vec{\delta M})^{\alpha} = \sum_{\beta=1}^{3} \chi^{\alpha\beta} H^{\beta} \tag{6.12}$$

we will get the formula

$$\chi^{\alpha\beta} = \frac{\mu_B}{\lambda^2} \{(3\lambda - \rho b)\delta^{\alpha\beta} -(\lambda-\rho b)\}, \tag{6.13}$$

where

$$b = 2S[D(v + \rho) - 2\rho(J + K) + 4\rho K] . \tag{6.14}$$

The tensor (6.13) has thus the form

$$\hat{\chi} = \begin{pmatrix} A & B & B \\ B & A & B \\ B & B & A \end{pmatrix}, \tag{6.15}$$

where

$$A = 2\mu_B \lambda^{-1}, \tag{6.16}$$

$$B = \mu_B \lambda^{-2}(\rho b - 2) . \tag{6.17}$$

By means of the transformation

$$R = \begin{pmatrix} \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \\ \dfrac{1}{\sqrt{6}} & \dfrac{1}{\sqrt{6}} & -\dfrac{2}{\sqrt{6}} \\ \dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} \end{pmatrix} \tag{6.18}$$

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this tensor will become diagonal

$$R \overset{\wedge}{\chi} R^{-1} = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_{||} \end{pmatrix} \qquad (6.19)$$

where

$$\chi_\perp = A - B = \mu \lambda^{-2}(3\lambda - \rho b), \qquad (6.20)$$

$$\chi_{||} = A + 2B = 2\mu_B \rho b \lambda^{-2}. \qquad (6.21)$$

Since expression (6.13) has been obtained in the first step of the iteration procedure, then its validity depends on the convergency of this procedure. It seems to us that the first step is effective.

VII. The Curie Temperature

In order to make an estimation of the calculated quantities and the parameters of our Hamiltonian it would be useful to have the formula for the Curie temperature. Therefore we will derive in this Section some very approximate expression for T_c , linearizing the Hamiltonian in the same manner as we did it in derivation of (3.12). Of course, now this method is much worst than in the case of $T = 0°K$, because of very unadequate treatment of the crystal field anisotropy, and we use it only for its simplicity leaving a refinement to a subsequent paper.

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Thus we apply the usual scheme of the molecular field theory using the effective field as defined in (3.12) ($H = 0$)

$$\vec{H}_i^{\bullet ff} = 2\sigma \vec{\Gamma}_i = \lambda_i (\sigma) \vec{M}_i \ . \tag{7.1}$$

The formula for the length of the sublattice magnetization is

$$\sigma_i = S B_s (\beta S H_i^{\bullet ff}) \ , \tag{7.2}$$

where $B_s(x)$ denotes the Brilloin's function and $\beta = \dfrac{1}{R\Gamma}$. Since

$$\vec{H}_i^{\bullet ff} = \{\vec{H}_i^{\bullet ff} \cdot \vec{H}_i^{\bullet ff}\}^{\frac{1}{2}} = |\lambda_i (\sigma)| \tag{7.3}$$

therefore, expanding r.h.s. of (7.2) for the limit $\sigma \to 0$ we get

$$k T_c = \frac{2}{3} S(S + 1) \vec{\Gamma}_i \vec{M}_i \tag{7.4}$$

or

$$k T_c = \frac{1}{3} (S + 1) \lambda \tag{7.5}$$

with λ as given by (3.18).
Assuming $S = 2$ we have

$$k T_c = \lambda = 4 [4\nu(3\nu + 2\rho)(J + 2K) + 4\rho^2 K + D(\nu + \rho)^2] . \tag{7.6}$$

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We will use this formula in our estimations for its simplicity but having in mind its limitations. It certainly over-estimates the contribution coming from the single-ion anisotropy and it could be refined if we will use more adequate version of the molecular field approxima-tion as, e.g., described in [19].

VIII. Application to $U_3 P_4$

In order to get some idea how does this theory work we will apply our formulae to the case of $U_3 P_4$. We assume here $S = 2$ and use $T_c = 140°K$ [1]. We will take the value of D from [10] ($D = 3B_2$ of their notation).

Thus we have

$$kT = \lambda = 1.92 \cdot 10^{-14} \text{ ergs}, \qquad D = 1.28 \cdot 10^{-14} \text{ ergs}. \qquad (8.1)$$

Let us assume $\theta = 30°$ [9]. Then, from (4.8) it follows

$$\frac{J + K}{D} = 0.146 \qquad J + K = 1.87 \cdot 10^{-15} \text{ ergs} \qquad (8.2)$$

and

$$v = 0.3, \qquad \rho = 0.6, \qquad u = 0.9. \qquad (8.3)$$

Using this in (7.6) we get

$$K = -2.6 \cdot 10^{-15} \text{ ergs}, \qquad J = 4.5 \cdot 10^{-15} \text{ ergs}. \qquad (8.4)$$

By means of (5.8-5.12) we estimate the magnitude
of saturation field: it follows that the magnetization
differs from full saturation less than 1% for the fields
of order $10^7 - 10^8$ Oe.

Let us estimate the initial susceptibility. Making
use of the formula (4.17) we obtain

$$\chi_{111} = 2.5 \cdot 10^{-7} \text{ cgs} . \tag{8.5}$$

This value should be compared with $\chi_{||}$ from the approxima-
te formula (6.21). Since $b = 1,2 \cdot 10^{-14}$ ergs we have

$$\chi_{||} = 3.7 \cdot 10^{-7} \text{ cgs} . \tag{8.6}$$

Thus we see that the procedure used in derivation of
(6.13) gives the overestimated values for χ .

For the magnetic field applied along [100] we have
from (6.16).

$$\chi_{(100)} = A = 9.7 \cdot 10^{-7} \text{ cgs} . \tag{8.7}$$

Hence, for the fields as high as 10^5 Oe we will obtain an
increase of magnetization about 0,6% for H along [lll]
and about 3.2% for H along [100] direction.

IX. Discussion

In the present paper we propose a model, given by (3.1) to describe magnetic properties of U_3X_4 compounds. We have in mind, first of all, compounds belonging to the 5th column of the periodic table. The most important term in our Hamiltonian is the three-axial crystal field anisotropy which makes the structure noncollinear.

Moreover, since this term breaks the commutativity of the Hamiltonian with the full-spin component, it leads to the lack of the full saturation of the magnetization. The restriction of exchange interactions to the nearest neighbours seems to be not very essential. Thus we have no critical field and the character of the field-induced phase transition will be qualitatively different from that of uniaxial case [19].

Our calculation are done in the zero-temperature limit in framework of a semiclassical approximation. Therefore all the formulae we derived should be corrected for the temperature dependence. We have to remember also that this approach is especially unsatisfactory with respect to the single-ion anisotropy and probably overestimates its contribution. Moreover, as it is well known [19,20], the effective crystal field anisotropy is strongly temperature dependent.

In the estimations made in Sec. 8 we used for D value obtained in $/10/$ and for the angle noncollinearity $\theta_\infty = 30°$ $/9/$. Especially the last is very suspicious. But we see that all the quantities we calculated strongly depend on this angle, therefore it is very important to establish the correct value.

In spite of all of these shortmings we see that our estimations are in qualitative agreement with the magnetization data $/7/$. Unfortunately, due to the extremely high anisotropy, the region of magnetic fields where we could expect the spin flopping lies far beyond the experimentally accessible one.

Acknowledgements

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