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Synopsis

The application of Landau's theory of second-order phase transitions to magnetic phase transitions is examined, with special regard to the superposed magnetic structures. The role of mixed invariants in the description of canted magnetic structures is emphasized. An extension is given to many-step magnetic phase transitions and the concept of "quasi phase transition" is introduced. The magnetic structure of $MnSO_4$, $Fe_3(PO_4)_2 \cdot 8H_2O$ and some dihydrated formats is examined in detail.

I. Introduction

As it is well known the Landau theory of second-order phase transitions /see Landau and Lifshitz[1], Lyubarskii[2]/ enables us to determine the symmetry of the new phase arising in a second-order phase transition. Dzyaloshinsky[3] and Kovalyov[4] applied the theory to the case of magnetic phase transitions. In the old form of the theory the structures attainable by second-order phase transition were rather simple, the linear dimensions of the new magnetic unit cell could be at most four times larger than that of the paramagnetic one. Therefore the Landau theory, in its old form, was not able to explain

the occurence of the spiral magnetic structures. Dzyaloshinsky[5] and Kovalyov[6] were able to extend the theory to account for these structures. Their considerations are completely different. Dzyaloshinsky's considerations give not only the criteria for the existence of spiral structures but also enables us to calculate the turning angle of the spiral. Unfortunately his method can be applied only to those cases when the turning angle is small. The extension given by Kovalyov can be only used to decide whether the spiral structure can arise in a second-order phase transition or not, and to describe the possible orientations of the magnetic moment.

The structures obtained by Kovalyov are more complicated, than the structures proposed earlier for MnO_2 and obtained by Dzyaloshinsky. Kovalyov has not said anything of the cause of this disagreement. In our opinion Kovalyov's method is more appropriate to treat the non-collinear magnetic structures in insulators but one has to distinguish, as Dzyaloshinsky did, invariants of exchange type and relativistic origine. The so-called mixed invariants have an important role in this description. In the case of MnO_2 one can show, that the deviation from the simple spiral structure is small and only very accurate measurements can point it out. The perturbational method is the reason, why Dzyaloshinsky obtained only a simple spiral structure.

Another problem in the theory of the magnetic structures is the existence of superposed magnetic structures and the taking place of more successive phase transitions. There are magnetic structures, which cannot arise directly from the paramagnetic phase. These transitions appear in the temperature dependence of the susceptibility and specific heat as peaks. But as it will be shown not every peak corresponds to a real

phase transition, we shall introduce the concept of "quasi phase transition". Also in this case the mixed invariants have an important role.

First we shall give a thorough discussion of the method, with special regard to the superposition of simple magnetic structures and the successive phase transitions. As an application the magnetic structure of $MnSO_4$, $Fe_3(PO_4)_2 \cdot 8H_2O$ and some dihydrated formate salts will be examined in detail. In $MnSO_4$ we have a three-step phase transition and the magnetic structure may deviate a little from the described one. In $Fe_3(PO_4)_2 \cdot 8H_2O$ we explain the two peaks of the specific heat by the aid of a real and a quasi phase transition. In the case of the dihydrated format salts we shall examine the problem whether there are oriented magnetic moments on both sublattices or only on one of them.

II. The role of mixed invariants in the description of second-order phase transitions

Let $G \times R$ be the magnetic symmetry group of the considered crystal in the paramagnetic phase. Here G denotes the ordinary space group of the crystal, R is the time-reversal that reverses all magnetic moments. Let $\underline{M}(\underline{r})$ denote the density of the magnetic moment in the crystal.

As it is well known the basis functions of all non-equivalent irreducible representations of a group form a complete set, i.e. any function can be expanded in terms of these basis functions. All the irreducible representations of the group G are known. The irreducible representations of the group $G \times R$ can be obtained by taking the direct product of the irreducible representations of group G and group R, which contains only the elements E /unit element/ and R. The group R has only two one-dimensional irreducible representations: $E=1$, $R=1$, $E=1$, $R=-1$.

Let $\varphi_j^{(\ell)}(\underline{r})$ be the j-th basis function of the ℓ-th irreducible representation of the group G. In the even representations of the group $G\times R$ $R\varphi_j^{(\ell)}(\underline{r})=\varphi_j^{(\ell)}(\underline{r})$, in the odd representations $R\varphi_j^{(\ell)}(\underline{r})=-\varphi_j^{(\ell)}(\underline{r})$. For the magnetic moment is odd with respect to the time-reversal, in its expansion only the basis functions belonging to the odd representations of the group $G\times R$ can occur. Expanding each component of $\underline{M}(\underline{r})$ in terms of $\varphi_j^{(\ell)}(\underline{r})$'s we get

$$M_\alpha(\underline{r})=\sum_{\ell,j} c_{\alpha j}^{(\ell)}\,\varphi_j^{(\ell)}(\underline{r})$$

$$\underline{M}(\underline{r})=\sum_{\ell,j,\alpha} c_{\alpha j}^{(\ell)}\,\underline{e}_\alpha\varphi_j^{(\ell)}(\underline{r}) \qquad /1/$$

where $\underline{e}_\alpha$ $(\alpha=x,y,z)$ is the unit axial vector in the α direction. In the paramagnetic phase $\underline{M}(\underline{r})=0$ i.e. $c_{j\alpha}^{(\ell)}=0$. In the magnetic phase some of the coefficients $c_{j\alpha}^{(\ell)}$ are different from zero. As in a second-order phase transition the density of magnetic moment varies continuously as a function of temperature, the coefficients $c_{j\alpha}^{(\ell)}$ change continuously, too. The free energy of the system is expansible in terms of either of them. /We shall use them alternatingly in the applications, in the general treatment we shall work with the coefficients $c_{j\alpha}^{(\ell)}$ ./ The free energy of the system must be invariant under any symmetry transformation of the group $G\times R$. For this reason one has to know the transformation properties of $\underline{M}(\underline{r})$ and the coefficients $c_{j\alpha}^{(\ell)}$. Under a symmetry transformation the basis functions $\varphi_j^{(\ell)}(\underline{r})$ and the axial vectors $\underline{e}_\alpha$ respectively transform among one another in a known way, the coefficients remain unchanged. Equivalently the $c_{j\alpha}^{(\ell)}$'s can transform among one another and the functions $\varphi_j^{(\ell)}(\underline{r})$ and the vectors $\underline{e}_\alpha$ are unchanged. The transformation properties of $\varphi_j^{(\ell)}(\underline{r})$ and $\underline{e}_\alpha$ determine that of $c_{j\alpha}^{(\ell)}$. Bearing in mind this it is possible to set up all the invariants and to write the free energy in the following way

$$\Phi = \Phi_0 + A_\nu f_\nu^{(2)}(\ldots c_{j\alpha}^{(\ell)}\ldots) + B_\nu f_\nu^{(4)}(\ldots c_{j\alpha}^{(\ell)}\ldots) + \ldots \qquad /2/$$

where $f_\nu^{(2)}(\ldots c_{j\alpha}^{(\ell)}\ldots)$ and $f_\nu^{(4)}(\ldots c_{j\alpha}^{(\ell)}\ldots)$ are the invariants of second- and fourth-order respectively. Minimizing the free energy with respect to $c_{j\alpha}^{(\ell)}$'s, the value of these coefficients can be determined and the density of magnetic moment, too.

The $c_{j\alpha}^{(\ell)}$'s /with the same index ℓ / transform according to the direct product of the ℓ-th irreducible representation and the axial vector representation. The $3n_\ell$ coefficients / n_ℓ is the dimension of the ℓ-th irreducible representation, $j = 1,2,\ldots n_\ell$ / form a reducible representation of the space group. The direct product representations with different indices ℓ can contain common irreducible representations. Therefore besides the invariants, consisting of coefficients with the same index ℓ, there are invariants consisting of coefficients with different indices ℓ. These so-called mixed invariants play an important role, if the aim is to determine the orientation of the magnetic moments and not only the magnetic space group. The occurence of the mixed invariants is the consequence of the vector character of the magnetic moment. In the case of ordering of alloys the probability distribution of the atoms is written in a series like /1/. In that problem a scalar function is examined, every irreducible representation occurs once and only once. Each invariant in the expansion of the free energy belongs to one of the irreducible representations, there are no mixed invariants.

In the paramagnetic state $A_\nu > 0$ for all ν. A phase transition takes place, when one of the A_ν 's, say A_i /the coefficient of the second-order invariant, consisting of some of the $c_{j\alpha}^{(i)}$'s/ will be negative, the values of these $c_{j\alpha}^{(i)}$ will be different from zero. At the same time also some other $c_{\alpha j}^{(\ell)}$'s that form a mixed

invariant with the former $c^{(i)}_{\alpha j}$'s will be different from zero. Thus we get two or more sets of non-vanishing coefficients, e.g. $c^{(i)}_{j\alpha}$ $(j = 1,2,\ldots n_i)$ and $c^{(k)}_{\beta j}$ $(j = 1,2,\ldots n_k)$ Generally α and β may be different and the magnetic moment obtained in this way had α and β components, too.

That part of the free energy which has total spherical symmetry corresponds to an exchange type interaction. The other part is the energy of anisotropy or represents a Dzyaloshinsky-Moriya type anisotropic superexchange interaction. These are of relativistic origin. So it is possible to determine the order of magnitude of the different components.

The mixed invariants play an important role in the description of canted magnetic structures and weak ferromagnetism. Dzyaloshinsky's consideration of weak ferromagnetism[3] is quite different in form as the above treatment. He writes the free energy in terms of the invariants formed from the magnetic moments of the sublattices, instead of using the $c^{(l)}_{j\alpha}$'s /apparently the two methods give the same result/. There are two combinations of the moments which transform according to the same representation and the corresponting mixed invariant represents the anisotropic superexchange interaction. The above treatment clearly shows why an irreducible representation can occur more than once.

Those coefficients $c^{(l)}_{j\alpha}$, from which no mixed invariant can be constructed, may be treated separately, they cannot have non-vanishing value at the same time.

The irreducible representations of a space group are labelled by two indices, one is the wave vector $\underline{k}$ which is characteristic to the translational properties, the other index distinguishes the representations belonging to the same vector $\underline{k}$. More exactly not one

vector but a set of vectors /which can be obtained from one another by symmetry transformations/ is characteristic to a representation. This set of vectors forms the star of the representation. We shall call two vectors different, if they belong to different stars. Because of the real character of the magnetic moment a non-real representation τ_j and its complex-conjugate representation τ_j^* most occur in the expansion /1/ with complex-conjugate coefficients. The representation $\tau_j + \tau_j^*$ is called a physically irreducible representation.

From the coefficients belonging to the representations of the space group with different wave vector $\underline{k}$ it is impossible to form a mixed invariant. Only such magnetic structure can arise in a second-order phase transition, at which the different components of the magnetic moment belong to the same $\underline{k}$, i.e. they have the same translational symmetry. If the components of the magnetic moment have different translational properties, the structure could arise only in more successive phase transitions, in every step with different $\underline{k}$.

To a given wave vector $\underline{k}$ some representations of the group belong. Generally not all of them can describe a magnetic structure. A condition was given by Kovalyov[4] to decide which irreducible representations must be taken into account in the expansion /1/. Let $\hat{G}(A)$ denote the proper point group of the magnetic atom A, let h' be the elements of this group. The symmetry transformations h' leave the position of the atom A unchanged. The representation τ_l of the point group $\hat{G}$ of the crystal is reducible with respect to the point group $\hat{G}(A)$. In the expansion /1/ one get magnetic moment from the representation τ_l only if it contains the unit representation of the group $\hat{G}(A)$. Physically it means, that the corresponding basis functions $\varphi_j^{(l)}(\underline{r})$ have non-vanishing value at the position of the atom. The mathematical formulation

of this condition is the following: those representations can describe magnetic structure for which

$$\sum_{\hat{G}(A)} \chi(h') \neq 0 \qquad /3/$$

where $\chi(h')$ is the character of the group element h'. In a structure with more sublattices it is possible to fulfil this condition only on one sublattice. The corresponding structure has magnetic moment only on one sublattice. This it the situation in the antiferromagnetic phase of $FeRh$ /7/.

III. Many-step magnetic phase transitions, "quasi phase transition"

The above described procedure can be applied not only to paramagnetic-magnetic transitions but also to transitions between two different magnetic phases, if the transition is of second-order. Let us suppose that the considered crystal has two successive second-order phase transitions at temperatures T_1 and T_2 /$T_1 \geq T_2$/. Let $\underline{M}_1(\underline{r},T)$ and $\underline{M}_2(\underline{r},T)$ denote the moment density above the lower Néel point and below it respectively. Let us examine the following function:

$$\underline{M}_d(\underline{r},T) = \begin{cases} \underline{M}_2(\underline{r},T) - \underline{M}_1(\underline{r},T_2) & \text{if } T < T_2 \\ 0 & \text{if } T > T_2 \end{cases} \qquad /4/$$

In a second-order phase transition $\underline{M}_2(\underline{r},T_2) = \underline{M}_1(\underline{r},T_2)$ and therefore $\underline{M}_d(\underline{r},T)$ is a continuous function of temperature. We can expand this function in terms of the basis functions of the irreducible representations like /1/. Minimizing the free energy the coefficients $C_{j\alpha}^{(l)}$ can be determined. The magnetic moment density corresponding to these values of coefficients $C_{\alpha j}^{(l)}$ gives only $\underline{M}_d(\underline{r},T)$, the magnetic moment corresponding to the phase above T_2 is also present. In such

a way in several steps one after the other very complicated magnetic structures can arise.

If the transitions are near in temperature, one may suppose that the expansion /1/ is valid in the nieghbourhood of T_2 , too./ It is not a necessary condition, the results are valid also in the more general case, but the treatment is more appropriate in this simplified model./ For the sake of simplicity let us assume, that the free energy has the form

$$\Phi = \Phi_0 + A_1 f^{(2)}(c_j^{(i)}) + A_2 f^{(2)}(c_j^{(k)}) + \alpha f^{(2)}(c_j^{(i)}, c_j^{(k)}) + \dots \quad /5/$$

$f^{(2)}(c_j^{(i)})$ and $f^{(2)}(c_j^{(k)})$ are second-order invariants consisting of the coefficients $c_j^{(i)}$ and $c_j^{(k)}$ respectively, $f^{(2)}(c_j^{(i)}, c_j^{(k)})$ is a mixed invariant. Let us assume that the latter term is caused by a relativistic interaction or a weak exchange interaction between the sublattices. Decreasing the temperature from the paramagnetic phase, a phase transition takes place at T_1 when A_1 or A_2, say A_1 , becomes negative. There appears a magnetic structure described by the coefficients $c_j^{(i)}$. Because of the existence of the mixed invariant there appears also the magnetic moment described by the coefficients $c_j^{(k)}$, but it means only a small perturbation in the structure. Further decreasing the temperature A_2 becomes negative at T_2 , $c_j^{(k)}$ can have larger value. The moment that was earlier less oriented, begins to become more oriented. At T_2 no phase transition takes place in the rigorous sense of the word but in the temperature dependence of the specific heat and the susceptibility a peak can appear. In the zeroth approximation, leaving the term $\alpha f^{(2)}(c_j^{(i)}, c_j^{(k)})$ we get two separate phase transitions with two peaks in the specific heat and susceptibility. If this mixed invariant represents a small perturbation it does not destroy the second peak, but this peak does not mean the appearing of a new phase. We may say, that a "quasi phase transition" takes place in the crystal.

We think that this is the explanation of the two peaks in the specific heat of vivianite and $Ni[(NH_2)_2CS]_6Br_2$.

IV. Application to $MnSO_4$

Recently G. Will et al. /8-9/ have reported, that the orthorombic $MnSO_4$ at 4.2°K has a conical spiral magnetic structure. Neutron diffraction measurements were made at the temperatures 77°K and 4.2°K. The additional peaks, found at 4.2°K, indicate the magnetic ordering but no measurements were made in the neighbourhood of the transition. From other measurement it is known, that the Néel temperature of $MnOS_4$ is at 11.5°K. /10/. The z component of the magnetic moment of the Mn atoms are coupled ferromagnetically in the (001) sheets but the adjacent sheets are coupled antiparallel /so-called $CrVO_4$ type magnetic structure/. In the ab plane there is a cycloidal spiral arrangement of the magnetic moments, with the propagation vector directed along the a axis. This structure is the superposition of at least two simple structures /a simple antiferromagnetic and a spiral structure/. We will examine this structure in detail.

The space group of $MnSO_4$ is D_{2h}^{17} (Cmcm) . The Bravais cell is a base centred orthorombic cell. The Mn atoms are situated at the points (000), $(00\frac{1}{2})$ $(\frac{1}{2}\frac{1}{2}0)$ and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ of the Bravais cell /see Fig.1/. The symmetry elements of this space group are the following ones: the unit element h_1 , the rotation through 180° about the a axis and translation in the c direction with the half of the lattice parameter $g_2=\{h_2|00\frac{1}{2}\}$, the rotation through 180° about the b axis h_3, the rotation through 180° about the c axis and translation in the c direction $g_4=\{h_4|00\frac{1}{2}\}$ the inversion h_{25} and the products of these elements

$g_{26} = g_2 h_{25}$, $h_{27} = h_3 h_{25}$, $g_{28} = g_4 h_{25}$ ./We use the notation of Kovalyov's book /11/ ./

If one wants to determine all the possible magnetic structures, all the possible irreducible representations of the space group should be examined. One is up against a simpler problem, if the magnetic structure is roughly known and the problem is to decide whether this structure could arise in a second-order phase transition or not and to make some refinements upon the structure. In the knowledge of the neutron diffraction measurements we shall examine the magnetic structure of $MnSO_4$.

The z component of the moment transforms at a translation according to the wave vector $\underline{k} = 0$, because at a translation with each lattice vector the moments are the same.

The cycloidal spiral component in the ab plane transforms according to the wave vector $\underline{k} = \left(\frac{\pi\mu}{a}, 0, 0\right)$ of the reciprocal space. Namely this vector has the property, that at a translation with the lattice parameter in the b or c direction it gives parallel moments /the moment of the atom at the position $(00\frac{1}{2})$ may be parallel or antiparallel/, but in the a direction we obtain the same moment only after a translation a/μ . /According to the measurements $\mu \sim 1/6$ /.

As the z and x,y components of the magnetic moment have different translational symmetries, there is no mixed invariant from the corresponding coefficients $c_{j\alpha}^{(l)}$, the antiferromagnetic z component and the spiral component in the ab plane cannot arise in the same phase transition. There must be at least two phase transitions in $MnSO_4$ We must still examine the behaviour of the rotating component.

In this space group the vector $\underline{k} = \left(\frac{\pi\mu}{a}00\right)$ has four two-dimensional irreducible representations /see Kovalyov /11/ /

	h_1	g_2	h_3	g_4	h_{25}	g_{26}	h_{27}	g_{28}
τ_1	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$
τ_2	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$
τ_3	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$
τ_4	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$

/6/

The functions $\varphi_j^{(\ell)}(\underline{r})$ in the expansion /1/ transform according to these representations. Which of these representations satisfy the condition /3/ ? The proper symmetry group of the Mn atoms is C_{2h}, the symmetry elements are h_1, h_3, h_{25}, h_{27}. One can easily see from the matrices that only τ_1 and τ_3 satisfy the condition /3/, these representations can describe magnetic structure.

$$\underline{M} = \underline{e}_\alpha \left(c_{1\alpha}^{(1)} \varphi_1^{(1)} + c_{2\alpha}^{(1)} \varphi_2^{(1)} + c_{1\alpha}^{(3)} \varphi_1^{(3)} + c_{2\alpha}^{(3)} \varphi_2^{(3)} \right) \qquad /7/$$

As $\tau(h_{25})\varphi_1^{(\ell)}(\underline{r}) = \varphi_1^{(\ell)}(-\underline{r}) = \varphi_2^{(\ell)}(\underline{r})$ and at the lattice points $\varphi_1^{(\ell)}(Rn) = \varphi_1^{(\ell)}(0) e^{ikRn}$, it is true that $\varphi_1^{(\ell)}(Rn) = \varphi_2^{(\ell)*}(Rn)$. For the magnetic moment must be real, we get $c_{1\alpha}^{(\ell)} = c_{2\alpha}^{(\ell)*}$.

The three unit axial vectors $\underline{e}_\alpha$ transform separately according to the following transformation rule:

	h_1	g_2	h_3	g_4	h_{25}	g_{26}	h_{27}	g_{28}
$\underline{e}_x$	1	1	-1	-1	1	1	-1	-1
$\underline{e}_y$	1	-1	1	-1	1	-1	1	-1
$\underline{e}_z$	1	-1	-1	1	1	-1	-1	1

/8/

From /6/ and /8/ we get the transformation properties of $c_{j\alpha}^{(l)}$'s.

$$c_{1x}^{(1)}, c_{2x}^{(1)} \to \tau_2 \qquad c_{1x}^{(3)}, c_{2x}^{(3)} \to \tau_4$$
$$c_{1y}^{(1)}, c_{2y}^{(1)} \to \tau_3 \qquad c_{1y}^{(3)}, c_{2y}^{(3)} \to \tau_1$$
$$c_{1z}^{(1)}, c_{2z}^{(1)} \to \tau_4 \qquad c_{1z}^{(3)}, c_{2z}^{(3)} \to \tau_2$$

As the x and y component of the magnetic moment transform according to different irreducible representations, they cannot occur in the same phase transition /there is no mixed invariant from the corresponding coefficients $c_{j\alpha}^{(l)}$ /. The spiral component of this structure must arise in two steps. As the oscillating components in the a and b directions occur at different temperatures, generally the amplitudes are different and the spiral structure is an elliptical spiral one.

It is interesting to note, that the coefficients $c_x^{(1)}$ and $c_z^{(3)}$ transform according to the same representation. The situation is the same in the case of $c_z^{(1)}$ and $c_x^{(3)}$. This means that there are mixed invariants consisting of $c_x^{(1)}$ and $c_z^{(3)}$ or $c_z^{(1)}$ and $c_x^{(3)}$. Writing the free energy in terms of these coefficients /we write here only the part that contains c_x and c_z because the terms with c_y can be treated separately/ we get

$$\begin{aligned}\phi = \phi_0 &+ A_1 c_{1x}^{(1)} c_{2x}^{(1)} + A_2 c_{1z}^{(3)} c_{2z}^{(3)} + \\ &+ \alpha_1 c_{1x}^{(1)} c_{2z}^{(3)} + \alpha_2 c_{1z}^{(3)} c_{2x}^{(1)} + \\ &+ \tfrac{1}{2} B_1 \left(c_{1x}^{(1)} c_{2x}^{(1)}\right)^2 + \tfrac{1}{2} B_2 \left(c_{1z}^{(3)} c_{2z}^{(3)}\right)^2 + \dots \\ &+ A_3 c_{1x}^{(3)} c_{2x}^{(3)} + A_4 c_{1z}^{(1)} c_{2z}^{(1)} + \\ &+ \alpha_3 c_{1x}^{(3)} c_{2z}^{(1)} + \alpha_4 c_{1z}^{(1)} c_{2x}^{(3)} + \\ &+ \tfrac{1}{2} B_3 \left(c_{1x}^{(3)} c_{2x}^{(3)}\right)^2 + \tfrac{1}{2} B_4 \left(c_{1z}^{(1)} c_{2z}^{(1)}\right)^2 + \dots\end{aligned} \qquad /9/$$

The terms with the coefficients A and B contain the energy of exchange interaction, the terms with the coefficient α correspond to a Dzyaloshinsky-Moriya type interaction. Writing the free energy in terms of the magnetic moments the latter terms have the form $D(\underline{S}_1 \times \underline{S}_2)$. The ratios α/A and α/B are much smaller than 1.

The above expression for the free energy can be separated into two parts, we shall deal only with the first part. For the free energy and the magnetic moment are real quantities, the $c_{j\alpha}^{(l)}$'s can be written in the following form: $c_{1x}^{(1)} = \eta_x e^{i\chi}$, $c_{2x}^{(1)} = \eta_x e^{-i\chi}$; $c_{12}^{(3)} = \eta_z e^{i\chi}$, $c_{2z}^{(3)} = \eta_z e^{-i\chi}$

$$\phi = \phi_0 + A_1 \eta_x^2 + A_2 \eta_z^2 + (\alpha_1 + \alpha_2)\eta_x \eta_z + \\ + \frac{1}{2} B_1 \eta_x^4 + \frac{1}{2} B_2 \eta_z^4 + \ldots \qquad /10/$$

Minimizing this expression with respect to η_x and η_z, the following equations are obtained

$$2A_1 \eta_x + (\alpha_1 + \alpha_2)\eta_z + 2B_1 \eta_x^3 = 0$$
$$2A_2 \eta_z + (\alpha_1 + \alpha_2)\eta_x + 2B_2 \eta_z^3 = 0 \qquad /11/$$

In the zeroth approximation, neglecting the relativistic interaction /the terms with α / we have for $A_1 < 0$ and $A_2 > 0$.

$$\eta_x = \sqrt{-\frac{A_1}{B_1}} \quad ; \quad \eta_z = 0 \qquad /12/$$

In the first approximation for the ratio η_z/η_x we get from the second equation of /11/ /neglecting the higher order term $B_2 \eta_z^3$/

$$\frac{\eta_z}{\eta_x} = -\frac{\alpha_1 + \alpha_2}{2A_2} \qquad /13/$$

It is clear from the above mentioned arguments, that $\eta_z/\eta_x \ll 1$. Together with the oscillating component in the a direction there must be an additional

oscillating component in the c direction. It seems, however, difficult to observe it in neutron diffraction measurement because of the small amplitude.

Summarizing the result: the described structure of $MnSO_4$ can arise only in three successive magnetic phase transitions, if all the transitions are of second-order. The x,y and z components of the moment appear at different temperatures. The spiral structure in the x,y sheet is an elliptical spiral one. A small oscillating component can settle on the antiferromagnetic z component.

V. The magnetic structure of vivianite

In the temperature dependence of the specific heat of vivianite two peaks were found by Forstat et al. /12/ /see Fig.2/. In the knowledge of the NMR measurements /13/ it was interpreted that two phase transitions take place at different temperatures. It is possible, however, to explain the two peaks in such a way that the peak at lower temperature corresponds to a "quasi phase transition".

Vivianite / $Fe_3(PO_4)_2 \cdot 8H_2O$ / is monoclinic with a space group $C_{2h}^3 (C2/m)$. There are two types of Fe^{++}, their positions are /as it is shown in Fig. 3/.

Type I: (000) and $(\frac{1}{2}\ \frac{1}{2}\ 0)$
type II: $\pm(0\ 0.39\ 0)$ and $(\frac{1}{2}\ \frac{1}{2}\ 0) \pm (0\ 0.39\ 0)$

The NMR measurements can be explained if we suppose that in the antiferromagnetic state type I ions are antiferromagnetically coupled and type II ion pairs are antiferromagnetically coupled /the ions in the pairs of type II can be coupled either ferromagnetically or antiferromagnetically/. The moments lie in the ac plane or along the b axis. For the sake of simplicity we examine the latter case but the result is the same in the former one, too.

In order to examine the structure let us denote the magnetic moments at the positions $(0\,0\,0), (\frac{1}{2}\,\frac{1}{2}\,0), \pm(0\;0.39\;0)$ and $(\frac{1}{2}\,\frac{1}{2}\,0) \pm (0\;0.39\;0)$ by $\underline{S}_1, \underline{S}_2, \ldots, \underline{S}_6$. According to the NMR measurements we assume that $\underline{S}_1 = -\underline{S}_2$, $\underline{S}_3 = -\underline{S}_5$, $\underline{S}_4 = -\underline{S}_6$. Instead of using the coefficients $C_{j\alpha}^{(l)}$ we expand the free energy in terms of these moments. /It makes the calculation easier, but it can be used only if the dimensions of the magnetic unit cell are known./ Let us write first the transformation properties of S_1, S_3 and S_4 /they denote the b component of the vectors/. The crystal has four symmetry elements: the unit element h_1, the rotation through 180° about the b axis h_4, the inversion h_{25}, and the reflection in the ac plane h_{28}. Examining only the b component of the moment the following transformation properties are valid:

h_1	h_4	h_{25}	h_{28}
S_1	S_1	S_1	S_1
S_3	S_3	S_4	S_4
S_4	S_4	S_3	S_3

S_1, $S_3 + S_4$ and $S_3 - S_4$ transform according to the following rule

	h_1	h_4	h_{25}	h_{28}
S_1	1	1	1	1
$S_3 + S_4$	1	1	1	1
$S_3 - S_4$	1	1	-1	-1

Up to the second order the free energy has the form

$$\phi = \phi_0 + \frac{1}{2} A_1 S_1^2 + \frac{1}{2} A_2 (S_3 + S_4)^2 + \qquad /14/$$

$$+ \frac{1}{2} A_3 (S_3 - S_4)^2 + B S_1 (S_3 + S_4) + \ldots$$

The term $BS_1(S_3+S_4)$ describes the exchange interaction between the two sublattices /it can be very weak in this case/. This can cause a "quasi phase transition". Let us assume that decreasing the temperature at T_1 the coefficient A_1 changes sign, at T_2 the coefficient A_2 does so i.e. $A_1=a_1(T-T_1), A_2=a_2(T-T_2)$. Below T_1 there is an aligned magnetic moment on the first sublattice and there is a small ordering on the second sublattice, the moments in the pairs are ferromagnetically coupled. Below T_2 the moments on the second sublattice are more oriented but no change of symmetry, no real phase transition takes place at T_2. If B/a_1, and B/a_2 are much smaller than 1, one can expect a peak at T_2 in the temperature dependence of the specific heat.

Maybe the second peak corresponds to a real phase transition but in that case the magnetic structure is not so simple. Let us suppose, that A_1 and A_3 change sign at T_1 and T_2 respectively. When A_3 becomes negative there appears magnetic moment only on the second sublattice, with antiferromagnetic coupling in the pairs. At temperatures below the second phase transition there is a small component on the second sublattice with ferromagnetic coupling in the pairs and a big component with antiferromagnetic coupling in the pairs, i.e. the magnitude of S_3 and S_4 are different.

The two peaks found in the temperature dependence of specific heat on $Ni[(NH_2)_2CS]_6Br_2$ /14/ can be explained in the same way. A quasi phase transition can take place also in this compound.

VI. On the structure of some dihydrated formates

From x-ray studies it is known that the dihydrated formates of Mn^{++}, Ni^{++} and Fe^{++} have common monoclinic

structure. The unit cell contains two each of two inequivalent types of metal ion sites. In spite of this fact different magnetic structures were concluded from susceptibility measurements, ESR, NMR and Mössbauer experiments. In $Mn(HCOO)_2 \cdot 2H_2O$ two peaks were found in the susceptibility [15]. One of them can originate from Fe^{++} impurities[16] but it can be the result of a "quasi phase transition", too. Oriented magnetic moment is only on one sublattice. In Fe^{++} and Ni^{++} salts[17] there is one phase transition. In the Fe^{++} salt there is oriented magnetic moment on both sublattices while in the Ni^{++} salt only on one of them. Supposing that the phase transitions are of second-order we will examine this problem.

The space group of these salts is $C_{2h}^5 (P2_1/c)$ The metal ions are situated on the edges of the elementary cell and on the centre of the faces /see Fig. 4/. The origine of the symmetry transformations is at $(0\,\frac{1}{4}\,\frac{1}{4})$. The symmetries of the crystal are: the unit element h_1, the rotation through 180° about the b axis and translation in the b direction $g_4=\{h_4|0\,\frac{1}{2}\,0\}$, the inversion followed by a translation $g_{25}=\{h_{25}|0\,\frac{1}{2}\,\frac{1}{2}\}$, the reflection in the ac plane followed by a translation in the c direction $g_{28}=\{h_{28}|00\,\frac{1}{2}\}$. These transformations connect the atoms in the bc plane but the adjacent planes are independent.

Let us denote the magnetic moment of the ions at $(000), (0\,\frac{1}{2}\,\frac{1}{2}), (\frac{1}{2}\,0\,\frac{1}{2})$ and $(\frac{1}{2}\,\frac{1}{2}\,0)$ by $\underline{S}_1, \underline{S}_2, \underline{S}_3$ and $\underline{S}_4$. Transforming the components of these axial vectors we get the following: $S_{1x}-S_{2x}$, $S_{1y}+S_{2y}$, $S_{1z}-S_{2z}$ $S_{3x}-S_{4x}$, $S_{3y}+S_{4y}$, $S_{3z}-S_{4z}$, $S_{3z}+S_{4z}$ transform according to the unit representation of the space group, $S_{1x}+S_{2x}$, $S_{1y}-S_{2y}$, $S_{1z}+S_{2z}$, $S_{3x}+S_{4x}$, $S_{3y}-S_{4y}$, $S_{3z}+S_{4z}$ transform according to the τ_3 representation.

	h_1	g_4	g_{25}	g_{28}
τ_1	1	1	1	1
τ_3	1	-1	1	-1

It is possible to set up mixed invariants from both sets. The invariants of $(S_{1x}-S_{2x})(S_{1y}+S_{2y})$ type correspond to a Dzyaloshinsky-Moriya type interaction, the invariants of $(S_{1x}-S_{2x})(S_{3x}-S_{4x})$ type correspond to the exchange interaction between the two sublattices. The minimization of the free energy gives that the members of either the first or the second set will be different from zero. In the former case we get $S_{1x}=-S_{2x}$, $S_{1y}=S_{2y}$, $S_{1z}=-S_{2z}$, $S_{3x}=-S_{4x}$, $S_{3y}=S_{4y}$, $S_{3z}=-S_{4z}$, in the latter case $S_{1x}=S_{2x}$, $S_{1y}=-S_{2y}$, $S_{1z}=S_{2z}$, $S_{3x}=S_{4x}$, $S_{3y}=-S_{4y}$, $S_{3z}=S_{4z}$.

The exchange interaction between the two sublattices causes that moments must appear on both sublattices at the same time. This interaction can be weak and the moment on the second sublattice can be small in comparison with the moment on the first sublattice. The magnitude of the interaction depends on the type of the metal ion, in the Fe^{++} salt it may be stronger than in the Ni^{++} and Mn^{++} salts. As a result of this the moments on the second sublattice will be more oriented in Fe^{++} salt than in other salts.

These salts have a resulting weak ferromagnetic moment in the b direction or in the ac plane.

There is a possibility that "quasi phase transition" takes place in these salts /there are a lot of mixed invariants in the free energy/. The two peaks in the susceptibility of the Mn^{++} salt can be explained in this way, too.

VII VII. Summary

The above considerations show the application of Landau's theory of second-order phase transitions to three different cases. First one can determine the orientation of the magnetic moments in the magnetic phase. We have shown that the formate dihydrates of iron, nickel and manganese are weak ferromagnets and there is magnetic moment on both sublattices. The moments on the second sublattice can be oriented more or less. Second it is possible to investigate many-step magnetic phase transitions and to determine the so arising complicated structures. In connection with this we have pointed out that the conical-spiral magnetic structure of $MnSO_4$ has to arise in three steps. At last we have called attention to the fact that not every peak in the temperature dependence of the susceptibility or the specific heat corresponds to a real phase transition. Introducing the concept of the "quasi phase transition" we could explain the behaviour of vivianite.

The experimental investigation of these transitions would be of interest. First of all neutron diffraction measurements ought to be made. This is not an easy job because the intensity ratios have to be measured with great accuracy. NMR and Mössbauer experiments are also favourable to determine the moments from the internal field. Care should be taken of the small components of the magnetic moment. In the case of $MnSO_4$ the existence of the three successive phase transitions can be examined with the aid of specific heat and susceptibility measurements, too.

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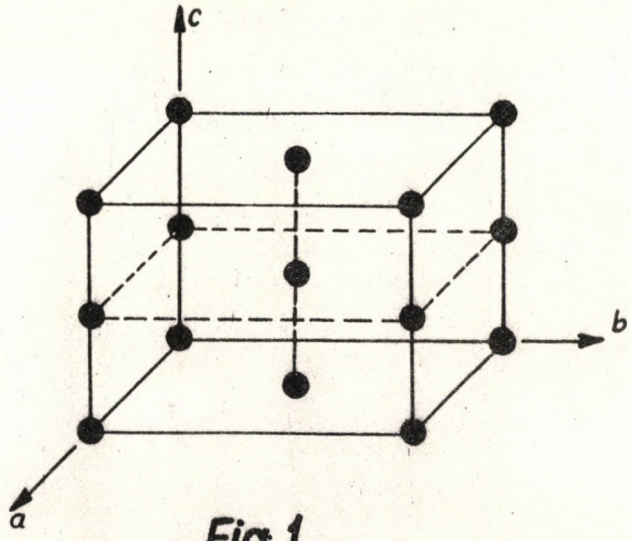

Fig. 1.

The Bravais cell of $MnSO_4$ with the positions of the Mn atoms.

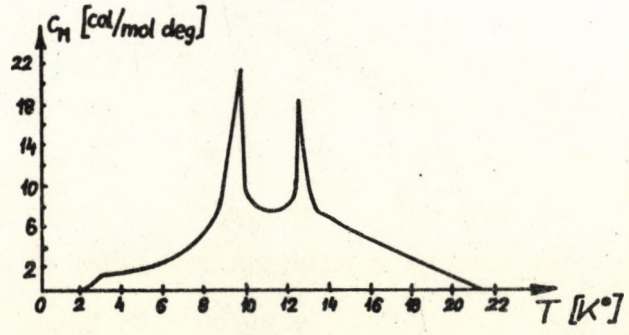

Fig. 2.

The magnetic-specific-heat- versus-temperature curve for vivianite.

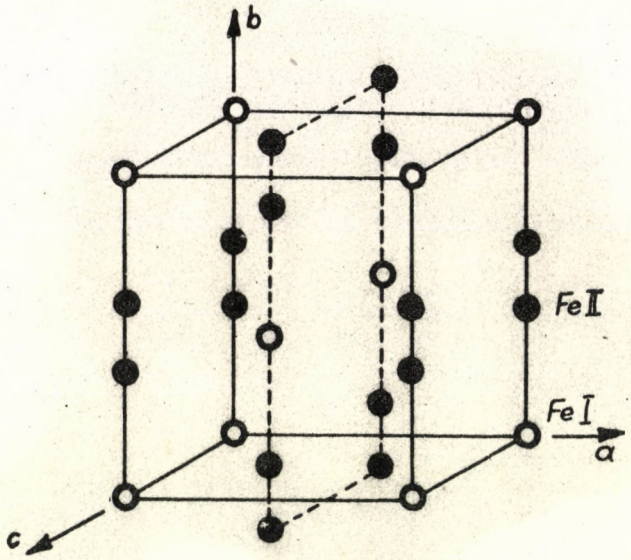

Fig. 3.

The unit cell of vivianite. Only the iron positions are shown

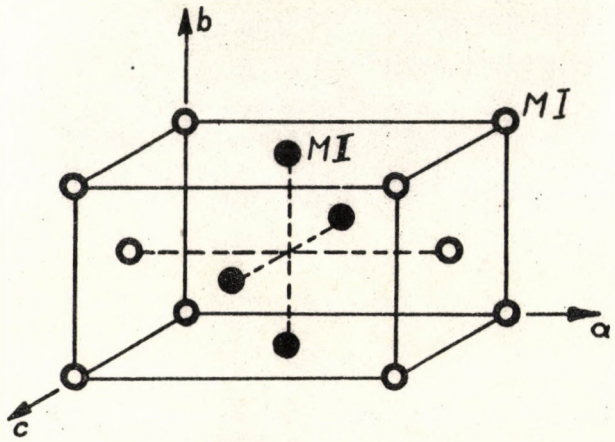

Fig. 4.

The unit cell of the dihydrated formate salts. Only the metal ion positions are shown.

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