Magnetization distribution in noncollinear magnetic systems with mutually perpendicular crystal axes

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The method of reconstruction of magnetization distribution in the crystal with noncollinear ordering of magnetic moments in the cubic, tetragonal and orthorhombic crystal structures was described. As an example the neutron diffraction data for $ScFe_4Al_8$ were used. It has been shown that in this case noncollinear magnetic system can be conveniently described as composed of three collinear systems. From the analysis of the magnetic structure factors the components of the magnetic moment of each atom in the system can be estimated what further allows for the synthesis of "partial" structure factors. The "partial" structure factors were used as the input data for the reconstruction of "partial" magnetization distributions using the Maximum Entropy Method (MEM). Finally, the full vectorial map of the magnetization distribution was obtained as a linear combination of the "partial" distributions.

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1. Introduction

The noncollinear magnetism is observed in many systems. Such behaviour can arise from a competition between FM and AFM interactions, geometric frustration of AFM interactions or anisotropy caused by the preferred direction of magnetization. Although the magnetization density is not an observable [1,2] and thus cannot be directly observed, it plays a fundamental role in the interpretation of magnetic scattering of neutrons. Moreover, the magnetization, especially of the 3d electron systems, is built by the outer electrons, thus it can give ~~a~~ very precise insight into the distribution of the outer electrons in the unit cell.

Complex magnetic systems are often studied by means of the polarized neutron diffraction with strong external magnetic field. In this technique the only one parameter – the flipping ratio *R* – is measured, and thus the determination of the vectorial map of the internal magnetization distribution is not easy. In addition, an external magnetic field destroys the '*natural*' ordering of magnetic moments, so the fine features of the magnetic ordering like the question on noncollinearity or incommensurability, may have not unique interpretation. This was somehow warned in the paper [2] in which one reads: *"It may be true that studies on systems which are not fruitfully analyzed within the conventional collinear scheme are avoided, or not published."* [2].

In this article we propose relatively simple method of the reconstruction of magnetization density distribution in noncollinear magnetic system. The method presented is restricted for the cubic, tetragonal and orthorhombic crystal structures. The only information desired are the unpolarized neutron diffraction data, collected without ~~an~~ external magnetic field. It will be shown that after the conventional magnetic structure refinement the reduction of the noncollinear system to the proper number of the collinear magnetic systems can be performed and then, for each of these resulting "collinear systems", the distribution of the proper component of magnetization density can be reconstructed by the Maximum Entropy Method. Finally - as an example - we will present the reconstruction of the magnetization density distribution for the noncollinear and incommensurate $ScFe_4Al_8$ compound.

2. The method

Our goal consists in reconstruction of the spatial distribution of magnetization in a crystal using the magnetic neutron diffraction data. In the neutron diffraction experiments the Fourier transform of the magnetization is observed. The intensity of magnetically scattered neutrons is proportional to the square of the moduli of magnetic structure factor, which is vectorial [3]:

$$\vec{F}_M(\vec{K}) = \sum_j \vec{q}_j \mu_j f_j(\vec{K}) \exp(i\vec{K}\cdot\vec{r}_j) \quad (1)$$

where:

$\vec{q}_j = \hat{e}\times(\hat{m}_j \times \hat{e})$ - Halpern's vector

$\hat{e} = \frac{\vec{K}}{|\vec{K}|}$ - unit vector in the direction of scattering vector

$\hat{m}_j = \frac{\vec{\mu}_j}{|\vec{\mu}_j|}$ - unit vector in the direction of magnetic moment of *j-th* atom

μ_j - magnetic moment of j'th atom (in Bohr magnetons)

$f_j(\vec{K})$ - form factor of *j-th* atom

and the sum is restricted to the magnetic atoms.
The Halpern's vector can be written as:

$$\vec{q} = \hat{m} - (\hat{e} \cdot \hat{m}) \cdot \hat{e} \tag{2}$$

Since

$$\hat{e} \cdot \hat{e} = 1 \quad \text{and} \quad \hat{m} = \frac{\mu_x \hat{x} + \mu_y \hat{y} + \mu_z \hat{z}}{|\vec{\mu}|}$$

where (x, y, z) denotes coordinates connected with the crystal, Halpern's vector can be written in the form:

$$\vec{q} = \frac{\mu_x \hat{x} + \mu_y \hat{y} + \mu_z \hat{z}}{|\vec{\mu}|} - \frac{\hat{e} \cdot \mu_x \hat{x} + \hat{e} \cdot \mu_y \hat{y} + \hat{e} \cdot \mu_z \hat{z}}{|\vec{\mu}|} \cdot \hat{e}$$

But

$$\frac{\hat{e} \cdot \mu_x \hat{x} + \hat{e} \cdot \mu_y \hat{y} + \hat{e} \cdot \mu_z \hat{z}}{|\vec{\mu}|} =$$

$$= \frac{\mu_x}{|\vec{\mu}|} \cos\alpha + \frac{\mu_y}{|\vec{\mu}|} \cos\beta + \frac{\mu_z}{|\vec{\mu}|} \cos\gamma$$

where α, β and γ are the angles between the unique vector $\hat{e}$ and X, Y and Z axes, respectively. Thus, we can write the Halpern's vector in the form:

$$\vec{q} = \frac{\mu_x}{|\vec{\mu}|}(\hat{x} - \cos\alpha \cdot \hat{e}) + \frac{\mu_y}{|\vec{\mu}|}(\hat{y} - \cos\beta \cdot \hat{e}) + \frac{\mu_z}{|\vec{\mu}|}(\hat{z} - \cos\gamma \cdot \hat{e})$$

The unit vector $\hat{e}$ can be written in the form:

$$\hat{e} = \cos\alpha\hat{x} + \cos\beta\hat{y} + \cos\gamma\hat{z}$$

Let's define a new, not orthogonal in general case, set of basic vectors:

$$\begin{aligned} \hat{a}_1 &= \hat{x} - \cos\alpha(\cos\alpha\hat{x} + \cos\beta\hat{y} + \cos\gamma\hat{z}) \\ \hat{a}_2 &= \hat{y} - \cos\beta(\cos\alpha\hat{x} + \cos\beta\hat{y} + \cos\gamma\hat{z}) \\ \hat{a}_3 &= \hat{z} - \cos\lambda(\cos\alpha\hat{x} + \cos\beta\hat{y} + \cos\gamma\hat{z}) \end{aligned} \tag{3}$$

The Halpern's vector ~~can be written~~ in the basis (3) is:

$$\vec{q} = \frac{\mu_x}{|\vec{\mu}|}\hat{a}_1 + \frac{\mu_y}{|\vec{\mu}|}\hat{a}_2 + \frac{\mu_z}{|\vec{\mu}|}\hat{a}_3 \tag{4}$$

Now, using (4), the magnetic structure factor (1) can be written in the form:

$$\vec{F}_M(\vec{K}) = \sum_j \left(\frac{\mu_{x,j}}{\mu_j}\hat{a}_1 + \frac{\mu_{y,j}}{\mu_j}\hat{a}_2 + \frac{\mu_{z,j}}{\mu_j}\hat{a}_3 \right) \mu_j f_j(\vec{K}) \exp(i\vec{K} \cdot \vec{r}_j) =$$
$$= \hat{a}_1 \sum_j \mu_{x,j} f_j(\vec{K}) \exp(i\vec{K} \cdot \vec{r}_j) + \hat{a}_2 \sum_j \mu_{y,j} f_j(\vec{K}) \exp(i\vec{K} \cdot \vec{r}_j) +$$
$$+ \hat{a}_3 \sum_j \mu_{z,j} f_j(\vec{K}) \exp(i\vec{K} \cdot \vec{r}_j)$$

Thus we can write the structure factor as the sum of three components – the "partial" structure factors, each of them dependent on different components of the atomic magnetic moment:

$$\vec{F}_M(\vec{K}) = \vec{F}_{M,\mu_x}(\vec{K}) + \vec{F}_{M,\mu_y}(\vec{K}) + \vec{F}_{M,\mu_z}(\vec{K})$$

where:

$$\begin{aligned} \vec{F}_{M,\mu_x}(\vec{K}) &= \hat{a}_1 \sum_j \mu_{x,j} f_j(\vec{K}) \exp(i\vec{K} \cdot \vec{r}_j) = \hat{a}_1 S_x(\vec{K}) \\ \vec{F}_{M,\mu_y}(\vec{K}) &= \hat{a}_2 \sum_j \mu_{y,j} f_j(\vec{K}) \exp(i\vec{K} \cdot \vec{r}_j) = \hat{a}_2 S_y(\vec{K}) \\ \vec{F}_{M,\mu_z}(\vec{K}) &= \hat{a}_3 \sum_j \mu_{z,j} f_j(\vec{K}) \exp(i\vec{K} \cdot \vec{r}_j) = \hat{a}_3 S_z(\vec{K}) \end{aligned} \tag{5}$$

When continuous $\vec{M}(\vec{r})$ - the magnetization distribution throughout the unit cell is considered, the magnetic structure factor can be written in the form:

$$\vec{F}_M(\vec{K}) = \int_V \vec{q}(\vec{r}) M(\vec{r}) \exp(i\vec{K} \cdot \vec{r}) dV$$

The unit vector of local magnetization is:

$$\vec{m}(r) = \frac{M_x(\vec{r})\hat{x} + M_y(\vec{r})\hat{y} + M_z(\vec{r})\hat{z}}{M(\vec{r})}$$

Thus again:

$$\vec{F}_M(\vec{K}) = \vec{F}_{M_{M_x}}(\vec{K}) + \vec{F}_{M_{M_y}}(\vec{K}) + \vec{F}_{M_{M_z}}(\vec{K})$$

where:

$$\begin{aligned} \vec{F}_{M_{M_x}}(\vec{K}) &= \hat{a}_1 \int_V M_x(\vec{r}) \exp(i\vec{K} \cdot \vec{r}) dV = \hat{a}_1 S_x(\vec{K}) \\ \vec{F}_{M_{M_y}}(\vec{K}) &= \hat{a}_2 \int_V M_y(\vec{r}) \exp(i\vec{K} \cdot \vec{r}) dV = \hat{a}_2 S_y(\vec{K}) \\ \vec{F}_{M_{M_z}}(\vec{K}) &= \hat{a}_3 \int_V M_z(\vec{r}) \exp(i\vec{K} \cdot \vec{r}) dV = \hat{a}_3 S_z(\vec{K}) \end{aligned} \tag{6}$$

When every $\mu_{x,j}$, $\mu_{y,j}$ and $\mu_{z,j}$ can be unambiguously found during the refinement of the neutron diffraction data, the set of desired number of "partial" structure factors can be calculated.

Because $M_x(\vec{r})$, $M_y(\vec{r})$ and $M_z(\vec{r})$ defined by (7) are scalar functions of vectorial argument, one can try to reconstruct them by Maximum Entropy Method and obtain finally the full vectorial map of magnetization:

$$\vec{M}(\vec{r}) = M_x(\vec{r})\hat{x} + M_y(\vec{r})\hat{y} + M_z(\vec{r})\hat{z} \tag{7}$$

MEM seems to be promising because the results are independent from the model and the required distribution can be obtained from incomplete data set.

3. Maximum Entropy Method

In the present work we used the program MEED [4] modified for magnetization density reconstruction. Because the map reconstructed by MEM has to be positive, the original procedure [4] had to be modified in

order to deal with *positive/negative* magnetization directions. The modified procedure was similar to this one described by Papoular [5].

The maximum entropy was introduced in crystallography by Collins [6]. Using the Jaynes [7] entropy formula:

$$S = -\sum_{i=1}^{P} p_i \ln \frac{p_i}{\tau_i} \tag{8}$$

where p_i is the probability distribution in the *i-th* pixel of the unit cell divided into P grid points and τ_i is so-called *prior* distribution. Assuming the positive distribution $M(\vec{r})$, the proper probability distributions can be expressed in the forms:

$$p(\vec{r}_i) = p_i = \frac{M(\vec{r}_i)}{\sum_{i=1}^{P} M(\vec{r}_i)}$$

and

$$\tau(\vec{r}_i) = \tau_i = \frac{M_0(\vec{r}_i)}{\sum_{i=1}^{M} M_0(\vec{r}_i)}$$

The subscript zero refers to the *prior* density.

Once the misfit function of the form (9) is introduced

$$C = \chi^2 = \frac{1}{N} \sum_{k=1}^{N} \frac{\left| F_k^{obs}(\vec{K}) - F_k^{cal}(\vec{K}) \right|^2}{\left[\sigma(F_k^{obs})\right]^2} , \tag{9}$$

where N denotes the number of observed structure factors $F(\vec{K})$, the functional:

$$Q(\lambda) = S - \lambda\chi^2 \tag{10}$$

where λ is the undetermined Lagrange multiplier can be maximized, so to obtain maximum entropy of the distribution which would agree with the experimental data within chosen cut-of value of *C*. This results in a set of equations:

$$\frac{\partial Q(\lambda, M)}{\partial M(\vec{r})} = 0 \tag{11}$$

whose final solution has the form:

$$M(\vec{r}) = M_0(\vec{r}) \exp\left(-\lambda \frac{\partial \chi^2}{\partial M(\vec{r})} \right) \tag{12}$$

The equations (12) are strongly nonlinear and has to be solved iteratively [4]. Starting with the assumed *prior* distribution $M_0(\vec{r})$ the new distribution $M(\vec{r})$ is obtained and this is used as the *prior* distribution in the next iteration. Assuming the Gaussian distribution of the experimental uncertainties $\sigma(F_k^{obs})$ the procedure is terminated by us when C = 1 is reached [4].

Let's consider a collinear magnetic system in which the magnetic moments are either parallel or antiparallel to a given direction. Let $M^+(\vec{r})$ and $M^-(\vec{r})$ denote the magnetization parallel (*positive*) and antiparallel (*negative*) to the chosen direction. The signs +/- are chosen arbitrarily. For each *positive/negative* part of the magnetization directions the MEM procedure can be applied in a simple manner. It is obvious that in general case we need calculate the six sets of "partial" structure factors for μ_x^+, μ_x^-, μ_y^+, μ_y^-, μ_z^+, and μ_z^- respectively. In case of collinear systems both the negative and positive part of the magnetization distribution can be treated in a separate manner and the final distribution can be found as the difference of the M^+ and M^- partial distributions. The procedure is relatively simple if one knows the magnetization of the sample, i.e. also the structure factor for (0,0,0) reflection. However, in the case of aniferromagnets, and noncollinear systems the situation may be by far more complicated.

4. The example

As an illustration of the method we used the experimental data collected on $ScFe_4Al_8$ system [8].
The sample crystallizes in a tetragonal $ThMn_{12}$ type structure, see Fig. 1.

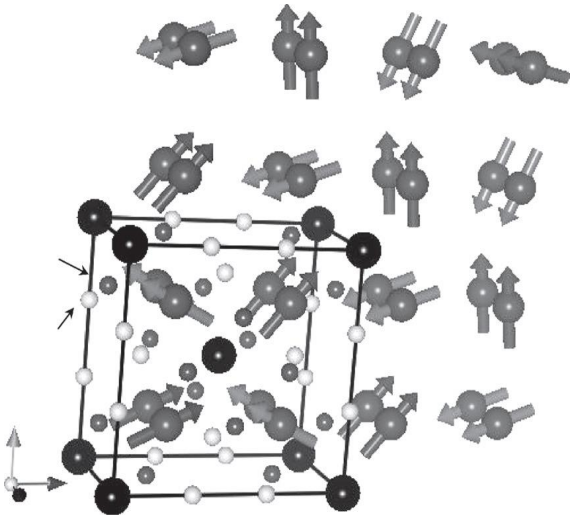

Fig. 1 The magnetic moment arrangement in the one of 225 chemical unit cells building the single magnetic supercell according to (0.13, 0.13, 0) modulation or one of 2500 chemical unit cells building the single magnetic supercell according to (0.18, 0.18, 0) modulation [8].

In general, the iron atoms occupy (8f) positions of the space of I 4/mmm symmetry. The studies of MFe_4Al_8 compounds have shown that the magnetic properties of this family of alloys are sensitive to changes in iron

concentration as well as to the disorder in the lattice [9]. The excess of Sc atoms substitute Fe and have a pronounced effect on the magnetic properties. The value of Fe magnetic moment is close to 1.0 μ_B per atom at 4 K.

The experiments [9] carried out on $ScFe_4Al_8$ in temperature range 4 – 320 K have shown that below 120 K the magnetic structure of the alloy forms a double cycloid with magnetic moments rotating according to the incomensurate in-plane wave vector, which is temperature independent up to 160 K. The double cycloid structure formed by the iron magnetic moments exhibits the phase shift equal to 150(7) degree at 4 K. The shift decreases with temperature increase and at 120 K achieves limiting value.

This double cycloid system discloses the dominant antiferromagnetic character of Fe–Fe coupling in the basal plane of the tetragonal cell. The canting angle $\alpha = 27(3)^0$ at 4 K exists below 120 K [8]. The n = 12 of magnetic structure factors for the modulation vector $\vec{q} = (0.13, 0.13, 0)$ [9] was found during the magnetic structure refinement in the region of $0.07 \le \frac{\sin\theta}{\lambda} \le 0.30$. The positions of the iron atoms together with the components of their magnetic moments in the unit cell are stored in Table 1.

Table 1. The positions of iron atoms in the starting "0" unit cell of $ScFe_4Al_8$. M_x and M_y are the x and y components of each magnetic moment.

Atom	x	y	z	M_x	M_y
Fe1	0.250	0.250	0.250	+0.96	+0.28
Fe2	0.750	0.250	0.250	-0.85	+0.53
Fe3	0.750	0.750	0.250	+0.44	+0.90
Fe4	0.250	0.750	0.250	-0.85	+0.53
Fe5	0.250	0.250	0.750	+0.96	+0.28
Fe6	0.750	0.250	0.750	-0.85	+0.53
Fe7	0.750	0.750	0.750	+0.44	+0.90
Fe8	0.250	0.750	0.750	-0.85	+0.53

Because in $ScFe_4Al_8$ system the *z* component of each individual magnetic moment is always equal to zero, the $S_z(\vec{K})$ "partial" structure factors are equal to zero too (see eq. 7). As in the system the μ_x^+, μ_x^- and μ_y^+ components are present only (see Table 1) the three sets - each of them containing a number of 50 of "partial" magnetic structure factors given by eqs. (5) have been calculated using the data stored in Table 1. In order to be close to the experimental conditions the real and imaginary parts of this "partial" magnetic structure factors were calculated in the region of $\frac{\sin\theta}{\lambda} \le 0.30$.

In all three cases the MEM reconstructions of magnetization density distribution were performed in the 64x64x64 grid points, assuming the P1 symmetry. Instead of the unknown statistical uncertainty $\sigma(F_k^{obs})$ required by MEM [4] the values defined by eq. (13) were used:

$$\sigma_F = \frac{1}{\sqrt{\sin\theta \sin 2\theta}} \tag{13}$$

where θ is the angular position of a given Bragg peak. In each step of iteration the magnetization distribution was normalized and the normalization factors P_x^+, P_x^- and P_y were found from the formulas:

$$\sum_j \mu_{x,j}^+ = P_x^+ \sum_i M_x^+(\vec{r}_i)$$
$$\sum_j \mu_{x,j}^- = P_x^- \sum_i M_x^-(\vec{r}_i)$$
$$\sum_j \mu_y = P_y \sum_i M_y(\vec{r}_i)$$

The convergence of the procedure was measured by the R-factor value [4]:

$$R = \frac{\sum_{i=1}^{160} \left| F_i^{calc}(\vec{K}) - F_i^{obs}(\vec{K}) \right|^2}{\sum_{i=1}^{160} \left| F_i^{obs}(\vec{K}) \right|^2}$$

The calculations were stopped when factor R was equal to 0.01. The presence of the modulation vectors in the system does not create any additional troubles from the point of view of the MEM procedure.

The convergence of the MEM procedure was reached in about 50 iterations for all of components of magnetic moments. As the results of MEM applied to those three set of "partial" structure factors we obtain also three of $M_x^+(\vec{r})$, $M_x^-(\vec{r})$ and $M_y^+(\vec{r})$ and magnetization distributions corresponding to x and y components of magnetic moments and for positive and negative directions of magnetization. Then, the final magnetization density distribution was calculated using eq. (9), where:

$$M_x(\vec{r}) = M_x^+(\vec{r}) - M_x^-(\vec{r})$$
$$M_y(\vec{r}) = M_y^+(\vec{r})$$

The MEM applied to this calculated set of the structure factors leads to the results shown in Fig. 2. The vectors show the direction of the local magnetization and their lengths are proportional to the value of local magnetization. Due to the very wide dynamic range of the local magnetization vector, the lengths of this vector are given in logarithmic scale.

The number of 10 contours are drawn in linear scale in the regions up to 0.002 $\mu_B/Å^3$ for z = 0.0, up to 0.005 $\mu_B/Å^3$ for z = 0.5 and and up to 1.45 $\mu_B/Å^3$ for z = 0.25 and z = 0.75. The noncollinearity of the magnetization vectors is clearly seen. The details of the magnetization distribution in $ScFe_4Al_8$ will be discussed elsewhere.

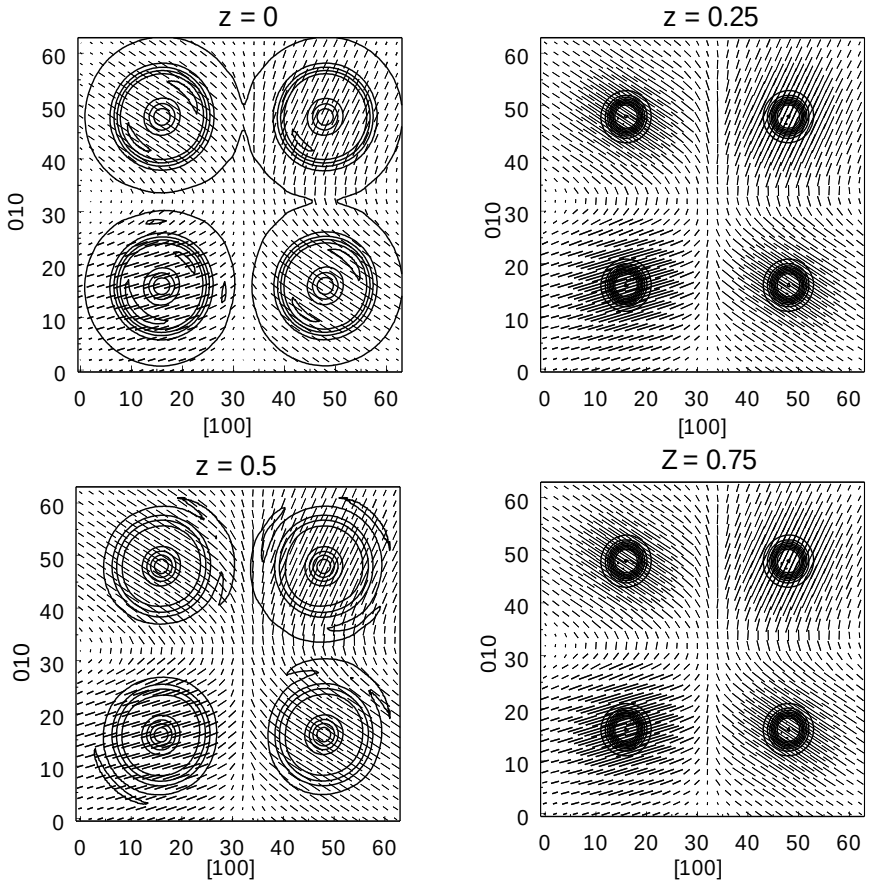

*Fig.2 The magnetization density distribution in XY plane for different z coordinates. The every second point in each direction was shown for better readability. The length of the magnetization vectors are given in a logarithmic scale. The number of 10 contours are drawn in linear scale in the regions from 0.0 $\mu_B/Å^3$ to 2.0*10^{-3} $\mu_B/Å^3$ for z = 0.0, from 0.0 $\mu_B/Å^3$ to 5.0*10^{-3} $\mu_B/Å^3$ for z = 0.5 and from 0.0 $\mu_B/Å^3$ to 1.45 $\mu_B/Å^3$ for z = 0.25 and z = 0.75.*

5. Conclusions

It has been shown that the magnetic structure factors can be expressed as the combination of the "partial" magnetic structure factors. Each partial structure factor depends on different component of magnetic moments of the atom in the system. From the other hand, the same set of these "partial" magnetic structure factors can be expressed as the functions of the internal magnetization distribution. Once the set of these "partial" structure factors was obtained, the Maximum Entropy Method can be easily applied and the distribution of the magnetization in the noncollinear magnetic system can be fully reconstructed

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