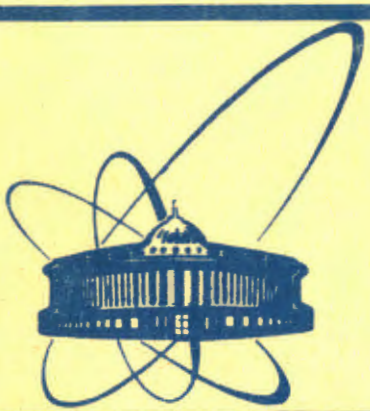

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W.Sikora, V.N.Syromiatnikov

HEXAGONAL PEROVSKITES.

I. Symmetric Analysis on the Basis of Paramagnetic Group $C_{6v}^{3} \cdot 1'$

1981

INTRODUCTION

The group-theoretical analysis of a great amount of magnetic structures shows that in most cases the magnetic structure of crystals is described by one irreducible representation of the symmetry group of the paramagnetic phase. This has allowed the authors of ref.[1-5] to put forward the concept of one irreducible representation according to which both the magnetic phase and structure phase transitions are described by one irreducible representation of the space group (IRS). When this rule is violated, it turns out that the data of compounds possess unusual physical properties. An example is represented by the magnetic structure realized on the family of hexagonal perovskites $ReMnO_3$ (Re: Er, Ho, Lu, Sc, Tm, Y). According to data of refs.[6-10] the crystal symmetry of these compounds in a state before the magnetic transition is described by the space group C_{6v}^3. The symmetry analysis of the magnetic structure of $ReMnO_3$ on the basis of the group C_{6v}^3, which is dealt with in the present work, has shown that the magnetic transition is described by two (IRS) entering into different magnetic multiplets[4] and are not attendant[11]. Just this has let to the assumption that the compaunds of the family $ReMnO_3$ in the paramagnetic phase should exist in a state with a crystal symmetry higher than C_{6v}^3.

1. DESCRIPTION OF EXPERIMENTAL RESULTS

The family of compounds of the type $ReMnO_3$ (Re: Er, Ho, Lu, Sc, Tm, Y) was investigated experimentally by the method of X-ray diffraction and by the neutron-diffraction method by many authors[6-10]. From the results obtained it is found that near the point of magnetic transition these compounds form the structure of perovskites with the hexagonal symmetry of the group C_{6v}^3. Atoms of Re are in positions (2a) and (4b); atoms of the Mn, in position (6c); oxygen atoms O_I, in (2a); O_{II}, in (4b); O_{III}, in (6c); O_{IV}, in (6c), where:

$$(2a):\ 1\,(0,0,z)\ ;\ 2(0,0,z+\frac{1}{2})\,, \tag{1.1}$$

$$(4b):\ 1\,(\frac{1}{3},\frac{2}{3},z)\ ;\ 2(\frac{2}{3},\frac{1}{3},z)\ ;\ 3(\frac{1}{3},\frac{2}{3},\frac{1}{2},+z)\ ;\ 4(\frac{2}{3},\frac{1}{3},\frac{1}{2}+z)\,,$$

(6 c): 1 (x,o,z); 2(o,x,z); 3(x,x,z); $4(\bar{x},o,\frac{1}{2}+z)$; $5(o,\bar{x},\frac{1}{2}+z)$; $6(\bar{x},\bar{x},\frac{1}{2}+z)$.

Running parameters are not determined exactly, but for the atom of Mn in all compounds of the family it is indicated that x is almost equal to 1/3. For the case of $LuMnO_3$ it is approximately found that

$$\begin{aligned} &Lu_I\,(4b):\ z=0.27;\quad Lu_{II}\,(2a):\ z=0.23 \\ &Mn\,(6c):\ x=\frac{1}{3};\quad z=0 \\ &O_I\,(2a):\ z\simeq\frac{1}{2};\quad O_{II}\,(4b):\ z\simeq 0 \\ &O_{III}(6c):\ x\simeq\frac{1}{3};\quad z\simeq\frac{1}{6} \\ &O_{IV}(6c):\ x\simeq\frac{2}{3},\quad z\simeq\frac{1}{3}. \end{aligned} \tag{1.2}$$

The magnetic structure is formed from the spin localized on Mn atoms, and the authors of experimental studies [6-10] do not define them uniquely proposing experimentally indistinguishable different models of noncollinear "triangular" structures with magnetic moments on the xy -plane: Koehler[7] admits structures that result from the mixing of model 1 with 2, or 3 with 4, which leads to structures with spins placed at an angle α to the hexagonal axis a. The angle α is different for

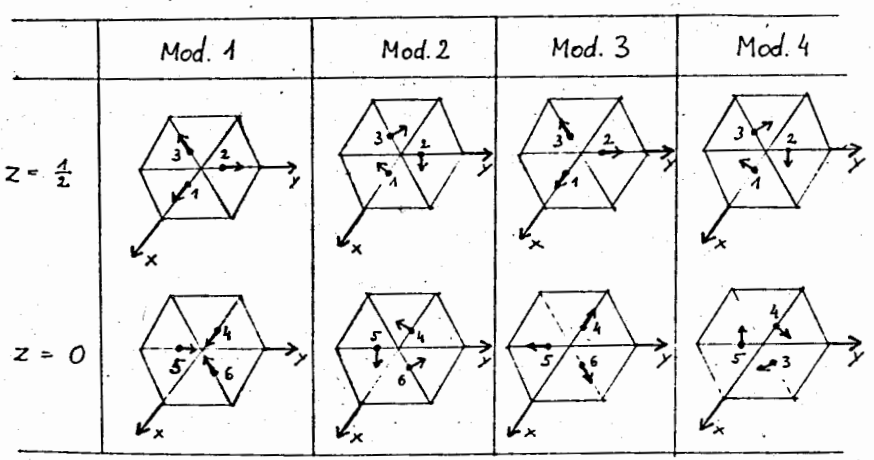

Fig. 1

different compounds of the family. For the case of $YMnO_3$ also a weak ferromagnetism is discovered. It means that z -components are nonzero. Including the z -component and assuming (Koehler) that $\vec{S}_1=\pm\vec{S}_4$, $\vec{S}_2=\pm\vec{S}_5$, $\vec{S}_3=\pm\vec{S}_6$ these models may be written as

Table 1

Model	$\vec{S}_1$	$\vec{S}_2$	$\vec{S}_3$	$\vec{S}_4$	$\vec{S}_5$	$\vec{S}_6$
1	(u,0,w)	(0,u,w)	$(\bar{u},\bar{u},w)$	(u,0,w)	(0,u,w)	$(\bar{u},\bar{u},w)$
2	(u,2u,w)	$(2\bar{u},\bar{u},w)$	$(u,\bar{u},w)$	(u,2u,w)	$(2\bar{u},\bar{u},w)$	$(u,\bar{u},w)$
3	(u,0,w)	(0,u,w)	$(\bar{u},\bar{u},w)$	$(\bar{u},0,\bar{w})$	$(0,\bar{u},\bar{w})$	$(u,u,\bar{w})$
4	(u,2u,w)	$(2\bar{u},\bar{u},w)$	$(u,\bar{u},w)$	$(\bar{u},2\bar{u},\bar{w})$	$(2u,u,\bar{w})$	$(\bar{u},u,\bar{w})$

With the z -component taken into account, as may be easily seen, still furhter models can be suggested:

Table 2

Model	$\vec{S}$	$\vec{S}$	$\vec{S}$	$\vec{S}$	$\vec{S}$	$\vec{S}$
5	(u,0,w)	(0,u,w)	$(\bar{u},\bar{u},w)$	$(u,0,\bar{w})$	$(0,u,\bar{w})$	$(\bar{u},\bar{u},\bar{w})$
6	(u,2u,w)	$(2\bar{u},\bar{u},w)$	$(u,\bar{u},w)$	$(u,2u,\bar{w})$	$(2\bar{u},\bar{u},\bar{w})$	$(u,\bar{u},\bar{w})$
7	(u,0,w)	(0,u,w)	$(\bar{u},\bar{u},w)$	$(\bar{u},0,w)$	(0,u,w)	(u,u,w)
8	(u,2u,w)	$(2\bar{u},\bar{u},w)$	$(u,\bar{u},w)$	$(\bar{u},2\bar{u},w)$	(2u,u,w)	$(\bar{u},u,w)$

where $\vec{S}_i\equiv\vec{S}(\vec{r}_i)$; (u, v, w) is the spin vector written in components in the coordinate system connected with the primitive cell of hexagonal symmetry C^3_{6v}.

2. THE SYMMETRY ANALYSIS OF MAGNETIC STRUCTURE ON THE BASIS OF PARAMAGNETIC SPACE GROUP $C^3_{6v}1'$

As has been shown in ref.[1] instead of representations of the group $C^3_{6v}1'$ in the symmetric analysis it is sufficient to consider the representations of group C^3_{6v}. For the symmetric analysis one should define the wave vector $\vec{k}$ that describes the translational properties of the structure and symmetry-allowed magnetic modes (basis vectors of irreducible representations of space group (IRS) for positions where magnetic moments ("spins") are localized).

In the considered family of compounds the magnetic and chemical cells coincide, and hence, it follows that $\vec{k}=0$ (star$\{\vec{k}_{11}\}$ by tables of Kovalev [12]). To obtain all possible magnetic modes allowed by the group G, according to refs.[1,3] the following is required:

1. To construct the magnetic representation $d_M^{\vec{k}}$ of the group $G_{\vec{k}}$ by the formula:

$$\{d_M^{\vec{k}}(g)\}_{i\alpha,j\beta} = e^{-i\vec{k}\vec{a}_P(g,j)}\delta_{i,gj}\delta_n R_n^{\alpha\beta}, \qquad (2.1)$$

where $e^{-i\vec{k}\vec{a}_P(g,j)}\delta_{i,gj}$ is simply a permutation representation $d_P^{\vec{k}}(g)$ for definite positions restricted to the zero cell, $\vec{a}_P(g,j)$ is the returning translation, $R_n^{\alpha\beta}$ is the rotation matrix of a polar vector by action of the rotational part h of element $g\equiv(h|\vec{t}+r)$, $\delta_n\equiv|R_n^{\alpha\beta}|$ (due to the "spin" vector being axial).

2) To expand the representation $d_M^{\vec{k}}$ over the irreducible representations $d^{\vec{k}\nu}$ by the formula:

$$d_M^{\vec{k}} = \sum_\nu n_M^\nu d^{\vec{k}\nu} \qquad (2.2)$$

$$n_M^\nu = \frac{1}{n(G_{\vec{k}}^\circ)}\sum_{g\in G_{\vec{k}}^\circ}\chi_M^{\vec{k}}(g)\,\chi^{*\vec{k}\nu}(g), \qquad (2.3)$$

where $G_{\vec{k}}^\circ\equiv\{(h_i|r_i)_{\vec{k}}\}$ is the group of the vector $\vec{k}$ of zero block, $n(G_{\vec{k}}^\circ)$ is the number of elements $G_{\vec{k}}^\circ$, $\chi_M^{\vec{k}}(g)$ and $\chi^{\vec{k}\nu}(g)$ are characters of the magnetic and ν-th IRS, respectively.

3. To calculate the basis functions in the expansion of IRS as a direct sum of atomic components $S^\alpha(\overset{\vec{k}}{\lambda}\nu|i)$ where:

$$S^\alpha(\overset{\vec{k}}{\lambda}\nu|i) = \sum_{g\in G_{\vec{k}}^\circ} d^{*\vec{k}\nu}_{\lambda[\mu]}(g)\, e^{-i\vec{k}\vec{a}_P(g,j)}\delta_{i,g[j]}\delta_h R_h^{\alpha[\beta]} \qquad (2.4)$$

(indices in brackets are fixed) with

$$S^\alpha(\overset{\vec{k}_L}{\lambda}\nu|i') = e^{-i\vec{k}_L\vec{a}_P(g_L,i)}\delta_{h_L}\sum_\beta R_{h_L}^{\alpha\beta}S^\beta(\overset{\vec{k}}{\lambda}\nu|i), \qquad \vec{k}_L = g_L\vec{k}. \qquad (2.5)$$

In this way, for hexagonal perovskites in the group C_{6v}^3 and position (3c) of magnetic atoms, with the vector $\vec{k}=0$ we arrive at the following expansion for $d_M^{\vec{k}}$:

$$d_M^{\vec{k}}11 = \tau_1\oplus 2\tau_2\oplus 2\tau_3\oplus\tau_4\oplus 3\tau_5\oplus 3\tau_6. \qquad (2.6)$$

The matrix dimension in $d_M^{\vec{k}}$ is here 18x18. The IRS of τ_1, τ_2, τ_3, τ_4 are one-dimensional, and those of τ_5, τ_6 are two-dimensional (the notation is from ref.[12]).

The magnetic modes calculated are presented in Table 3. In brackets three components ($S^x(\overset{\vec{k}}{\lambda}\nu|i)$, $S^y(\overset{\vec{k}}{\lambda}\nu|i)$, $S^z(\overset{\vec{k}}{\lambda}\nu|i)$) are written.

Table 3

Representation	Basis vectors	Magnetic modes: Positions of Atoms 1	2	3	4	5	6
τ_1	ψ^{τ_1}	(120)	(210)	(110)	(120)	(210)	(110)
τ_2	$I\psi^{\tau_2}$	(100)	(010)	(110)	(100)	(010)	(110)
	$I\psi^{\tau_2}$	(001)	(001)	(001)	(001)	(001)	(001)
τ_3	$I\psi^{\tau_3}$	(100)	(010)	(110)	(100)	(010)	(110)
	$I\psi^{\tau_3}$	(001)	(001)	(001)	(001)	(001)	(001)
τ_4	ψ^{τ_4}	(120)	(210)	(110)	(120)	(210)	(110)
τ_5	$I\psi_1^{\tau_5}$	(100)	$(0\varepsilon^*0)$	$(\bar\varepsilon^{*2}\bar\varepsilon^{*2}0)$	(100)	$(0\varepsilon^*0)$	$(\bar\varepsilon^{*2}\bar\varepsilon^{*2}0)$
	$I\psi_2^{\tau_5}$	(100)	$(0\bar\varepsilon\,0)$	$(\varepsilon^2\varepsilon^20)$	(100)	$(0\bar\varepsilon\,0)$	$(\varepsilon^2\varepsilon^20)$
	$I\psi_1^{\tau_5}$	(010)	$(\bar\varepsilon^*\bar\varepsilon^*0)$	$(\varepsilon^{*2}00)$	(010)	$(\bar\varepsilon^*\bar\varepsilon^*0)$	$(\varepsilon^{*2}00)$
	$I\psi_2^{\tau_5}$	(110)	$(\bar\varepsilon\;00)$	$(0\bar\varepsilon^20)$	(110)	$(\bar\varepsilon\;00)$	$(0\bar\varepsilon^20)$
	$I\psi_1^{\tau_5}$	(001)	$(00\varepsilon^*)$	$(00\varepsilon^{*2})$	(001)	$(00\bar\varepsilon^*)$	$(00\bar\varepsilon^{*2})$
	$I\psi_2^{\tau_5}$	(001)	$(00\bar\varepsilon)$	$(00\bar\varepsilon^2)$	(001)	(00ε)	$(00\varepsilon^2)$
τ_6	$I\psi_1^{\tau_6}$	(100)	$(0\varepsilon^*0)$	$(\bar\varepsilon^{*2}\bar\varepsilon^{*2}0)$	(100)	$(0\bar\varepsilon^*0)$	$(\varepsilon^{*2}\varepsilon^{*2}0)$
	$I\psi_2^{\tau_6}$	(100)	$(0\bar\varepsilon\,0)$	$(\varepsilon^2\varepsilon^20)$	(100)	$(0\varepsilon\,0)$	$(\bar\varepsilon^2\bar\varepsilon^20)$
	$I\psi_1^{\tau_6}$	(010)	$(\bar\varepsilon^*\bar\varepsilon^*0)$	$(\varepsilon^{*2}00)$	(010)	$(\varepsilon^*\varepsilon^*0)$	$(\bar\varepsilon^{*2}00)$
	$I\psi_2^{\tau_6}$	(110)	$(\bar\varepsilon\;00)$	$(0\bar\varepsilon^20)$	(110)	$(\varepsilon\;00)$	$(0\varepsilon^20)$
	$I\psi_1^{\tau_6}$	(001)	$(00\varepsilon^*)$	$(00\varepsilon^{*2})$	(001)	$(00\varepsilon^*)$	$(00\varepsilon^{*2})$
	$I\psi_2^{\tau_6}$	(001)	$(00\bar\varepsilon)$	$(00\bar\varepsilon^2)$	(001)	$(00\bar\varepsilon)$	$(00\bar\varepsilon^2)$

$$\varepsilon \equiv e^{i\frac{2\pi}{3}}$$

From Table 3 it is seen that in case a given IRS occurs in the magnetic expansion n times, by ranning over different fixed indices we obtain n different basis vectors of the given representation. By comparing the obtained modes with earlier listed 8 models of magnetic structures of compounds $ReMnO_3$ one can see that all of them follow from the basis vectors of IRS, τ_1, τ_2, τ_3, and τ_4.

Table 4

	Models of the Magnetic Structure							
component	1	2	3	4	5	6	7	8
$S_{x,y}$	$^{I}\psi^{\Gamma_3}$	ψ^{Γ_4}	$^{I}\psi^{\Gamma_2}$	ψ^{Γ_1}	$^{I}\psi^{\Gamma_3}$	ψ^{Γ_4}	$^{I}\psi^{\Gamma_2}$	ψ^{Γ_1}
S_z	$^{II}\psi^{\Gamma_2}$	$^{II}\psi^{\Gamma_2}$	$^{II}\psi^{\Gamma_3}$	$^{II}\psi^{\Gamma_3}$	$^{II}\psi^{\Gamma_3}$	$^{II}\psi^{\Gamma_3}$	$^{II}\psi^{\Gamma_2}$	$^{II}\psi^{\Gamma_2}$

Models 1-4 proposed by experimental observations and models which result from mixing of 1 with 2 or 3 with 4 are described, as is clear from Table 4, by more than one IRS. It is just this that has initiated the detailed symmetric analysis of hexagonal perovskites.

As a rule, the fact of participation of several IRS in the magnetic transition points to a complicated nature of this transition. The connection between IRS describing the magnetic structure gives us an information on physical features of the paramagnetic state.

Thus, for instance, 2 IRS describing the magnetic structure can belong to one exchange multiplet, and their simultaneous participation in the magnetic transition signifies that after splitting the multiplet by the crystal anisotropy the corresponding levels turn out to be weakly splitted /4/.

Another reason of the participation of two IRS in the magnetic transition may be their attendance /5,11/ which points to the interaction of two parameters of the transition.

And finally, if the structure of the paramagnetic phase is a weakly-distorted version of a certain highly symmetric structure, then on the basis of the symmetry group of this highly symmetric phase in describing the magnetic structure we may arrive at the case of one IRS /5/.

What magnetic multiplets are possible is defined (in accordance with /4/) by the expansion of the magnetic representation in the irreducible representation of the exchange group (IRE) by means of the formula

$$\vec{d}^{k}_{M} = \sum_{\nu} n_{P}^{\nu} \left(\vec{d}^{k\nu}_{P} \times V'\right), \qquad (2.7)$$

where $\vec{d}^{k\nu}_{P} \times V'$ is the IRE written as a direct product of the permutation representation $\vec{d}^{k\nu}_{P}$ by representation V'; V'is the representation by which a pseudovector is transformed, n_{P}^{ν} defines the decomposition of the permutation representation over IRS and simultaneously the decomposition of $\vec{d}^{k}_{M}$ over IRE. The representation $\vec{d}^{k\nu}_{P} \times V'$ is irreducible for the exchange group but its restriction on the space group may be reducible. The expansion

$$\vec{d}^{k\nu}_{P} \times V' = \sum_{\mu} r_{\mu}^{\nu} d^{k\mu}, \qquad (2.8)$$

where

$$r_{\mu}^{\nu} = \frac{1}{n(G^{o}_{k})} \sum_{g \in G^{o}_{k}} \vec{\chi}^{k\nu}(g)\, \chi^{*\vec{k}\mu}(g)\, (1+2\cos\phi_{n}), \qquad (2.9)$$

$(1+2\cos\phi_n)$ is the character of the representation V'. Numbers r_{μ}^{ν} define the composition of a given magnetic multiplet. The calculation is performed for hexagonal perovskites in the group C^{3}_{6v} (positions 3c)) and it shows that

$$\vec{d}^{k}_{M}11 = \Gamma_1 \times V' \oplus \Gamma_4 \times V' \oplus \Gamma_5 \times V' \oplus \Gamma_6 \times V', \qquad (2.10)$$

i.e., there appear four exchange multiplets with the following composition

$$\Gamma_1 \times V' = \Gamma_2 \oplus \Gamma_5, \quad \Gamma_4 \times V' = \Gamma_3 \oplus \Gamma_6, \quad \Gamma_5 \times V' = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5 \oplus \Gamma_6,$$

$$\Gamma_6 + V' = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_6. \qquad (2.11)$$

From (2.11), it is seen that the representations, which occur several times in the expansion of d^{k}_{M}, enter into different multiplets (for instance, one Γ_2 into $\Gamma_5 \times V'$, another into $\Gamma_1 \times V'$). In the case of $ReMnO_3$ (C^{3}_{6v}, (3c)) the permutation expansion contains the following basis vectors:

Table 5

Basis vector	Atomic number in the primitive cell					
	1	2	3	4	5	6
φ^{Γ_1}	1	1	1	1	1	1
φ^{Γ_4}	1	1	1	-1	-1	-1
$\varphi_1^{\Gamma_5}$	1	ε	ε^2	-1	$-\varepsilon$	$-\varepsilon^2$
$\varphi_2^{\Gamma_5}$	1	ε^*	ε^{*2}	-1	$-\varepsilon^*$	$-\varepsilon^{*2}$
$\varphi_1^{\Gamma_6}$	1	ε	ε^2	1	ε	ε^2
$\varphi_2^{\Gamma_6}$	1	ε^*	ε^{*2}	1	ε^*	ε^{*2}

The multiplet $\tau_1 \times V'$ describes the structure which may be written in the form $\vec{s}_1 = \vec{s}_4$, $\vec{s}_2 = \vec{s}_5$, $\vec{s}_3 = \vec{s}_6$. From repeating representations of τ_2 only the basis function $^{II}\psi^{\tau_2}$ describes such a structure. From Table 3 for IRS τ_1, τ_2, τ_3, τ_4 and Table 5 it is seen that:

Table 6

Basis vector	ψ^{τ_1}	$^{I}\psi^{\tau_2}$ $^{II}\psi^{\tau_2}$	$^{I}\psi^{\tau_3}$	$^{II}\psi^{\tau_3}$	ψ^{τ_4}
Magnetic Multiplet	$\tau_5 \times V'$	$\tau_5 \times V'$	$\tau_1 \times V'$	$\tau_6 \times V'$	$\tau_4 \times V'$	$\tau_6 \times V'$

From Tables 4 and 6 it is easily seen that all the 8 listed models of the magnetic structure are described by representations entering into two different multiplets. Also it is clear that the mixing of $S_{x,y}$ components of models 1 with 2 and 3 with 4 leaves the structure in the initial multiplet. The analysis performed shows that the existence of exchange multiplets cannot be the reason for simultaneous appearance of the components $S_{x,y}$ and S_z in the family of hexagonal perovskites.

A second possibility to understand this experimental fact comes from the relation of attendance /11/. When the transition, structure or magnetic, proceeds over two IRS τ_1 and τ_2 and the first of them leads to the group G_1, while the second to the group G_2, where G_1 is a subgroup of G_2, the representation τ_1 is relevant while τ_2 is attendant. It is seen that the addition of τ_2 does not contradict the symmetry established after transition. In the case of models of the magnetic structure of hexagonal perovskites proposed by experimentators the symmetry of the component $S_{x,y}$ is described by one magnetic group of the family of space group C^3_{6v}; and the component S_z, by another group of the same family (representations τ_1, τ_2, τ_3, τ_4 are one-dimensional). This means that they are not connected by the relation group-subgroup. The simultaneous appearance of components $S_{x,y}$ and S_z cannot be explained by the attendance of representations. This is possible for models 5 and 7 which are described by one IRS and one magnetic group. From the above it is seen that only two of 8 models, just those not proposed by experimentalists, can be explained on the basis of paramagnetic group $C^3_{6v} \cdot 1'$. Structure data (proximity of running parameters to "good" values) indicates that the structure C^3_{6v} can be considered as a weak deformation of a certain highly symmetric structure. The search of this structure and analysis of possible structure and magnetic transitions will be published elsewhere.

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