Proposed third long-range order in multiferroics

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We proposed that in multiferroics, there exists a third long-range order besides the electric polarization and magnetic order. This long-range order reduces the symmetry of the spatial part of the wave functions of electrons. Thus the cancellation in the "spin-current" model can be avoided. As a result, the expectation value of electric polarization will be larger by an order of magnitude. We have derived a distinct form of electric polarization $\vec{P} \sim -\hat{Q} \times (\hat{s}_j \times \hat{s}_{j+1})$, where $\vec{Q}$ is the wave vector of this long-range order.

I. INTRODUCTION

Multiferroic materials[1] have several coexisting long-range orders. Kimura *et al.*[2] found very interesting properties in TbMnO₃. The ferroelectric transition temperature coincides with a magnetic transition which was identified later to be the transition from sinusoidal magnetic order to spiral order.[3] It was also found[4] that with sufficiently strong magnetic field, the electric polarization switches direction. These are clear experimental evidences that the electric polarization and magnetic orders are closely related. Electromagnetic (EM) field is one of the fundamental interactions and electricity and magnetism are unified. It should not have been surprising that electric and magnetic properties are coupled. However, in this case there seems to be neither charge current nor time-dependent electric field nor varying magnetic flux in the system. So the fundamental question is by what mechanism electricity and magnetism are coupled. As the list of multiferroic material grows rapidly, their mechanisms and the varieties of physical properties also multiply.[5,6] van der Brink and Khomskii classified them into two types.[7] Type-I multiferroics usually have high ferroelectric temperature but weak coupling between electric polarization and magnetic order. In type-II multiferroics, there are strong electric polarization and magnetic order coupling. With a few exceptions such as Ca₃Co₂₋ₓMnₓO₆ (Ref. 8) and the scenario proposed by Sergienko *et al.*,[9] these compounds are originated from spin-orbit interaction and possess spiral-spin configuration. This is the focus of this work. Katsura *et al.* (KNB) (Ref. 10) proposed the spin-current model of multiferroics in which the coupling between electric polarization and magnetic order is due to spin-orbit interaction. The mechanism can be interpreted as the coupling between electric field and spin current or the Aharonov-Casher (AC) effect[11] and it gives polarization,

$$\vec{P} \simeq -eI\left(\frac{V}{\Delta}\right)^3 \hat{e}_{12} \times (\hat{e}_1 \times \hat{e}_2), \tag{1}$$

where V is the hybridization energy, Δ is the charge-transfer energy, $\hat{e}_1$ and $\hat{e}_2$ are the unit vectors of two adjacent spins, and $\hat{e}_{12}$ is the direction of bond. $eI = e|\int \psi_d^*(\vec{r})\vec{r}\psi_p(\vec{r})d^3\vec{r}|$ is the expectation value of electric polarization of the hybridized state of d orbitals of transition element atoms and p orbitals of oxygen atoms. The factor $\hat{e}_1 \times \hat{e}_2$ fits nicely with spiral-spin configuration. It predicts that the electric polarization is

perpendicular to the screw direction. Furthermore, it was able to explain the results of Kimura *et al.*,[4] applied magnetic field can flip the direction of spiral spins and hence, that of electric polarization. The generalization to a bulk system with active e_g orbitals was also performed.[12]

Though the spin-current model has been successful in many aspects, it has the quantitative problem. For example, assuming $V \approx 0.5$ eV and $\Delta \approx 2$ eV, I has to be of the order 0.1 nm in order that $P \approx 1000$ μC/m², the magnitude in TbMnO₃. This raised doubt of the relevance of the model.[13,14] First-principles calculation by Malashevich and Vanderbilt[15] indicated that in TbMnO₃ the electric polarization of purely electronic nature is an order of magnitude smaller than experimental data. This problem has to be addressed before the spin-current model can be viewed as an accomplished model. This is also the subject of this work.

The electric polarization in Eq. (1) which has the factor (V/Δ) to the third power, is the remains of catastrophic cancellation which comes from the symmetry of the system. In KNB's words: "the dominant term comes from the difference of the normalization factors between two perturbed states." The electric polarization exists only in the systems without inversion symmetry. In many compounds, it is the spiral-spin configuration which breaks the symmetry. However, as one can see from the calculation of KNB, this effect, to the leading order, is only manifest in the spin part of the wave functions and it bears the factor $\hat{e}_1 \times \hat{e}_2$. The spatial part of the wave functions, to the leading order, still possess space inversion symmetry. Hence, the expectation values of electric polarization suffers cancellation. There are other evidences that the lower the symmetry of the system, the greater the electric polarization. In Ref. 9, it was found that atom displacement enhanced electric polarization in E-type antiferromagnetism. The results in Ref. 15 provide even stronger support. Their calculation showed that the spin-orbit interaction is indispensable to the existence of electric polarization while lattice distortion enhances electric polarization by at least tenfold. However, Bridges *et al.*[16] did not find evidence of lattice distortion within experimental accuracy, which is 5×10^{-3} Å. It must be said that a displacement of O^{2-} ions approximately 1×10^{-3} Å is sufficient to give the electric polarization found in TbMnO₃. It will be even smaller for the displacement of Cu^{2+} ions (4×10^{-4} Å) in the compounds with smaller polarization, like LiCu₂O₂.[17] At this stage, experimental data can neither support nor rule out lattice dis-

tortion contribution in TbMnO$_3$ and LiCu$_2$O$_2$. Therefore, it is likely that in the compounds with large electric polarization such as TbMnO$_3$ and CuO (Ref. [18]), there is an extra factor which reduce the symmetry. *As a result, the spatial part of the system also has lower symmetry to avoid the catastrophic cancellation.*

In this work, we proposed that there should be a third long-range order besides the electric polarization and magnetic order. It can be structure distortion, charge order, or orbital order (OO). OO occurs in transition-metal (TM) compounds with crystal field, Jahn-Teller or GdFeO$_3$-type distortions.[19] For example, in manganites, $\psi_{3x^2-r^2}$ and $\psi_{3y^2-r^2}$ orbitals are favored on two interpenetrating sublattices due to crystal field.[20] However, other effects such as superexchange interaction and spin-orbit interaction can also change the orbital configuration. In the spin-orbital model,[19] different combinations of orbitals can give different exchange energies. Hence, there are various competing mechanisms. As a result, the OO should not have such a simple structure. We can provide another argument for the existence of OO. In $3d$ transition elements, the spin-orbit coupling strength is of the order 0.05 eV or 600 K. It is much higher than the Néel temperature. This means that the spin and orbital angular momenta are aligned in opposite direction long before the magnetic order is established. If there is experimental evidence of say, sinusoidal magnetic order, it is also an indication of OO with a wave-vector commensurate with that of spins.

Even if in a system without OO, structure distortion, such as cooperative Jahn-Teller effect or GdFeO$_3$-type distortions can also play the role of the third long order. The d orbitals are anisotropic. The magnitude of oxygen bond angle can influence hybridization. The third possible candidate is charge order or its multipole expansion. For apparent reason, it can cause an additional periodic potential and hence, affects wave functions.

Here is a brief summary of this work. By introducing a third long-range order into the system, we show that the electric polarization can be enhanced by an order of magnitude. A distinct form of electric polarization is derived. This long-range order can reduce the spatial symmetry of the spatial wave functions. Therefore, the catastrophic cancellation is avoided. More specifically, long-range orders with wave vector $\vec{Q}$ affect the hybridization energy. The state of crystal momentum $\vec{k}$ mixes with the state of $\vec{k} \pm \vec{Q}$. In evaluation of electric polarization, one has to sum over entire bands up to the Fermi surface for multiferroic insulators. The cancellation will *not* be complete if the wave function is a mixture.

II. WAVE FUNCTIONS

To see the origin of the catastrophic cancellation, we start with a U(1)×SU(2) gauge-invariant action which will give the equation of motion as the Pauli equation,

$$S = \int d^4x \left[i\hbar\psi^* D_0 \psi - \frac{\hbar^2}{2mc} \sum_{k=1}^{3} (D_k\psi)^*(D_k\psi) \right.$$
$$\left. - \frac{1}{16\pi c} \sum_{\mu,\nu=0}^{3} F_{\mu\nu}F^{\mu\nu} \right] \tag{2}$$

with $x^0 = ct$ and the covariant derivatives $D_0 = \partial/\partial x^0$

$-(ie/\hbar c)A_0 + (ie/2mc^2)\Sigma_a\rho_{0a}\sigma^a$ and $D_k = \partial/\partial x^k + (ie/\hbar c)A_k + (ie/4mc^2)\Sigma\rho_{ka}\sigma^a$ are introduced in order to show clearly the charge and spin currents. A term of EM field is also present. Here, we use the notations of Fröhlich and Studer[21] with a little simplification. The SU(2) fields $\rho_{0a} = B^a$ and $\rho_{ka} = \Sigma_b\varepsilon_{kab}E^b$ are related the components of magnetic and electric field. However, it should be noted that the action is correct only to the order $O(m^{-2})$. Above action illustrates the origin of AC effect in which the electric field is coupled to moving spins or magnetic moments. By taking variation in ρ_{ka}, multiplying by ε_{kab} and summing over a, and assuming the system is charge neutral, we obtain

$$\frac{E_b}{4\pi c} = \frac{-\hbar e}{8m^2 c^3} \sum_{a,k=1}^{3} \left\{ \left[\left(\frac{\hbar}{i} \frac{\partial}{\partial x^k} + \frac{e}{c} A_k \right) \psi \right]^* \varepsilon_{kab}\sigma^a \psi \right.$$
$$\left. + (\varepsilon_{kab}\sigma^a\psi)^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x^k} + \frac{e}{c} A_k \right) \psi \right\}, \tag{3}$$

where a term of the order m^{-3} is discarded. The right-hand side (rhs) is clearly the spin current. It is the gist of the spin-current model of multiferroics. From the equation $\vec{D} = \vec{E} + 4\pi\vec{P}$, one finds that when there is no free charge, the electric polarization $\vec{P} = \vec{E}/4\pi$ can be generated by spin current. Nevertheless, we can see the reason why the electric polarization given by the spin-current model usually is small in magnitude. In insulators such as multiferroics, there is no movement of free charge carriers and thus no spin current on the rhs of Eq. (3). KNB had to invoke superexchange interaction. This is exactly the reason why there is catastrophic cancellation because only by going to the higher orders can one find spin current. The cancellation can be avoided if there is a long-range order in the system which can give the wave-function modulation, produce significant derivative of ψ and hence, give rise to large the electric polarization.

Our model is quite simple. A crystal of transition element atoms with valence d orbitals and oxygen atoms with p orbitals are considered. The transition-metal atoms have spiral-spin configuration and OO so that the jth transition-metal atom has the combined spin and orbital state,

$$\Psi_j = \begin{pmatrix} e^{-i\phi/2} \cos(\vec{q} \cdot \vec{R}_j/2) \\ e^{i\phi/2} \sin(\vec{q} \cdot \vec{R}_j/2) \end{pmatrix}$$
$$\otimes \begin{pmatrix} [A + B\cos(\vec{Q} \cdot \vec{R}_j)]\psi_{d1}(\vec{r} - \vec{R}_j) \\ B\sin(\vec{Q} \cdot \vec{R}_j)\psi_{d2}(\vec{r} - \vec{R}_j) \end{pmatrix}, \tag{4}$$

where $\psi_{d1(2)}(\vec{r} - \vec{R}_j)$ is the first and second d orbital of the transition element atom at site $\vec{R}_j$, $\vec{q}$, and $\vec{Q}$ stand for the wave vectors of spin order and orbital order, respectively, and ϕ is the angle between x axis and the spin. We assume that there are two active orbitals like those of e_g orbitals and have reserved the freedom of OO with nonorthogonal orbitals, like $|3x^2-r^2\rangle$ and $|3y^2-r^2\rangle$. B is approximately a constant. If on the other hand, the third long-range order is lattice distortion and there is no OO, then $A=1$ and $B=0$, (or one can set $Q=0$). The effect of lattice distortion will appear in the Hamiltonian in next paragraph in the form of modulated hybridization energy.

The hybridization energy is affected by the orbital states and lattice distortion due to the anisotropies of the orbitals. It is also influenced by spins. The spins of the hopping electrons are aligned with localized spins. Hence, the Hamiltonian has the form

$$H = \sum \varepsilon_p c_{pi,l\sigma}^\dagger c_{pi,l\sigma} + \sum \varepsilon_d c_{dj}^\dagger c_{dj} + \sum_{n.n.}$$

$$\times [AV_l + BV \cos(\vec{Q} \cdot \vec{R}_j - \alpha_l)]\cos(\vec{Q}' \cdot \vec{R}_j)$$

$$\times [e^{-i\phi/2} \cos \theta_j c_{dj}^\dagger c_{pi,l\uparrow} + e^{i\phi/2} \sin \theta_j c_{dj}^\dagger c_{pi,l\downarrow}] + \text{H.c.}$$

$$+ \lambda \sum \vec{l}_j \cdot \vec{s}_j, \tag{5}$$

where l is the index of the oxygen atoms (position $\vec{R}_j + \vec{r}_l$) in the basis, and $\theta_j = \vec{q} \cdot \vec{R}_j / 2$. V_l and V_l' are the hybridization energies of the p orbital of the lth oxygen atoms with the first and second d orbital of the transition-metal atoms, $V = \sqrt{V_l^2 + V_l'^2}$ and $\cos \alpha_l = V_l / V$. The last term is the spin-orbit interaction. The factor $AV_l + BV \cos(\vec{Q} \cdot \vec{R}_j - \alpha_l)$ in hybridization comes entirely from OO. The modulation $BV \cos(\vec{Q} \cdot \vec{R}_j - \alpha_l)$ contains contribution from the first and second orbitals with the factors $\cos \alpha_l$ and $\sin \alpha_l$, respectively. If there is no OO, then $A=1$, $B=0$, and $\alpha_l=0$. The factor $\cos(\vec{Q}' \cdot \vec{R}_j)$ comes from the displacements of atoms. For example, if the oxygen atom between two transition-metal atoms moves laterally such that the bond angle of TM-O-TM is reduced, then the hybridization will be reduced for e_g electrons. Hence the hybridization energy acquires the modulation of lattice distortion (wave vector $\vec{Q}'$). If both OO and lattice distortion are present, then our case is viable only if they are commensurate to each other. In that case, two effects are superimposed on each other and the hybridization energy will has the form above. In the following calculation, we will consider the case with OO only. The extension to additional lattice distortion effect is not difficult.

The Hamiltonian without spin-orbit interaction can be diagonalized by making the substitution: $\vec{R}_{i,l} = \vec{R}_i + \vec{r}_l$, $p_{il,\uparrow} = e^{-i\phi/2} \cos(\vec{q} \cdot \vec{R}_{i,l}/2) c_{pi,l\uparrow} + e^{i\phi/2} \sin(\vec{q} \cdot \vec{R}_{i,l}/2) c_{pi,l\downarrow}$, and $p_{il,\downarrow} = e^{i\phi/2} \cos(\vec{q} \cdot \vec{R}_{i,l}/2) c_{pi,l\downarrow} - e^{-i\phi/2} \sin(\vec{q} \cdot \vec{R}_{i,l}/2) c_{pi,l\uparrow}$, and taking Fourier transform. For our purpose, it suffices to assume that $\varepsilon_d - \varepsilon_p > |V|$ and analyze the perturbed wave function. The resulting wave function can be expressed with the following tight-binding wave functions: $\psi_{d,\vec{k}}(\vec{r}) = \sum_j e^{i\vec{k} \cdot \vec{R}_j} \Psi_j$ and $\psi_{p,l,\vec{k}}(\vec{r}) = \sum_j e^{i\vec{k} \cdot \vec{R}_j} \psi_p(\vec{r} - \vec{R}_j - \vec{r}_l)(e^{-i\phi/2} \cos \theta_j, e^{i\phi/2} \sin \theta_j)^T$ and it is

$$\psi_{\vec{k}}(\vec{r}) = C \left\{ \psi_{d,\vec{k}}(\vec{r}) + \sum_l \frac{V_l}{\varepsilon_d - \varepsilon_p} \right.$$

$$\left. \times \left[A\psi_{p,l,\vec{k}}(\vec{r}) + \frac{B}{2} \sum_\zeta e^{-i\zeta\alpha_l} \psi_{p,l,\vec{k}+\zeta\vec{Q}}(\vec{r}) \right] \right\}, \tag{6}$$

where $\psi_p(\vec{r} - \vec{R}_j - \vec{r}_l)$ is the p orbitals of the oxygen atoms at site $\vec{R}_j + \vec{r}_l$, $\zeta = \pm 1$, and C is a normalization constant.

We apply the spin-orbit interaction to the wave functions in Eq. (6) as a perturbation and gain a term $-(\lambda/\Delta)\vec{l} \cdot \vec{s}\Psi_j$, where $\Delta = J_H - \Delta_{cf}$ with J_H being the Hund's coupling energy

and Δ_{cf} the crystal-field splitting between e_g and t_{2g} orbitals. (The perturbed states have minority spin and t_{2g} orbitals.) Now we are in position to calculate the electric polarization with Eq. (6),

$$\vec{P} = \frac{e|C^2|\lambda}{(\varepsilon_d - \varepsilon_p)\Delta} \sum_{\vec{k},l} V_l \left[a\langle\psi_{d,\vec{k}}|(\vec{l} \cdot \vec{s})\vec{r}|\psi_{p,l,\vec{k}}\rangle \right.$$

$$\left. + \sum_\zeta \frac{be^{-i\alpha_l\zeta}}{2}\langle\psi_{d,\vec{k}}|(\vec{l} \cdot \vec{s})\vec{r}|\psi_{p,l,\vec{k}+\zeta\vec{Q}}\rangle \right] + \text{c.c.} \tag{7}$$

The unperturbed wave functions do not contribute to electric polarization because of cancellation. It is due to crystal structure inversion symmetry despite of spiral-spin configuration. The first term vanishes after summing over $\vec{k}$. It is again due to the inversion symmetry of the spatial part of the wave function. The net electric polarization comes from the second term in Eq. (7). The reason the catastrophic cancellation is avoided is that with the third long-range order, the energy bands open gaps at $2\vec{k} \cdot (\vec{Q} + \vec{G}) = (\vec{Q} + \vec{G})^2$, where $\vec{G}$ is a reciprocal-lattice vector. The gap is comparable to the hybridization energy if OO or lattice distortion is significant. Different mini bands not only have different energies but also have different linear combinations of wave functions. In other words, the symmetry of the entire band is lower. Introducing phonons into the system[14] has the same effect. The importance of $\vec{Q}$ is manifest. Calculation of the contribution of the highest mini band gives

$$\vec{P} \simeq \hat{e}_z \frac{4eI'AB\lambda V \cos \alpha}{\pi\Delta(\varepsilon_d - \varepsilon_p)}$$

$$\times [\cos(Q_x a_0)\sin(Q_x a_0/2)\sin(q_x a_0/2)\cos \phi$$

$$+ \cos(Q_x a_0)\sin(Q_y a_0/2)\sin(q_y a_0/2)\sin \phi], \tag{8}$$

where a_0 is the lattice constant and $I' = \int \psi_{zx}^*(\vec{r} - \vec{R}_j)z\psi_x(\vec{r} - \vec{R}_j - \vec{r}_l)d^3\vec{r}$. We define $\cos \alpha = |\cos \alpha_l|$, note that for $x^2 - y^2$ orbital $V_x = -V_y$ and for $3z^2 - r^2$ orbital, $V_x = V_y$ so that $\cos \alpha_x = \pm \cos \alpha_y$. In the continuum limit where $a_0 \to 0$, we found

$$\vec{P} \simeq -\frac{2eI'V\lambda}{\pi(\varepsilon_d - \varepsilon_p)\Delta}\hat{Q} \times (\hat{s}_j \times \hat{s}_{j+1}). \tag{9}$$

Here, $\hat{s}$ is the unit vector of the spin. In a crystal with a long-range order other than spins and electric polarization, the wave vector of the long-range order Q, emerges in the expression of electric polarization in place of the bond direction in Eq. (1), as shown in Fig. 1.

Since we are concerned with the magnitude of the electric polarization, we now make a practical estimation: $|V_l| \approx 0.5$ eV, $\varepsilon_d - \varepsilon_p \approx \Delta \approx 1$ eV, $\lambda \approx 0.05$ eV, and $AB \approx 0.5$. Note that above calculation is purely of hybridization. It does not involve double occupancy in the transition-metal atoms and hence, the on-site Coulomb repulsion does not have any effect. For this reason $\varepsilon_d - \varepsilon_p$ and Δ are smaller than those calculated with local-density approximation plus U density-functional theory. The magnitude of electric polarization is $|\vec{P}| \sim 3000–5000(I')$ $\mu C/m^2$. Since the order of magnitude of I' is a fraction of. The result of our calculation is compat-
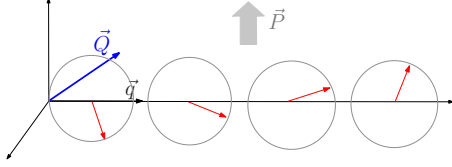
FIG. 1. (Color online) Schematic graph showing the directions of spins (red (short) arrows), electric polarization (gray (thick) arrow) $\vec{q}$ (black arrow), and $\vec{Q}$ (blue (light) arrow). $\vec{q}$ and $\vec{Q}$ can be parallel to each other.

ible with the experimental data of say, TbMnO$_3$.

III. SPIN CURRENT AND POLARIZATION

On reflection of Eq. (3), one sees clearly the origin of the electric polarization in Eq. (9). The ψ in Eq. (3) is just that in Eq. (6). The scattering of electrons with the third long-range order, which can be seen from our calculations in Eqs. (4)–(6), mixes different plane waves and hence, enable ψ to sustain current. With the magnetic moments provided by spiral spins in leading order, the spin current on the rhs of Eq. (3) gives rise to electric field on the left-hand side which in turn, causes electric polarization in the form $-\vec{E} \cdot \vec{P}$. With linear-response formalism,

$$\vec{P} = -e^2 \sum_n \frac{\langle 0|\vec{E} \cdot \vec{r}|n\rangle\langle n|\vec{r}|0\rangle}{E_0 - E_n}, \qquad (10)$$

one finds that $\vec{P}$ in Eqs. (9) and (10) has the same form. We have the following correspondence: $E_n - E_0 \sim \Delta$, $\vec{E} \cdot \vec{r}$ gives spin-orbit interaction with $\vec{E}$ in Eq. (3) and the spin operator in Eq. (3) gives the now well-quoted factor $\hat{s}_j \times \hat{s}_{j+1}$. Since spins and orbitals are closely related, wave vectors of magnetic orders and orbital order very likely have the relation $\vec{Q} = r\vec{q}$, where r is a rational number. Our calculation showed that only incommensurate OO can suppress catastrophic cancellation. If not, OO can be accounted for with an enlarged unit cell, and the electric polarization still suffers catastrophic cancellation. This can explain why magnetoelectric phenomenon usually occurs with incommensurate magnetic orders.

Our result has several implications. For example, it was found that[14,22] there is modulated electric polarization (antiferroelectricity) in multiferroics. Its absolute magnitude is much greater than that of the net polarization. The existence of OO makes things more complex. If the modulated polarization and OO are commensurate to each other, then an enhancement can occur. A related phenomenon is electromagnons[23] in multiferroic material.[24] It was suggested[25] that the dominant term is of the form $\vec{P} = \Sigma \vec{\Pi}_{ij} \vec{S}_i \cdot \vec{S}_j$. According to Moriya,[23] $|\vec{\Pi}_{ij}| \sim I'J/\Delta$ where the superexchange interaction J (V in Moriya's notation) is of the order $(V^2/\Delta)^2/U$ with U being the on-site Coulomb repulsion. Comparing to this $\vec{P}$, our polarization in Eq. (9) is more favorable or the spin-orbit coupling (0.05 eV) is relatively stronger compared to exchange interaction. The additional long-range order can give rise to extra magnon excitations. These are of purely electronic origin. The wave vector of the magnons can also be different. It is equal to $\vec{Q}$ for one-magnon processes and $\vec{k}$ and $\vec{k} \pm \vec{Q}$ for bimagnon processes. Its effect will be manifest in optical spectra, susceptibility, and electric polarizability measurement. This will be related to the vector spin chirality[26] $\hat{s}_j \times \hat{s}_{j+1}$. The study on this subject is under way.

In conclusion, we have proposed that with third long-range order in the system, the catastrophic cancellation of electric polarization can be avoided. The resulting magnitude is comparable to experimental data. The long-range order can be either OO or cooperative Jahn-Teller distortion but it has to be incommensurate. Lastly but perhaps most importantly, the cause of electric polarization and multiferroics is firmly established and it is spin current coming from the spin-orbit interaction.

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