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Magnetic structures upon ordering of e_g orbitals in a square lattice

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Abstract
The exchange mechanism effect on the ordering of electrons on e_g orbitals in a two-dimensional Heisenberg model with exchange anisotropy for a $S = 1/2$ spin is determined. The regions of existence of long-range quasi-one- and two-dimensional antiferromagnetic order with the special exchange topology are calculated by a quantum Monte Carlo method. The Nèel temperature and quantum reduction of spin on site for an antiferromagnet with the stripe structure is estimated as a function of exchange anisotropy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetic materials with double orbital quasi-degeneration are characterized not only by spin-dependent interactions, but also by the dependence of the exchange integral on the mutual position of the orbitals. The interplay of spins with the charge-orbital ordering changes not only magnetic properties, but also transport characteristics, for example, gives rise to giant magnetoresistance in manganites. The orbital ordering forms a quasi-one-dimensional antiferromagnetic ordering in $KCuF_3$ [1] and two-dimensional antiferromagnetic ordering in NH_4CuCl_3 [2] at low temperatures.

When studying the ground state and low-temperature effects in low-dimensional systems, one should remember that the quantum fluctuations in a spin system are of significant importance and, in the case of the strong interaction of spins with orbitals through the exchange interaction, it must be taken into account that the hopping integrals between the neighboring 3d ions depends on both the orbital type and on the mutual position of the sites, because the electron-density distribution is not spherically symmetric.

The interrelation between the spin order and orbital ordering is clearly illustrated in a Kugel'–Khomskii model [1] for the Hamiltonian of perovskites (e_g ions at the sites of a simple cubic lattice), which is obtained from the multi-electron Hamiltonian with the same exchange parameters $J = 4t^2/U$, where t is the hopping integral and U is the Coulomb-repulsion parameter at the site between electrons.

The physical origin of this peculiar situation is the strong spatial anisotropy of the e_g orbital wavefunctions. This type of orbital ordering provides the largest energy gain due to the quantum spin fluctuations. An orbital flip modulates the strength of the neighboring exchange bond and causes the existence of a strong antiferromagnetic exchange interaction directed along the overlap of the orbitals, with a strong space anisotropy of the exchange interactions that is typical of the quasi-one-dimensional system in the presence of a gap in an orbital excitation spectrum.

In addition to the ferro and antiferromagnetic ordering of the $d_{3z^2-r^2}$ orbitals, the ordering of the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals is also possible on account of the fact that the hopping integral between these orbitals may differ substantially due to strong electron correlations. The strength of the antiferromagnetic interaction is determined by the region of the overlap of the $2p_3d$ orbitals and depends on the orbital e_g state of an electron. The overlap integral between the $d_{x^2-y^2}$ and p_x orbitals is $E_{x,\alpha}(l,m,n) = (\sqrt{3/2})l(l^2 - m^2)(pd\sigma)$, where $(pd\sigma)$ is the overlap integral between the $d\sigma$- and $p\sigma$ orbitals and (l,m,n) is the unit vector along the direction from a cation to an anion. The overlap integral between $d_{2x^2-z^2-y^2}$ and p_x-orbitals is expressed as $E_{x,\beta}(l,m,n) = l[n^2 - (l^2+m^2)/2](pd\sigma)$ [3]. Then, the hopping amplitude between adjacent copper ions via the p-orbital along the x-axis is evaluated as $t^x_{\alpha\beta} = E_{x,\alpha}(1,0,0)E_{x,\beta}(-1,0,0)/(e_p - e_d)$ [3], where e_p and e_d are the energy levels for the d- and p-orbitals,

respectively, and $E_{x,\alpha}$ and $E_{x,\beta}$ are the overlap integrals of the $d_{x^2-y^2}$ and p_x orbitals and p_x and $d_{2x^2-z^2-y^2}$ orbitals, which will be denoted as d_x^2.

When the ratio of the hopping integrals is written as $t_{\alpha\alpha}/t_{\beta\beta} = 3/4$ and $t_{\alpha\beta}/t_{\beta\beta} = 1/4$, the exchange interactions between electrons on the $d_{x^2-y^2}$ and $d_{2x^2-z^2-y^2}$ orbitals differ by a factor of two: $J_{\alpha\alpha}/J_{\beta\beta} = 0.56$, whereas $J_{\alpha\beta}/J_{\beta\beta} = 0.063$.

The account for the Coulomb interaction between electrons located both at a site and between different orbitals will also lead to modification of the exchange parameters and an alternation of the $J_{\alpha\alpha}/J_{\beta\beta}$ relation between them. Below we consider a model with one electron (hole) on the e_g orbital with an exchange interaction between them specified by a parameter. This model is applicable to perovskites containing Mn^{3+}, Ni^{3+}, Cu^{2+}, and Fe^{2+} ions in octahedral environment.

This study is aimed at determining the effect of the exchange interaction between e_g electrons on the ordering of $d_{2x^2-z^2-y^2}$ and $d_{x^2-y^2}$ orbitals in a Mott insulator and the estimation of a region of the parameters, at which the magnetic order dimensionality changes from quasi-two-dimensional to quasi-one-dimensional antiferromagnetic. The exchange alternating in the spin Peierls quasi-two-dimensional antiferromagnetic gives rise to disappearing long-range order and to the formation of a singlet state. Possible the alternation of exchange along one direction of the lattice as a result of orbital ordering causes the instability of AF order.

2. Model and discussion

Let us consider a model with antiferromagnetic exchange alternation and a stripe structure for a spin $S = 1/2$: the Hamiltonian has the following form:

$$\begin{aligned} H = &-\sum_{i,j,\alpha}(1+\delta)J^{\alpha\alpha}S^{\alpha}_{i+1,j}S^{\alpha}_{i+2,j} \\ &+ K^{\alpha\alpha}(S^{\alpha}_{i+1,j}S^{\alpha}_{i+1,j+1} + S^{\alpha}_{i+2,j}S^{\alpha}_{i+2,j+1}) \\ &+ J^{\alpha\alpha}S^{\alpha}_{i,j}S^{\alpha}_{i+1,j} + (1-\delta)J^{\alpha\alpha}S^{\alpha}_{i,j}S^{\alpha}_{i,j+1} \\ &+ J^{\alpha\alpha}S^{\alpha}_{i+2,j}S^{\alpha}_{i+3,j} + (1-\delta)J^{\alpha\alpha}\big(S^{\alpha}_{i+3,j}S^{\alpha}_{i+4,j} \\ &+ S^{\alpha}_{i+3,j}S^{\alpha}_{i+3,j+1}\big) - \sum_i H_i S^z_i \end{aligned} \tag{1}$$

where $J(1+\delta)$, $J(1-\delta)$, $J(J<0)$ are the exchange interactions between electrons located at the nearest d_{2x^2}–d_{2x^2}, $d_{x^2-y^2}$–$d_{x^2-y^2}$, $d_{x^2-y^2}$–d_{2x^2} orbitals, H is the external magnetic field, $\eta = J^{zz} - J^{xx(yy)}/J^{zz}$ is the exchange anisotropy value, $K < 0$ is the interchain exchange value fixed in our calculations as $K/J = 1/16$. As a calculation method, we have selected the quantum Monte Carlo method that combines two algorithms, namely the world-line algorithm and the continuous time algorithm for the spin $S = 1/2$ [4]. The continuous time world-line Monte Carlo approach is based on an expansion of a statistical evolution operator $e^{-H/T}$ by exchange interaction strength. The Hamiltonian is divided into two parts: the diagonal part $H_0 \sim JS^z_iS^z_j$ and the nondiagonal part $V_J \sim J/2(S^+_iS^-_j + S^-_iS^+_j)$. Following [4] we express operators $\exp[-\tau_0(H_0/2 + V_J)]$ on the imaginary time segments τ_0 in terms of the evolution operator σ_{ev} in the interaction representation $\exp(-\tau_0 H) = \exp(-\tau_0 H_0)\sigma_{ev}$, where

$$\begin{aligned} \sigma_{ev} = 1 &- \int_0^{\tau_0} d\tau\, V_{J,\alpha}(\tau) + \ldots + (-1)^m \\ &\times \int_0^{\tau_0} d\tau_m \ldots \int_0^{\tau_2} d\tau_1 V_{J,\alpha}(\tau_m)\ldots V_{J,\alpha}(\tau_1) + \cdots \end{aligned} \tag{2}$$

and $V_{J,\alpha}(\tau) = e^{\tau H_0}V_{J,\alpha}e^{-\tau H_0}$, $V_{J,\alpha}|\beta\rangle = -q_{\gamma\beta}(J,\alpha)|\gamma\rangle$.

The summation and integration of operator V_J in equation is carried out using a stochastic procedure of sampling various kink–antikink configurations in accordance with their weights. The probability of the formation of a kink–antikink pair is given by

$$\begin{aligned} W &= |q_{\gamma\beta}(J,\alpha)|^2 \exp((\tau_2-\tau_1)E_{\gamma\beta}), \\ E_{\gamma\beta} &= E_\gamma - E_\beta, \qquad H_0|\gamma\rangle = E_\gamma|\gamma\rangle, \\ H_0|\beta\rangle &= E_\beta|\beta\rangle, \qquad (\tau_2-\tau_1) < \tau_0. \end{aligned} \tag{3}$$

A subprocess of kink shift along the time axis with probability $W = \exp(\Delta\tau E_{\gamma\beta})$ is possible. The use of global spin flips at a site leads to a finite transition probability $W \sim q_{\gamma\beta}$ on interval τ_0. As a result, the total projection of the spin changes and discontinuities are observed on world lines with even numbers. Since computations lead only to an even number of nondiagonal changes of trajectories $q^{2n}_{\gamma\beta}(J)$ we can avoid obtaining the minus sign due to an increase in the systematic error [5]. As an eigenfunction of Hamiltonian H_0, we choose the S^z representation of $\uparrow$ and $\downarrow$ spins.

In the calculations a square lattice with $L = 40, 48, 60, 72$ and periodic boundary conditions is used. From 40 000 to 60 000 Monte Carlo steps (MCS) per site are spent to reach equilibrium and another 80 000–100 000 MCS are used for the averaging.

We consider two types of the orbital ordering that are illustrated in figure 1. The d_{2x^2}–d_{2x^2} orbitals overlap gives rise to a strong antiferromagnetic exchange and space anisotropy of the exchange interactions in a lattice, which differ by more than an order of magnitude. The magnetic properties of such a system are similar to those of a quasi-one-dimensional antiferromagnet. Alternation of pairs of the d_{2x^2}–d_{2x^2}, $d_{x^2-y^2}$–$d_{x^2-y^2}$ orbitals induces stripes along the [01] direction and alternation of the exchange interactions along the [10] direction, as one can see in figures 1(c) and (d). The magnetic properties of systems with the two types of orbital ordering have been analyzed on the basis of a spin–spin correlation function $\langle S^z(0)S^z(r)\rangle$, staggered magnetization m_s, a magnetic structure factor $S(q) = \frac{1}{N}\sum_r \exp(-iqr)S^z(0)S^z(r)$, energy E and specific heat $Ck_B/N = dE/dT$. The temperature dependences of the staggered magnetization and specific heat are plotted in figure 2 for anisotropic AF with various parameters of alternating exchange. The temperature at which specific heat has its maximum and staggered magnetization tends to zero is associated with the Nèel temperature.

Alternation of exchange along one of the lattice directions enhances the quantum fluctuations, which results in a reducing spin on site in the limit of 5%–9% in the range of parameters $0 < \delta < 0.4$ and decreasing Nèel temperature. The normalized Nèel temperature, plotted in the inset to figure 3,

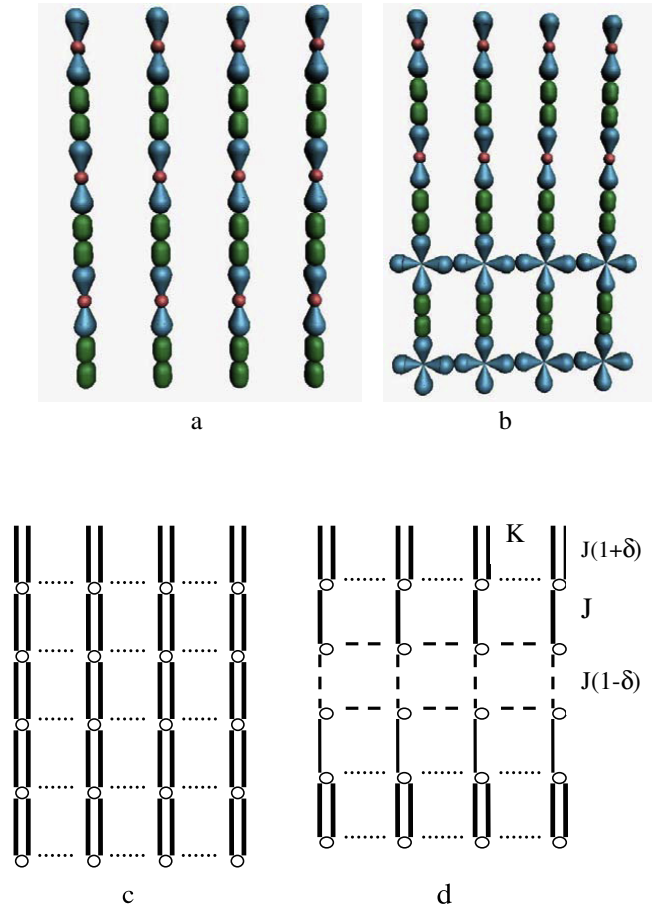

Figure 1. d_{2x^2}–d_{2x^2} (a) and $d_{x^2-y^2}$–d_{2x^2} (b) orbital ordering. Arrangement of the strong intrachain $J(1+\delta)$ and weak interchain K exchanges in a square lattice. The J-exchange is related to the overlap of d_{2x^2}–$d_{x^2-y^2}$ orbitals; $J(1+\delta)$ is related to the d_{2x^2}–d_{2x^2} orbitals, $J(1-\delta)$ is the $d_{x^2-y^2}$–$d_{x^2-y^2}$ orbitals overlap.

is well fitted by the linear function $T_N(\delta)/T_N(0) = 1 - 0.6\delta$ for a series of anisotropy parameters. Monte Carlo simulation of thermodynamic characteristic at larger δ and interpolation of the linear function $T_N(\delta)/T_N(0)$ indicate the stability of AF order as compared to disordered spin state. A similar effect of the reduction of spin arises from the exchange anisotropy. Staggered magnetization and Nèel temperature of AF having the stripe structure rise with increasing anisotropy as is shown in figure 3. The dependence of $T_N(\eta)$ versus exchange anisotropy is interpolated better by a power function $T_N(\eta)/J = 1/4\eta^{1/6}$ than a logarithmic law. It differs from the behavior of an anisotropic Heisenberg antiferromagnet with $S = 1/2$ on a square lattice that reveals a logarithmic dependence $T_N(\eta)/J = 2/\ln(11/\eta)$ [6] and a linear dependence of $1/\sigma$ versus $\ln(1/\eta)$ for $\eta > 0.01$ [7]. A stripe structure is also observed at static charge disproportional between the 3d elements in the oxide compounds [8, 9] and the magnetic properties are considered in terms of the Heisenberg model with a nonuniform distribution of exchange in the lattice [10, 11].

We have determined the basic magnetic properties of a two-dimensional magnet with the orbital ordering presented in figure 1(b). As a consequence of low dimensionality of

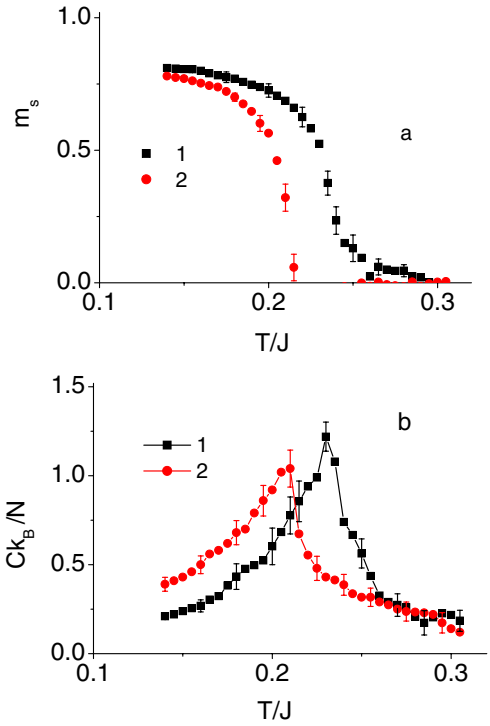

Figure 2. Staggered magnetization m_s (a) and specific heat Ck_B/N (b) of a magnet with the orbital ordering (figures 1(b) and (d)) for the anisotropy $\eta = 0.5$, $\delta = 0.1(1).0.3(2)$, $L = 60$ versus temperature.

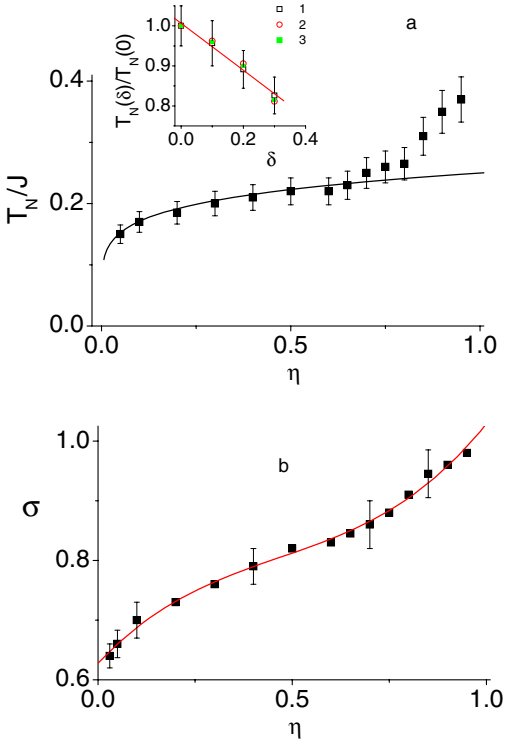

Figure 3. Nèel temperature T_N/J of the quasi-two-dimensional AF at $\delta = 0.3(1)$ and fitting function $T_N/J = \eta^{1/6}/4$ (solid line) as a function of exchange anisotropy (a). Inset: normalized Nèel temperature $T_N(\delta)/T_N(0)$ versus alternating exchange at $\eta = 0.25(1), 0.5(2), 0.75(3)$. Magnetization on the site σ calculated by MC at $T/T_N = 0.2$, $L = 60$ versus exchange anisotropy (b).

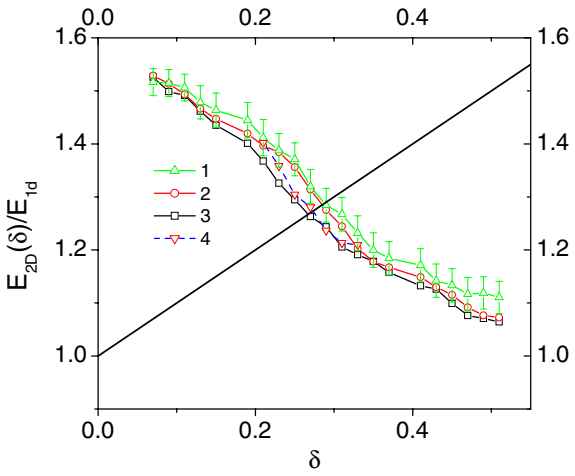

Figure 4. Energy of a quasi-two-dimensional antiferromagnetic E_{2D} (figure 1(d)) and a quasi-one-dimensional antiferromagnetic with the strong intrachain $J(1+\delta)$ exchange normalized to the energy of the E_{1D} antiferromagnetic with the exchange ratio $K/J = 1/16$ for $\eta = 0.25$, $L = 40(1), 48(2), 60(3), 72(4)$ calculated at $T/T_N = 0.2$ as a function of the exchange alternation.

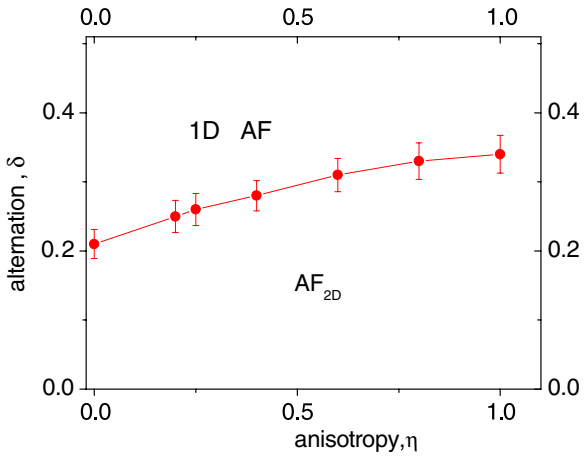

Figure 5. Phase diagram of a magnet containing the regions of quasi-two-dimensional AF with the orbital ordering d_{2x^2}, $d_{x^2-y^2}$ (lower line) and quasi-one-dimensional AF with d_{2x^2}–d_{2x^2} orbital ordering (upper line) in a plane alternation–anisotropy exchange.

the system, the quantum spin fluctuations may cause orbital correlations and the ordering of the d_{2x^2}–d_{2x^2} orbitals. In this case, spin interactions are quasi-one-dimensional along a chain and favor a rise of exchange energy, which is proportional to $E/J = 0.44(1+\delta)$. Ising-like anisotropy suppresses the quantum spin fluctuations and decreases the absolute energy value from $E/J = 0.44$ to 0.25 with an increase in the exchange anisotropy. With the growth of the exchange alternation along the [10] direction, the energy of a 2D system decreases due to a decrease in the interchain interaction. Figure 4 illustrates the energy of a 2D magnet calculated for several lattice sizes. The intersection of energies of the 1D and 2D magnets with the arrangement of bonds in a lattice as in figures 1(c) and (d) determines the region of stability of the 2D magnetic ordering with a stripe structure. A phase boundary separating the region of existence of magnets with the d_{2x^2}–d_{2x^2} and d_{2x^2}–$d_{x^2-y^2}$ orbital ordering is given in figure 5.

The quasi-one-dimensional AF ordering becomes stable at $\delta > 0.2, \eta = 0, \delta > 0.34, \eta \to 1$. The ratio of exchanges in $KCuF_3$ is $J(d_{x^2-y^2}$–$d_{x^2-y^2})/J(d_{2x^2}$–$d_{x^2-y^2}) \simeq 0.78$ that corresponds to $\delta \sim 0.22$. Exchange anisotropy is small for the cubic crystal and according to our results the ordering of the d_{2x^2}–d_{2x^2} orbitals is preferred. Orthorhombic distortion of a structure in NH_4CuCl_3 induces modification in a crystal field and in the intra-atomic Coulomb interaction U_{dd} between electrons in the orbital. The change in distance and in angle of a bond between the nearest cations modifies the overlap of the integral of the wavefunctions of the d_{2x^2} and $d_{x^2-y^2}$ orbitals. As a result, the ratio of amplitudes of the hopping integrals may vary in the wide range $0.1 < t_{\alpha\alpha}/t_{\beta\beta} < 1$ because the hopping integral is $t = E^2/(e_p - e_d + U_{dd})$. The exchange interaction between electrons on the d_{2x^2}–d_{2x^2} orbitals decreases and the ratio of exchanges $J(d_{x^2-y^2} - d_{x^2-y^2})/J(d_{2x^2} - d_{2x^2})$ grows; this corresponds to a decrease of the alternation parameter. As a consequence, the variation of exchange interaction causes rearrangement of the d_{2x^2} and $d_{x^2-y^2}$ orbitals and leads to strongly decreasing Nèel temperature in NH_4CuCl_3 [2]. Orbital rearrangement leads to modification of the spectral electron density near the top of a valence band and near the bottom of a conductivity band.

3. Conclusion

We have analyzed the exchange mechanism of the ordering of electrons on the e_g orbitals using the Heisenberg model with the special exchange topology on a square lattice. We have found the exchange parameters associated with the relation of the exchange interaction of electrons on the d_{2x^2}–d_{2x^2} and $d_{x^2-y^2}$–$d_{x^2-y^2}$ orbitals and exchange anisotropy, under which the ordering of pairs of the d_{2x^2}–d_{2x^2}, $d_{x^2-y^2}$–$d_{x^2-y^2}$ orbitals form a two-dimensional antiferromagnetic state with a stripe structure. The region of existence of an quasi-one-antiferromagnetic in the plane of anisotropy–alternation of exchange has been calculated. Quantum reduction of spin on a site for a quasi-two-dimensional antiferromagnet with stripe structure versus exchange anisotropy has been estimated.

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