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Formation of a Gapless Quantum Spin Liquid upon Orbital Ordering in a Chain

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The exchange mechanism of the ordering of electrons on e_g orbitals has been estimated by the quantum Monte Carlo method with the inclusion of the hopping integrals through an anion in a one-dimensional system. A magnetic state in the form of a gapless quantum spin liquid has been found. The plateau existence region in the field-dependence of the magnetization, as well as the wave vector of the modulation of the magnetic structure with $Q = \pi/2$ in the (magnetic field–exchange alternating) plane, is determined.

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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. This property changes not only the magnetic properties but also the transport characteristics, for example, gives rise to giant magnetoresistance in manganites. The orbital ordering forms a quasi-low-dimensional structure in $KCuF_3$ [1] and likely results in the formation of quantum states without the long-range magnetic order in $KCuCl_3$ [2] and NH_3CuCl_3 [3]. When investigating the ground state and low-temperature effects in low-dimensional systems, quantum fluctuations in the spin system are of significant importance and, in the case of the strong interaction of spins with orbitals through the exchange interaction, it is necessary to take into account that the hopping integrals between the neighboring 3*d* ions depend both on the orbital type and on the mutual position of the sites, because the electron-density distribution is not spherically symmetric.

The relation of the spin order to the orbital ordering is illustrated in the Kugel'–Khomskiĭ model [1] for the Hamiltonian of perovskites (e_g ions at the sites of the simple cubic lattice), which is obtained from the multielectron 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 the d_{z^2}–d_{z^2} and $d_{x^2-y^2}$–$d_{x^2-y^2}$ orbitals. More accurate calculation of the hopping integrals of electrons between neighboring cations along the x axis through an anion (oxygen, fluorine, chlorine, etc.) yields the expression $t^x_{\alpha\beta} = E_{x,\alpha}E_{x,\beta}/(\epsilon_p - \epsilon_d)$, where ϵ_p and ϵ_d are the level energies for the p and d orbitals, respectively; $E_{x,\alpha}$ is the overlap integral between the $d_{x^2-y^2}$ and p_x orbitals; and $E_{x,\beta}$ is the overlap integral between the $d_{2x^2-z^2-y^2}$ and p_x orbitals calculated in [4]. When the ratio of the hopping integrals is written in the form $t_{\alpha\alpha}/t_{\beta\beta} = 3/4$ and $t_{\alpha\beta}/t_{\beta\beta} = \sqrt{3/2}$ and the exchange interactions between electrons on the d_{z^2} and $d_{x^2-y^2}$ orbitals differ by a factor of almost 2, $J_{\alpha\alpha}/J_{\beta\beta} = 0.56$, whereas $J_{\alpha\beta}/J_{\beta\beta} = 0.75$. The Coulomb interaction between electrons both at a site and between different orbitals should also be taken into account when calculating exchanges, and the inclusion of this interaction modifies the relation between the exchanges. Below, we consider a model with one electron (hole) on the e_g orbital with the inclusion of only the electron exchange mechanism. This model is applicable to perovskites containing the Mn^{3+}, Ni^{3+}, Cu^{2+}, and Fe^{2+} ions in the octahedral environment.

It is known that low-dimensional systems with alternating exchange imitating the spin Peierls transition are in a more stable state and have an energy gain of $E/J \sim \delta$, where $\delta = J_{i,i+1} - J_{i+1,i+1}$. The interaction of the electrons on the e_g orbitals with various octahedron oscillation modes forms orbital ordering. The most widespread type of the orbital ordering is associated with the alternating of the $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals, whose schematic arrangement has the form ⇳⇔⇳⇔. For oxides and ions located in a distorted octahedron, this corresponds to the distortion axis rotation in the xy plane by an angle of $\pi/2$. The effective interaction

between the orbitals is $\sim g_k^2 \omega_k^{-1}$ (g is the electron–phonon coupling constant and ω is the octahedron oscillation frequency) and reaches a maximum at the edge of the Brillouin zone for perovskite-like crystals [5]. Another case is associated with the removal of the degeneration of the e_g orbitals and with the doubling of the unit cell along the c axis. For example, the alternating of prolonged and flattened octahedra along the tetragonal axis gives rise to the redistribution of the electron density on the d_{z^2} and $d_{x^2-y^2}$ orbitals. The exchange energy between spins on the neighboring orbitals can decrease when pairs of orbitals are ordered as $\Updownarrow\Updownarrow\Leftrightarrow\Leftrightarrow$ and $d_{z^2}-d_{z^2}-d_{x^2-y^2}-d_{x^2-y^2}$ for the first and second cases, respectively. Exchange alternating reduces the system energy due to quantum spin fluctuations in low-dimensional systems. Competition between the exchange energy and effective interaction between orbitals can change the orbital and spin orderings at low temperatures or can soften the optical oscillation mode in the middle of the Brillouin zone.

Let us consider the model with the symmetric alternating exchange described by the Hamiltonian

$$H = -\sum_i [J(1+\delta)\hat{S}_i\hat{S}_{i+1} + J\hat{S}_{i+1}\hat{S}_{i+2} + J(1-\delta)\hat{S}_{i+2}\hat{S}_{i+3} + J\hat{S}_{i+3}\hat{S}_{i+4}] - \sum_i H_i S_i^z, \quad (1)$$

where $J \sim t_{\alpha\beta}^2$ is the exchange interaction determined by the hopping of electrons between the different orbitals at the neighboring sites and H is the external magnetic field. The unit cell contains four spins coupling by the exchanges J, $J(1 \pm \delta)$.

As a calculation method, we take the quantum Monte Carlo method unifying two algorithms, worldlines and continuous time [6], for the spins $S = 1/2$ located at the sites of the chain $L = 400$ with the nonuniform exchange distribution and periodic boundary conditions. The calculation method was described in detail in [7]. The following quantities are calculated in the framework of this method: the magnetization $m = 2\langle S^z\rangle$, the spin–spin correlation function, the correlation radius, the static susceptibility $\chi = m/H$ in the external magnetic field directed along the quantization axis, the energy, and the entropy $S(T_i) = \int_0^{T_i} dT/T(dE/dT)$.

Figure 1 shows the correlation radius determined by fitting the function $\langle S^z(0)S^z(r)\rangle = A/r^\eta \exp(-r/\xi)$ to the calculated distance dependence of the spin–spin correlation function. As the alternating magnitude increases, the correlation radius decreases sharply (the power exponent remains almost unchanged, $\eta = 1 \pm 0.08$). The derivative $d\xi/dT$ has a maximum at a certain temperature T^* (see the inset in Fig. 1). The interpolation of

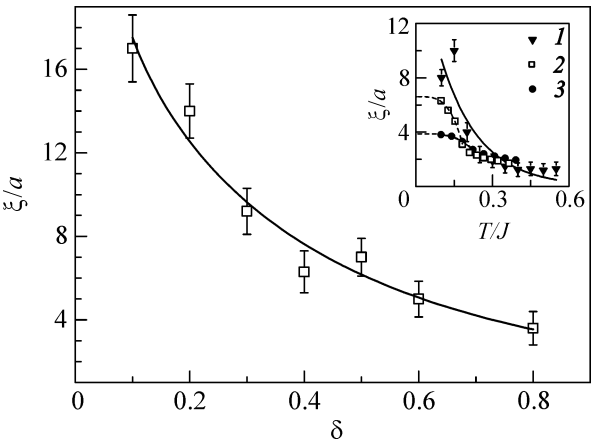

Fig. 1. Correlation radius of the magnet normalized to the lattice constant a with the ordering of orbital pairs and the approximation dependence $\xi(\delta)$ given by Eq. (2) vs. the exchange alternating magnitude. The inset shows the temperature dependence of the correlation radius for $\delta = (1)$ 0, (2) 0.4, and (3) 0.8 and $\xi =$ (solid line) A/T and (dotted line) $A - BT^3$.

$\xi(T)$ by a third-order polynomial for low temperatures $T < T^*$ provides the asymptotic value of the correlation radius. The approximation of the calculated results for $\xi(\delta)$ by the function

$$\xi = \frac{A}{(1+\delta)^\alpha}\exp\left(\frac{1}{B\delta}\right) \quad (2)$$

with the parameters $\alpha = 3$, $B = 60(2)$, and $A = 11(1)$ provides the minimum dispersion as compared to the power function. In a limiting case of $\delta \longrightarrow 1$, the correlation radius is on the order of the lattice constant. In a limiting case of $\delta \longrightarrow 0$, the spin–spin correlation function of the Heisenberg chain with the antiferromagnetic exchange is a power function.

The exchange alternating in the spin Peierls chain induces a gap in the spectrum of the triplet excitations and gives rise to a finite correlation radius in the ground state. Using the calculated dependences of the magnetization and spin correlation functions on the external magnetic field, we determine the critical fields H_c corresponding to the formation of the long-range magnetic order and the gap in the triplet-excitation spectrum. The calculations provide a linear dependence, $\Delta \cong 2\delta$, of the gap on the exchange alternating and are in good agreement with the limiting case for one dimer, $H_c = gS^zJ(1+\delta) = 2J$. The thermodynamic characteristics—the specific heat and susceptibility capacity—decrease according to the exponential law below this temperature.

The ordered arrangement of the orbital pairs described by Hamiltonian (1) gives rise to the appearance of the plateau on the magnetization curve $m(H)$ shown in Fig. 2 at a critical external field H_{c1}. The corresponding magnetization is equal to $m = 0.5\mu_B$. The

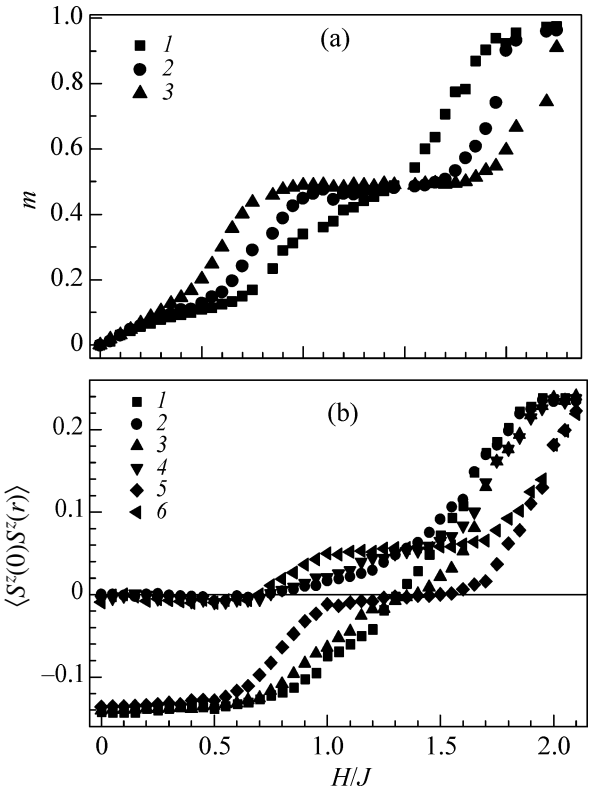

Fig. 2. Field dependences of the (a) magnetization m and (b) spin–spin correlation functions $\langle S^z(0)S^z(r)\rangle$ at the distance r = (*1*, *3*, *5*) 1 and (*2*, *4*, *6*) 31 for δ = (*1*) 0.2, (*2*) 0.4, and (*3*) 0.6. The symbol sizes correspond to the errors.

magnetic structure factor determined from the spin–spin correlation function

$$S(q) = \frac{1}{N}\sum_{r_j} \exp(-iqr_j)S^z(0)S^z(r_j)$$

has a main maximum and a number of satellites (see Fig. 3). The magnetic field aligns the spins of the kinks along the field and stabilizes the long-range ferromagnetic order, which does not coincide with the short-range order calculated by chain-averaging of the spin–spin correlation function in the first coordination sphere. As the magnetic field increases, the modulation of the magnetic structure with the wave vector $q = \pi/2$ is observed near the magnetic field $H \sim H_{c1}$. The linear dependence $m(H)$ for low external fields indicates the absence of a gap in the spectrum of triplet spin excitations and the magnetic state is a quantum spin liquid with a finite correlation radius.

The data can be treated assuming that the spin of the unit cell in the ground state is equal to zero, whereas the excited state corresponds to a triplet with $S^z = 1$. In the presence of the magnetic field, these states are split and the multiplet energies with $S^z = 1$ and $S^z = 0$ intersect at H_{c1}. The arrangement of the spins in the chain in the

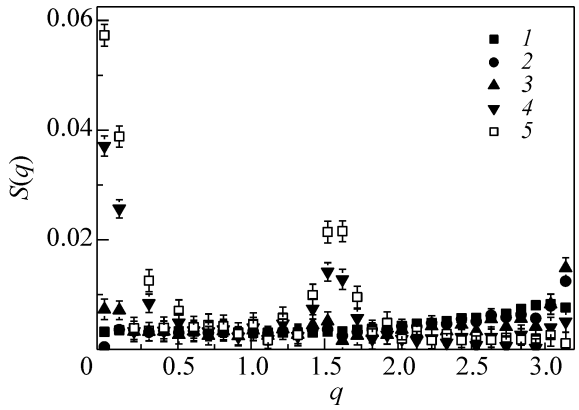

Fig. 3. Magnetic structure factor $S(q)$ of a magnet with the orbital ordering of pairs for $\delta = 0.6$ in the external magnetic field H/J = (*1*) 0.1, (*2*) 0.3, (*3*) 0.5, (*4*) 0.7, and (*5*) 1.1.

plateau region $H_{c1} < H < H_{c2}$, which is determined from the analysis of the spin–spin correlation functions (see Fig. 2b), can be represented as ↑↑↑↓↑↑↑↓. The modulation of the magnetic structure is well described by the wave vector $Q = \pi/2$.

The multiplets with $S^z = 1$ and 2 intersect in the field H_{c2}, the short-range order coincides in sign with the long-range ferromagnetic order, and the ferromagnetic modulation disappears. This interpretation is confirmed by the critical fields H_{c1} and H_{c2} determined by means of the exact diagonalization of a four-spin cluster at $\delta \longrightarrow 1$; these data are shown in Fig. 4. The ordering of the orbital pairs in the magnetic field provides three types of the magnetic order: short-range antiferromagnetic order; ferromagnetic order; and modulated ferromagnetic order with $Q = \pi/2$, depending on the relation of the magnetic field and exchange alternating. Figure 4 shows the regions of these phases in the (magnetic field, exchange alternating) plane.

The plateau on the magnetization curve $m(H) = 1/2$ is also observed for other models, e.g., in an antiferromagnetic chain with easy-plane anisotropy and with a spin of $S = 3/2$ at the site [8] and in a zigzag chain with alternating exchange and exchange interaction between the spins $S = 1/2$ of the second neighbors [9]. This effect is explained by the formation of the dimers and spinons in the former model and the induced XY anisotropy in the latter model. Anisotropy induced by the internal parameters of the Hamiltonian gives rise to the formation of the gap in the triplet-excitation spectrum. To reveal the activation character of the excitation spectrum in the phase with the modulated ferromagnetic order in the field range $H_{c1} < H < H_{c2}$, we calculate the temperature dependences of the magnetic state and the magnetic structure factor in the field range where the plateau $m = 1/2$ is observed. The gap ΔE in the spin excitation spectrum is responsible for the exponential behavior of the susceptibility $\chi \sim \exp(\Delta E/k_B T)$.

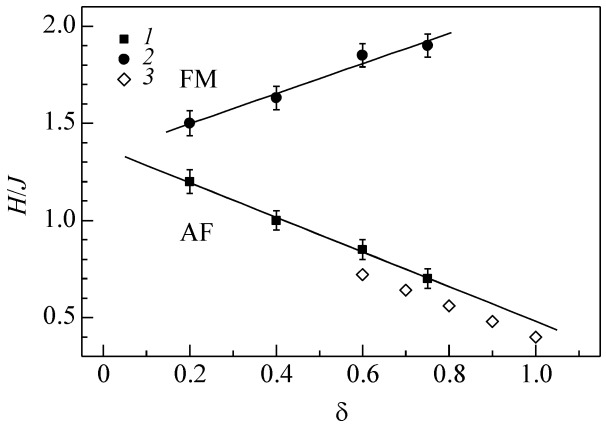

Fig. 4. Phase diagram of the magnet with the orbital ordering of pairs containing the regions with the short-range antiferromagnetic order (AF), ferromagnetic order (FM), and modulated ferromagnetic order with the plateau $m(H) = 1/2\mu_B$ in the field interval $H_{c1}(1) - H_{c2}(2)$ in the (magnetic field, exchange alternating) plane. The critical fields $H_{c1}(3)$ correspond to the singlet–triplet transition in a four-spin cluster.

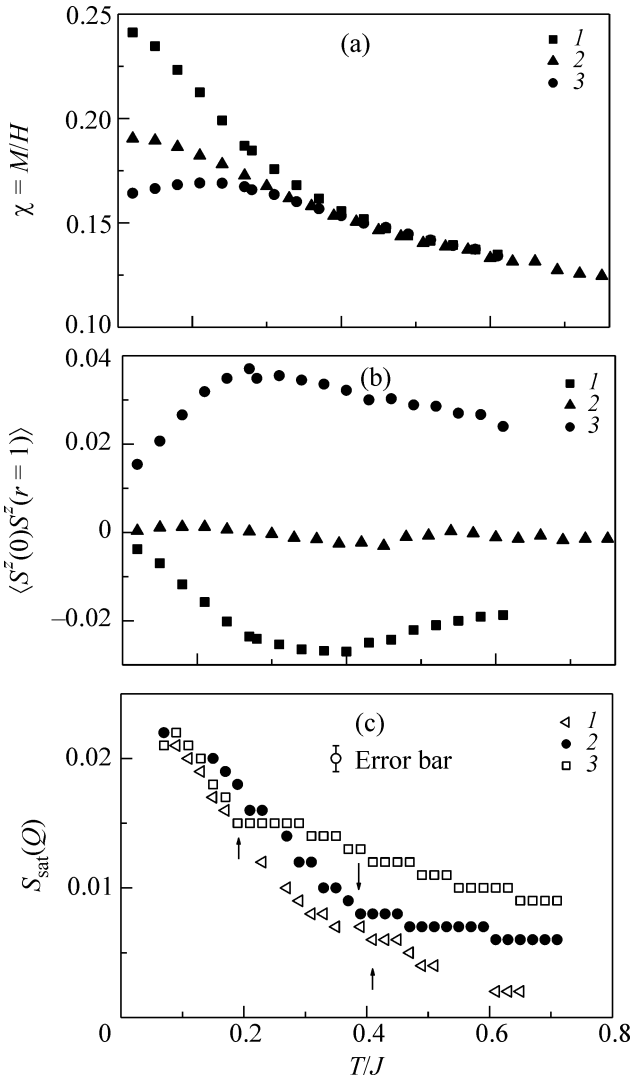

Fig. 5. Temperature dependences of the (a) susceptibility $\chi = M/H$, (b) spin correlation functions $\langle S^z(0)S^z(r = 1)\rangle$ (the symbol sizes correspond to the errors), and (c) superstructure reflection intensity $S_{sat}(Q)$ of the alternating chain with $\delta = 0.6$ in the field $H/J = (1)$ 1, (2) 1.3, and (3) 1.6. The temperature corresponding to the disappearance of the modulated ferromagnetic structure with $Q = \pi/2$ is marked by the arrows.

Figure 5 shows the temperature dependences of the susceptibility at a given exchange alternating as calculated for various fields. The behavior of the susceptibility $\chi(T)$ is smooth and approximated by a power law. Here, the temperature behaviors of the spin correlation functions are different in two magnetic field regions $H < H^*$ and $H > H^*$, where $H^* \cong (H_{c1} + H_{c2})/0.5$. In particular, the short-range antiferromagnetic order in the fields $H < H^*$ is recovered with increasing temperature (see Fig. 5b) and the temperature dependence of the magnetic structure factor is similar to the behavior of an antiferromagnet in the spin-flop phase. The wave vector of the superstructure reflection (see Fig. 5c) disappears at a certain temperature T^* increasing monotonically with the exchange alternating magnitude. The disappearance of the modulation of the structure correlates with the increase in the entropy growth at $T^* \sim 0.45$ ($\delta = 0.6$). The increase in the magnetization (see Fig. 5a) and the appearance of the short-range ferromagnetic order (see Fig. 5b) with increasing the temperature in high fields $H > H^*$ indicate the suppression of quantum fluctuations of the magnetic field. The temperature at which the magnetization is maximal and the wave vector of the superstructure disappears (see Fig. 5c) corresponds to the crossover region of the transition from the regime of quantum fluctuations to the regime of classical fluctuations. This effect is likely manifested also when the short-range antiferromagnetic order is induced in the field $H < H^*$. In particular, an inflection point is observed on the entropy curve $S(T)$ in the temperature interval $T = 0.25$–0.3 ($\delta = 0.6$).

The magnetic state (see Fig. 6) of the magnets with the orbital ordering is maximal at the temperature T_{max}. The temperature dependence of the susceptibility in this region is similar to the dependence of the susceptibility of the two-level singlet–triplet system. The excitation spectrum of uncoupled four-spin clusters at $\delta = 1$ is significantly different from the spectrum of the clusters interacting with each other ($\delta \longrightarrow 1$). In the former case, the energy of the triplet state is $E_t = -J$. For the continuous chain, $\delta \longrightarrow 1$, the excited states correspond to the spinons with an energy of $E_s = -1.5J$; i.e., the energy gap between the ground state and excited states of the spinons is half the value for the magnon excitations.

The decrease in the energy of the antiferromagnetic chain with the nonuniform periodic distribution of exchange is caused by the decrease in the effective

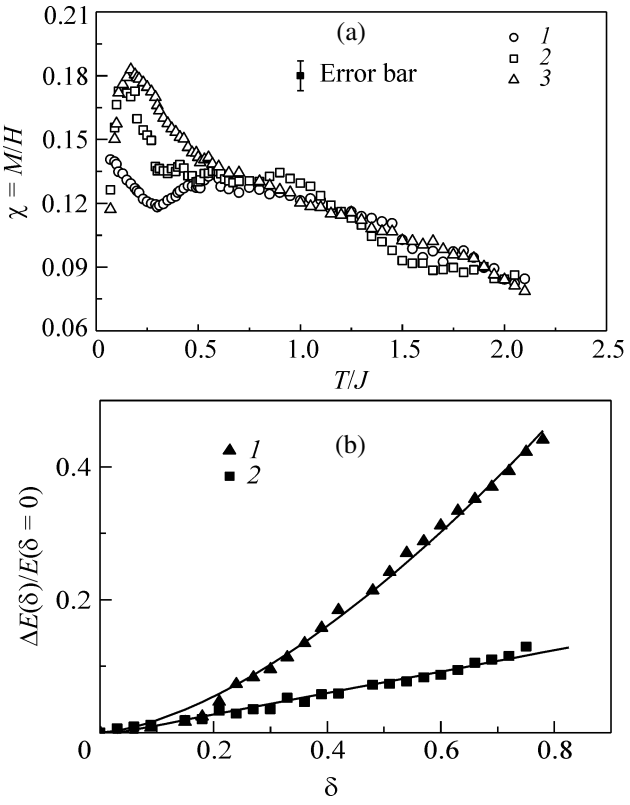

Fig. 6. (a) Temperature dependence of the susceptibility of the magnet with the orbital ordering for δ = (*1*) 0.2, (*2*) 0.4, and (*3*) 0.6 calculated by the Monte Carlo method in the field $H/J = 0.1$. (b) Exchange-alternating dependence of the relative energy change $\Delta E = (E(\delta) - E(\delta = 0))$ for (*1*) the spin Peierls model, (*2*) ordering of the orbitals, and power-law approximation functions $\Delta E/E(\delta = 0) = A\delta^{\alpha}$ with the parameters (*1*) $A = 0.67(2)$ and $\alpha = 1.50(4)$ and (*2*) $A = 0.15(1)$ and $\alpha = 1$ (orbital ordering). The errors correspond to the symbol sizes.

chain length owing to a change in the correlation radius. In particular, in the limiting cases, the energies per spin in the infinite antiferromagnetic chain and dimer are $E_{\text{chain}} = -2\ln 2 + 0.5 \simeq -0.4433J$ and $E_{\text{d}} = -0.75J$, respectively. As a result, the energy of the alternating chain depends on the wave vector of the exchange modulation; i.e., the larger the number of the spins coupled by the strong exchange, the lower the change in the energy of the chain after the exchange alternating. The unit cell contains two and four spins in a spin Peierls magnet and in a magnet with orbital ordering, respectively. Figure 6b shows the Monte Carlo calculations of the relative energy change as a function of the exchange-alternating magnitude. These data are well approximated by the power function $\Delta E/E = A\delta^{\alpha}$ with the parameters $A = 0.67(2)$ and $\alpha = 1.50(4)$ (spin Peierls model) and $A = 0.15(1)$ and $\alpha = 1$ (orbital ordering). The results for $\delta \longrightarrow 1$ almost coincide with the energy change calculated for the four-spin cluster for the spin Peierls model $\Delta E/E$ = (exact) 0.69 and (Monte Carlo) 0.67 and for the orbital ordering $\Delta E/E$ = (exact) 0.14 and (Monte Carlo) 0.15(1).

Using the typical parameters of the hopping integrals from the cation to anion $t_{d_{z^2}-p} = 2$ eV, $t_{d_{x^2}-p} = 0.5$ eV, and $t_{d_{x^2-y^2}-p} = 1.5$ eV; the charge gap $\epsilon_p - \epsilon_d = 3$ eV; and $U = 6$ eV, we estimate the gain in the exchange energy as $\Delta E_{\text{ex}} \sim 0.05$ and 0.017 eV for the $\Updownarrow\Updownarrow\Leftrightarrow\Leftrightarrow$ ordering of pairs of d_{z^2} orbitals and for the $d_{z^2}-d_{z^2}-d_{x^2-y^2}-d_{x^2-y^2}$ ordering, respectively. Owing to the competition between the Coulomb and exchange interactions between the electrons on the neighboring orbitals, a certain orbital order with the structure wave vector $Q = \pi/2$ can be induced. In magnets with narrow optical bands and weak dispersion of the optical oscillation mode and the electron–phonon coupling constant $\sim g_k^2\omega_k^{-1}$ near the band edge, the exchange mechanism possibly gives rise to a change in the magnetic and orbital orders with decreasing the temperature.

Thus, in a quasi-low-dimensional magnet with one electron (hole) on the e_g orbital and competing Coulomb and exchange interactions, the appearance of the orbital order with the structure wave vector $Q = \pi/2$ or the softening of the elastic oscillation mode near this vector is possible. The magnetic state after the ordering of orbital pairs is a gapless quantum spin liquid with a finite correlation radius. The phase diagram of the modulated ferromagnet is determined. This diagram has a plateau $m(H) = 1/2$ on the magnetization curve in the (magnetic field, exchange alternating) plane.

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