Impurity effects on the long-range ordered state are one of the attractive themes in recent study of correlated electron systems [1]. A small amount of non-magnetic impurities dramatically destroy the superconductivity in cuprates, and induce the antiferromagnetic long-range order in the low-dimensional quantum spin-liquids. Doped impurities also cause striking effects on the charge- and orbital-orders; substitution of Cr ions for Mn in colossal magnetoresistive (CMR) manganites immediately destroys the charge-orbital orders [2]. Origin of CMR itself is studied from the viewpoint of randomness and/or percolation [3].

Recently, the dilution effects in KCuF₃ by substituting Zn for Cu is reported experimentally by Tatami et al. [4]. A Cu²⁺ ion in the cubic-crystalline field shows the t₆²e₃ configuration which has the e₈ orbital degree of freedom. The Cu ions in the perovskite crystal form the three-dimensional (3D) simple-cubic (SC) lattice, and exhibit the long-range orbital order (OO) in room temperatures, where the dₓ²−y² and dₓz−yঀ-like orbitals are aligned with momentum \( \mathbf{Q} = (\pi, \pi, \pi) \). Since the five d orbitals are fully occupied in Zn²⁺, substitution of Zn for Cu corresponds to dilution of orbital. The resonant x-ray scattering (RXS) studies in KCu₁₋ₓZnₓF₃ reveal that a decrease in the orbital-ordering temperature \( T_{OO} \) by dilution is remarkable in comparison with the randomly diluted magnets, and OO disappears around \( x = 0.5 \), as shown in the inset of Fig. 1. These observations may not be explained by the conventional percolation scenario; the site-percolation threshold in 3D SC lattice is \( x_c (= 1 - p_c) = 0.69 \) which is applicable well to the several diluted magnets such as KMn₁₋ₓMgₓF₂ [5, 6].

We examine, in this Letter, the dilution effects on the long-range order of the e₈ orbital degree of freedom. As well known, the doubly degenerate e₈ orbital is treated by the pseudo-spin (PS) operator with a magnitude of 1/2; \( \mathbf{T}_i = \frac{1}{2} \sum_{\gamma, \gamma'} d_{i \gamma}^\dagger \sigma \gamma \sigma \gamma' d_{i \gamma'} \), where \( d_{i \gamma} \) indicates the annihilation operator of a hole with spin \( s \) and orbital \( \gamma \) at site \( i \), and \( \sigma \) is the Pauli matrices. A shape of the electronic orbital is described by an angle \( \theta \) of the PS vector as \( |\theta\rangle = \cos(\theta/2)|d_3z\rangle + \sin(\theta/2)|d_2\rangle \). For example, \( \theta = 0, 2\pi/3 \) and \( 4\pi/3 \) correspond to the \( d_3z\ ), \( d_3y\ ), and \( d_2\ ) orbitals, respectively, and \( \theta = \pi/3, \pi \) and \(-\pi/3 \) to \( d_2\ ), \( d_3\ ) and \( d_2\ ) orbitals, respectively. As shown below, the Hamiltonian for the diluted orbital system is described by the PS operators and seems to be on the same footing with the spin models. However, the obtained results are qualitatively different from the diluted magnets. The main results are shown in Fig. 1. The impurity-concentration \( x \) dependences of \( T_{OO} \), calculated by the two different methods, show rapid decreases in comparison with that in the spin models. The results can explain the experimentally discovered anomalous dilution effects in KCu₁₋ₓZnₓF₃ [4].

The model Hamiltonian adopted here describes the orbital interaction between the nearest-neighbor (NN) Cu sites in a
3D SC lattice:

$$\mathcal{H} = 2J \sum_{\langle ij \rangle} \tau_i \tau_j \epsilon_i \epsilon_j,$$

(1)

where $J(>0)$ is the interaction, and $\langle ij \rangle$ indicates a pair of the NN sites along the direction $l(=x,y,z)$. The operator $\tau_i$ depends explicitly on the bond direction and is defined by a linear combination of the PS operators as

$$\tau_i = \cos \left( \frac{2\pi}{3} n_i \right) T_{ix} + \sin \left( \frac{2\pi}{3} n_i \right) T_{ix},$$

(2)

with $(n_x, n_y, n_z) = (1,2,3)$. The quenched impurities without the orbital degree of freedom are introduced by $\epsilon_i$ taking one and zero for Cu and Zn, respectively.

The Hamiltonian in Eq. (1) without impurities ($\epsilon_i = 1$ for $\forall i$) does not concern an origin of the interaction, i.e. the electronic and/or phononic interactions. In the electronic view point, this is derived by the generalized-Hubbard model with the $e_g$ orbital degree of freedom. Through the perturbational expansion with respect to the NN electron transfer $t$, the spin-orbital superexchange model is obtained [23]; $\mathcal{H}_S = -2J_1 \sum_{\langle ij \rangle} \left( \frac{1}{2} S_i \cdot S_j + \frac{1}{2} \tau_i \tau_j \right) - 2J_2 \sum_{\langle ij \rangle} \left( \frac{1}{2} S_i \cdot S_j - \frac{1}{2} \tau_i \tau_j \right)$. Here, $S_i$ is the spin operator at site $i$ with magnitude of 1/2, and $J_1(=t^2/(U-3t))$ and $J_2(=t^2/U)$ are the superexchange interactions with the on-site intra-orbital Coulomb interaction $U$ and the exchange interaction $I$. Since the Néel temperature ($T_N$) in KCu$_{1-x}$Zn$_x$F$_3$ is far below $T_{OO}$ in a whole range of $x$ [24], taking $S_i \cdot S_j = 0$ is a good assumption, and Eq. (1) with $J = \frac{1}{2} J_1 - \frac{1}{2} J_2$ is obtained. In the phononic viewpoint, the orbital model is derived based on the cooperative Jahn-Teller (JT) effects. Start from the linear JT coupling Hamiltonian $\mathcal{H}_{JT} = \sum_{m=x,y,z} Q_m T_{im}$ with the vibrational modes $Q_m$ ($m=x,z$) in a F$_6$ octahedron, and the lattice potential $K$ between NN Cu-F bonds. After rewriting $Q_m$ by the phonon coordinates $q_m$, we obtain Eq. (1) with $J = 2g^2/(9K)$ by integrating out $q_m$ [10]. A sign of $J$ is positive in both the two processes. A unique aspect of the orbital model to be noticed here is that the explicit form of the interaction depends on the bond direction $l$ and the order parameter is of a staggered type, and the lattice po-

ential $K$ between NN Cu-F bonds.

We have performed the finite-size scaling analyses in the MC simulation to determine $T_{OO}$. The correlation length $\xi$ is calculated by the second-moment method in the PS correlation function for several sizes $L$. In Fig. 2(b), we demonstrate the scaling plot for $\xi/L$ as a function of $(T - T_{OO})/L^\nu$ at $x = 0$. The scaling analyses work quite well for $L = 10$, 12 and 14. $T_{OO}$ and the exponent $\nu$ are determined through the least-square fitting by the polynomial expansion and obtained as $T_{OO}/J = 0.344 \pm 0.002$ and $\nu = 0.69 \pm 0.81$. However, statistical errors are not enough to obtain the precise value of $\nu$. Even in the diluted case [see the inset of Fig. 2(b)], the precision is enough to determine $T_{OO}$ = $(0.248 \pm 0.003)/J$ for $x = 0.15$. Beyond $x = 0.15$, the scaling analyses do not work well.

In Fig 3(a), the temperature dependence of the normalized-order parameter $m_0(x,T)$ is presented. First, focus on the region of $x \leq 0.15$. As expected, $m_0(x=0,T)$ abruptly increases at $T_{OO}$ and is saturated to 0.5 at $T \to 0$. By doping impurity, $m_0(x,T)$ does not reach 0.5 even far below
staggered-type orbital order at \( x \), and \( m_0(x \neq 0, T \rightarrow 0) \) gradually decreases with increasing \( x \). Although the system sizes are not sufficient to estimate \( m_0(x, T) \) in the thermodynamic limit, \( m_0(x \neq 0, T \rightarrow 0) \) does not show the smooth convergence to 0.5 in contrast to the diluted spin models. Beyond \( x = 0.15 \), the situation is changed qualitatively; in spite of the fact that \( m_0(x, T) \) grows around a certain temperature (e.g. \( \sim 0.18J \) at \( x = 0.2 \), \( m_0(x, T \rightarrow 0) \) becomes small abruptly and decreases weakly with increasing \( L \). Anomalies in the specific heat and the susceptibility around this temperature become weak, and some of the physical quantities, e.g. \( N_0 = \sum_{m=-x}^{x}(T_{O0})^2 \) with \( Q = (\pi, \pi, \pi) \), depend on the initial states in the MC simulation. It seems that the orbital correlation grows up below this temperature, but the long-range order does not. We suppose that a possible orbital state in this region is a short-range ordered state or a glass state [18], although we do not identify this phase correctly at the present stage. Thus, in \( x > 0.15 \), a temperature where \( dm_0(x, T)/dT \) in \( L = 18 \) takes a maximum is interpreted to be the cross-over and/or glass-transition temperature. Above \( x = 0.3 \), estimation of \( T_{O0} \) becomes severe, because of the weak temperature dependence of \( m_0(x, T) \). Thus, as a supplementary information of the ordering temperature, we calculate a temperature \( T_{O0} \) where \( dN_0/dT \) takes a maximum, and consider its full width at half maximum as an error. The initial state in the calculation for \( T_{O0} \) is assumed to be the ordered state, although the initial-state dependence of \( T_{O0} \) is much weaker than that of the \( N_0 \) amplitude.

The \( x \) dependences of \( T_{O0} \) and \( T_{OOS} \) presented in Fig. 1(a) are obtained by the MC (filled-red squares) and CE (blue lines) methods introduced above. For comparison, the \( x \) dependences of \( T_N \) in the spin models are plotted. \( T_{OOS} \) are also shown by the open-red squares. Starting to dope impurities in the orbital model, decrease of \( T_{O0} \) is more remarkable than that of \( T_N \) in the spin models. Around \( x = 0.15 \), the clear transition to the long-range order becomes obscure, explained above. \( T_{OOS} \) obtained by \( N_0 \) are close to \( T_{O0} \) below \( x = 0.2 \), and decrease smoothly up to \( x = 0.3 \), although the critical \( x \), where \( T_{O0} \) disappears, is not determined due to large statistical errors. A rapid decrease of \( T_{O0} \) is also obtained by the CE method. It is seen that difference between the calculated \( T_{O0} - x \) curves for the cluster sizes \( N_C = 1 \) (bold line) and 2 (broken line) is within a few percent. \( T_{O0} \) in the CE method disappears around \( x = 0.5 \) being much smaller than \( x_c = 0.69 \) for the 3D SC lattice. We also calculate \( T_{O0} \) in the CE method where the quantum PS operators are replaced by the classical vectors. The calculated results plotted by the one-point chain line are close qualitatively to the \( T_{O0}(T_{O0}) - x \) curve obtained by the classical MC method.

Now we introduce the physical picture of the diluted orbital-ordered state. The real-space configurations of the orbital PSs help us to understand the calculated \( T_{O0} - x \) curve. The MC snapshots of the PSs on a plane are shown in Figs. 3(b) and (c) for \( x = 0.1 \) and 0.3, respectively. The staggered-type O0 with the orbital angles \( (\theta_A/\theta_B) = (0/\pi) \) is seen in the back-ground of Fig. 3(b). At the neighboring sites of the impurities indicated by the open circles, tiltings of the PS vectors are observed. Disturbing the PS configuration from \( (0/\pi) \) becomes violent at \( x = 0.3 \). These observations are caused by the local-symmetry breaking by dilution. Consider the orbital state at a neighboring site of an impurity on the \( x \) axis. On account of the impurity, one of the interactions along \( x \) vanishes. Since the interaction depends on the bond direction explicitly in the orbital model, the PS at this site tilts to gain the interaction energies for other five bonds. This is the essence of the diluted orbital systems and is in contrast to
at the different three-neighboring sites is obtained: $q$ produce this type of OO, the higher-order JT coupling is $J_{\text{JT}}$ effects. By rewriting approximately this term based on the theory of the cooperative orbital-ordering temperature ($T_{\text{OO}}$) of the XY model (reverse triangles), and $T_{\text{OO}}$ at $J'/J=0$ by the CE method (bold line) are also plotted.

Finally, to compare the present theory with the experiments in KCu$_{1-x}$Zn$_x$F$_3$, more directly, we introduce the higher-order JT coupling. From the RXS experiments [4] and the lattice distortion in KCuF$_3$ [12], the OO in KCuF$_3$ is expected to be the $d_{z^2}$-type; the cant-type OO with the orbital angles $(\theta - \varphi) / (\theta \sim \pi/3)$ and $Q = (\pi, \pi, \pi)$. To reproduce this type of OO, the higher-order JT coupling is required, $\mathcal{H}_{\text{JT}}' = g' \sum_i \left\{ (Q_{iz}^2 - Q_{ax}^2) T_{iz} - 2Q_{ia}^2 T_{ax} \right\}$ which provides the anisotropy in the PS space. Here we treat approximately this term based on the theory of the cooperative JT effects. By rewriting $Q_{\alpha(z)}$ by the phonon coordinates $q_{\text{ph}}$, and integrating out $q_{\text{ph}}$, the interaction between orbitals at the different three-neighboring sites is obtained: $\mathcal{H}'' = J' \sum_{i,j,k} \left\{ (T_{iz}T_{jz} + T_{iz}T_{kz} - 2T_{iz}T_{jk}) \right\} \epsilon_{i} \epsilon_{j} \epsilon_{k}$. Here, $J' = (16g^2\epsilon^2)/(9K^2)$ is the coupling constant and $(ijk)$ indicates a sum of the neighboring three sites. The MF energy of $\mathcal{H}''$ is proportional to $\frac{J'}{2} \cos 3\varphi$ implying the anisotropy. A value of $g'$ for a Cu$^{2+}$ ion was estimated by the adiabatic potential barrier in a molecule [20] and corresponds to $J'$ being about 0.3 $J$. We have performed the MC calculations in the model of $\mathcal{H} + \mathcal{H}''$, and observed that the cant-type OO at $x=0$ is realized. The doping dependences of $T_{\text{OO}}$ (and $T_{\text{OO}}$) with including $\mathcal{H}''$ are presented in Fig. 4 for $J'/J = 0.3$ and 3. The filled and open symbols are for $T_{\text{OO}}$ and $T_{\text{OO}}$, respectively, which are obtained by the same ways with those in Fig. 1. With increasing $J'$, the $T_{\text{OO}}(T_{\text{OO}} - x)$ curves approach to those for the spin models, because the anisotropy suppresses the tilting of PSs. However, we confirm that the rapid reduction of $T_{\text{OO}}$ by dilution survives even in the calculation with the realistic value of $J'$, and is consistent with the RXS experimental results shown in the inset of Fig. 1.

In summary, we have investigated the dilution effects on the long-range order of the $e_g$ orbital degree of freedom. We confirm, by both the MC and CE methods, that $T_{\text{OO}}$ decreases rapidly with doping, in comparison with the diluted magnets. The tilting of the orbital PSs around impurities, which is distinguished qualitatively from the spin models, is the essence for the rapid decrease of $T_{\text{OO}}$. The present theory provides a new view point for the recent experiments in a diluted orbital systems of KCu$_{1-x}$Zn$_x$F$_3$. A broad peak profile observed by the RXS experiments [4] may be attributed to the orbital tilting around impurities. Observations of the tilting by the scanning-tunneling microscope and/or the scanning-electron microscope are a direct check for the present results.

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