Incident-energy-dependent spectral weight of resonant inelastic x-ray scattering in doped cuprates

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(Dated: April 11, 2018)

We theoretically investigate the incident-photon energy $\omega_i$ dependence of resonant inelastic x-ray scattering (RIXS) tuned for the Cu $L$ edge in cuprate superconductors by using the exact diagonalization technique for a single-band Hubbard model. Depending on the value of core-hole Coulomb interaction in the intermediate state, RIXS for non-spin-flip channel shows either a $\omega_i$-dependent fluorescencelike or $\omega_i$-independent Raman-like behavior for hole doping. An analysis of x-ray absorption suggests that the core-hole Coulomb interaction is larger than on-site Coulomb interaction in the Hubbard model, resulting in a fluorescence-like behavior in RIXS consistent with recent RIXS experiments. A shift on the high-energy side of the center of spectral distribution is also predicted for electron-doped systems though spectral weight is small. Main structures in the spin-flip channel exhibit a Raman-like behavior as expected, accompanied with a fluorescencelike behavior with small intensity.

PACS numbers: 78.70.Ck, 78.20.Bh, 74.72.-h

I. INTRODUCTION

Resonant inelastic x-ray scattering (RIXS) experiments tuned for the Cu $L$ edge have provided a lot of new insights about spin dynamics of the spin-flip channel in cuprate superconductors when incident photon has the $\pi$ polarization [1, 2]. The non-spin-flip channel involving charge dynamics as well as two-magnon excitations can be predominantly detected by $\sigma$ polarization for the incident photon.

Not only polarization dependence but also incident-photon energy $\omega_i$ dependence of the RIXS spectrum gives us useful information on the electronic states of cuprates. Experimentally it has been reported that the $\omega_i$ dependence for the $\pi$-polarized incident photon gives a Raman-like behavior independent of $\omega_i$, while the $\sigma$ polarization induces a fluorescencelike shift of spectral weight with increasing $\omega_i$ [3, 4]. Theoretically it has been pointed out that the $\omega_i$ dependence is sensitive to particle-hole excitations of quasiparticles $\pi, \sigma$ depending on band structures of materials [5]. On the other hand, a model calculation for the$d$oped-Mott insulator, i.e., a calculation of the single-band Hubbard model, has also captured Raman-like and fluorescencelike behaviors [4]: The Raman-like excitation comes from collective spin excitations, while the fluorescencelike shift is due to the continuum of particle-hole excitations.

In the fluorescence of the normal x-ray emission spectroscopy (XES), there is no correlation between a photoexcited electron in the vacuum continuum and a valence electron decaying into the core hole so that the emission spectrum is almost independent of $\omega_i$. Then the energy loss of the x ray increases as $\omega_i$ increases. In the present RIXS, however, the fluorescencelike behavior would come from a different origin [5, 6] since these electrons are rather correlated.

The intermediate state of the RIXS process contains a core hole created by an incident photon. Therefore, the Coulomb interaction between the core hole and valence electron ($3d_{x^2-y^2}$ electron in cuprates) acting in the intermediate state influences the RIXS spectrum. It is thus expected that the core-hole Coulomb interaction also affects the $\omega_i$ dependence of the RIXS spectrum.

In this paper, we perform the Lanczos-type exact diagonalization calculation of the RIXS spectrum for the single-band Hubbard model describing hole- and electron-doped cuprates. Examining the $\omega_i$ dependence of non-spin-flip RIXS spectra, we find that the dependence is strongly affected by the value of core-hole Coulomb interaction in hole doping: A $\omega_i$-dependent fluorescencelike behavior appears when the core-hole Coulomb interaction is larger than the on-site Coulomb interaction in the Hubbard model, while a $\omega_i$-independent Raman-like behavior appears for smaller core-hole Coulomb interaction although the distribution of spectral weight depends on $\omega_i$. Analyzing main and satellite structures in x-ray absorption (XAS) for hole doping, we find that it is reasonable to take the core-hole Coulomb interaction in modeling RIXS by a single-band model of cuprates. This suggests a fluorescence-like behavior in RIXS for the $\sigma$-polarized geometry detecting non-spin-flip excitations, being consistent with recent experiments [3, 4]. In such a case, the dynamical charge structure factor is observed through $\sigma$-polarized RIXS by tuning $\omega_i$ to a satellite structure in XAS for hole doping.

Using the larger core-hole Coulomb interaction, we
predict a shift on the high-energy side of the center of spectral distribution in electron doping, which has not yet been observed experimentally. In the spin-flip channel, main structures exhibit a Raman-like behavior as expected. In addition, there is a fluorescencelike behavior similar to the non-spin-flip channel, although spectral weight is very small. The behavior is enhanced with increasing hole carriers. A detailed experimental work to detect these behaviors is desired in the future.

This paper is organized as follows. The Hubbard model and RIXS spectra decomposed into spin-flip and non-spin-flip channels are introduced in Sec. II. In Sec. III we calculate the dependence of XAS on the core-hole Coulomb interaction for both hole and electron doping. The ω dependence of RIXS spectra are shown in Sec. IV and the origin of fluorescencelike and Raman-like behaviors is discussed. Finally, a summary is given in Sec. V.

II. MODEL AND METHOD

In order to describe 3d electrons in the CuO$_2$ plane, we take a single-band Hubbard model given by

$$H_{3d} = -t \sum_{i\delta\sigma} c_{i\sigma}^{\dagger} c_{i+\delta\sigma} - t' \sum_{i\delta'\sigma} c_{i\sigma}^{\dagger} c_{i+\delta'\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow},$$

(1)

where $c_{i\sigma}^{\dagger}$ is the creation operator of an electron with spin σ at site i, number operator $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$, and $i + \delta$ (i + δ′) represents the four first (second) nearest-neighbor sites around site i, and t, t′, and U are the nearest-neighbor hopping, the next-nearest-neighbor hopping, and on-site Coulomb interaction, respectively. We take $U/t = 10$ and $t'/t = -0.25$, which are typical values appropriate for cuprates.

Based on the Hubbard model, the XAS for the L edge accompanied by the excitation of an electron from the core Cu2p to Cu3d orbital can be described by

$$I^{\text{XAS}}(\omega) = \frac{1}{\pi} \text{Im} \left[ \sum_{l\delta\sigma} c_{l\sigma}^{\dagger} \frac{1}{\omega - H_{l}^{\uparrow} + E_0 + i\Gamma} c_{l\sigma} |0\rangle \right],$$

(2)

where |0⟩ represents the ground state with energy $E_0$; j is the total angular momentum of Cu2p with either j = 1/2 or j = 3/2; Γ is the relaxation time of the core hole; and $H_{l}^{\uparrow} = H_{3d} - U_{c} \sum_{i} n_{i\sigma} + \varepsilon_j$ with $U_{c}$ and $\varepsilon_j$ being the Cu 2p-3d Coulomb interaction and energy level of Cu 2p, respectively. Here, we assume the presence of a Cu2p core hole at site l.

In RIXS, tuning polarization of incident and outgoing photons, we can separate excitation with the change of total spin by one ($\Delta S = 1$) and excitation with no change of total spin ($\Delta S = 0$) \cite{11}. We call the former (the latter) spin-flip (non-spin-flip) process hereafter. The two excitations can be defined as

$$I_{q}^{\Delta S=0}(\Delta \omega) = \sum_{f} |\langle f | N_{q}^{f} |0\rangle|^{2} \delta (\Delta \omega - E_{f} + E_0),$$

(3)

$$I_{q}^{\Delta S=1}(\Delta \omega) = \sum_{f} |\langle f | S_{q}^{f} |0\rangle|^{2} \delta (\Delta \omega - E_{f} + E_0),$$

(4)

with $S_{q}^{f} = (B_{q}^{f\uparrow\uparrow} - B_{q}^{f\downarrow\downarrow})/2$, $N_{q}^{f} = B_{q}^{f\uparrow\uparrow} + B_{q}^{f\downarrow\downarrow}$, and

$$B_{q}^{f\sigma\prime\sigma} = \sum_{l} e^{-i\mathbf{q}\cdot\mathbf{R}_{l}} c_{l\sigma'}^{\dagger} \frac{1}{\omega_{l} - H_{l}^{\uparrow} + E_0 + i\Gamma} c_{l\sigma},$$

(5)

where |f⟩ represents the final state with energy $E_{f}$; and R$_{l}$ is the position vector at site l.

When Γ is much larger than the remaining terms in the denominator of (5), $S_{q}^{f}$ and $N_{q}^{f}$ reduce to $S_{q}^{f} = \sum_{l} e^{-i\mathbf{q}\cdot\mathbf{R}_{l}} S_{l}^{f}$ and $N_{q}^{f} = \sum_{l} e^{-i\mathbf{q}\cdot\mathbf{R}_{l}} N_{l}$, respectively, with the z component of the spin operator $S_{l}^{f}$ and electron-number operator $N_{l}$ (the first-collision approximation). In this approximation, (3) and (4) read the dynamical charge structure factor,

$$N(q, \omega) = \sum_{f} |\langle f | N_{q}^{f} |0\rangle|^{2} \delta (\omega - E_{f} + E_0),$$

(6)

and the dynamical spin structure factor,

$$S(q, \omega) = \sum_{f} |\langle f | S_{q}^{f} |0\rangle|^{2} \delta (\omega - E_{f} + E_0),$$

(7)

respectively.

When Γ is comparable with the remaining terms in (5), intersite operators emerge as effective operators of (5) in addition to the on-site charge $N_{l}$ and spin $S_{l}^{f}$ \cite{12}. In the non-spin-flip process, a two-magnon-type operator is easily expected to contribute to $N_{q}^{f}$. We thus define the q-dependent dynamical two-magnon correlation function,

$$M(q, \omega) = \sum_{f} |\langle f | M_{q}^{f} |0\rangle|^{2} \delta (\omega - E_{f} + E_0),$$

(8)

with $M_{q}^{\pm} = \sum_{k} (\cos k_{x} \pm \cos k_{y}) S_{k+q} S_{-k}$, where + (−) corresponds to $A_{1g}$ ($B_{1g}$) representation.

In order to calculate Eqs. (3), (4), (6), (7), and (8), we use a Lanczos-type exact diagonalization technique on a $\mathbf{18} \times \mathbf{18}$ cluster under periodic boundary conditions. We consider hole and electron doping with the carrier concentration $x = n/18$, corresponding to 18 − n electrons and 18 + n electrons in the cluster for hole and electron doping, respectively. We set Γ = t for both XAS and RIXS.

III. X-RAY ABSORPTION SPECTRUM (XAS)

The value of $U_{c}$ used in the literature is ranged from $\sim U/2$ \cite{12} to $\sim 3U/2$ \cite{11} in describing L-edge RIXS for cuprates. In Fig. 3 the $U_{c}$ dependence of XAS spectrum
the carrier already creates the occupied state and a core hole, respectively. We note that the \( U_c \) dependence of XAS spectra is strong in hole doping.

The Cu \( L_3 \)-edge XAS in hole-doped cuprates has detected two structures near 930 eV \[13, 14\]. One is a large peak coming from the process \( 3d^0 \rightarrow 2p3d^{10} (2p = \text{Cu}2p \text{ core hole}) \) and the other is a weak structure related to carrier concentration \[15\] given by the process of \( 3d^0 L \rightarrow 2p3d^{10} L \) (\( L = \text{oxygen ligand hole} \)). The latter structure is higher by roughly 1.5 eV in energy than the former one \[13, 15\]. By using Cu-O clusters with appropriate parameters, the two structures have been obtained in hole doping \[16\]. A two-band CuO model used in RIXS calculations \[11\] also reproduced a two-structure behavior similar to the experiments (not shown).

In comparing the experimental data with the XAS in the single-band Hubbard model, it would be reasonable to assign \( 3d^0 \rightarrow 2p3d^{10} (3d^0 L \rightarrow 2p3d^{10} L) \) to \( d^1 \rightarrow 2d^2 \) (\( d^0 \rightarrow 2d^2 \)) by taking into account the correspondence between the Zhang-Rice singlet state (\( 3d^0 L \)) and the lower-Hubbard-band state (\( d^0 \)). Taking a standard value of \( t = 0.35 \text{ eV} \), we can find that the energy separation of the two structures in hole-doped XAS shown in Fig. 1(b) becomes an experimental value (1.5 eV) when \( U_c \sim 12t \). This means that \( U_c > U = 10t \). However, a smaller value of \( U_c \) satisfying \( U_c < U \) has been used in the literature \[11, 12\]. Therefore, it is interesting to examine the effect of \( U_c \) on the \( \omega \) dependence of the RIXS spectrum. In the following, keeping \( U = 10t \), we use \( U_c = 12t \) and \( U_c = 8t \) as a representative parameter for \( U_c > U \) and \( U_c < U \), respectively.

### IV. RIXS SPECTRUM

#### A. Non-spin-flip channel

##### 1. Hole doping

The incident-photon energy \( \omega \) dependence of non-spin-flip intensity \( I_{QS=0}^{xS} \) at \( q = (2\pi/3, 0) \) in hole doping with \( x = 0.11 \) is shown for the case of \( U_c = 12t > U \) in Fig. 2(a). The bottom spectrum exhibits the spectrum obtained by tuning \( \omega \) at the edge of the lowest-energy peak in the XAS spectrum shown in Fig. 1(b). Here, the edge is defined as the lowest-energy eigenstate represented by the lowest-energy vertical bar in Fig. 1(b). There are two peaks at \( \omega = 1.8t \) and \( \omega = 0.2t \) together with a broad tail around \( \omega = 3t \). The peak at \( \omega = 1.8t \) is similar to that at half filling, which is originated from two-magnon excitation. We note that in this energy re-
region there are also charge excitations coming from hole carrier as seen from the dynamical charge structure factor $N(q, \omega)$ in Fig. 2(c). On the other hand, the peak at $\omega = 0.2t$ does not have a corresponding structure $N(q, \omega)$, indicating that the peak is related to an excitation beyond a simple two-particle response. Actually, we find that the peak at $\omega = 0.2t$ appears in $M(q, \omega)$ with $B_{1g}$ as shown in Fig. 2(d). The broad tail around $\omega = 3t$ may partly come from charge excitations, but its spectral shape is different from $N(q, \omega)$. This is reasonable since the edge of XAS is mainly composed of the $\tilde{c}$ state to which hole carriers do not contribute.

When $\omega_i$ is increased by $t$ from the edge, $I_{q, \omega}^{S=0}$ increases as shown in Fig. 2(a). This is simply due to the fact that the peak of the XAS is located slightly above the edge position and thus resonance becomes maximum when $\omega_i$ is larger than the edge energy. With further increasing $\omega_i$, spectral weight gradually decreases as $t$ increases and resonance condition becomes weaker. Furthermore, $t$ distribution of spectral weight becomes wider, accompanied by the reduction of peak heights. When $\omega_i$ is higher than the edge position by $5t$, where the incident photon resonates to a satellite structure in XAS, spectral distribution becomes similar to $N(q, \omega)$. This is again reasonable since the incident photon resonates mainly to the $\tilde{c}d^1$ state [see Fig. 1(b)] and thus hole carriers contribute to the RIXS process through the intermediate state. As a consequence, a characteristic structure in $t$ spectral weight gradually changes from the low-energy peak near $\Delta \omega = 2t$ to the high-energy broad peak near $\Delta \omega = 4t$ with increasing $\omega_i$. This evolution of $I_{q, \omega}^{S=0}$ with $\omega_i$ exhibits a fluorescence-like $\omega_i$ dependence: $t$-dependence at $\omega = 0$ is higher than that at $\omega = 11$. As for $U_i = 12t$, low-energy two-magnon excitations as expected from $N(q, \omega)$ in Fig. 3(c). It is clear in Fig. 3(a) that, with increasing $\omega_i$ from the edge position, the spectral distribution smoothly shifts to the high-energy side accompanied by the reduction of low-energy weight similar to the charge excitations shown in Fig. 2(c).

The fluorescence-like $\omega_i$ dependence at $U_i = 12t$ becomes more clear when hole carriers are increased. Figure 3 shows $I_{q, \omega}^{S=0}$, $N(q, \omega)$, and $M(q, \omega)$ at $q = (2\pi/3, 0)$ for the hole-doped $\sqrt{18} \times \sqrt{18}$ Hubbard cluster with $x = 2/18 \sim 0.11$. (a) $U_i = 12t$ and (b) $U_i = 8t$. Parameters are $U = 10t$, $t' = -0.25t$, and $\Gamma = t$. $\omega_i$ at the bottom panel is set to the edge of the XAS spectrum and increases by $t$ from bottom to top. (c) The dynamical charge structure factor $N(q, \omega)$ at $q = (2\pi/3, 0)$. (d) The $q$-dependent dynamical two-magnon correlation function $M(q, \omega)$ at $q = (2\pi/3, 0)$. Black (red) line, $B_{1g}$ ($A_{1g}$) mode.
This smooth shift indicates that the fluorescence-like behavior can be seen more clearly in the overdoped region. On the other hand, $\omega_i$ dependence at $U_c = 8t$ exhibits a Raman-like behavior consistent with the case of $x = 0.11$.

We note that these $\omega_i$ dependencies mentioned above are not only for $q = (2\pi/3, 0)$ but also for $q = (\pi/3, \pi/3)$ defined in the $\sqrt{18} \times \sqrt{18}$ cluster (not shown).

The $\omega_i$ dependence of the RIXS spectrum has been measured in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [5]. In the experiment, the $\sigma$ polarization of the incident photon approximately correspond to non-spin-flip spectrum $I_q^{\Delta S=0}$. Comparing the calculated $I_q^{\Delta S=0}$ in Figs. 2 and 3 with the experimental data at $q = (0.74\pi, 0)$ for the overdoped sample [5], we find that the $U_c = 12t$ case corresponds to the experiment, since there is a fluorescence-like behavior. Encouraged by the correspondence, we use $U_c = 12t$ in the following as a representative value for cuprates.

![FIG. 3. (Color online) Same as Fig. 2 but $x = 4/18 \sim 0.22$.](image)

Fig. 3. (Color online) Same as Fig. 2 but $x = 4/18 \sim 0.22$.

2. Electron doping

Figure 4 shows the $\omega_i$ dependence of the non-spin-flip spectrum $I_q^{\Delta S=0}$ at $q = (2\pi/3, 0)$ for electron doping. When $\omega_i$ is tuned to the edge, there are two main structures at $\Delta \omega = 1.2t$ and $2.5t$. The latter is partly contributed from charge excitations due to electron carriers as expected from $N(q, \omega)$ shown in Fig. 3(b). In $N(q, \omega)$, however, there is no corresponding structure for the former structure, indicating a possible two-magnon origin. In fact, $M(q, \omega)$ shown in Fig. 4(c) exhibits an enhancement at the former energy. We further notice that there is no prominent structure at $\omega = 6t$ where $N(q, \omega)$ shows a peak structure.

With increasing $\omega_i$, the two main structures gradually lose their weight and a broad structure near $\Delta \omega = 3t$ remains accompanied with an small enhancement around $\Delta \omega = 6t$. The spectral distribution, for example, for $\omega_i$ higher by $\sim 3t$ from the edge, resembles $N(q, \omega)$. With further increasing $\omega_i$, the center of spectral distribution shifts to the high-energy side, although the spectral weight is strongly reduced as compared with the case of hole doping.

We note that the origin of such a fluorescence-like be-
behavior is different from the case of hole doping. In hole doping, the spectral weight similar to \( N(i, \omega) \) at high \( \omega \) is constructed by hole carriers through the \( \tilde{d}^1 \) state. On the other hand, in electron doping there is no direct contribution from electron carriers in the intermediate state in RIXS, since the carriers already make an inactive \( \tilde{d}^2 \) states for XAS. Therefore, the spectral weight similar to \( N(i, \omega) \) in electron doping may be due to an indirect effect of electron carriers appearing in the XAS spectra as a broad structure with small spectral weight above the main peak as seen in Fig. 1(a). This is the reason for weak fluorescence-like intensity in electron doping. Detailed examinations of \( \omega \) dependence in the \( \sigma \)-polarized RIXS is desired to confirm theoretical predictions for electron doping.

### B. Spin-flip channel

Since particle-hole excitations are involved in not only the non-spin-flip channel but also the spin-flip one, it is interesting to examine how the spin-flip spectrum \( f_{q}^{\Delta S=1} \) is dependent on \( \omega \). Figure 5 shows \( f_{q}^{\Delta S=1} \) at \( q = (2\pi/3, 0) \) for both electron and hole dopings. Comparing Figs. 5(a) and 5(b) for electron doping and Figs. 5(c) and 5(d) for hole doping, we find that \( f_{q}^{\Delta S=1} \) for \( \omega \) tuned to the absorption edge resembles \( S(q, \omega) \). This is in contrast to the case of \( f_{q}^{\Delta S=0} \) as discussed in Sec. IV A. With increasing \( \omega \) from the edge, low-energy spin-flip excitations below \( \omega = 2t \) in both dopings remain showing a Raman-like behavior. In addition, there is a dispersive fluorescence-like structure, which is similar to the case of the non-spin-flip spectrum \( f_{q}^{\Delta S=0} \), although the intensity is very small above \( \Delta \omega = 2t \). This indicates the presence of particle-hole excitations in the spin-flip channel.

In order to make clear the effect of hole carriers on the \( \omega_i \) dependence, we show the contour map of \( f_{q}^{\Delta S=1} \) at \( q = (2\pi/3, 0) \) together with the non-spin flip \( f_{q}^{\Delta S=0} \) for the realistic value of \( U_c = 12t \) in Fig. 5. At half filling \( x = 0 \) [Figs. 5(a) and 5(d)], both spectra exhibit Raman-like \( \omega_i \) dependence. \( f_{q}^{\Delta S=0} \) clearly shows fluorescence-like \( \omega_i \) dependence with increasing \( x \) as expected. The spin-flip spectra in Figs. 5(b) and 5(c) also show fluorescence-like \( \omega_i \) dependence in the same \( \Delta \omega \) region as \( f_{q}^{\Delta S=0} \), though its intensity is weak as compared with low-energy excitations. We can find that the fluorescence-like intensity increases with increasing \( x \), being consistent with the view that particle-hole excitations contribute to RIXS spectra in the spin-flip channel when carriers become more itinerant. A detailed examination of \( \omega_i \) dependence of RIXS for the \( \pi \)-polarized incident photon and different carrier concentrations is desired in the near future.

### V. Summary

Examining the \( \omega_i \) dependence of non-spin-flip RIXS spectra by the exact diagonalization calculation for the single-band Hubbard model, we have found that the dependence is strongly affected by the value of the core-hole Coulomb interaction in hole doping: A fluorescence-like behavior appears when the core-hole Coulomb interaction \( U_c \) is larger than the on-site Coulomb interaction \( U \) in the Hubbard model \( U_c > U \), while a Raman-like be-
havior appears for $U_c < U$, although the distribution of spectral weight depends on $\omega_i$. Comparing the calculated energy separation between a main peak and a satellite structure in XAS with the corresponding experimental data, we have confirmed that $U_c > U$ for the single-band Hubbard model, suggesting a fluorescencelike behavior in RIXS for the $\sigma$-polarized geometry detecting non-spin-flip excitations. This is consistent with recent experimental observations for overdoped YBa$_2$Cu$_3$O$_{6+x}$ [3]. We predict that the dynamical charge structure factor is observed through RIXS by tuning $\omega_i$ to the satellite structure. Using the same $U_c$ value, we predict a shift on the high-energy side of the center of spectral distribution in electron doping, whose intensity is reduced as compared with the case of hole doping. In the spin-flip channel, main structures exhibit a Raman-like behavior as expected but there is a fluorescencelike behavior similar to the non-spin-flip case, although the spectral weight is very small. A detailed experimental work to detect these behaviors is highly desired in the near future.

FIG. 6. (Color online) The contour plot of incident-phonon energy $\omega_i$ dependence of spin-flip spectra $I_{4}^{\Delta S=1}$ and non-spin-flip spectra $I_{4}^{\Delta S=0}$ at $q = (2\pi/3, 0)$ for the hole-doped $\sqrt{18} \times \sqrt{18}$ Hubbard cluster with parameters $U = 10t$, $t' = -0.25t$, $U_c = 12t$ and $\Gamma = t$. (a) $x = 0$, (b) $x = 2/18 \sim 0.11$, and (c) $x = 4/18 \sim 0.22$ for $I_{4}^{\Delta S=1}$. (d) $x = 0$, (e) $x \sim 0.11$, and (f) $x \sim 0.22$ for $I_{4}^{\Delta S=0}$.

ACKNOWLEDGMENTS

This work was supported by the Japan Society for the Promotion of Science, KAKENHI (Grants No. 26287079, 15H03553 and 16H04004) and by HPCI Strategic Programs for Innovative Research (Grants No. hp140078) and Computational Materials Science Initiative from Ministry of Education, Culture, Sports, Science, and Technology.

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