per super-cell. The wave function and energy eigenvalue are denoted as $\psi^{(0)}_{\sigma n\mathbf{k}}(\mathbf{r})$ and $\epsilon^{(0)}_{\sigma n}(\mathbf{k})$, respectively. All the lowest $N_e = N_c \times n_e$ levels are occupied in the ground state.

The final states $|f\rangle$'s are constructed by using the one-electron states calculated in the presence of the core-hole in accordance with the following procedure. Defining $n^{(0)}_\sigma(\mathbf{k})$ by the number of levels with spin σ and wave vector $\mathbf{k}$ below the Fermi level in the ground state, we distribute $n^{(0)}_\sigma(\mathbf{k})$ electrons with spin σ and wave vector $\mathbf{k}$ in the states given in the presence of core hole. The final state $|f_0\rangle$ containing no e-h pair is constructed by distributing electrons from the lowest energy level up to the $n^{(0)}_\sigma(\mathbf{k})$'th level with spin σ for each wave vector $\mathbf{k}$. The final states $|f_\nu\rangle$'s containing ν e-h pairs are constructed by annihilating ν electrons in the occupied conduction states and creating ν electrons in the unoccupied conduction states from $|f_0\rangle$.

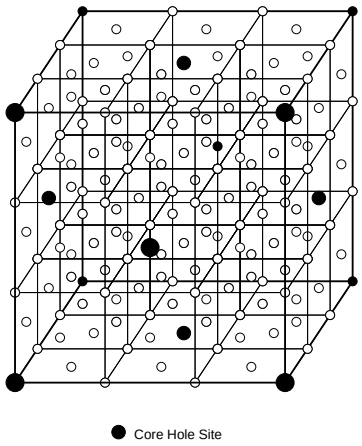

Figure 1: Sketch of a super-cell containing core-holes in fcc structure. Core-hole sites indicated by solid circles are assumed forming a $3 \times 3 \times 3$ fcc lattice. The super-cell for the bcc structure is shown in fig. 1 in Ref. 19.

C. Overlap integrals

We assume that the transition matrix elements between the core state and the photo-excited states are constant. The remaining matrix elements connecting the ground and final states are expressed by

$$\langle f_\nu | s_\sigma | g\rangle = \begin{vmatrix} S_{1,1} & S_{2,1} & ..... & S_{N_e,1} \\ S_{1,2} & S_{2,2} & ..... & S_{N_e,2} \\ .... & .... & .... & .... \\ S_{1,N_e} & S_{2,N_e} & ..... & S_{N_e,N_e} \end{vmatrix}, \qquad (3)$$

with

$$S_{i,i'} = \int \phi^*_i(\mathbf{r})\phi^{(0)}_{i'}(\mathbf{r})\mathrm{d}^3 r, \qquad (4)$$

where the integral is carried out within a unit cell. Subscripts $i = (\sigma, n, \mathbf{k})$ and $i' = (\sigma', n', \mathbf{k}')$ are running over occupied conduction states in the presence of core hole and in the ground state, respectively. We eliminate the overlaps between the wave functions for the core levels. The corresponding energies difference is given by

$$\begin{aligned} \Delta E &= E_{f_\nu} - E_g \\ &= E_{f_\nu} - E_{f_0} + E_{f_0} - E_g, \end{aligned} \qquad (5)$$

where $E_{f_0} - E_g$ includes the energy of core hole, and is treated as an adjustable parameter in the present study such that the threshold of XPS spectra coincides with the experimental value. The excitation energy $E_{f_\nu} - E_{f_0}$ with ν e-h pairs is given by

$$E_{f_\nu} - E_{f_0} = \sum_{(i,j)} (\epsilon_j - \epsilon_i), \qquad (6)$$

where ϵ_i's are the Kohn-Sham eigenvalues, and $\epsilon_j - \epsilon_i$ stands for the energy of e-h pair of an electron at level j and a hole at level i. Although the Kohn-Sham eigenvalues may not be proper quasi-particle energies, they practically give a good approximation to quasi-particle energies, except for the fundamental energy gap.[22,23] Substituting Eqs. (3) and (5) into Eq. (1), we obtain the XPS spectra.

In the actual calculation, instead of N_c $\mathbf{k}$-points, we pick up only the Γ point as the sample states for calculating XPS spectra. For Ni, we pick up the X point (and the equivalent Y and Z points) in addition to the Γ point, since the $3d$ band states at the Γ point are fully occupied by both up-spin and down-spin electrons even though the $3 \times 3 \times 3$ fcc super-cell is used.

Before closing this section, we briefly mention the XPS intensity at the energy of threshold. The final state $|f_0\rangle$ with the lowest energy (no e-h pair) has a finite overlap with the ground state $|g\rangle$, giving rise to intensities at the threshold. In principle, such overlap converges at zero with $N_e \to \infty$, according to the Anderson orthogonality theorem.[1] In such infinite systems, energy levels become continuous near the Fermi level and thereby infinite numbers of e-h pairs could be created with infinitesimal excitation energies, leading to the so called Fermi edge singularity in the XPS spectra. The finite contribution obtained above arises from the discreteness of energy levels and could be interpreted as the integrated intensity of singular spectra near the threshold, in consistent with the model calculations for other systems.[6,24]

III. RESULTS AND DISCUSSION

A. Ferromagnetic Transition Metals

In this subsections, we refer to majority(minority) spin as up(down)-spin. The Ni metal takes an fcc structure. For simplicity, the Co metal is assumed to take an fcc structure, although it actually takes an hcp structure.