Bulk- and Surface-Sensitive High-Resolution Photoemission Study of Two Mott-Hubbard Systems: SrVO₃ and CaVO₃

R. Eguchi,[1,2] T. Kiss,[1] S. Tsuda,[1] T. Shimojima,[1] T. Mizokami,[1] T. Yokoya,[1] A. Chainani,[2] S. Shin,[1,2] I. H. Inoue,[3] T. Togashi,[2] S. Watanabe,[1] C. Q. Zhang,[4] C. T. Chen,[4] M. Arita,[5] K. Shimada,[5] H. Namatame,[5] and M. Taniguchi[5,6]

[1]*Institute for Solid State Physics (ISSP), University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*
[2]*RIKEN, SPring-8 Center, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan*
[3]*Correlated Electron Reserch Center (CERC), National Institute of Advance Industrial Science and Tecnology (AIST),*
Tsukuba Central 4, Tsukuba 305-8562, Japan
[4]*Beijing Center for Crystal R&D, Chinese Academy of Science, Zhongguancun, Beijing 100080, China*
[5]*Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[6]*Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
(Received 4 February 2005; published 23 February 2006)

We study the electronic structure of Mott-Hubbard systems SrVO₃ and CaVO₃ with bulk and surface-sensitive high-resolution photoemission spectroscopy, using a vacuum ultraviolet laser, synchrotron radiation, and a discharge lamp ($h\nu = 7$–21 eV). A systematic suppression of the density of states (DOS) within ~0.2 eV of the Fermi level (E_F) is found on decreasing photon energy, i.e., on increasing bulk sensitivity. The coherent band in SrVO₃ and CaVO₃ is shown to consist of surface and bulk-derived features, separated in energy. The stronger distortion on surface of CaVO₃ compared to SrVO₃ leads to a higher surface metallicity in the coherent DOS at E_F, consistent with recent theory.

The electronic properties of $3d$ transition metal oxides with strong electron correlations have been extensively studied, particularly since the discovery of high T_c superconductivity and colossal magnetoresistance [1,2]. Carrier doping and/or bandwidth control leads to attractive and complicated phase transitions, such as superconducting and metal-insulator transitions (MITs) in various perovskite-type compounds [1,2]. Such MITs are known to occur systematically by filling control due to the closing of a Mott-Hubbard (MH) type gap. According to MH theory [3], such a MIT is controlled by the relative magnitude of on-site Coulomb interaction U and bandwidth W. Valence band photoemission spectroscopy (PES) studies validate this picture [4]. The dynamical mean-field theory (DMFT) has helped to elucidate the ultraviolet photoemission spectroscopy and optical conductivity of the MH MIT [5,6]. It is now well-known that strongly correlated materials exhibit a coherent and incoherent band and, currently, DMFT is considered the most powerful theoretical method to elucidate their electronic structure (ES).

The perovskite-type $3d^1$ configuration metals Ca₁₋ₓSrₓVO₃ are typical materials whose valence band spectra are compared with DMFT. This is because it is believed that d bandwidth is controlled by the V-O-V bond angle, which changes from 180° for cubic SrVO₃ to 160° for orthorhombic CaVO₃ [7] i.e., the d bandwidth W of SrVO₃ is larger than that of CaVO₃ [8], while on-site U is similar for d^1 (V⁴⁺) oxides. Early PES and inverse-PES of Ca₁₋ₓSrₓVO₃ in the V $3d$ region showed a three-peak structure [9], namely, the coherent band (quasiparticle band) at E_F and the incoherent band corresponding to upper and lower Hubbard bands, located at a few electron volts above and below E_F. Ultraviolet photoemission spec-

troscopy experiments were also interpreted to show systematic spectral weight transfer from coherent band to the incoherent band with increasing U/W, consistent with early DMFT studies [10]. However, a very recent local-density approximation +DMFT study shows that SrVO₃ and CaVO₃ are very similar, consistent with thermodynamic and bulk-sensitive experiments [11]. In particular, it was clarified that the V-O-V bond angle change involves (i) a decreasing d-p-d hybridization and (ii) a compensating, increasing d-d hybridization, resulting in a very small change in t_{2g} bandwidth [11].

The bulk and surface contributions in the ES of Ca₁₋ₓSrₓVO₃ have been studied using photon-energy-dependent PES [12]. The surface sensitivity of PES can be varied by changing the exciting photon energy, since the mean free path (MFP) of electrons depends sensitively on their kinetic energy [13]. Based on a U/W analysis of spectral weight transfer between the coherent and incoherent features, it was concluded that the bulk and surface ES of SrVO₃ is metallic, while the surface of CaVO₃ is a MH insulator and its bulk is metallic [12]. This analysis does not take into account the possibility of separate features due to surface and bulk ES within the coherent band. DMFT studies show that the reduced coordination number leads to a charge transfer of 0.06 electrons from the surface d_{xy} band to the surface d_{xz}, d_{yz} bands [14]. The effective mass gets enhanced at the surface with a narrowing of the coherent band, effectively leading to higher density of states (DOS) at E_F. Further, recent bulk-sensitive PES measurements of CaVO₃ and SrVO₃ using soft x-ray synchrotron radiation ($h\nu = 900$ eV) [15] have shown that V $3d$ DOS at E_F is similar for both systems, indicating absence of spectral weight transfer between coherent and

incoherent features, as explained in detail in Ref. [11]. In very profound studies of d^1 MH titanate systems [16], recent experiments and theory have established "electronic reconstruction" leading to a metallic surface of a MH insulator, and a metallic interface between a MH insulator and band insulator. This behavior is also derived from charge density transferred to the surface or interface [16].

Thus, there exist discrepancies of the results in terms of surface versus bulk ES of $CaVO_3$ and $SrVO_3$ that need to be addressed. In this work, we investigate surface versus bulk ES within the coherent band of $CaVO_3$ and $SrVO_3$. We adopt a different route to study surface and bulk ES: low-energy PES, simply because the universal MFP curve has a minimum at about 30–50 eV electron kinetic energy [13]. Along with higher bulk sensitivity, we get the added advantage of very high resolution, using a new laser system ($h\nu = 6.994$ eV), low-energy ($h\nu = 9$–13 eV) synchrotron radiation, and a discharge lamp ($h\nu = 21.218$ eV). The photoelectron MFP at $h\nu = 6.994$ eV, the lowest photon energy used in the present study, is ~ 100 Å [13]. This is much more bulk sensitive than previous PES measurements done with Al $K\alpha$ ($h\nu = 1486.6$ eV, MFP $\approx$ 20 Å) or soft x-rays ($h\nu = 900$ eV, MFP ≈ 15 Å). At the highest energy used here ($h\nu = 21.218$ eV), the MFP is ≈ 5 Å, and hence we progressively span from very surface-sensitive to very bulk-sensitive measurements.

PES experiments were carried out using (i) a Scienta SES2002 PES spectrometer and a GAMMADATA He discharging lamp with a monochromator, (ii) a wide-angle-lens ($\pm 14°$) Scienta R4000 PES spectrometer and a VUV laser at ISSP [17]. The VUV laser system, developed recently [18], employs the 6th harmonic light of energy 6.994 eV, obtained by using the second harmonic $KBe_2BO_3F_2$ crystal with a frequency tripled single-mode Nd:YVO$_4$ laser. The intensity is more than 10^{15} photons per second with a line width of 0.25 meV. PES experiments were also carried out using Scienta SES2002 PES spectrometer and synchrotron radiation ($h\nu = 13.8$ eV and 9.2 eV) at BL-9A, at HiSOR [19]. All systems use a flowing liquid He cryostat with a thermally shielded sample holder. PES measurements were carried out at a vacuum of $\sim 10^{-10}$ Torr at 6–200 K. Single crystals of $SrVO_3$ and $CaVO_3$ samples were fractured *in situ* to obtain a clean surface. Optical micrographs showed shiny stepped terraces (~ 10–20 μm wide), which is much smaller than the photon source spot size (>100 μm) for PES experiments. Since the photon energies are low, we ensured that all the spectra reported here are angle-integrated by actually checking for angle-resolved effects by varying the incidence angle so as to cover the first Brillouin zone. The energy resolutions were set to 8 meV to get reasonable signal intensity. The E_F was referenced to that of a gold film evaporated onto the sample holder.

Figure 1 shows the comparison of spectra measured using 21.218 eV and 13.8 eV photon energy at 6 K for $SrVO_3$ and $CaVO_3$. The spectra are normalized for area
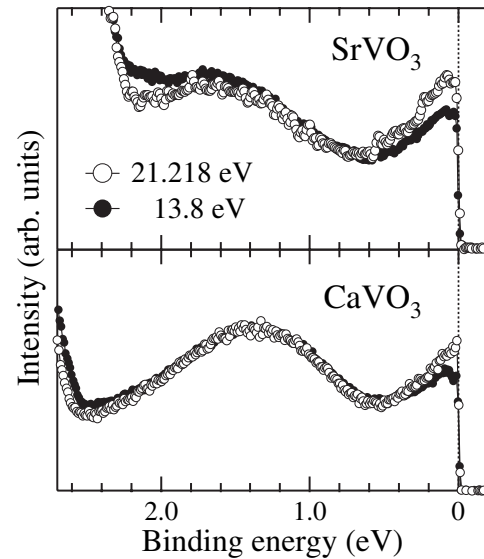

FIG. 1. Photoemission spectra of $SrVO_3$ (top) and $CaVO_3$ (bottom) measured using 21.218 eV and 13.8 eV photon energy at 6 K.

under the curve. The 21.218 eV spectra are consistent with early work [10]. Small differences are seen in the lower binding energy coherent part, at and near E_F, which we investigate in detail. Figs. 2(a) and 2(b) show bulk-sensitive PE spectra of $SrVO_3$ and $CaVO_3$ measured using the laser source ($h\nu = 6.994$ eV) at 6 K. The experimental spectra are normalized to match at the dip feature around 0.6 eV, assuming a similar behavior as in Fig. 1. This normalization suggests that spectral weight in the coherent feature is significantly different ($\sim 50\%$ at E_F) between $SrVO_3$ and $CaVO_3$. However, since it is impossible to investigate the lower Hubbard band with $h\nu = 6.994$ eV,
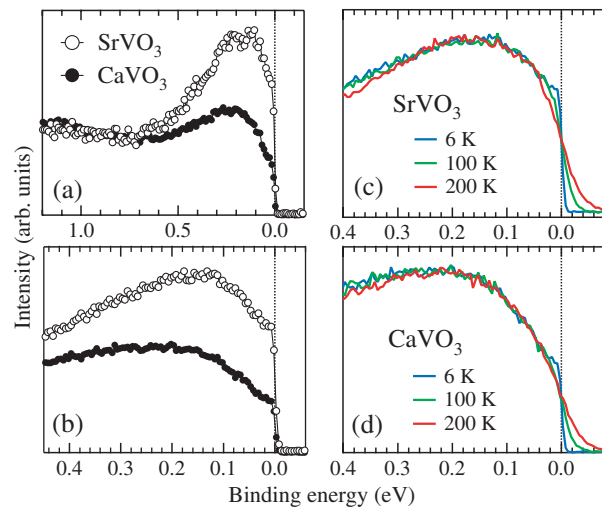

FIG. 2 (color). (a) Photoemission spectra of $SrVO_3$ and $CaVO_3$ measured using laser source ($h\nu = 6.994$ eV) at 6 K. (b) Expanded view of the coherent band near E_F. Temperature-dependent photoemission spectra of (c) $SrVO_3$ and (d) $CaVO_3$ near E_F at 6 K, 100 K, and 200 K.

and the normalization used above does not separate out bulk versus surface contributions and an ambiguous background, it leads to a difference between SrVO$_3$ and CaVO$_3$. This is inconsistent with thermodynamic and bulk-sensitive experiments [8,11,12,15].

More significantly, we observe that the peak of the coherent feature is not at E_F [Fig. 2(b)], but at an energy of ~0.2 eV in both SrVO$_3$ and CaVO$_3$. The intensity suppression observed at E_F is more in laser excited spectra than in the spectra measured using $h\nu = 21.218$ eV and 13.8 eV (Fig. 1). It suggests that this intensity suppression is more in the bulk, while the intensity at E_F is higher in the surface ES. This behavior within the coherent band has not been addressed in earlier studies. The ratio of the spectral intensity at E_F to the coherent peak (at 0.18 eV binding energy) intensity is about 0.7 and 0.5 in SrVO$_3$ and CaVO$_3$, respectively. We have also checked the temperature dependence of this behavior. Figs. 2(c) and 2(d) show the temperature-dependent spectra near E_F measured using laser source at 6, 100, and 200 K. The spectral intensity suppression does not change with temperature.

In order to confirm and establish spectral changes as a function of photon energy, and hence bulk sensitivity, we compare high signal to noise ratio photon-energy-dependent spectra of SrVO$_3$ and CaVO$_3$ at and near E_F measured using 21.218, 13.8, 9.2, and 6.994 eV photons in Fig. 3. The spectra for SrVO$_3$ and CaVO$_3$ are independently normalized at 0.5 eV binding energy so as to see the relative change with photon energy. The intensity at and near E_F is systematically suppressed with lower photon energy. The relative spectral change is much larger in CaVO$_3$ than in SrVO$_3$. A clear structure is seen within 40 meV of E_F in the surface-sensitive spectra obtained with 21.218 and 13.8 eV, particularly for CaVO$_3$.

In order to estimate surface and bulk contributions within the coherent band at and near E_F, and approximate MFPs, we have carried out the following analysis : The
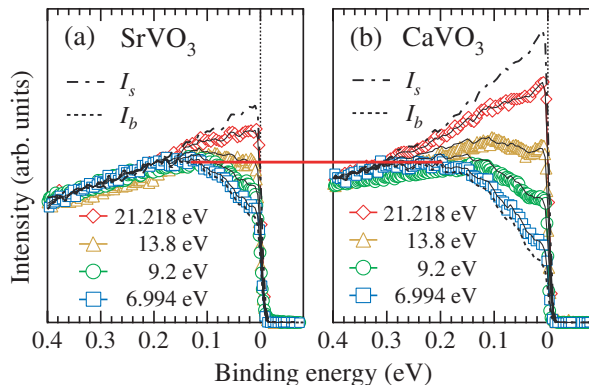

FIG. 3 (color). Photon-energy-dependent photoemission spectra of (a) SrVO$_3$ and (b) CaVO$_3$ near E_F measured using 21.218, 13.8, 9.2, and 6.994 eV photons at 6 K. The extracted bulk (I_b) and surface (I_s) spectra of SrVO$_3$ and CaVO$_3$ are also plotted (dotted and dot-dashed lines) with the reproduced spectra (thin lines) at each excitation energy.

normalized PE spectral intensity $I(E)$ is expressed as $I(E) = \exp(-d/\lambda)I_b(E) + [1 - \exp(-d/\lambda)]I_s(E)$, where I_b and I_s is the normalized bulk and surface spectra, d is the thickness of the surface layer, and λ is the MFP, respectively [20]. We obtain I_b and I_s spectra, using the 21.218 eV and 6.994 eV excited spectra, and assuming $d = 7.5$ Å, $\lambda_{21.218} = 5 \pm 1$ Å, and $\lambda_{6.994} = 85 \pm 10$ Å. The extracted I_b and I_s spectra of SrVO$_3$ and CaVO$_3$ [see Figs. 3(a) and 3(b)] also consistently reproduce the spectra obtained with $h\nu = 13.8$ eV ($\lambda_{13.8} = 11 \pm 1$ Å) and $h\nu = 9.2$ eV ($\lambda_{9.2} = 23 \pm 2$ Å). The results are in very good agreement with experimental spectra, including the fine structures below 0.1 eV binding energy. See Ref. [21] for a complete analysis. The error bars in estimating MFPs are approximately ± 10–20%, but the qualitative trend is consistent with He I data being more surface sensitive and the lower photon energy (~14 to 7 eV) data is progressively more bulk sensitive, consistent with the universal MFP curve [13]. The surface versus bulk analysis is done independently for SrVO$_3$ and CaVO$_3$, but for a relative comparison between them which eliminates photon energy dependence of cross section, we normalize the intensities at the peak ($\equiv 0.18$ eV) in the bulk-derived spectra in Figs. 3(a) and 3(b) (red horizontal line), assuming the analysis of Ref. [15] as correct. This leads to a difference in the DOS at E_F in the extracted bulk contribution of ~25% between SrVO$_3$ and CaVO$_3$, while Ref. [15] estimates it as ~15%. These values are consistent with thermodynamic [8] and bulk-sensitive experiments [11,12,15], as well as calculated quasiparticle weight Z or effective mass $m^*/m = 1/Z$, which varies between 2.1–2.4 [11,15] or 2.2–3.5 [22]. Thus, the normalization presented in Fig. 3 is appropriate for the bulk ES. On separating out the bulk component, the surface-sensitive spectra at E_F exhibit higher metallicity in CaVO$_3$, and also in SrVO$_3$ but to a lesser extent, consistent with recent studies [14,16,23]. In contrast with Ref. [12], the surface ES of CaVO$_3$ is not a MH insulator.

The operative interactions responsible for the observations need careful discussion. First, the observed suppression in bulk-sensitive PES cannot be elucidated by band structure calculations, which indicate a maximum at E_F in the occupied DOS [24]. Secondly, while it is known that magnetic or charge fluctuations can lead to a pseudogap in the DOS [25], a magnetic or charge density wave transition has not been observed in any experimental study of SrVO$_3$ and CaVO$_3$. The phonon DOS in SrVO$_3$ and CaVO$_3$ has also not been reported. In related materials like SrTiO$_3$, BaTiO$_3$, LaTiO$_3$, and YTiO$_3$, the optical phonon mode is observed at 67, 62, 66, and 70 meV, respectively [26]. Thus, the 0.2 eV energy pseudogaplike feature in the present experiment is considered too large to be related to phonons. Moreover, there is no report indicating strong electron-phonon coupling in SrVO$_3$ and CaVO$_3$.

DMFT calculations for the bulk ES of SrVO$_3$ and CaVO$_3$ also predict a peak at E_F. However, DMFT calcu-

lations of the surface ES revealed strong modifications of the coherent and incoherent bands of d^1 MH systems [14,16,23]. At the surface, the t_{2g} degeneracy is lifted, leading to a separation of d_{xy} and $d_{yz,zx}$ derived states. The d_{xy} band lies in the plane and exhibits strong dispersion within the surface plane. The DOS of the more strongly correlated $d_{yz,zx}$ states is narrower, leading to an enhancement of its spectral weight at E_F. These changes are caused by electronic charge density being transferred to the surface. Experiments and theory show very similar results for the surface of a MH insulator and the interface ES of a MH and band insulator, which actually makes the surface or interface metallic [16]. We believe the feature within 40 meV of E_F is the surface $d_{yz,zx}$ states, followed by the surface d_{xy} states between 40 meV to ~0.2 eV (Fig. 3). These are suppressed in the bulk, revealing the bulk t_{2g} feature at ~0.2 eV with a pseudogap at E_F. The present experimental results demonstrate that the t_{2g} degeneracy is indeed lifted on the surface, observed by increasing photon energy from 7 to 21 eV or increasing surface sensitivity. The relative change in $CaVO_3$ is significantly larger than in $SrVO_3$, and we attribute it to the difference between their surface ES. Recent DMFT calculations show that the MH transition is driven by an interplay of correlation effects and a structural ($GdFeO_3$-type) distortion due to a reduction, not only of the bandwidth, but also of the effective orbital degeneracy [22]. This indicates that in distorted $CaVO_3$, the t_{2g} degeneracy is lifted on the surface, leading to stronger spectral weight changes as observed in our photon-energy-dependent PE results.

It is also noted that the spectral intensity at E_F can be suppressed by Coulomb interactions. This was shown by Monte Carlo calculations [27] of spectral changes across the MH transition for a three-dimensional Hubbard model. The results indicated a 4-peak structure in the DOS as a function of temperature, with the quasiparticle peak at E_F splitting into two peaks at low temperature, in addition to the presence of upper and lower incoherent peaks [27]. The calculated results suggest similarity with the pseudogap-like behavior in the quasiparticle peak observed in our PES results. However, this theoretical calculation assumes an intermediate correlation regime [27], rather than the strongly correlated regime. This is in contrast to the fact that $SrVO_3$ and $CaVO_3$ are usually considered as strongly correlated systems as estimated from PE and inverse PE spectra, with $U \sim 4$ eV and $W \sim 2.5$ eV [9].

In conclusion, we studied the bulk and surface ES of $SrVO_3$ and $CaVO_3$ with very high resolution using low-energy (7–21 eV) PES. The coherent spectral weight of $SrVO_3$ and $CaVO_3$ shows a systematic suppression up to 0.2 eV binding energy on reducing incident photon energy from 21 to 7 eV, due to increasing bulk sensitivity. The bulk ES of $SrVO_3$ and $CaVO_3$ are similar. The results show evidence for the t_{2g} degeneracy being lifted on the surface, and a separation of d_{xy} and $d_{yz,zx}$ derived states from the bulk t_{2g} feature. The stronger distortion on the surface of $CaVO_3$ compared to $SrVO_3$ is directly reflected in the coherent DOS at E_F, consistent with recent theory.

[1] E. Dagotto, Rev. Mod. Phys. **66**, 763 (1994).
[2] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
[3] J. Hubbard, Proc. R. Soc. A **276**, 238 (1963).
[4] A. Fujimori *et al.*, Phys. Rev. Lett. **69**, 1796 (1992).
[5] X. Y. Zhang, M. J. Rozenberg, and G. Kotliar, Phys. Rev. Lett. **70**, 1666 (1993).
[6] M. J. Rozenberg *et al.*, Phys. Rev. Lett. **75**, 105 (1995).
[7] B. L. Chamberland and P. S. Danielson, J. Solid State Chem. **3**, 243 (1971).
[8] I. H. Inoue *et al.*, Phys. Rev. B **58**, 4372 (1998).
[9] K. Morikawa *et al.*, Phys. Rev. B **52**, 13 711 (1995).
[10] I. H. Inoue *et al.*, Phys. Rev. Lett. **74**, 2539 (1995).
[11] I. A. Nekrasov *et al.*, Phys. Rev. B **72**, 155106 (2005).
[12] K. Maiti *et al.*, Europhys. Lett. **55**, 246 (2001).
[13] M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).
[14] A. Liebsch, Phys. Rev. Lett. **90**, 096401 (2003).
[15] A. Sekiyama *et al.*, Phys. Rev. Lett. **93**, 156402 (2004).
[16] A. Ohtomo, D. A. Muller, J. L. Grazul, and Y. Hwang, Nature (London) **419**, 378 (2002); A. Ohtomo and H. Y. Hwang, Nature (London) **427**, 423 (2004); S. Okamoto and A. J. Millis, Nature (London) **428**, 630 (2004).
[17] T. Kiss *et al.*, Phys. Rev. Lett. **94**, 057001 (2005).
[18] T. Togashi *et al.*, Opt. Lett. **28**, 254 (2003).
[19] M. Taniguchi and J. Ghijsen, J. Synchrotron Radiat. **5**, 1176 (1998); T. Matsui *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **467–468**, 537 (2001); M. Arita *et al.*, Surf. Rev. Lett. **9**, 535 (2002).
[20] L. Z. Liu *et al.*, Phys. Rev. B **45**, 8934 (1992).
[21] See EPAPS Document No. E-PRLTAO-96-036609 for a complete analysis of the surface and bulk components in $SrVO_3$ and $CaVO_3$. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[22] E. Pavarini *et al.*, Phys. Rev. Lett. **92**, 176403 (2004).
[23] M. Potthoff and W. Nolting, Phys. Rev. B **60**, 7834 (1999); S. Schwieger, M. Potthoff, and W. Nolting, Phys. Rev. B **67**, 165408 (2003).
[24] K. Takegahara, J. Electron Spectrosc. Relat. Phenom. **66**, 303 (1994).
[25] E. Jurczek and T. M. Rice, Europhys. Lett. **1**, 225 (1986); A. Kampf and J. R. Schrieffer, Phys. Rev. B **41**, 6399 (1990).
[26] T. Katsufuji and Y. Tokura, Phys. Rev. B **50**, R2704 (1994); D. A. Crandles, T. Timusk, and J. E. Greedan, Phys. Rev. B **44**, 13 250 (1991); A. S. Barker, Jr., Phys. Rev. **145**, 391 (1966).
[27] N. Tomita, M. Yamazaki, and K. Nasu, Phys. Rev. B **68**, 035117 (2003); M. Yamazaki, N. Tomita, and K. Nasu, J. Phys. Soc. Jpn. **72**, 611 (2003).