

# Evidence against strong correlation in 4d transition metal oxides, CaRuO<sub>3</sub> and SrRuO<sub>3</sub>

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We investigate the electronic structure of 4d transition metal oxides, CaRuO<sub>3</sub> and SrRuO<sub>3</sub>. The analysis of the photoemission spectra reveals significantly weak electron correlation strength ( $U/W \sim 0.2$ ) as expected in 4d systems and resolves the long standing issue that arose due to the prediction of large  $U/W$  similar to 3d-systems. It is shown that the bulk spectra, thermodynamic parameters and optical properties in these systems can consistently be described using first principle approaches. The observation of different surface and bulk electronic structures in these weakly correlated 4d systems is unusual.

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Hubbard model consisting of inter-site hopping energy,  $t$  ( $\propto W$ =bandwidth) and on-site Coulomb repulsion energy,  $U$  has been widely accepted as the simplest model to capture correlation effects in the electronic structure. Thus, effective electron correlation strength can be described by a single parameter,  $U/W$  ( $U/W > 1 \Rightarrow$ insulator,  $U/W < 1 \Rightarrow$ metal). Correlation effects in 3d transition metal oxides (TMO) have extensively been studied using this model during the past few decades following the discovery of many exotic properties in these systems.<sup>1</sup> Despite simplicity of the model, the major difficulty arises from large  $U$  leading to non-perturbative nature of the problem, and the presence of various competing effects such as different types of long-range order, interplay between localization and lattice coherence etc.

4d orbitals in 4d TMOs are more extended than 3d orbitals in 3d TMOs. Thus, correlation effect is expected to be less important in these systems and provide a suitable testing ground for the applicability of various *ab initio* approaches. This is reflected by only a small mass enhancement<sup>2,3</sup> ( $m^*/m_b = 3.0$  in SrRuO<sub>3</sub>;  $m^*$  = effective mass,  $m_b$  = band mass) in the specific heat measurements. However, photoemission<sup>4,5</sup> and optical<sup>6</sup> data reported so far are significantly different from their *ab initio* results. All these studies predict a large  $U/W$  similar to that observed in 3d TMO in contrast to the behavior expected from the highly extended nature of 4d systems. It is thus believed that various approximations (slave boson, techniques in the limit of infinite dimensions, exact calculations for finite size system *etc.*) are necessary to simulate the material properties of these systems. In addition, tetravalent ruthenates have drawn significant attention recently due to the discovery of interesting magnetism,<sup>2-8</sup> unconventional superconductivity,<sup>9</sup> metal-insulator transitions,<sup>10</sup> *etc.*

In this paper, we present evidence for weak correlations among 4d TMOs. We report the results of our investigation of the electronic structure of 4d TMOs, SrRuO<sub>3</sub> and CaRuO<sub>3</sub>. SrRuO<sub>3</sub> is a ferromagnetic metal. Isostructural and isoelectronic, CaRuO<sub>3</sub> (with slightly differ-

ent Ru-O-Ru bond angle; 150° in CaRuO<sub>3</sub> and 165° in SrRuO<sub>3</sub>) exhibits antiferromagnetic behavior.<sup>2,11</sup> Photoemission spectra at different photon energies reveal different electronic structures for surface and bulk in *both* the cases. It is to note here that early 3d TMOs as well as rare-earth systems are known to exhibit different surface and bulk electronic structures,<sup>12-15</sup> which was attributed to an enhancement of  $U/W$  at the surface compared to that in the bulk. It was necessary to employ the dynamical mean field theoretical approach (DMFT) within the limit of infinite dimensional Hubbard model to determine the bulk electronic structure in these 3d systems.<sup>16</sup> Interestingly, the bulk spectra in this study could be described remarkably well using *ab initio* approaches. Present results, thus, resolve three fundamental issues in these systems. (a) Electron correlation is significantly weak in 4d TMOs ( $U/W \sim 0.2$ ). (b) First principle approaches are sufficient to simulate the bulk photoemission and optical responses, and to reproduce  $m^*/m_b$  obtained from the specific heat measurements. (c) The surface and bulk electronic structures can be different even in weakly correlated systems.

High quality polycrystalline samples (large grain size achieved by long sintering at the preparation temperature) were prepared by solid state reaction method using ultra-high purity ingredients and characterized by *x*-ray diffraction (XRD) patterns and magnetic measurements as described elsewhere.<sup>2,4,11</sup> Sharp XRD patterns reveal pure GdFeO<sub>3</sub> structure with similar lattice constants as observed for single crystalline samples.<sup>2</sup> Magnetic susceptibility measurements exhibit a ferromagnetic transition in SrRuO<sub>3</sub> at 165 K and the signature of antiferromagnetic interactions in CaRuO<sub>3</sub> at 180 K. The magnetic moment of 2.7  $\mu_B$  in SrRuO<sub>3</sub> and 3  $\mu_B$  in CaRuO<sub>3</sub> in the paramagnetic phase is close to their spin-only value of 2.83  $\mu_B$  for  $t_{2g\uparrow}^3 t_{2g\downarrow}^1$  configurations at Ru sites. Photoemission measurements were performed on *in situ* ( $4 \times 10^{-11}$  torr) scraped samples<sup>17,18</sup> using SES2002 Scienta analyzer at room temperature (paramagnetic phase) in order to avoid complications due to different long-range orders. The experimental resolution was 7 meV,

0.8 eV and 0.9 eV for measurements with monochromatic He II, Mg  $K\alpha$  and Al  $K\alpha$  lines.

Valence band spectra obtained at He II, Mg  $K\alpha$  and Al  $K\alpha$  excitation energies are shown in Fig. 1. The signature of three discernible features is evident in the figure. While the features appearing at binding energies  $> 2.5$  eV are large in He II spectra, the relative intensity between 2.5-0 eV binding energies is significantly enhanced in the  $x$ -ray photoemission (XP) spectra. Considering strong dependence of the relative transition matrix elements on excitation energies,<sup>19</sup> the 0-2.5 eV feature can be attributed to essentially Ru  $4d$  electron excitations with the O  $2p$  contributions appearing beyond 2.5 eV.

In order to understand these results, we calculated the electron density of states (DOS) of CaRuO<sub>3</sub> and SrRuO<sub>3</sub> using full potential linearized augmented plane wave method (FLAPW) within the local density approximations (LDA) for the experimentally obtained crystal structure in the paramagnetic phase.<sup>20</sup> The convergence was achieved using 512  $k$ -points within the first Brillouin zone. Total DOS (TDOS) and partial DOS (PDOS) corresponding to Ru  $4d$  and O  $2p$  states are shown in Fig. 2. No significant contribution from Ca and Sr states are observed in this energy range. Three distinct groups of peaks are evident in the figure in the occupied part. Non-bonding O  $2p$  states appear between 2-4 eV and the bonding states with dominant O  $2p$  contributions appear at higher binding energies. This is also manifested in Fig. 1 by an enhancement in intensity at 7 eV in the XP spectra compared to the He II spectra. He II spectra exhibit a peak below 6 eV. The intensity at  $E_F$  arises primarily due to Ru  $4d$  split  $t_{2g}$  bands. The broad and empty  $e_g$  bands appear beyond 1 eV above  $E_F$ .

Small distortion of RuO<sub>6</sub> octahedra lifts the degeneracy of the  $t_{2g}$  band as shown in the insets of Fig. 2. While  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  bands in SrRuO<sub>3</sub> have similar width ( $W = 2.4$  eV), the total bandwidth is about 3.1 eV due to the splitting of  $t_{2g}$  band. In CaRuO<sub>3</sub>, the total bandwidth is about 2.4 eV. Interestingly, the width of  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  bands varies between 2.3-2.4 eV which is similar to those in SrRuO<sub>3</sub>. *This reveals that the small change in Ru-O-Ru bond angle between SrRuO<sub>3</sub> and CaRuO<sub>3</sub> has essentially no influence on  $W$  (the bandwidth of the individual  $d$ -bands) and thus,  $U/W$  in these systems.* The center of mass for  $d_{xy}$  band appears very close to  $E_F$  in both the cases, while  $d_{xz}$  and  $d_{yz}$  bands appear at lower energies.

It is now clear that the feature close to  $E_F$  has primarily Ru  $4d$  character. High resolution in the He II spectra leads to a minimal overlap between O  $2p$  and Ru  $t_{2g}$  bands (see Fig. 1). Hence, it is possible to delineate Ru  $t_{2g}$  contributions quite reliably by subtracting O  $2p$  tail as shown in the inset (I) of Fig. 1 for SrRuO<sub>3</sub>. Ru  $t_{2g}$  bands, thus extracted for *both* CaRuO<sub>3</sub> and SrRuO<sub>3</sub> are shown in Fig. 3(a). Large intensity at  $E_F$  represents the extended states as also seen in the band structure calculations and is commonly known as 'coherent feature'. Interestingly, the maximum intensity appears

around 1.2 eV as observed before,<sup>4,5</sup> while the theoretical intensity peaks at about 0.5 eV with negligible contributions beyond 1 eV (see Fig. 3(b)). Thus, this feature is often attributed to the signature of the electronic states essentially localized due to electron correlations and is termed as 'incoherent feature'. Spectral modifications observed in Fig. 3(a) indicate larger correlation effects in CaRuO<sub>3</sub> compared to SrRuO<sub>3</sub> as predicted from the structure. While large intensity at  $E_F$  indicates metallic character, the complete dominance of this apparent incoherent feature was taken as evidence of the presence of strong correlation effects in previous studies.<sup>4-6</sup> We present our results below establishing that this feature essentially arises due to the contributions from the surface electronic structure.

Interestingly, the XP spectra in Fig. 1 exhibit highest intensity at 0.5 eV for the Ru  $4d$  band even though the intensities at higher energies contain contributions from resolution broadened O  $2p$  band-tails. In order to subtract these contributions from the XP spectra, we broadened the peaks 1 and 2 in inset (I) representing the O  $2p$  features in the He II spectra upto the resolution broadening of the XP measurements and the relative intensities of the features 1 and 2 were obtained *via* least-square-error-fit. The subtracted spectra shown in Fig. 3(c) clearly possess different lineshape compared to the solid lines representing resolution broadened He II spectra. The  $x$ -ray photoelectrons has significantly larger escape depth compared to the ultra-violet photoelectrons, which leads to a significantly larger bulk sensitivity in XPS compared to that in UPS. Thus, it is obvious that the bulk and surface electronic structures are significantly different in these systems. *We do not observe any change in lineshape of the  $t_{2g}$  band in the XP spectra of CaRuO<sub>3</sub> and SrRuO<sub>3</sub> as expected from the band structure results described above.*

Photoemission intensity can be expressed as  $I(\epsilon) = [1 - e^{-d/\lambda}]f^s(\epsilon) + e^{-d/\lambda}f^b(\epsilon)$ , where  $d$  is the thickness of the surface layer and  $\lambda$  is the escape depth of the photoelectrons.  $f^s(\epsilon)$  and  $f^b(\epsilon)$  represent the surface and bulk spectral functions, respectively. Since  $d$  and  $\lambda$  are expected to change in the same way due to the difference between  $3d$  and  $4d$  sites, experimentally estimated  $d/\lambda$ -values in a similar system CaSrVO<sub>3</sub><sup>12</sup> are a good approximation to extract  $f^s(\epsilon)$  and  $f^b(\epsilon)$  in these systems. We observe that a change in  $d/\lambda$  values by more than 10% leads to unphysical intensities providing confidence in this procedure. The extracted  $f^s(\epsilon)$  and  $f^b(\epsilon)$  are shown in Fig. 4.  $f^s(\epsilon)$  in both the cases is dominated by the intensity centered at 1 eV.  $f^b(\epsilon)$  exhibit large coherent feature with the peak at about 0.5 eV as observed in the *ab initio* calculations. The feature around 2 eV indicates the presence of some degree of correlation effects, which is estimated below.

The spectral function can be expressed as,  $f^b(\epsilon) = -\frac{1}{\pi}Im \sum_k G_k(\epsilon)$ , where  $G_k(\epsilon)$  is the retarded Green's function representing the many electron system and is given by  $G_k(\epsilon) = 1/(\epsilon - \Sigma_k(\epsilon) - \epsilon_k)$ .  $\Sigma_k(\epsilon)$  is the self

energy of the system. For small  $U$ ,  $\Sigma_k(\epsilon)$  can be calculated using perturbation approach upto the second order term<sup>21</sup> within the local approximations. We have used Ru  $t_{2g}$  PDOS for these calculations. The calculated spectral functions are shown by solid lines in Fig. 4. The fit to the experimental spectra is remarkable. Most interestingly,  $U/W$  is found to be significantly small (0.24 for CaRuO<sub>3</sub> and 0.21 for SrRuO<sub>3</sub>;  $U = 0.6 \pm 0.05$  eV in both the cases) in sharp contrast to all previous predictions.<sup>4-6</sup> A small variation in  $U/W$  leads to significantly large spectral weight transfer as shown in Fig 4(a). We calculated the mass enhancement factor following the relation,  $\frac{m^*}{m_b} = 1 - \frac{\partial}{\partial \epsilon} (Re\Sigma(\epsilon))|_{\epsilon=E_F}$ . Interestingly,  $m^*/m_b$  for SrRuO<sub>3</sub> is almost the same (= 2.9) as that obtained (= 3.0) from specific heat measurements. While  $U/W$  in CaRuO<sub>3</sub> is little larger than that in SrRuO<sub>3</sub>,  $m^*/m_b$  in CaRuO<sub>3</sub> is found to be close to SrRuO<sub>3</sub> and somewhat smaller than its experimental value.

It is important to realize here that the optical response (particularly in transmission mode) corresponds essentially to the bulk electronic structure.<sup>6</sup> Thus, the description of weak correlation effects in the bulk electronic structure should also be reflected in the optical spectra. We, thus, calculated the optical response by calculating the joint density of states using Wien-program.<sup>20</sup> The calculated spectra (correlation effects are not considered) shown in the inset of Fig. 4(b) resemble the experimental spectra by Ahn *et al.*<sup>6</sup> remarkably well. *This study, thus, establishes for the first time that these weakly correlated 4d TMOs provide a model systems for the applicability of the first principle approaches in determining the thermodynamic, optical and spectroscopic properties.*

Differences in the surface and bulk electronic structures in 3d TMOs as well as in rare earths were attributed to the enhancement of  $U/W$  due to the band narrowing at the surface.<sup>12,16</sup> Thus, the observation of different  $f^s(\epsilon)$  and  $f^b(\epsilon)$  in these weakly correlated 4d TMOs as well is unusual. Most surprisingly, the surface peak appears at lower binding energies than the incoherent peak in the bulk spectra. It is observed that small distortion of RuO<sub>6</sub> octahedra in the orthorhombic structure lifts the degeneracy of the bulk  $t_{2g}$  band (see insets in Fig. 2). Whether the surface layer consists of Sr/Ca-O or Ru-O layer, the absence of periodicity along the surface will enhance this distortion leading to a different crystal field symmetry presumably close to  $D_{4h}$  symmetry ( $t_{2g} \Rightarrow e_g + b_{2g}$ ); where,  $d_{xz}$  and  $d_{yz}$  bands exhibit  $e_g$ -symmetry and  $d_{xy}$  band has  $b_{2g}$ -symmetry.<sup>14</sup> Thus, the peak around 1 eV in the surface spectra may be attributed to an essentially filled  $e_g$  band with  $b_{2g}$  band appearing above  $E_F$ .

In summary, correlation effects are found to be significantly weak in these 4d systems. This resolves the long standing issue that arose due to the prediction of large electron correlation in these systems similar to 3d-TMOs. We find that the photoemission and optical responses, and thermodynamic parameters can be consistently described for the first time within the first principle ap-

proaches. The first observation of different surface electronic structure in these weakly correlated 4d systems may possibly be attributed to the change in symmetry at the surface.

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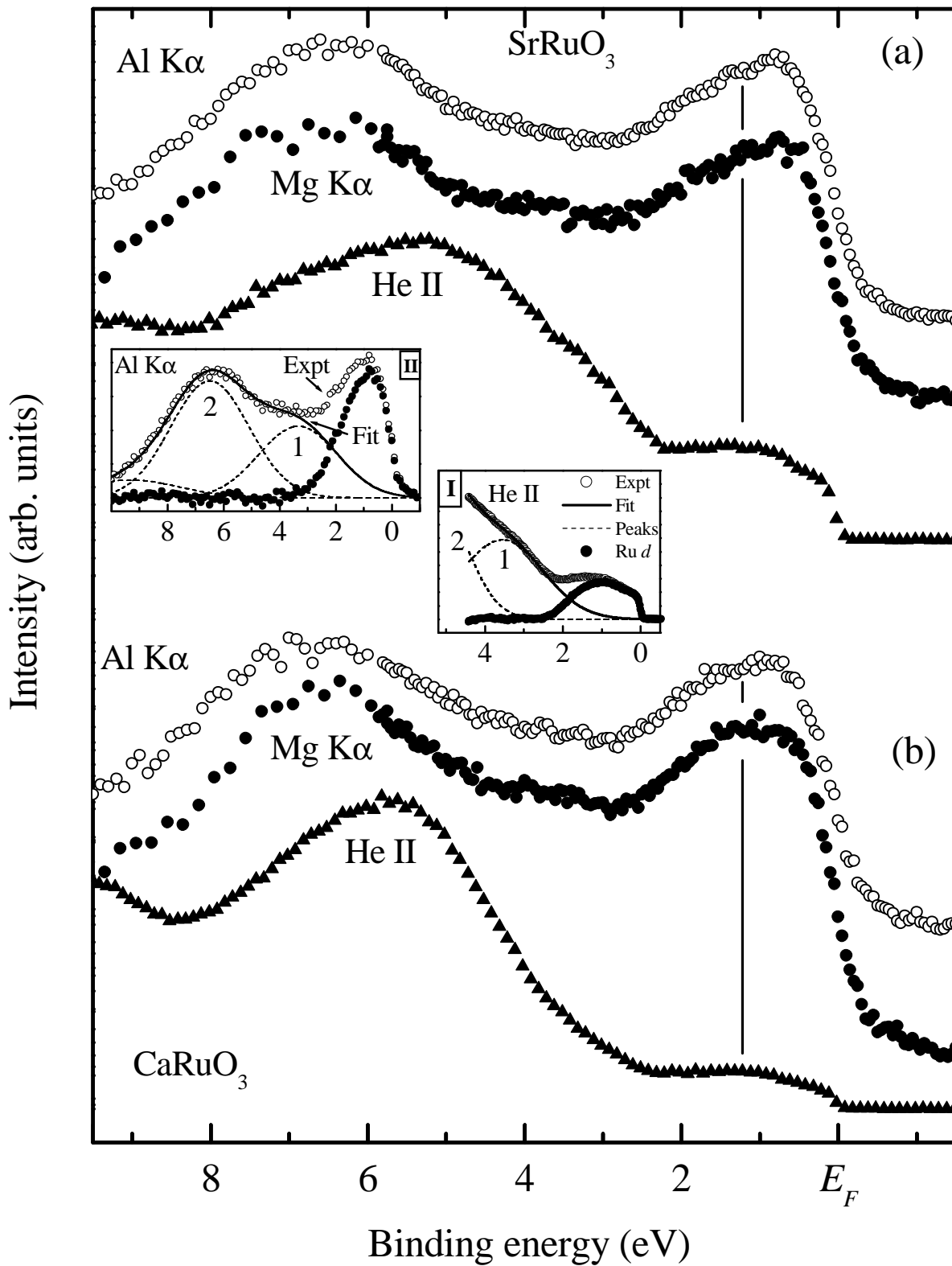
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- <sup>17</sup> Since, perovskite structure has no cleavage plane, scraping has sufficiently high probability to expose intrinsic bulk material through intragrain fracture [Susaki *et al.* Phys. Rev. Lett. **78**, 1832 (1997)]. We have verified this on a similar system, SrVO<sub>3</sub>. We find that the spectra collected from scraped and cleaved single crystals are identical [K. Maiti *et al.* (unpublished)].
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FIG. 1. Valence band spectra of (a) SrRuO<sub>3</sub> and (b) CaRuO<sub>3</sub>. Subtraction of O 2*p* contributions from He II spectrum of SrRuO<sub>3</sub> is demonstrated in inset (I). The peaks 1 and 2 represent the non-bonding and bonding features. These two peaks are broadened upto XP resolution to obtain O 2*p* contributions in the XP spectrum of SrRuO<sub>3</sub> as shown in inset (II). The relative intensity of the features is obtained by least square error method.

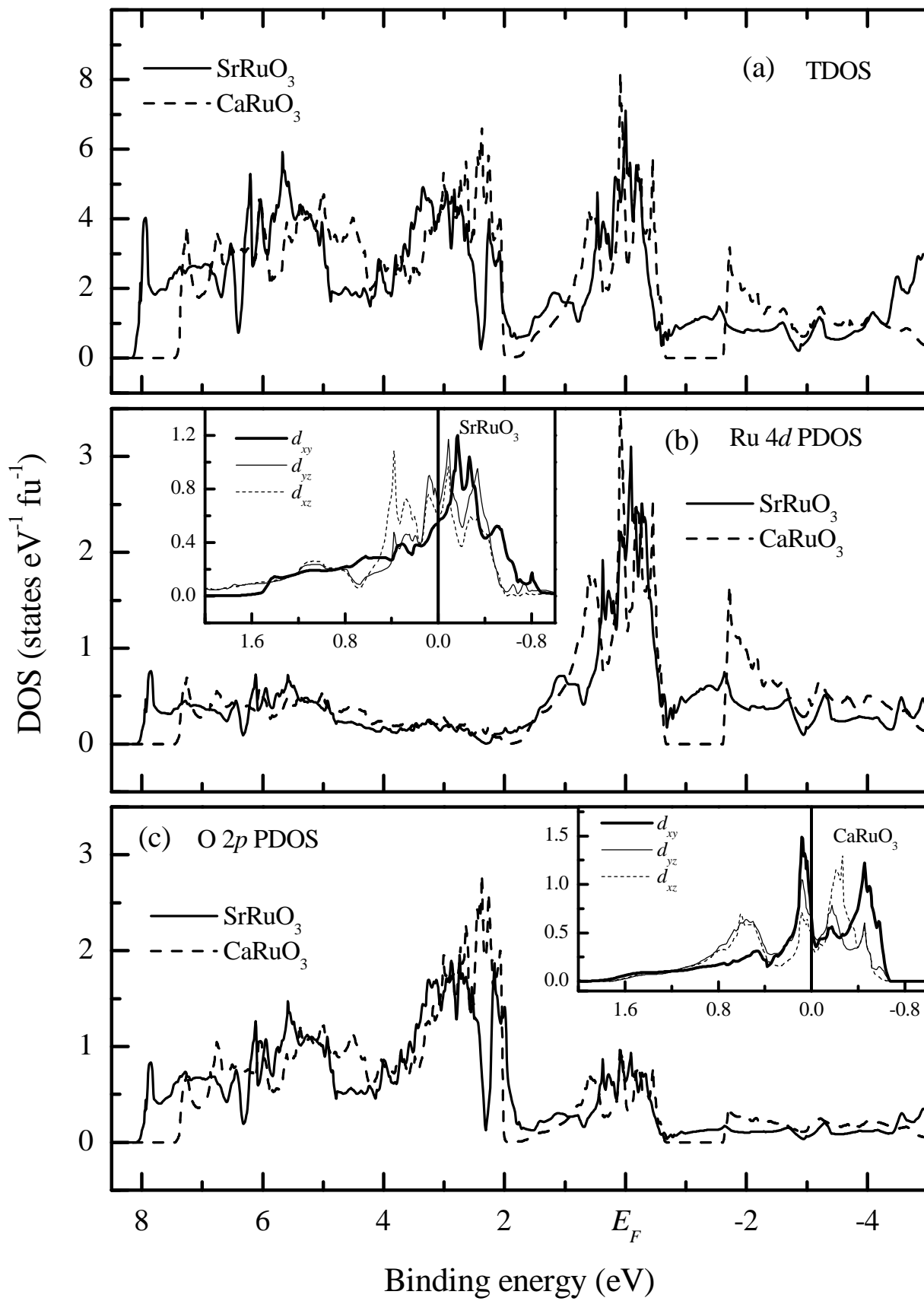
FIG. 2. (a) TDOS, (b) Ru 4*d* PDOS and (c) O 2*p* PDOS in SrRuO<sub>3</sub> and CaRuO<sub>3</sub>. *d*<sub>*xy*</sub>, *d*<sub>*yz*</sub> and *d*<sub>*xz*</sub> bands are shown in the inset in (b) for SrRuO<sub>3</sub> and in (c) for CaRuO<sub>3</sub>.

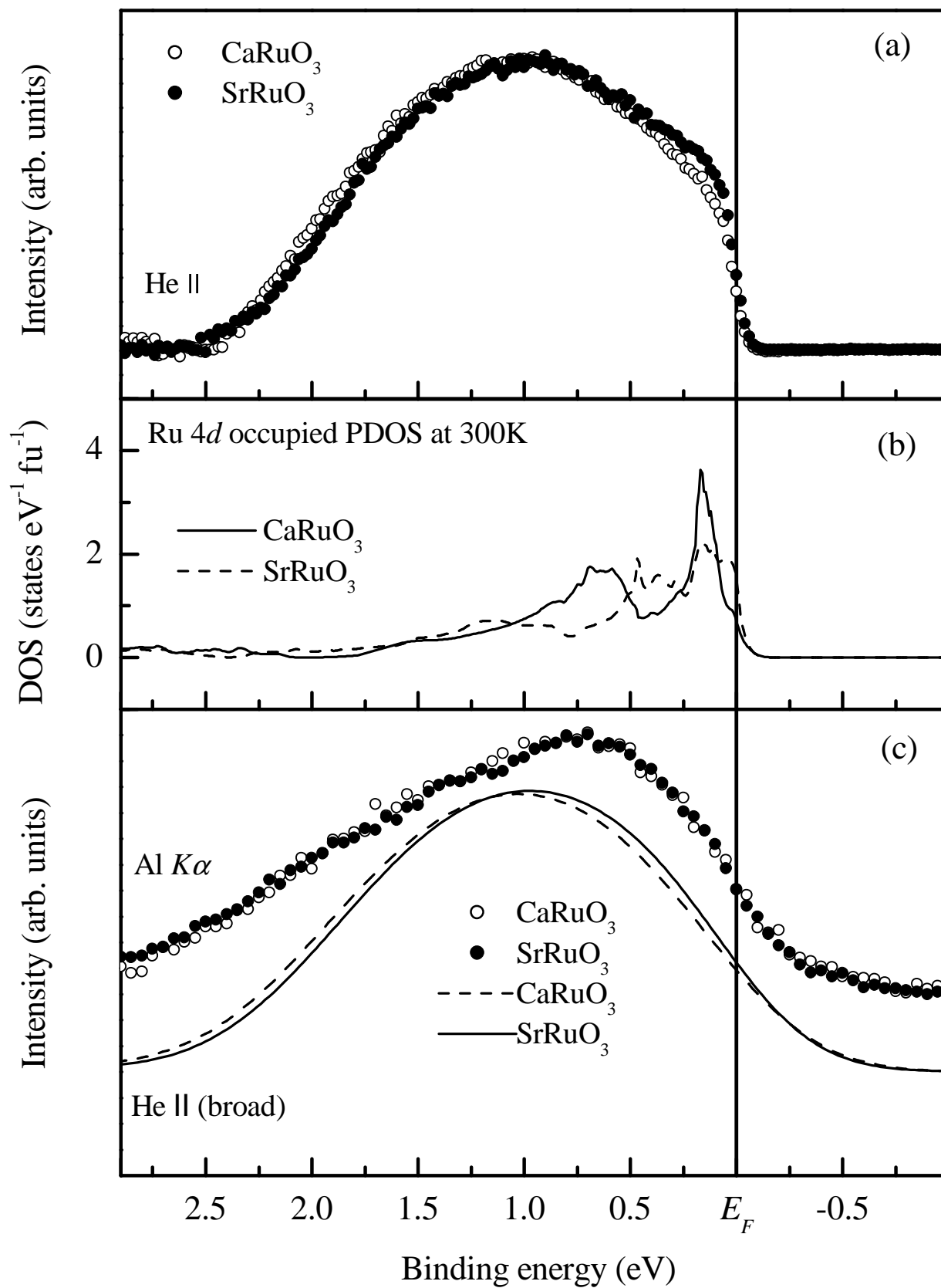
FIG. 3. (a) Ru *t*<sub>2*g*</sub> band extracted from He II spectra for CaRuO<sub>3</sub> and SrRuO<sub>3</sub>. (b) Ru 4*d* PDOS convoluted with Fermi distribution function at 300 K. This represents the signature of coherent feature. (c) Ru *t*<sub>2*g*</sub> band extracted from XP spectra for CaRuO<sub>3</sub> and SrRuO<sub>3</sub>. The resolution broadened He II spectra are also shown for comparison.

FIG. 4. Surface and bulk spectra in (a) CaRuO<sub>3</sub> and (b) SrRuO<sub>3</sub>. The solid lines represent the simulated spectra from first principle calculations. The dashed and dot-dashed lines in (a) represent the simulated spectra for  $U/W = 0.12$  and  $0.36$ , respectively. The calculated optical response are shown in the inset. The lineshape is found to be similar to that observed experimentally.<sup>6</sup>

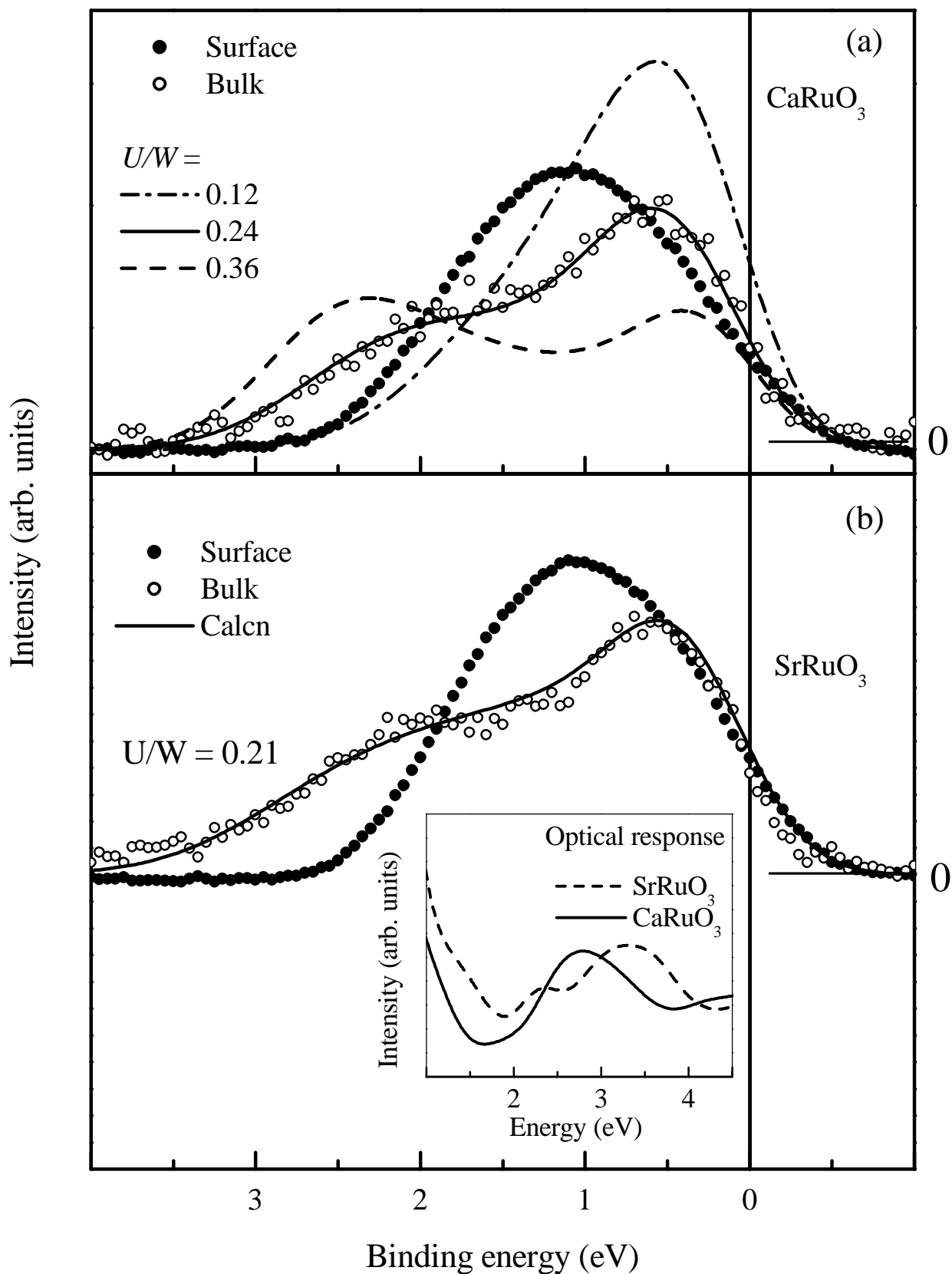


Rev. Fig.1 Maiti and Singh





Rev. Fig.3 Maiti and Singh



Rev. Fig.4 Maiti and Singh