Comment on "Electronic structure and orbital ordering of SrRu$_{1-x}$Ti$_x$O$_3$: GGA+$U$ investigations"

Kalobaran Maiti

Department of Condensed Matter Physics and Materials’ Science,
Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai - 400 005, INDIA

(Dated: July 18, 2008)

In the paper, PRB 77, 085118 (2008), the authors conclude that the observation of Ti-doping induced half-metallicity in SrRu$_{1-x}$Ti$_x$O$_3$ within the limit of local density approximations is not valid as the experimental results indicate insulating behavior. It was described that the metal-insulator transition (MIT) at $x=0.5$ observed in this system appears due to the enhancement of on-site Coulomb repulsion strength, $U$ with Ti substitutions, $x$. The MIT primarily depends on $U$ and partially on $x$ and/or disorder. All these conclusions are in sharp contrast to the experimental observations, which predicted Anderson insulating phase at $x=0.5$ (finite localized density of states at the Fermi level). The hard gap due to electron correlation appears at much higher $x$ ($\sim 0.8$). In addition, it is well established that homovalent substitution has negligible influence on on-site $U$ (a local variable). These inconsistencies appear due to the fact that the calculated results representing the bulk electronic structure are compared with the experimental results dominated by surface contributions. The experimental bulk spectra, already available in the literature exhibit finite density of states at the Fermi level even for $x \geq 0.5$ sample, which suggests that the conclusion of half metallic phase in an earlier study is reasonable. Thus, the insulator to metal transition in these systems is driven by bandwidth, $W$ rather than $U$ and disorder plays dominant role in the metal-insulator transition. One needs to consider the bulk spectra to reproduce numerically the bulk electronic structure.

PACS numbers: 71.27.+a, 71.30.+h, 71.20.-b, 79.60.Bm

Ruthenates have drawn significant attention in the recent times due to many interesting properties exhibited by these systems such as non-Fermi liquid behavior, unusual magnetism, superconductivity etc. SrRuO$_3$ forms in perovskite structure and is a ferromagnetic metal. It was observed experimentally that Ti doping at the Ru sites in SrRuO$_3$ (SrRu$_{1-x}$Ti$_x$O$_3$) thin films leads to an interesting evolution of the electronic properties ranging from weakly correlated metal to a band insulator via several intermediate phases for different values of $x$. A recent study based on generalized gradient approximations (GGA) using vasp package observed that Ti substitution at the Ru sites in SrRuO$_3$ leads to a metal to half-metal transition around $x=0.5$. The authors conclude that such observation is in disagreement with the experimental observation of a metal-insulator transition as a function of Ti-dopant concentration. It was suggested that a larger $U$ would be more reasonable in the dopant concentration to achieve an insulating ground state. In addition, it was predicted that observed metal insulator transitions in this system is primarily driven by on-site Coulomb repulsion. Disorder and/or Ti substitution are only partially responsible in determining the metal-insulator transition.

All the above conclusions are in sharp contrast to the experimental results. Firstly, the experimental results based on transport measurements on thin films suggest an Anderson insulating phase at $x=0.5$. This phase correspond to finite electronic density of states at the Fermi level, which are localized due to the effect of disorder. Both transport and photoemission studies do not indicate signature of hard gap at $x=0.5$. The occurrence of hard gap is predicted at much higher Ti concentration ($x \sim 0.8$). It is clear that disorder play a significant role in determining the electronic properties in this system. In addition, it is already well known that even in strongly correlated 3$d$ transition metal oxides, the magnitude of on-site Coulomb repulsion strength, $U$ is not significantly sensitive to the homovalent substitutions. This is reasonable as $U$ is a local variable. Thus, a conclusion of change in $U$ with Ti substitution is unusual.

Various photoemission studies of such ruthenates reveal that the intensity of the correlation induced lower Hubbard band is significantly weaker than the intensity of the coherent feature that represents the delocalized electronic states in the vicinity of the Fermi level. Thus, the electron correlation strength is significantly weak in these systems compared to that often found in highly correlated 3$d$ transition metal oxides. This again rules out the possibility of Ti-substitution induced enhancement of $U$ in such a weakly correlated electron systems leading to insulating phase. We believe that the inconsistencies observed here have a different origin as described below.

The results from band structure calculations represent the bulk electronic structure. Therefore it is desirable to compare the calculated results with the properties obtained from bulk materials and the spectral function representing the bulk electronic structure of the concerned systems. All the experimental results referred in the paper are obtained from thin film samples. The photoemission spectra provide the direct representation of the electronic density of state. The experimental photoemission results referred in the paper have significant surface con-
SES2002 and monochromatized photon sources. The entries were obtained using Gammadata Scienta analyzer, figure for a representative case. The experimental significantly different. Part of the results are reproduced in the electronic structures.

**FIG. 1:** (color online) (a) X-ray photoemission spectra, (b) He I spectra, (c) bulk spectra and (d) surface spectra of SrRuO$_3$ (open circles) and SrRu$_{0.5}$Ti$_{0.5}$O$_3$ (solid circles), respectively.

Contributions. While it is often considered that sufficiently thick films exhibit properties close to that expected in the bulk of the material, it is observed that the substrate induced strain persists even in thick films and the two-dimensional topology of these films lead to significantly different electronic and magnetic properties. Such confinement effects are used in numerous occasions to generate quantum wells, in-plane magnetizations etc.

In addition, experiments on various transition metal oxides reveal significantly different surface and bulk electronic structures. Even the samples in the form of thin films also exhibit surface-bulk differences in the electronic structure. Moreover, in the present case, it has been demonstrated experimentally that the surface and bulk electronic structure in SrRu$_{1−x}$Ti$_x$O$_3$ are significantly different. Part of the results are reproduced in the figure for a representative case. The experimental spectra were obtained using Gammadata Scienta analyzer, SES2002 and monochromatized photon sources. The energy resolution for x-ray photoemission (XP) and He II photoemission measurements were set at 300 meV and 4 meV, respectively. The details of sample preparation and characterizations are described elsewhere.

In Fig. 1(a) and 1(b), we show the x-ray photoemission and He I spectra of SrRuO$_3$ (open circles) and SrRu$_{0.5}$Ti$_{0.5}$O$_3$ (solid circles). The spectral region shown here represents the density of states having primarily Ru 4$d$ character as also found in previous studies. It is evident that spectral lineshape changes significantly with the change in photon energy. The He I spectra are most surface sensitive (~80%). The surface contribution in the x-ray photoemission spectra is significantly small (~40%). Thus, the different spectral lineshape in Fig. 1(a) and 1(b) indicates that the surface and bulk electronic structures are significantly different.

The extracted surface and bulk spectra are shown in Fig. 1(c) and 1(d). It is evident that the ultraviolet photoemission spectra collected using thin films as well as the bulk samples in the present study are very similar to the surface spectra obtained from bulk samples. In the surface spectra and in the He I spectra, the peak position of the most intense feature moves towards higher binding energies with increase in $x$. While such change may indicate a change in $U$ in the surface electronic structure, it can have other origin too. For example, the crystallographic symmetry at the surface is different from that in the bulk leading to different crystal field effect, surface defects, surface reconstructions etc. In fact it is believed that the later effects are more reasonable in these systems.

The bulk spectra exhibit finite density of states at the Fermi level for all the $x$ values studied. Most importantly, the bulk spectra and/or the raw spectra obtained by x-ray photoemission spectroscopy reveal that the energy position of the electron correlation induced feature (lower Hubbard band) as marked by vertical dashed lines in Fig. 1(a) and 1(c) moves towards the Fermi level with the increase in Ti-dopant concentration in sharp contrast to the conclusions of the concerned paper. Most importantly, this observation is visible in the raw data of the x-ray photoemission spectra and is independent of any data analysis procedure. Thus, it is important to extract the surface and bulk contributions from the experimental spectra to obtain realistic representation of the bulk electronic structure. This also echoes the view that the insulating nature observed at these compositions are 'Anderson insulator' kind, which correspond to disorder induced localized finite density of states at the Fermi level.

We now turn to the question of half-metallic phase, which is also observed in earlier studies. The main aim of that study was to grow half-metallic phase via Ti substitution induced band narrowing. Since, the Ti 3$d$ levels has significantly different eigen energies compared to the eigen energies of Ru 4$d$ levels and Ti 3$d$ band is almost completely empty appearing above the Fermi level, the hopping of electrons from one Ru site to another via Ti sites is smaller than that expected for Ru-O-Ru hopping strength. Hence, Ti substitution leads to a significant narrowing of the Ru 4$d$ bands. This in turn pulls the up spin band completely below the Fermi level and only the down spin band contributes at the Fermi level resulting to half metallicity. It is already known that the electron correlation strength is significantly weak in these systems. Thus, the consideration of $U$ would slightly enhance the energy gap in the up spin channel. The down spin channel will continue to contribute at the Fermi level as finite intensity is observed in the experimental bulk spectra. Thus, the conclusion of half metallic phase will not be influenced significantly by the weak electron correlation in the vicinity of $x = 0.5$ compositions.

In summary, the surface and bulk electronic structure in Ti-substituted SrRuO$_3$ are significantly different. The bulk spectra in these ruthenates exhibit finite den-
sity of states at the Fermi level for $x$ as high as 0.6 in SrRu$_{1-x}$Ti$_x$O$_3$. This is consistent with the other experimental results indicating Anderson insulating phase rather than the hard gap insulators. The insulator to metal transition in these systems are primarily driven by bandwidth, $W$ rather than $U$, and disorder plays an important role in determining the electronic properties of these systems.

* Electronic mail: kbmaiti@tifr.res.in

1 J. Kim, J.-Y. Kim, B.-G. Park, and S.-J. Oh, Phys. Rev. B 73, 235109 (2006).
2 M. Abbate, J.A. Guevara, S.L. Cuffini, Y.P. Mascarenhas, and E. Morikawa, Eur. Phys. J. B 25, 203 (2002).
3 K.W. Kim, J.S. Lee, T.W. Noh, S.R. Lee, and K. Char, Phys. Rev. B 71, 125104 (2005).
4 P.-A. Lin, H.-T. Jeng, and C.-S. Hsue, Phys. Rev. B 77, 085118 (2008).
5 M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
6 A. Georges, G. Kotliar, W. Krauth, and M.J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
7 K. Maiti and R.S. Singh, Phys. Rev. B 71, 161102(R) (2005).
8 M. Takizawa, D. Toyota, H. Wadati, A. Chikamatsu, H. Kumigashira, A. Fujimori, M. Oshima, Z. Fang, M. Lippmaa, M. Kawasaki, and H. Koinuma, Phys. Rev. B 72, 060404(R) (2005).
9 G. Cao, S. McCall, M. Shepard, J.E. Crow, and R.P. Guertin, Phys. Rev. B 56, 321 (1997).
10 K. Maiti, Priya Mahadevan, and D.D. Sarma, Phys. Rev. Lett. 80, 2885 (1998).
11 R.S. Singh, V.R.R. Medicherla, K. Maiti, and E.V. Sampathkumaran, Phys. Rev. B 77, 201102(R) (2008).
12 K. Maiti, R.S. Singh, and V.R.R. Medicherla, Phys. Rev. B 76, 165128 (2007); ibid., arXiv/0704.0327.
13 K. Maiti, Phys. Rev. B 73, 235110 (2006).
14 David J. Singh, J. Appl. Phys. 79, 4818 (1996).
15 K. Maiti, Phys. Rev. B 77, 212407 (2008); ibid, arXiv/0704.0321.