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Electronic structure of bulk- and Na-intercalated TiS_2 determined from a GGA+*U* study with the Hubbard terms obtained *ab initio*

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A theoretical study on the electronic structure of titanium sulfide compounds TiS_2 intercalated with Na is presented using generalized gradient approximation (GGA)+*U* calculations. Na-intercalated TiS_2 compounds are well-known materials in the field of battery systems. The atomic structure of available experimental ultraviolet photoemission spectroscopy (UPS) data is discussed and modeled on a $Na_3Ti_{12}S_{24}$ unit cell. The on-site effective correlation term *U* is determined from first principles following a linear-response method for the Ti 3*d* electrons of this compound and the corresponding host TiS_2. Valence electronic structures obtained from subsequent GGA+*U* calculations are compared to experimental UPS available data and to standard GGA results for both compounds. The improvement achieved with the *ab initio* GGA+*U* method and the agreement with the experimental spectra are discussed.

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I. INTRODUCTION

Transition metal dichalcogenide compounds (TMDC) intercalated with alkali atoms are well-known materials for their possible application in battery systems.[1] Several theoretical and experimental works specifically on Na_xTiS_2 have been carried out.[2–4] On the other hand the TMDC TiS_2 has been one of the most controversial compounds. There are a number of experiments which conclude that it has a semimetallic behavior[5,6] and others that propose that it is a semiconductor.[7,8] Furthermore, recent theoretical studies[9–12] show diverse results and have also formulated different theories about the electronic structure of TiS_2. In this work using an *ab initio* density-functional theory (DFT) we study results of experimental valence photoemission spectra obtained in parent and Na-intercalated TiS_2 compounds.[3,4]

DFT framework[13,14] has been used widely for obtaining a number of properties of materials. Its most extended formulations, the local-density approximation (LDA) and generalized gradient approximation (GGA), have been successful in describing many properties but fail to obtain accurately the electronic structure of materials with strong Coulomb interactions.

One of the most popular approaches that has arisen to take into account these interactions in a more proper way is the GGA+*U* method [or analogous LDA+*U* (Ref. 15)]. It includes a correction for the energetic contribution of strongly correlated electronic shells (typically *d* or *f* valence shells of transition metals or rare earths, respectively) constructed in a Hartree-Fock manner, which essentially discourages partial occupations. The main advantage of GGA+*U* over other methods is that the computational time is not considerably increased when compared to standard DFT approximations.

One drawback of GGA+*U* is that the correction is introduced through a term, *U*, which in the initial formulations of the method was taken as a parameter used to adjust the results with known experimental properties for obtaining its optimal value. A linear-response method for obtaining *U* from first-principles calculations has been determined by means of its relationship to the spurious curvature of the total GGA energy of a system as a function of the number of electrons.[16]

In a previous theoretical work for TiS_2 the Hubbard term *U* was adjusted in order to obtain experimental properties.[17] In the present work we obtain the on-site effective correlation term *U* from first principles following the above linear-response method[16] for both TiS_2 and Na_xTiS_2 compounds.

This paper is organized as follows. In Sec. II a discussion about the compounds studied in this work is presented. In Sec. III the method used is briefly described. In Sec. IV the results obtained using the *ab initio* GGA+*U* method for the electronic structure of bulk TiS_2 and intercalated Na_xTiS_2 compounds are presented and compared with those of standard GGA calculations and photoemission measurements. In Sec. V summary with the main conclusions is shown.

II. COMPOUNDS

Bulk TiS_2 and Na-intercalated TiS_2 compounds are studied in this work. 1*T*-TiS_2 crystallizes in the trigonal structure $P\bar{3}m1$ with cell parameters $a=3.407$ Å and $c=5.695$ Å. This layered compound consists of a sheet of Ti^{4+} atoms arranged triangularly in the *ab* plane (0,0,0) occupying octahedral sites created by another two adjacent sheets of S^{2-} atoms [S_1:(1/3,2/3,0.25) and S_2:(2/3,1/3,0.75)]. Consecutive TiS_2 layers are bonded by van der Waals forces generated between the closest S sheets in such a way that some elements can be intercalated in the interlayer area.

In situ ultraviolet photoemission spectroscopy (UPS) results on a Na-intercalated thin-film TiS_2 sample were obtained elsewhere by Tonti *et al.*[3,4] A broad valence band can be seen there which is mainly formed from S 3*p* states and the lower edge of a Ti 3*d* band. The occupation of the latter essentially comes from the additional charge injected by weakly bound 3*s* electrons of intercalated Na.

In the present study the Na concentration has been extracted from comparison of areas of the valence bands found using UPS measurements. A ratio of S 3*p* and Ti 3*d* peak areas taking into account the orbital-dependent cross sections for the He-I source (4.333 and 5.074 for S 3*p* and Ti 3*d*, respectively[18]) and subtracting background intensity using Shirley's method[19] present in the program XPSPEAK (Ref. 20) turned out to be about 108. If we now consider the $NaTiS_2$ compound, given the integration of the density of states (DOS), the corresponding ratio is 12, independent of the Ti 3*d* character inside the S 3*p* band. Therefore, supposing linear proportionality between both ratios, the compound predicted by this reasoning must have a low Na intercalation, namely, $Na_{0.1}TiS_2$.

There is still an open question about the Na intercalation. No concrete structure was reported in the experimental work for the intercalation process. In the known literature three stable crystalline Na_xTiS_2 phases appear depending on the amount of Na intercalated, namely, *II* for $0.17 \leq x \leq 0.33$,[21] *Ib* for $0.38 \leq x \leq 0.68$,[22] and *Ia* for $0.79 \leq x \leq 1$.[22] However, there is no definitive phase for low intercalations (0.1 or less) of Na. In fact these known phases have occupation factors different from 1. Although in the bulk 1*T*-TiS_2 structure the stacking of consecutive layers is carried out in the same way in the intercalated materials, there is a big variety of possible stackings of adjacent TiS_2 layers. Furthermore, there are also two different symmetries available for the Na intercalation sites, i.e., (quasi-)octahedral and trigonal prismatic.

Nevertheless, in this work it is argued that neither the geometry of the Na intercalation sites nor the relative position of adjacent TiS_2 layers have a significant effect over the valence electronic structure, but the main factor is the quantity of intercalated Na, whose effect is the opening of a band gap between the S 3*p* and Ti 3*d* bands. To prove this, electronic DOSs obtained from GGA calculations for different phases of $NaTiS_2$ compounds have been compared (see Fig. 1). Phase *II* was not included in the study because of its complexity which implies fractional structure factors that do not allow a specific unit cell to be used. In the *Ia*-$NaTiS_2$ compound the Na site has an octahedral symmetry, while in the other compound (based on the *Ib*-$Na_{0.55}TiS_2$ phase but changing the structure factor of Na from 0.55 to 1) the site is prismatic. Observing the main aspects of the valence electronic structure (the gap between the Ti 3*d* and the S 3*p* bands, the width of the latter, or the position of the principal peaks), it can be seen that the differences are not greater than 0.1 eV.

A calculation of a bulk Ti_3S_6 compound, a 1×1×3 supercell of the TiS_2 primitive cell, was also included in Fig. 1. The resemblance of both $Na_3Ti_3S_6$ valence bands with the host compound, except the absence of band gap which depends only on the amount of Na intercalated, is also significant, even though both $Na_3Ti_3S_6$ compounds have 3*R* stacking and Ti_3S_6 has 1*T* stacking.

Taking into account that the amount of Na introduced in these examples is much higher than that used in the calculations presented below, 3*R* stacking of the structures above was taken for modeling the low intercalated compound without worrying about obtaining an electronic structure significantly different from the one expected for the experimental measurements. Having selected the stacking 3*R*, the most probable site symmetry of Na seems to be octahedral on analogy of the bulk TiS_2 compound in which the stacking already provides octahedral sites.

The final structure is represented in Fig. 2. Due to the limited computational resources that impose a moderately large unit cell, we have to limit the size of the intercalated compound cell to $Na_3Ti_{12}S_{24}$, i.e., $x=0.25$, higher than 0.1 but within a low intercalation range.

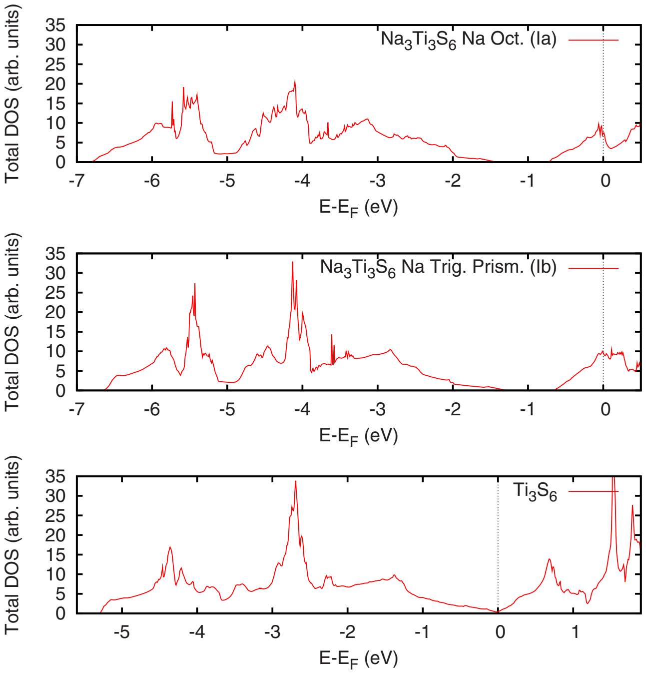

FIG. 1. (Color online) Comparison of DOS for two $Na_3Ti_3S_6$ compounds (one based on the *Ia*-Na_xTiS_2 phase and another based on the *Ib*-Na_xTiS_2 phase) and for a host Ti_3S_6 compound.

III. METHOD

The scheme followed in this study was introduced as a simplified version of the rotational invariant formulation of the GGA+*U* method (Ref. 16 and references therein). In this formulation an extra E_U component is introduced for total energy which depends on the occupation coefficients of the considered strongly correlated states $n^{i\sigma}_{mm'}$, and it is tuned by the term *U*,

$$E_U[n^{i\sigma}_{mm'}] = \frac{U}{2}\sum_{i,\sigma} \mathrm{Tr}[\mathbf{n}^{i,\sigma}(1-\mathbf{n}^{i,\sigma})]. \tag{1}$$

In the equation above $\mathbf{n}^{i,\sigma}$ is the total summation of occupations over all the strong correlated states of site *i* and spin σ. The occupation matrix coefficients are calculated as

$$n^{i\sigma}_{mm'} = \sum_{\mathbf{k},\nu} f^{\sigma}_{\mathbf{k}\nu}\langle\psi^{\sigma}_{\mathbf{k},\nu}|P^{i}_{mm'}|\psi^{\sigma}_{\mathbf{k},\nu}\rangle, \tag{2}$$

where $\psi^{\sigma}_{\mathbf{k},\nu}$ is the electronic wave function of the ν state in $\mathbf{k}$ with spin σ, $f^{\sigma}_{\mathbf{k}\nu}$ is the corresponding occupation number, and $P^{i}_{mm'}$ are the projection operators, which in our case correspond to Wannier functions.[23]

U is assigned to the value of the spurious curvature of the total energy of the system with respect to the variation in the number of electrons. It can be obtained following a linear-response method from constrained DFT calculations in which a small potential shift is applied to the correlated

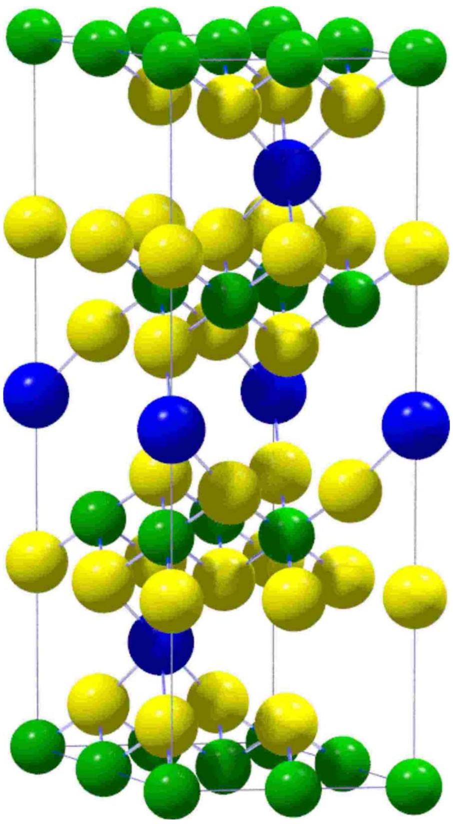

FIG. 2. (Color online) Structure of the modeled $Na_3Ti_{12}S_{24}$ compound. S, Ti, and Na atoms are filled in yellow (light gray), green (medium gray), and navy blue (dark gray), respectively.

states. If a potential shift α_j is applied to the atom j, the response function in the atom i is defined as

$$\chi_{ij} = \frac{\partial n_i}{\partial \alpha_j} \tag{3}$$

and the value of U corresponds to the diagonal term

$$U = (\chi_0^{-1} - \chi^{-1})_{ii}. \tag{4}$$

The response matrix χ_0 refers to the bare perturbation without allowing the redistribution of the whole electronic system toward the self-consistency, while χ refers to the self-consistent response function. In order to approach the full magnitude of the response function, it is necessary to perform calculations in unit cells as large as possible.

Plane-wave-based QUANTUM-ESPRESSO code[24] was used for the calculations with ultrasoft pseudopotentials.[25] The $Na_3Ti_{12}S_{24}$ whole atomic structure was allowed to be relaxed below the convergence thresholds of 0.4 mRy/bohr for the atomic forces and 0.5 kbar for the pressure. The PW91 functional[26] was selected to parametrize the exchange-correlation potential of the GGA calculations. A Methfessel-Paxton first-order technique[27] with 5 mRy of smearing was used to obtain the occupation of one-particle levels in the Brillouin zone, whose sampling was $7\times7\times13$ and $6\times6\times2$ for the $3\times3\times1$ supercell of TiS_2 and the unit cell of $Na_3T_{12}S_{24}$, respectively. The DOSs were calculated following the tetrahedron method.[28] Wannier-type projectors used in the GGA+U scheme to obtain the highly localized occupations were created by a postprocessing routine included in the QUANTUM-ESPRESSO package from converged Kohn-Sham states obtained in previous GGA calculations.

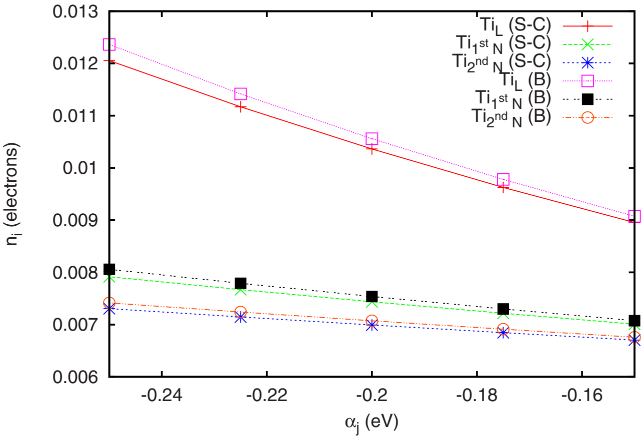

FIG. 3. (Color online) Occupation of localized levels of the different Ti_i atoms of TiS_2 compound with respect to α_j potential shifts, both allowing the relaxation to the self-consistency (S-C) and not (B) for constructing χ and χ_0, respectively. The Ti_L label corresponds to the same atom in which α_j is applied. Ti_{1stN} is referred to the six first Ti neighbors and Ti_{2ndN} corresponds to the two second neighbors of Ti_L.

IV. RESULTS

A. TiS_2

In the first stage the electronic valence-band structure for bulk TiS_2 was calculated. A $3\times3\times1$ supercell of TiS_2 was selected in order to calculate U following the scheme explained above. The use of this cell includes not only the contribution from the nearest Ti neighbors which are placed at 3.41 Å but also that one from the second-nearest neighbors located at 4.82 Å.

As can be seen from Fig. 3, in order to obtain the response functions χ and χ_0 the potential shifts employed on this occasion were not centered on zero, as is usual in the scheme of Ref. 16, but in −0.2 eV. The reason is that the 3d levels in the TiS_2 compounds are essentially empty, and therefore the additional discouragement which would be usually achieved by a positive potential shift applied is not originated properly. In these circumstances the use of small negative potential shifts allows this kind of difficulties to be overcome. Their use is guaranteed because the resulting occupations are above zero but almost negligible (always below 0.015 electron per Ti atom). A stable behavior of U at 2.1 eV has been checked when applying potential shifts around −0.2 eV.

Having obtained the value of 2.1 eV for U a GGA+U calculation was carried out. The resulting GGA+U DOS is shown against that obtained with GGA in Fig. 4. It can be seen that the use of the computed U has brought about a band gap of 1 eV between the S 3p and the Ti 3d bands, while in the GGA result this gap is not present.

In order to compare these results straightforwardly with the experimental UPS, the DOS followed a postprocess

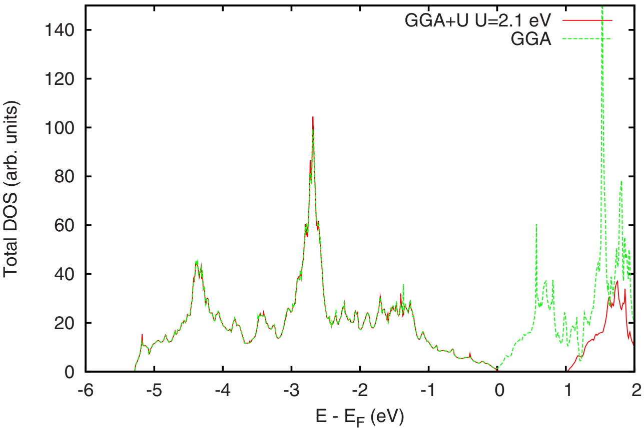

FIG. 4. (Color online) Total DOS for Ti_9S_{18} compound calculated with GGA and GGA+U scheme using an *ab initio* value for U of 2.1 eV.

method. First a Lorentzian convolution was made which simulates the finite lifetime of the excited electrons and whose full width at half maximum (FWHM) is linearly proportional with a coefficient 0.1 to the binding energy of the valence electrons.[29] Afterward there was applied a Gaussian convolution with a constant FWHM which in this case represents the spectrometer resolution—in this case 63 meV. Finally a background proportional to the integrated intensity of lower binding energies was added following a Shirley-type method.[30] The spectrum obtained is presented together with the experimental HeI-UPS results[3] in Fig. 5.

From Fig. 5 it can be seen that the locations of the three main peaks of the S 3p band in both spectra agree. The only feature that is not completely reproduced is the relative size of the peaks. However, it must be taken into account that UPS is essentially a surface technique, and therefore the crystal orientation is an important factor which can modify the peak intensities. Furthermore, background addition method could be improved by using a more refined method, but the differences due to this fact are not expected to be significant.

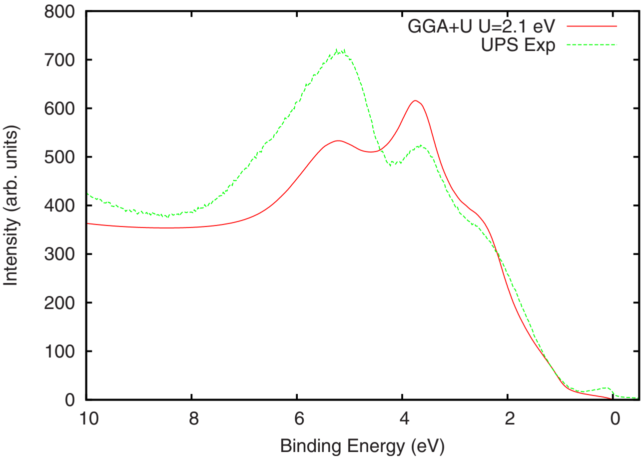

FIG. 5. (Color online) Photoemission spectra of Ti_9S_{18} compound obtained with GGA+U (U=2.1 eV) compared to UPS spectrum (HeI) from Ref. 3.

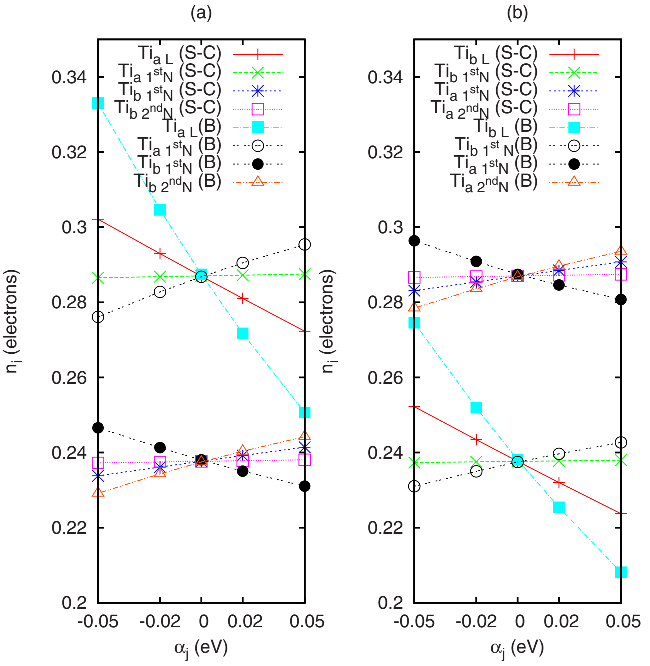

FIG. 6. (Color online) Occupation of localized levels of the different Ti_i atoms for $Na_3Ti_{12}S_{24}$ compound with respect to applied α_j potential shifts [over sites Ti_a and Ti_b for (a) and (b), respectively]. The labels have the same meaning as in Fig. 3, except that Ti_a and Ti_b are considered as independent species, and therefore local and neighbor sites noted here have been split into a and b types.

B. Na_xTiS_2

In this part of the work the electronic structure of $Na_3Ti_{12}S_{24}$ is calculated following a method analogous to that explained above, and thus the first step needed to be fulfilled is again the obtaining of the corresponding Hubbard term. In principle we suppose that the influence of the intercalated Na should not be important for the determination of U because Na atoms are located intentionally in a highly homogeneous arrangement. However in the compound shown in Fig. 2 not all the twelve Ti atoms are completely equivalent, but there are three of them (one per layer) which are surrounded by six first Na neighbors equidistant to them. From now on these Ti atoms will be labeled as Ti_a. The other nine (Ti_b) are surrounded by some Na atoms closer than others. This small difference is reflected in the localized occupations being 0.29 and 0.24 electrons for Ti_a and Ti_b, respectively. It is noted that if the twelve Ti were equivalent all the local occupations would be 0.25 electrons.

Therefore, a study taking these two Ti sites as independent atomic species was carried out for the calculation of U. The resulting occupations obtained for the localized states and for the different potential shifts applied are shown in Fig. 6. The results of the on-site screened correlation term turned out to be $U_{Ti_a}=2.62$ eV and $U_{Ti_b}=2.60$ eV, which implies that all the Ti atoms can be considered as equivalent.

Consequently, the DOS at GGA+U level for $Na_3Ti_{12}S_{24}$ was calculated using a unique value of U=2.6 eV for the twelve Ti atoms. In Fig. 7 this DOS is shown with another

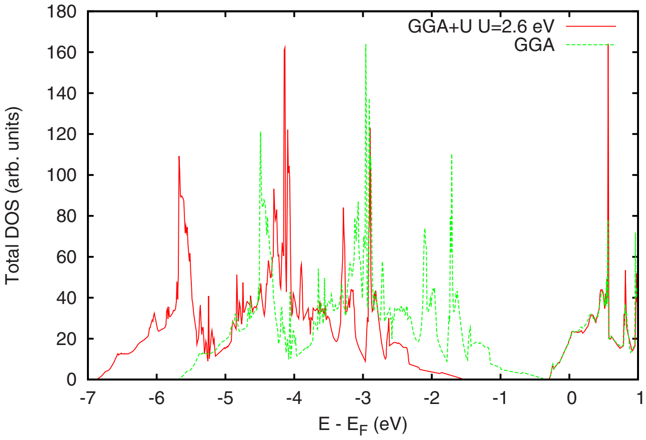

FIG. 7. (Color online) Total DOS for $Na_3Ti_{12}S_{24}$ compound calculated with GGA and GGA+U using an *ab initio* value for U of 2.6 eV.

one calculated following the GGA scheme. It can be seen that a band gap of 1.2 eV appears for the GGA+U results, while in the GGA standard DOS there is no appreciable gap.

Finally, postprocess tasks analogous to those introduced above were performed in order to compare the GGA+U results with the available experimental UPS spectra (see Fig. 8), including again Lorentzian and Gaussian broadenings and Shirley-type background addition. There is resemblance between both spectra, and the main peaks binding energies are close to the experimental ones. However there are few features that are different in them. On one hand, and as happened to the TiS_2 case, the sizes of the different S 3p peaks disagree and the explanation proposed is the same as that explained above. On the other hand a small new peak appears with binding energy at about 8 eV. This peak is assigned in Ref. 4 to a slightly different hybridization of S atoms caused probably for some disorder in the slab stacking.

Nevertheless, calculated spectra of Fig. 8 have been shown to reproduce a band gap between S 3p and Ti 3d bands that agrees to a large extent with the experimental measurements, unlike GGA, which was not able to predict a significant band gap in the Na-intercalated TiS_2.

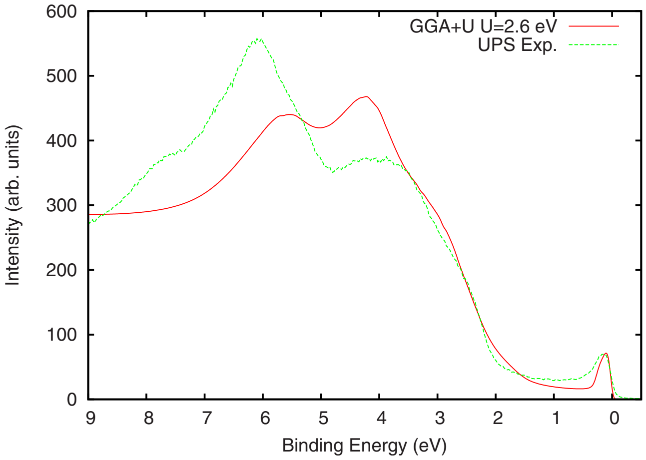

FIG. 8. (Color online) Photoemission spectra of $Na_3Ti_{12}S_{24}$ compound obtained with GGA+U (U=2.6 eV) compared to UPS spectrum (HeI) from Ref. 3.

V. SUMMARY AND CONCLUSIONS

In the present work an *ab initio* GGA+U study has been applied in order to obtain the valence electronic structure of TiS_2 compounds, both bulk and Na intercalated with a composition approximate to $Na_{0.1}TiS_2$. A $Na_3Ti_{12}S_{24}$ unit cell was modeled for carrying out the GGA+U study for the intercalated material. It is argued that the only important factor that affects the valence electronic structure of Na_xTiS_2 compounds is the quantity of intercalated Na, while the geometry of its site and the stacking of the TiS_2 layers are largely irrelevant.

Following the method set out by Cococcioni and de Gironcoli[16] the on-site correlation term U of Ti 3d electrons of Ti_9S_{18} compound has been calculated as 2.1 eV. In the case of $Na_3Ti_{12}S_{24}$, even though there is slightly inhomogeneous arrangement of the surrounding Na atoms, the obtained result of U was 2.6 eV for all of the Ti atoms considered as equivalent.

The difference found between the values of the strength of the Hubbard term in both compounds is attributed to the different valence states of the Ti atoms. In the case of TiS_2 all of the Ti atoms have a valence of 4+, while in the intercalated compound the additional charge provided by the Na 3s electrons is transferred to the Ti 3d levels resulting in a valence state close to $Ti^{3.75+}$.

This increase in the obtained Hubbard term is reflected in the subsequent GGA+U calculations carried out with the corresponding U values, showing band gaps of 1 and 1.2 eV for both bulk and Na-intercalated TiS_2, respectively. Those band gaps are originated by means of the enhancement of the single-particle energies of the Ti 3d electronic levels with respect to the other states. Standard GGA calculations did not produce a significant band gap in any of the compounds studied.

A postprocess work for calculated DOS has been carried out in order to compare the results with available UPS experimental data. The S 3p binding energies are close to those of the UPS measurements. Discrepancies in some relative intensities of the different peaks which make up the S 3p band can result from the influence of the sample orientation. In the case of the $Na_3Ti_{12}S_{24}$ calculations, they do not show a small experimental peak at 8 eV, but its origin seems to come from perturbations in the slab stacking.[4]

To conclude, the study presented here shows a considerable improvement in the electronic properties of these materials in comparison to previous calculations and predicts a semiconductor behavior for bulk and Na-intercalated TiS_2 which agrees with experimental UPS measurements without the need for U parameters to be adjusted *ad hoc*. Moreover, obtaining the Hubbard term through strict first-principles calculations can be extended to the prediction of electronic properties for novel materials in which correlations could play a significant role and whose measurements do not exist or are difficult to be obtained.

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[1] M. Broussely, P. Biensan, and B. Simon, Electrochim. Acta **45**, 3 (1999).

[2] J. Dijkstra, C. F. van Bruggen, and C. Haas, J. Phys.: Condens. Matter **1**, 4297 (1989).

[3] D. Tonti, C. Pettenkofer, and W. Jaegermann, Electrochem. Solid-State Lett. **3**, 220 (2000).

[4] D. Tonti, Ph.D. thesis, Freie Universität Berlin, 2000 (http://www.diss.fu-berlin.de/2000/145/).

[5] F. R. Shepherd and P. M. Williams, J. Phys. C **7**, 4416 (1974).

[6] C. A. Kukkonen, W. J. Kaiser, E. M. Logothetis, B. J. Blumenstock, P. A. Schroeder, S. P. Faile, R. Colella, and J. Gambold, Phys. Rev. B **24**, 1691 (1981).

[7] C. H. Chen, W. Fabian, F. C. Brown, K. C. Woo, B. Davies, B. DeLong, and A. H. Thompson, Phys. Rev. B **21**, 615 (1980).

[8] P. C. Klipstein and R. H. Friend, J. Phys. C **17**, 2713 (1984).

[9] C. M. Fang, R. A. de Groot, and C. Haas, Phys. Rev. B **56**, 4455 (1997).

[10] D. R. Allan, A. A. Kelsey, S. J. Clark, R. J. Angel, and G. J. Ackland, Phys. Rev. B **57**, 5106 (1998).

[11] S. Sharma, T. Nautiyal, G. S. Singh, S. Auluck, P. Blaha, and C. Ambrosch-Draxl, Phys. Rev. B **59**, 14833 (1999).

[12] A. H. Reshak and S. Auluck, Phys. Rev. B **68**, 245113 (2003).

[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[14] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[15] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[16] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).

[17] Q. Yan-Bin, Z. Guo-Hua, L. Di, W. Jiang-Long, Q. Xiao-Ying, and Z. Zhi, Chin. Phys. Lett. **24**, 1050 (2007).

[18] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[19] D. A. Shirley, Phys. Rev. B **5**, 4709 (1972).

[20] R. Kwok, http://www.phy.cuhk.edu.hk/~surface/XPSPEAK.

[21] H. J. M. Bouwmeester, E. J. P. Dekker, K. D. Bronsema, R. J. Haange, and G. A. Wiegers, Rev. Chim. Miner. **19**, 333 (1982).

[22] K. Cenzual, L. M. Gelato, M. Penzo, and E. Parthe, Acta Crystallogr. B **47**, 433 (1991).

[23] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

[24] P. Giannozzi *et al.*, http://www.quantum-espresso.org

[25] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[26] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992); **48**, 4978 (1993).

[27] M. Methfessel and A. T. Paxton, Phys. Rev. B **40**, 3616 (1989).

[28] P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).

[29] H. Höchst, P. Steiner, G. Reiter, and S. Hüfner, Z. Phys. B Condens. Matter **42**, 199 (1981).

[30] X. Li, Z. Zhang, and J. Henrich, J. Electron Spectrosc. Relat. Phenom. **63**, 253 (1993).