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# Localised Wannier orbital basis for the Mott insulators $\text{GaV}_4\text{S}_8$ and $\text{GaTa}_4\text{Se}_8$

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**Abstract** – We study the electronic properties of  $\text{GaV}_4\text{S}_8$  (GVS) and  $\text{GaTa}_4\text{Se}_8$  (GTS), two distant members within the large family of chalcogenides  $\text{AM}_4\text{X}_8$ , with  $\text{A} = \{\text{Ga}, \text{Ge}\}$ ,  $\text{M} = \{\text{V}, \text{Nb}, \text{Ta}, \text{Mo}\}$  and  $\text{X} = \{\text{S}, \text{Se}\}$ . While all these compounds are Mott insulators, their ground states show many types of magnetic order, with GVS being ferromagnetic and GTS non-magnetic. Based on their band structures, calculated with density functional theory methods, we compute an effective tight-binding Hamiltonian in a localised Wannier basis set, for each of the two compounds. The localised orbitals provide a very accurate representation of the band structure, with hopping amplitudes that rapidly decrease with distance. We estimate the superexchange interactions and show that the Coulomb repulsion with Hund's coupling may account for the different ground states observed in GVS and GTS. Our localised Wannier basis provides a starting point for realistic dynamical mean-field theory studies of strong-correlation effects in this family compounds.

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The members of the family of chalcogenides compounds of formula  $\text{AM}_4\text{X}_8$  ( $\text{AMX}$ ), with  $\text{A} = \{\text{Ga}, \text{Ge}\}$ ,  $\text{M} = \{\text{V}, \text{Nb}, \text{Ta}, \text{Mo}\}$ ,  $\text{X} = \{\text{S}, \text{Se}\}$ , are paradigmatic examples of strongly correlated systems. Their recent experimental study has unveiled very interesting properties such as pressure-driven metal-insulator transitions, superconductivity above 11.5 GPa [1], and even resistive switching under electric pulsing [2,3].

Crystallographically, these compounds have a lacunar spinel structure with a FCC general symmetry [4,5]. They are formed by two types of units: clusters of the transition metal atoms surrounded by the X atoms,  $\text{M}_4\text{X}_8$ , and  $\text{AX}_4$  tetrahedrons, both ordered in a NaCl manner. As the distances between the four metal atoms of the cluster are significantly shorter than the inter-cluster ones, we can understand their basic electronic properties on the basis of molecular orbitals. Particularly, near the Fermi energy they form three molecular levels with a

$t_{2g}$  cubic symmetry, which may be filled with one or two electrons, or even with one hole, depending on the specific combination of the elements above [6]. The smaller overlap between inter-cluster orbitals gives place to relatively small hopping amplitudes which lead to narrow  $d$ -electron bands, where strong-correlation effects may be expected. In fact, the nominal occupation of the molecular orbitals should lead to partially filled metallic bands; however, all the experimental systems are good insulators at low temperatures.

There is another universal feature that runs through the whole family, namely, the occurrence of structural transitions at temperatures around 50 K. However, not all compounds adopt the same low-temperature structure, and several of those low- $T$  structures remain yet undetermined.

Regarding their ground-state properties, there are also striking differences. While some of them acquire a

magnetic order, such as  $\text{GaV}_4\text{S}_8$  and  $\text{GeV}_4\text{S}_8$ , which, respectively, become a ferro- and an antiferro-magnet [6,7], others, such as  $\text{GaNb}_4\text{S}_8$  and  $\text{GaTa}_4\text{Se}_8$ , seem to remain paramagnetic down to the lowest measured temperatures.

Since all these systems have uncompleted electronic shells but fail to become metals, they are generally considered to be a family of paradigmatic Mott insulators. Moreover, experimentally, it has been observed that pressure may dramatically decrease the resistivity of all these compounds, up to several orders of magnitude at low temperature, consistent with this classification. Some of them may even become superconductors under pressure, as, for instance,  $\text{GaTa}_4\text{Se}_8$ , with a critical temperature of just a few Kelvin degrees at 11.5 GPa [1]. The Mott transition in the AMX family has also been associated to their unusual resistive switching properties, which may be used for novel non-volatile memory devices [2,3].

While the universal classification of these insulators as of Mott type is appealing, it also poses the question on the origin of their observed differences. In this paper we begin to address this issue by obtaining a representation of the electronic structure in terms of localised orbitals, and studying the systematic differences by focusing in two distant members of the family, namely,  $\text{GaV}_4\text{S}_8$  (GVS) and  $\text{GaTa}_4\text{Se}_8$  (GTS). The former has more localised  $3d$  electrons while the latter has more extended  $5d$  ones. The possibility of representing the electronic band structure through a tight-binding Hamiltonian is important in two ways: Firstly, it justifies that by adding the correlation effects one would obtain a Hubbard-type model where Mott physics takes place in the strongly correlated limit, thus accounting for the universal insulator behaviour in the intermediate to high (room) temperature range. Secondly, the inter-cluster hopping matrix elements obtained in the tight-binding construction are closely connected with the effective short-ranged magnetic interactions, such as the superexchange mechanism. Therefore, their systematic changes may provide insights into the origins of the variety of ground states that are experimentally observed.

Our results show that the electronic structures of both studied compounds can in fact be faithfully reproduced by an effective tight-binding Hamiltonian defined on a localised orbital basis set, which we compute explicitly. The computed data for the two systems seem qualitatively similar, which is consistent with the observed universal Mott behaviour at intermediate to high temperature. However, the inter-cluster hopping amplitudes and the estimated superexchange interactions reveal significant differences, which may explain the variety of ground states that are also experimentally observed. In addition, our work also provides a suitable starting point for a dynamical mean-field theory (DMFT) study [8], which may eventually fully elucidate the detailed behaviour of the members of the AMX family.

Most of the previous theoretical work on compounds of this family has been restricted to density functional

theory (DFT) approaches [9,10], in general including correlation effects that are introduced as a static mean field, such as in the LDA +  $U$  methods [11]. However, unless a low-temperature structural transition is assumed, and a certain type of magnetic ordering is adopted, these approaches would usually fail to predict insulator states. Other approaches, such as the DMFT should be better adapted, as they may predict paramagnetic or magnetic Mott insulator states on equal footing. However, that methodology would also rely on two assumptions, namely the value of the onsite Coulomb interaction strength  $U$ , and the definition of a suitable localised basis set. Here we shall explicitly obtain such a localised basis for the two compounds previously mentioned, and we shall discuss their main similarities and differences.

The starting point of our approach is the DFT [12] electronic-structure calculation of the compounds GVS and GTS. To this end we use the Wien2K code [13], that is an implementation of the full-potential linearised-augmented plane-wave method (FP-LAPW) [14]. As we are interested in neither total energies nor magnetic states, we adopt the simplest local density approximation to represent the exchange correlation potential [15]. Results using the generalised gradient approximation are completely equivalent since band structures are, in general, insensitive to this choice. Even though within the DFT schemes the eigenvalues formally have no direct physical meaning, it is, nevertheless, broadly accepted that they provide a good approximation for the quasi-particle energies and band structure. Thus, here we shall adopt them as the reference for the calculation of the localised Wannier orbital basis. We restrict the energy window to the three  $t_{2g}$  bands that cross the Fermi energy. We note that these three bands are quite well separated from the rest of the band manifold, which is very advantageous in order to successfully obtain an accurate local orbital basis representation with short-ranged hopping amplitudes. The localised Wannier orbital basis is computed following the procedure described by Marzari, Vanderbilt and coworkers in a series of papers [16] and implemented in the code Wannier90 [17]. As the interface between the two programs we use the code wien2wannier [18].

In fig. 1 we show the electronic band structure obtained by the DFT calculations along with those computed from the effective tight-binding Hamiltonian on the localised Wannier orbital basis. We observe that the agreement is excellent for both, the GVS and the GTS compounds.

In fig. 2, we depict the Wannier orbitals constructed for GVS. These orbitals have the  $t_{2g}$  symmetry expected for the cubic lattice. However, they are molecular orbitals involving the four V atoms forming a cluster; thus, as can be seen in the figure, they are different from the familiar single-atom  $d$ -shell  $t_{2g}$  symmetry orbitals. The comparison of the two sets of Wannier orbitals computed for GVS and GTS shows that the former are relatively more confined. The spread of the orbital, taken as a representative of the

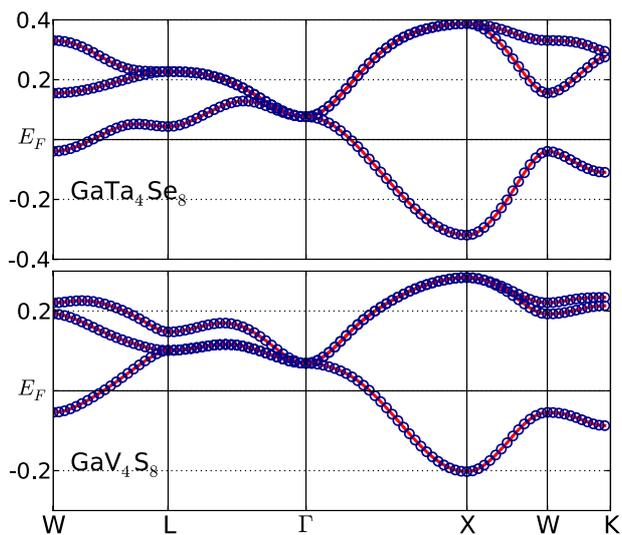


Fig. 1: (Color online) The red curves are the DFT electronic structure of the  $t_{2g}$  bands crossing the Fermi energy for GVS (bottom) and GTS (top). The blue-dot curves correspond to the respective tight-binding energy bands.

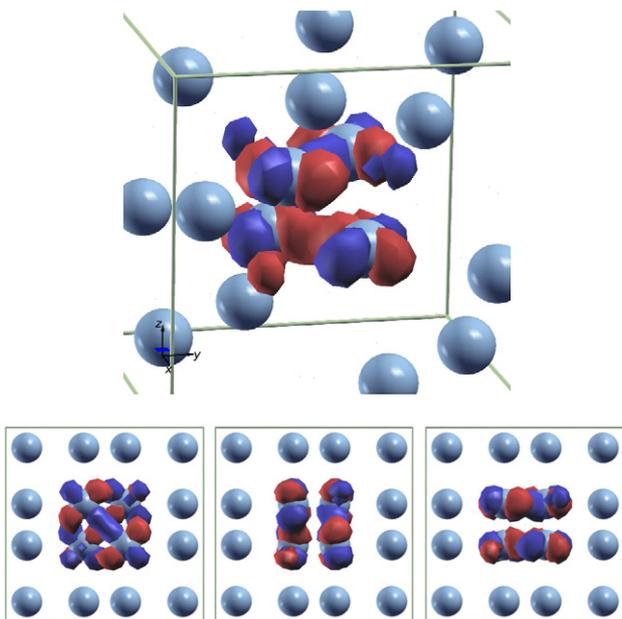


Fig. 2: (Color online) Top panel: spatial representation of one of the three  $t_{2g}$  Wannier orbitals of GVS. Bottom panels: side view (100) of the three Wannier orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  of GVS. For the sake of clarity, Ga and S atoms are not shown. The results for the corresponding orbitals of the GTS compound are qualitatively similar, hence, they are not displayed.

extension of the wave function, is around  $7.5 \text{ \AA}$  for GVS but slightly more than  $10 \text{ \AA}$  for GTS.

In fig. 3 we show the “fat bands”, which contain the information of the orbital content of each one of the bands. We observe that the GVS compound shows a relatively high degree of orbital character mixing in the three bands, while the GTS compound, in contrast, shows a smaller mixing.

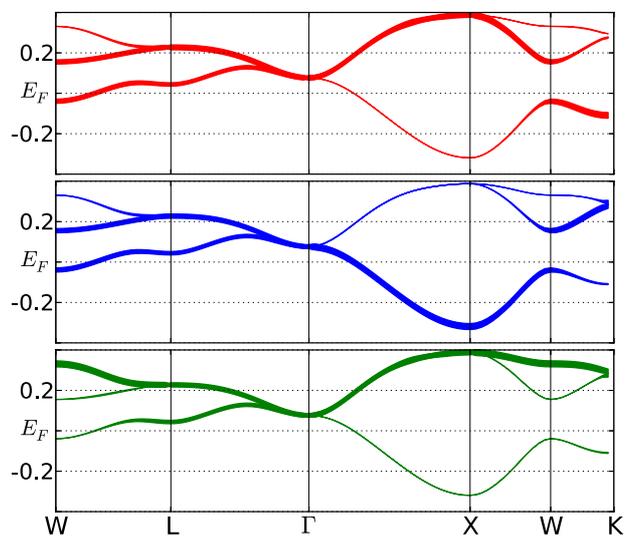
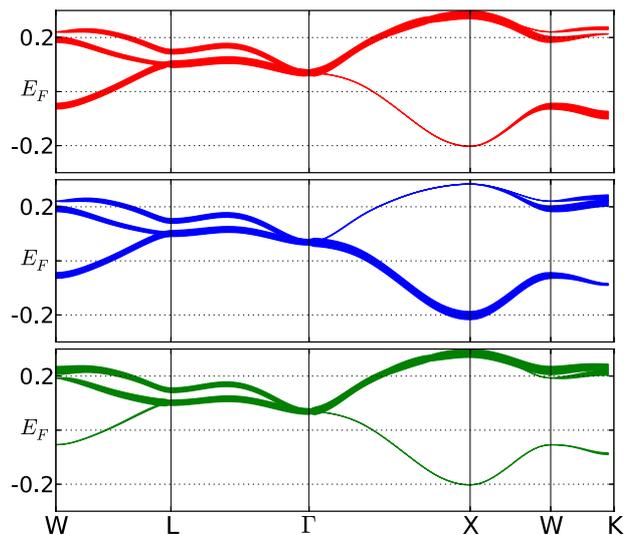


Fig. 3: (Color online) “Fat bands” for GVS (top) and GTS (bottom). Red, green and blue, respectively, correspond to  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  characters.

In fig. 4 we show the dependence of the orbital hopping elements  $t_{ij}$  on the distance. Notice that by symmetry  $t_{xy,xy}(\mathbf{r}) = t_{yz,yz}(\mathbf{r}) = t_{zx,zx}(\mathbf{r})$ , and  $t_{xy,yz}(\mathbf{r}) = t_{yz,zx}(\mathbf{r}) = t_{zx,xy}(\mathbf{r})$ . The results show that for both GVS and GTS the magnitude of the overlaps decreases very rapidly with distance. They become virtually negligible beyond the first nearest neighbours for GVS, while in GTS they reach a little longer. Moreover, quantitatively, the hopping elements of GVS are significantly smaller than those of GTS, which is consistent with the smaller band width of the former.

The calculation of the  $t_{ij}$ , shown in fig. 4, enables us to gain further insight into the possible origin of different ground states observed in GVS and GTS. If we consider the fact that both systems are in the large- $U$  Mott insulator regime, their conduction band electrons become actually localised by correlations, one occupying each transition metal tetrahedron. These localised states are highly degenerate since the electron may occupy

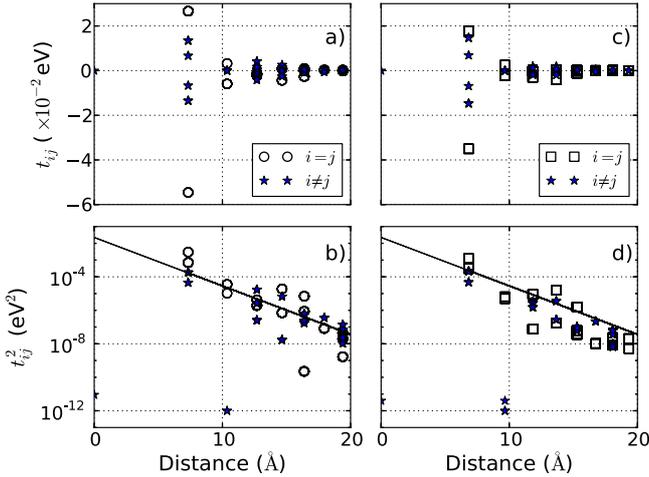


Fig. 4: (Color online) Orbital hopping amplitudes and square of the same quantity for GTS (a, b) and GVS (c, d). Open symbols are for same-orbital and full symbols for different-orbital hopping. The lines on the bottom plots are a guide for the eyes.

any of the three  $t_{2g}$  molecular orbitals with any of the two spin directions. In the simpler case of a one band Mott-Hubbard insulator in a bipartite lattice, this type of degeneracy would be lifted by the superexchange interaction ( $\sim t^2/U$ ), which drives the system towards an antiferromagnetically ordered ground state. Here the situation is more complex, due to the higher degeneracy and the more complex lattice structure. Nevertheless, in a first approximation, the examination of the generalised superexchange interaction terms should give clues on the different nature of the ground states in the different materials.

The generalisation of the superexchange interactions to the present multiorbital case is straightforward [19]. The magnitudes of the couplings are  $J_{i,j}^{se} = t_{ij}^2/(U - \nu J)$ , where  $J$  is Hund's interaction and  $\nu = 3, 2$  or  $0$ , depending whether the doubly occupied virtual state has different orbital and same spin, same orbital and different spin, or different orbital and different spin, respectively [19]. The first case,  $\nu = 3$ , is the one that may favour a localised ferromagnetic insulator ground state. We note that the stabilisation of a ferromagnetic state would imply the (anti-)orbital ordering of the electronic states in the lattice. From the relative values of the  $t_{ij}$  that are plotted in fig. 4, it is immediately apparent that the superexchange interactions are dominated by the nearest-neighbour same-orbital terms (*i.e.*,  $i = j$ ). An important uncertainty that we face are the values of the interactions  $U$  and  $J$ . A first-principle methodology for their calculation remains a matter of debate. Here we shall use a practical approach. The value of the interaction  $U$  may be estimated from optical conductivity experiments, which probe direct lower to upper Hubbard band transitions. The corresponding values for GVS and GTS are  $0.8$  and  $1.2$  eV [20]. These are in fact larger than

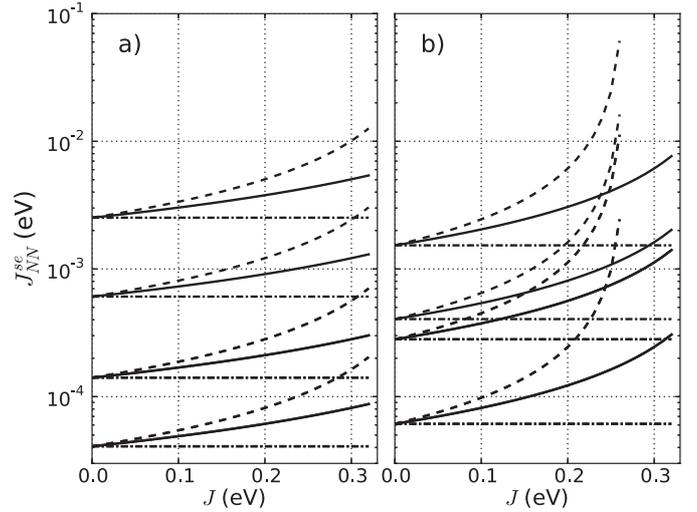


Fig. 5: First near-neighbour superexchange interaction for GTS (a) and GVS (b). The cases with  $\nu = 0, 2$  and  $3$  (see text) are shown by, respectively, dash-dotted, full and dashed lines. In both cases, the two topmost sets correspond to same-orbital exchange ( $i = j$ ) and the rest to the different-orbital case ( $i \neq j$ ).

the respective band width  $W$ ,  $0.5$  and  $0.7$  eV, and the ratio  $U/W$  is approximately  $1.6$  and  $1.71$  for GVS and GTS, respectively. These values should be taken as lower bounds for the estimate of the strength of the interaction.

On the other hand, from studies of DMFT in multi-orbital systems [21], it is known that the Mott insulator at  $T = 0$  occurs for a critical  $U_c$  of approximately  $10t$ , for a three-degenerate-band Hubbard model with one electron per site. In the case of a single-band model with one electron per site, the value of  $U_c$  is about  $6t$ . The total band width for the three degenerate bands it is  $W = 4\sqrt{3}t$ , while for the single-band case it is  $W = 4t$ . Hence,  $U_c/W \approx 1.44$  for the three-band case, and  $U_c/W \approx 1.5$  for the single-band case. The critical value for GTS and GVS should be somewhere in between these two cases, since the three-band degeneracy is partially lifted. Clearly, from the considerations made above, from DMFT one would expect both GVS and GTS to be Mott-Hubbard insulators.

The estimation of  $J$  is more difficult, so we shall simply consider it a free parameter. Reasonable values of  $J$ , however, would run up to about one-third of the interaction  $U$ . In fig. 5 we show the dependence of the superexchange couplings for nearest-neighbour sites at fixed interaction  $U$  and as a function of Hund's parameter  $J$ . From the figure results it is apparent that the GVS system has a stronger tendency towards ferromagnetic order, since the  $\nu = 3$  superexchange interaction is larger than the others, and relatively larger than in GTS. This result is consistent with the experimentally determined ground states.

While these observations are suggestive, we should emphasise, nevertheless, that the present study, based on a strong-coupling picture, remains inconclusive. In fact, an interesting open question, for instance, is: what would the actual orbitally ordered state that would correspond to

the ferromagnetic insulating Mott state of GVS be? Also, to go beyond this strong-coupling approach, one would need to perform a fully quantum-mechanical many-body calculation, such as in realistic DMFT. Our calculation and our effective tight-binding Hamiltonian should be a proper starting point for such a calculation, which we plan for future work. An additional complication that we have so far ignored is the fact that GVS, unlike GTS, has a structural transition to a  $R\bar{3}m$  structure that occurs before the ferromagnetic instability [22]. It remains an open question but, is in fact possible, that the ferromagnetic instability is further favoured by the distortion.

To conclude, we have studied the electronic states of GVS and GTS, which belong to a large family of correlated chalcogenides that are commonly classified as Mott insulators. These systems share the same high-temperature structure; however, they display different magnetic ground states. By means of density functional calculations and a maximally localised Wannier orbital construction, we explored the physical origin of the observed differences. We considered GVS and GTS as two test-case systems, since the first orders ferromagnetically while the second does not seem to order. From the orbital construction we computed the hopping amplitudes and obtained the effective superexchange interactions within a strong-coupling picture. We found quantitative differences, consistent with the experimental observations.

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