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We study the tight-binding dispersion of the recently discovered superconductor $K_2Cr_3As_3$, obtained from Wannier projection of Density Functional Theory (DFT) results. In order to establish quantitatively the actual degree of quasi-one-dimensionality of this compound, we analyze the electronic band structure for two reduced sets of hopping parameters: one restricted to the Cr-As tubes and another one retaining a minimal number of in-plane hoppings. The corresponding total and local density of states of the compound are also computed with the aim of assessing the tight-binding results with respect to the DFT ones. We find a quite good agreement with the DFT results for the more extended set of hopping parameters, especially for what concerns the orbitals that dominate at the Fermi level. Therefore, we conclude that one cannot avoid taking into account in-plane hoppings up to the next-nearest-neighbors cells even only to describe correctly the Fermi surface cuts and the populations along the k_z direction. Such a choice of a minimal number of hopping parameters directly reflects in the possibility of correctly describing correlations and magnetic interactions. © *2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5042740

I. INTRODUCTION

Systems such as heavy fermion compounds,[1–3] high transition-temperature cuprate superconductors,[4–14] strontium ruthenate superconductors[15–23] and iron-pnictide superconductors[24,25] have been investigated very thoroughly due to their unconventional properties determined by the existence of a superconducting phase that appears close to a magnetic one when the latter is suppressed by applying an *external* agent, such as for instance pressure. In recent years, this type of investigation has been extended to the search of superconductivity in Cr pnictides, although chromium is one of the few metallic elements that doesn't superconduct even under high pressures.[26] Thus, the discovery of superconductivity in chromium arsenide (CrAs) was only recent and rather unexpected. CrAs exhibits a superconducting transition of $T_c \approx 2$ K for a critical pressure of $P_c \approx 8$ Kbar, where its magnetically ordered phase is completely suppressed.[27–29] Then, another family of superconducting CrAs-based compounds has been discovered, that of $A_2Cr_3As_3$, where A is K,[26] Rb[30] or Cs.[31]

It is worth noting that while CrAs is a 3D compound and superconducts only under a sizable pressure, $A_2Cr_3As_3$ are considered quasi-one-dimensional (Q1D) superconductors at ambient pressure. In particular, $K_2Cr_3As_3$ has a $T_C \approx 6.1$ K, an hexagonal crystal structure at room temperature with a=9.9832 Å and c=4.2304 Å, and $[(Cr_3As_3)^{2-}]_\infty$ double-walled subnanotubes separated by columns of K^+ ions.[26] This material is very peculiar because it is considered Q1D and, at the same

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time, it is a superconductor: superconductivity is not so frequent in Q1D compounds due to the Peierls instability.[32,33] As regards $K_2Cr_3As_3$, a large specific heat coefficient of 70-75 mJ K^{-2} mol^{-1} indicates strong electron correlations, while a linear temperature dependence of the resistivity from 7 to 300 K supports the hypothesis of a Tomonaga-Luttinger liquid (TLL) behavior,[26] as foreseeable for fermions confined in 1D. Moreover, in their ARPES study of single crystals of the compound, Watson *et al.* have found two Q1D Fermi surface sheets with linear dispersions and a spectral weight of the Q1D bands decreasing near the Fermi level according to a linear power law, in an energy range of ∼200 meV; this has been interpreted as another point in favor of a TLL behavior.[34] On the other hand, Kong *et al.* report a T^3 dependence of resistivity from 10 to 40 K[35] and therefore the degree of unidimensionality of the system is still under current debate.

All experiments point to an unconventional type of superconductivity: an upper critical field that is 3-4 times the Pauli limit,[26] the absence of the Hebel-Schlichter coherence peak in $1/T_1$ just below T_C[36] and a linear temperature dependence of the penetration depth for $T \ll T_c$.[37] Muon spin rotation measurements show results consistent with a d-wave model with line nodes. The weak evidence of a spontaneous appearance of an internal magnetic field below the transition temperature is probably another proof that the superconducting state is not conventional.[38] The Debye temperature is found to be 220 K, the specific heat jump at the superconducting transition is $2.2\gamma T_c$ and the upper critical field is anisotropic with different amplitudes between fields parallel and perpendicular to the rodlike crystals.[35] NMR measurements on the compound show evidence for a strong enhancement of Cr spin fluctuations above T_c in the subnanotubes based on the nuclear spin-lattice relaxation rate $1/T_1$.[36]

From a theoretical point of view, first-principles calculations were performed by Jiang *et al.*[39] Since the Cr sub-lattice is magnetically strongly frustrated, they considered several different possible magnetic states and they found that all the magnetically stable states are energetically degenerate within the DFT errorbars. The presence of multiple degenerate magnetic configurations indicates that the ground state is paramagnetic.[39] They found also that the Cr-d_{xy}, $d_{x^2-y^2}$, d_{z^2} orbitals dominate close to the Fermi level, with three bands crossing E_F to form one 3D Fermi surface sheet and two Q1D sheets.[39] Wu *et al* predict that both $K_2Cr_3As_3$ and $Rb_2Cr_3As_3$ exhibit strong frustrated magnetic fluctuations and are close to a novel in-out coplanar magnetic ground state.[40] They also report that frustrated magnetism is very sensitive to the c-axis lattice constant and can thus be suppressed by increasing pressure.[40] Moreover, three- and six-band models have been built and they show in both weak and strong coupling limits that a triplet p_z-wave pairing is the leading pairing symmetry for physically realistic parameters.[41,42] Zhou *et al* have obtained, for $A_2Cr_3As_3$ (A=K, Rb or Cs), that at small U the pairing comes from 3D γ band and has spatial symmetry $f_{y(3x^2-y^2)}$, with line nodes in the gap function, while at large U a fully gapped p-wave state, $p_z\hat{z}$ dominates at the Q1D α-band.[43]

In this paper, we study the electronic properties of $K_2Cr_3As_3$ by implementing a tight-binding reduction procedure onto state-of-the-art DFT calculations in order to contribute to clarify the issue of the quasi-one-dimensionality of the compound. We obtain the band structure and the total and local density of states (DOS) considering two reduced sets of hopping parameters and compare them with the DFT results to establish the minimal number of in-plane hopping amplitudes necessary to get a reasonable agreement and an adequate description of the properties of the material. The hopping parameters have been extracted by means of the Wannier procedure applied to the DFT results. The paper is organized as follows: in the next section, we describe our tight-binding procedure and show the band structure obtained considering the two reduced sets of hopping parameters. In Sec. III, we focus on the total and the local DOS to check the reliability of the results from the previous section with respect to the DFT ones. In Sec. IV, we draw our conclusions and make some final remarks.

II. BAND STRUCTURE

To study the electronic properties of the material, we start from the following tight-binding Hamiltonian

$$H = \sum_{i,\alpha,\sigma} \varepsilon_i^{\alpha} c_{i\alpha\sigma}^{\dagger} c_{i\alpha\sigma} - \sum_{i,j,\alpha,\beta,\sigma} t_{ij}^{\alpha\beta} (c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} + h.c.), \quad (1)$$

where i and j indicate the positions of Cr or As atoms in the crystal, σ is the spin, α and β are the orbital indices. The two terms take into account the on-site energies and the hopping processes

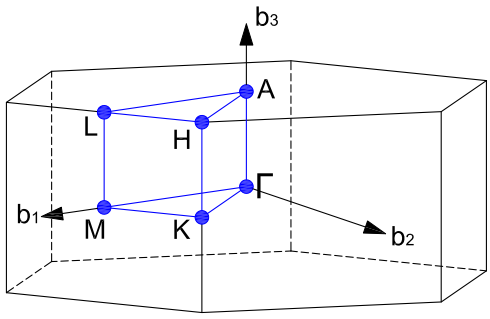


FIG. 1. High symmetry path in the hexagonal Brillouin zone chosen according to the notation of Ref. 44.

between Cr and As orbitals, respectively. The Hamiltonian corresponds to a 48×48 matrix because we have to consider the d orbitals of the Chromium and the p orbitals of the Arsenic and the primitive cell contains six Cr and six As atoms. As we have already discussed in the introduction, the hopping parameters are obtained by the DFT overlap integrals of the orbitals. Diagonalizing the Hamiltonian, we obtain the corresponding band structure, whose behavior will be discussed referring to the high symmetry path in the hexagonal Brillouin zone chosen according to the notation of Ref. 44 (see Fig. 1). In what follows, we use the notation $\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$ where $\mathbf{R}$ is a lattice vector in the direct space.

We analyze two cases that differ only for the chosen set of hopping parameters with the aim of assessing the degree of quasi-one dimensionality of the material. In the first case, we take into account only the hoppings between the orbitals of the atoms that lie within a single sub-nanotube extending along the z axis. Hence, we limit ourselves to consider the hoppings between the primitive cells in set A of Table I. In Fig. 2, we report the comparison between the band structure obtained in this case

TABLE I. Sets of primitive cells used in the calculations and in the figures.

set	primitive cells (n_1, n_2, n_3)
A	(0, 0, 0), (0, 0, 1), (0, 0, −1), (0, 0, 2), (0, 0, −2)
B	set A $\oplus$ (1, 0, 0), (−1, 0, 0), (0, 1, 0), (0, −1, 0), (1, −1, 0), (−1, 1, 0), (1, 1, 0), (−1, −1, 0)

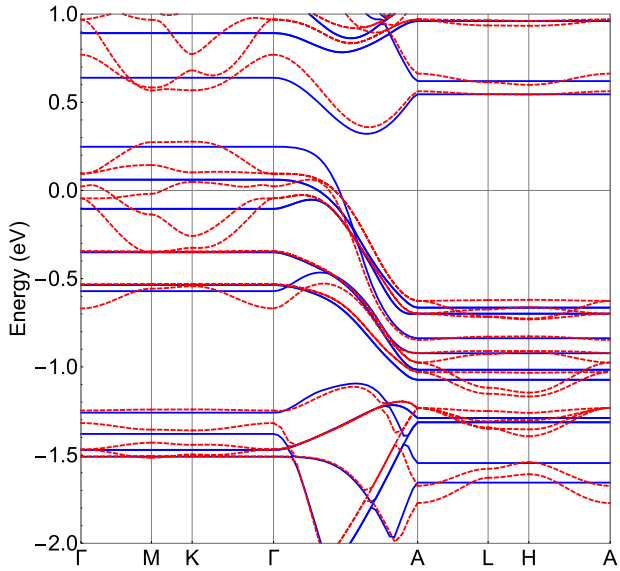


FIG. 2. Comparison between the tight-binding band structure (blue lines), obtained considering the primitive cells in set A of Table I and the DFT spectrum (red dashed lines). The zero of energy marks the position of the Fermi level.

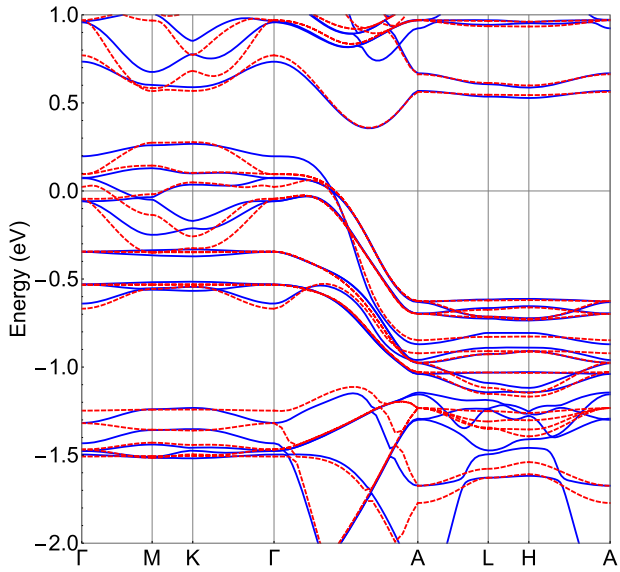


FIG. 3. Comparison between the tight-binding band structure (blue lines), obtained considering the primitive cells in set B of Table I, and the DFT spectrum (red dashed lines). The zero of energy marks the position of the Fermi level.

and the DFT spectrum. We can clearly see that this choice of hoppings not only misses completely the in-plane band structure, but it does not even allow to describe correctly the band structure along the z axis. This unveils an overlooked relevance of in-plane virtual processes that affect the z-axis physics.

Accordingly, in the second case we have also taken into account the in-plane hoppings between primitive cells in set B of Table I. In Fig. 3, we show how the agreement improves substantially not only for the in-plane paths, which was expected, but also for the Γ-A line of the Brillouin zone, that is for the k_z direction. This demonstrates that it is necessary to take into account not only the z-axis hopping processes, but also several in-plane ones to get a qualitatively good description of the band structure. This is in agreement with the results obtained by Taddei *et al.*, who have measured and modeled the spin wave excitations of this compound and found that inter-tube exchange terms are necessary to reproduce their experimental data.[45]

In the next section, we will check whether this reduced set of hoppings (set B) is also sufficient to obtain a qualitatively correct description, that is in agreement with the DFT results, of the orbital populations close to the Fermi surface.

III. DENSITY OF STATES

We obtain the total DOS from the usual definition:

$$\rho(\omega) = \frac{1}{N} \sum_{\boldsymbol{k}} \delta(\omega - \varepsilon_{\boldsymbol{k}}) \tag{2}$$

where $\varepsilon_{\boldsymbol{k}}$ is the energy dispersion of Hamiltonian (1) and the sum is carried out on the N values of momenta $\boldsymbol{k}$ in the Brillouin zone; our numerical grid contains $6 \times 6 \times 12$ **k**-points. The delta functions in Eq. (2) have been approximated by Gaussian functions with a variance of 0.025 eV.

In Fig. 4, we report the total DOS obtained taking hopping parameters related to set A and B of Table I, together with the DFT results: set B leads to a very good qualitative agreement with the latter, this showing that this set of hoppings manages to catch correctly also the overall populations close to the Fermi level, in contrast to set A, which exhibits evident limitations.

We can now check, by projecting the total DOS onto the Cr and As orbitals, if we obtain a correct description of the local orbital occupations close to the Fermi level. To this purpose, we have

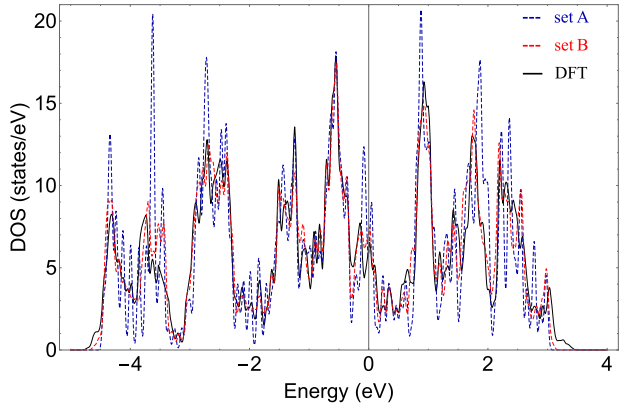


FIG. 4. Total DOS obtained considering the primitive cells in set A and B of Table I and the DFT results. The zero of energy marks the position of the Fermi level.

TABLE II. DOS at the chemical potential $\rho^{\#}_{\nu}(0)$ (states/eV) and related contribution to the total DOS at the chemical potential $\bar{\rho}^{\#}_{\nu}(0) = a_\nu b_\nu \rho^{\#}_{\nu}(0)/\rho^{\#}(0)$ for the different classes of orbitals (ν = 1: Cr $d_{xy}, d_{x^2-y^2}$, ν = 2: Cr d_{z^2}, ν = 3: Cr d_{yz}, d_{xz}, 4: As p_x, p_y, p_z) present in the system and different sets of hoppings # = *A*, *B*, *C* where *C* stands for the DFT results. $a_\nu = (2, 1, 2, 3)$ is the number of orbitals in the class, while $b_\nu = 6$ is the number of related atoms in the unit cell.

ν	$\rho^{A}_{\nu}(0)$	$\bar{\rho}^{A}_{\nu}(0)$	$\rho^{B}_{\nu}(0)$	$\bar{\rho}^{B}_{\nu}(0)$	$\rho^{C}_{\nu}(0)$	$\bar{\rho}^{C}_{\nu}(0)$
1	0.255	52.67%	0.349	58.51%	0.306	59.24%
2	0.162	16.73%	0.127	10.65%	0.116	11.23%
3	0.017	3.47%	0.028	4.69%	0.022	4.26%
4	0.087	27.12%	0.104	26.15%	0.087	25.27%

reported in Table II the values of the projected densities of states (PDOSs) at the Fermi level, and its contribution to the total DOS, related to (i) the Cr-*d* symmetrical orbitals with respect to the basal plane ($d_{xy}, d_{x^2-y^2}, d_{z^2}$), (ii) the Cr-*d* antisymmetrical orbitals (d_{yz}, d_{xz}) and (iii) the As-*p* orbitals, for the previous three cases: set A, set B and DFT. We notice that the value for each class, labelled by ν, has been obtained by averaging over all $a_\nu = (2, 1, 2, 3)$ orbitals and $b_\nu = (6, 6, 6, 6)$ atoms in the unit cell belonging to the class. We clearly find that the symmetrical orbitals with respect to the basal plane dominate, in agreement to what reported in Ref. 39, and that the values found for set B are evidently much closer to those coming from DFT (all discrepancies below 1%) with respect to those obtained for set A (discrepancies up to 6.5%). We conclude that set B is the minimal number of hoppings necessary to achieve a proper description of the band structure along the k_z direction as well as of its orbital occupations.

It is worth noting that, as already reported in the literature,[39] the orbital characterization of the spectrum reveals a high degree of covalency between the Cr-*d* and the As-*p* orbitals, as it happens for the CrAs.[46–48] This opens up a new quest for the minimal number of effective bands necessary to describe qualitatively, but also quantitatively, the system, at least close to the Fermi level. We are currently investigating this aspect too.

IV. CONCLUSIONS

We have used a tight-binding model, obtained through the Wannier projection of *DFT* results, to study the electronic properties of $K_2Cr_3As_3$ in order to explore its degree of unidimensionality. We have then analyzed the band structure and the total and the local DOS of the compound taking into account not only the usually considered hoppings along the *z*-axis, but also those up to the next-nearest-neighbor primitive cells in the plane. Only adding these latter, we managed to achieve a good qualitative agreement with the DFT spectrum near the Fermi level, demonstrating that the system does not exhibit a genuine one-dimensional character. Consequently, this study

gives clear hints on the minimal number of hopping parameters needed to perform further studies and understand the role of correlations, magnetic interactions and spin-orbit as well as the mechanism and the nature of the superconductivity in this material. A more detailed analysis of the electronic properties of the compound, aiming to derive a reliable minimal effective band model, is underway.

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