Unified description of the electronic structure of M_2AC nanolamellar carbides

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The nanolamellar M_2AC or carbon-based "211 MAX" phases, where M is an early transition metal, A belongs to groups 13–15, and C is carbon, can be described by rigid band models. The same band model applies to all possible A elements belonging to a given group of the periodic table. Changing M for a given A is then equivalent to shifting the Fermi energy E_F through a band structure common to all phases in the group. This is shown by comparing predictions of density functional theory (DFT) to angle-resolved photoemission spectroscopy (ARPES) measurements. In particular, the Fermi surface of a given Al-based MAX phase can be obtained with an acceptable degree of accuracy by simply selecting the appropriate ARPES isoenergy surface of another Al-based phase. In V₂AlC, and in addition to conventional metal energy bands, both DFT and ARPES show the existence of a gapped nodal line located around 0.2 eV below E_F or complex crossing points at E_F with Dirac-like features in some directions. Application of the rigid band model suggests that these topological features as well as others, also predicted by DFT, can be positioned at or close to E_F by an appropriate choice of M and A, or by using an appropriate combination of various M and A elements.

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I. INTRODUCTION

Rigid band models are useful for describing families of materials where varying a parameter does not appreciably modify the energy band structure but results in an appreciable sweep of the Fermi energy across the bands [1-3]. This parameter is typically a tunable atomic fraction of a given chemical element, which either directly enters into the composition of an alloy or a compound (see, e.g., [1-5]) or which is used for intercalating a nanolamellar phase (see, e.g., [6–8]). Alternatively, it was also noticed long ago that simple transition metals belonging to the same or neighboring groups could exhibit quite similar band structures, their electronic structure differing only by a shift in Fermi energy (see, e.g., [9]). Finally (as in this work), changing a chemical element in a compound belonging to a given family while keeping a similar band structure also justifies the use of a rigid band model [10,11]. For the latter to be applicable, the symmetry of the crystal structure must not only remain unchanged from one compound (or composition) to the next but the changes in electron correlations must also be small with respect to the electronic structure [12-14]. In contrast, when the structure is maintained but a noticeable change in electronic structure is observed, this failure of the rigid band model is often viewed as a good indication that electron correlations (or more simply, the electron potential) play an important role (see, e.g., [12–14]).

In this work we wish to demonstrate the applicability of rigid band models to a subfamily of nanolamellar compounds called MAX phases. The chemical formula of these phases is $M_{n+1}AX_n$, where M is an early transition metal, A belongs to groups 13–15, and X is either C or N, n = 1-3. These phases were discovered long ago in Nowotny's group in the 1960s (see, e.g., [15] and [16] for a description of the early work). Although some useful contributions were published during the following decades, MAX-phase research really started to grow in the late 1990s (see, e.g., [17]), and a number of review articles or books are now available in which the reader can get an exhaustive description of MAX-phase research history and status as well as of their physical and chemical properties (see, e.g., [18-26]). The number of different phases already synthesized definitely make them one of the largest families of nanolamellar phases known so far [26].

MAX phases are potentially useful for applications in harsh environments [18] or as precursors of a family of twodimensional systems called MXenes [27]. They are metallic compounds with a substantial number of partially occupied electron and hole bands at Fermi energy E_F [25]. The density of states (DOS) at E_F is thus most often quite high [18]. Numerous previous works already describe features related to the electronic structure and some of its anisotropies, both on theoretical and experimental grounds (see, e.g., [28–33]). They are more exhaustively listed in a recent review article up to year 2017 [24]. In this article, we focus on the subfamily with n = 1, also called "211 MAX phases." The similarity between the electronic structure of the 211 (and even 312) phases was noticed long ago: the calculated DOS profile of one compound, once correctly shifted in energy, could be

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roughly superimposed over the DOS of another compound [18,34,35]. Here, we go one step further and combine density functional theory (DFT) calculations to angle-resolved photoemission spectroscopy (ARPES) in order to show that not only the DOS but also the topology of the bands in reciprocal space is also conserved. All band structures are similar within a given A group and, quite remarkably, the Fermi surface (FS) of a given MAX phase can be deduced from ARPES measurements conducted on another phase simply by selecting the appropriate ARPES isoenergy surface. Additionally, the shift in energy required to obtain this agreement reasonably matches the shift in E_F predicted by DFT. These results allow one to use a unified description of the electronic structure of those phases. Such a unified description was not obvious a priori, because the Fermi surfaces of different MAX phases can differ enormously (as predicted and measured [36,37]). It thus turns out that this difference is almost entirely accounted for by a simple shift in E_F .

Applicability of the rigid band model to MAX phases offers interesting perspectives. As detailed below, the band structure of those phases exhibits many band inversions. These band inversions result in the existence of several nodes or band crossings at different energy levels. This leads, e.g., to the prediction of the existence of nodal lines at several locations of the band structure. Such features were studied very early in the history of quantum and solid-state physics [38]. However, they actually laid dormant in the literature until the two last decades. They then sparked a renewed and now very strong interest (see, e.g., [39–41] for recent reviews) due to the resulting electronic properties they may generate, e.g., protected surface states, or the specific responses to electromagnetic excitations they may lead to [39]. These include Weyl, Dirac, and nodal line semimetals [39-41], as well as other intricate band structure specificities (see, e.g., [42] for a hybrid parabolic and Dirac-like dispersion at the degeneracy points or [43] for other semi-Dirac points, or [44] for surface Dirac node arcs). In particular, nodal lines are now actively studied in a number of 3D materials and can be divided into gapped and symmetry-protected lines, depending on whether spin-orbit coupling lifts the degeneracy at the crossing point or not (see, e.g., [41]). In principle, gapped nodal lines positioned at E_F favor the existence of a strong spin Hall effect, a desired feature for generating spin currents in spintronic devices [41,45,46]. In the last section, we provide detailed theoretical and experimental evidence for the existence of such topological features in the V₂AlC phase (more precisely, a gapped nodal line slightly below E_F and a complex crossing point with some Dirac-like features at E_F). In MAX phases, such nodes are always accompanied by the presence of other, more conventional bands, but the possibility to change E_F appreciably by just changing the M element should allow one to position E_F at a given crossing point (this is predicted, e.g., in the case of the "simple" phases V₂AlC, Nb₂AlC, and Ti₂AlC). Combining conventional bands to nodal lines is indeed not expected to prevent one from obtaining a strong spin Hall effect (see, e.g., [46] and references therein). Hence, combining several M elements could possibly allow one to reach other interesting topological nodes experimentally. The 211 MAX phases thus form a family of semimetals incorporating a variety of interesting



FIG. 1. (a) Cr₂AlC Fermi surface mapping from ARPES plotted together with V₂AlC DFT isoenergy lines 0.6 eV above E_F . On (b), ARPES in-plane mapping of Cr₂AlC at $E = E_F - 0.56$ eV is compared with V₂AlC DFT Fermi surface cuts. (c) V₂AlC ARPES Fermi surface mapping. When shifting the energy 1.12 eV below the V₂AlC Fermi level, we obtain the in-plane mapping in (d), which is plotted vs Ti₂AlC DFT Fermi surface cuts. Dotted lines stand for isoenergy lines over the Γ and A planes.

topological features, which could reasonably be described by the use of a restricted number of rigid band models.

II. MATERIALS AND METHODS

Cr₂AlC and V₂AlC single crystals were grown by hightemperature solution growth using methods described in detail in [47,48]. Cr₂AlC platelets obtained in solution have an area of about a few square centimeters with a thickness of a few millimeters. V₂AlC platelets are somewhat smaller, typically less than 1 cm^2 large and 50–100 μm thick. Both were cut in 3 \times 3 mm squares using a diamond wire saw. Cr₂AlC samples were additionally cleaved to reach a thickness of about 500 μ m. They were later cleaved in situ for ARPES experiments performed at AichiSR BL7U under ultrahigh vacuum (typically less than 5×10^{-9} Pa) and at a temperature between 8 and 15 K. Horizontally polarized light perpendicular to the analyzer slit was used as described in [36,37]. The angle between the light beam and the detector was set to 45 degrees. The polarization vector lay in the horizontal plane (one can refer to Fig. 1 in [36], where the experimental configuration is very precisely described, for more insight on the experimental configuration). For most of the experimental results shown here, $h\nu$ was set to 100 eV. ARPES mapping in Figs. 1(a), 1(c), and 4 were already published in [36,37] and are compared here with DFT calculations made for other MAX phases in order to demonstrate the validity of the rigid band model. Additional ARPES experiments were performed at the Institute for Solid State Physics (ISSP), University of Tokyo [49], at T = 35 K using a quasi-continuous-wave laser source (hv = 6.994 eV) [Figs. 11(b), 11(d), and 12(b)]. Here, circularly polarized light was used in order to partially circumvent the low-photoionization cross section of some orbital contributions within the experimental range allowed by the detector. Energy resolution was set at about 5 meV.

All calculations were performed with the full potential LAPW+lo method implemented within the WIEN2K software. The non-spin-polarized Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional [50] was chosen. The following phases were chosen for computational analysis in this work (together with the references of the .cif files used for computations): Cr₂AlC [51], V₂AlC [52], Ti₂AlC [53], Nb₂AlC [54], Ti₂GaC [55], Ti₂GeC [15], and Ti₂SnC [15].

Wave functions were expanded up to a RKM cutoff parameter of 9 to make sure convergence was reached for all phases (RKM refers to the product of the smallest 'atomic sphere radius' R times the largest K vector of the LAPW expansion used). For the same reason, a very dense $73 \times 73 \times 14$ Monkhorst-Pack cell was used. The Fermi surfaces were calculated using X-CRYSDEN [56]. The level of convergence in energy was set to 0.001 mRy for Bader charge calculations with the WIEN2K AIM code.

III. ELECTRONIC STRUCTURE OF M_2 AlC (M =Cr, V, Ti)

Though the applicability of rigid band models to describe M_2 AlC phases has already been suggested [18,34,35], it has not been experimentally verified yet. One experimental technique that allows one to do so is ARPES, whose output is the wave-vector and energy spectra of the electronic states of the material probed [57,58]. Such a technique requires bulk single-crystalline samples, and MAX-phase single crystals were not available until recently [47,48]. The combination of ARPES experiments performed on MAX-phase single crystals and DFT calculations makes it possible to test the rigid band model beyond the mere assessment of the density of states [36,37]. This method allows us to study how the topology of the bands in reciprocal space (i.e., the band structure and the isoenergy surfaces) would evolve when going from one phase to another. Before detailing our analysis, it is useful to briefly summarize our previous findings [36,37]: Regarding the ARPES spectra of Cr₂AlC, it was found that most of the features of the experimental FS were well reproduced by DFT calculations. It mainly consists of quasitwo-dimensional (2D) tubes directed along c*. The most noticeable discrepancy was an additional pocket observed at the Γ point that accounts for a camel-back-like structure located just below E_F . Some renormalization effects were also observed. V₂AlC FS determined by ARPES showed an even better level of consistency with DFT but was found to be much less bidimensional than Cr₂AlC. For Cr₂AlC as for V₂AlC, all ARPES spectra were found to be consistent with both the angular dependence of the photoionization cross section and the orbital characters of the bands predicted by DFT.

Figure 1 displays a section, i.e., a 2D cut or a projection for a specific reciprocal space plane (here the ΓKM plane), of the FS of three MAX phases (Cr₂AlC, V₂AlC, and Ti₂AlC). For each image, the ARPES intensity map and DFT results at ΓKM and AHL planes are plotted together. The specificity of all figures is that we do not directly superimpose the DFT of one phase to the ARPES image of the same phase. For each image, the DFT and the ARPES come from two different phases. But we apply to the DFT (or to the ARPES) an overall energy shift which allows us to optimize the matching between the DFT and the ARPES maps. In other words, if we start from the ARPES FS of a given phase, we find the appropriate energy shift in the band structure of *another* phase, which is required to obtain the best fit of the ARPES image, and plot the resulting DFT isoenergy surface. Alternatively, if we directly plot the DFT FS, then we probe the ARPES isoenergy surface of another phase for an energy value which allows us to fit the DFT FS. The ARPES maps are therefore plotted versus the FS or isoenergy sections over the Γ or A plane. Thus, the ARPES spectra of several phases are directly compared, at and below E_F , to DFT Fermi lines or isoenergy surface lines of other phases.

In Fig. 1(a), the measured Cr₂AlC FS is compared to V₂AlC isoenergy lines 0.6 eV above the V₂AlC Fermi level, computed by DFT. They match to a remarkable extent. Even more strikingly, the V₂AlC isoenergy surface shows a pocket centered at Γ , a feature which was actually missing from Cr₂AlC DFT calculations but was spotted by ARPES [36]. Similarly, in Fig. 1(b) one can verify that a Cr₂AlC ARPES isoenergy section at $E = E_F - 0.56$ eV almost perfectly fits the V₂AlC DFT Fermi surface. (The additional features around M are due to surface states appearing just after crystal cleavage, already observed and commented on in [37] in the case of V₂AlC.) This ARPES isoenergy surface has a form that shows not only well-defined lines but also extended regions due to dispersion bands which are locally 3D, as expected for the V₂AlC FS. One can also check the very strong similarity existing between a direct ARPES measurement of the V_2AIC FS [Fig. 1(c)] and the shifted Cr_2AIC ARPES image of Fig. 1(b). (A 45-degree rotation needs to be applied in order to take into account the difference in orientation of the two crystals for those two measurements.) We summarize DFT FS results in Fig. 2, where V_2AlC FS and isoenergy surfaces are plotted in 3D within the first Brillouin zone (BZ). By shifting upwards by 0.6 eV with respect to the V₂AlC Fermi energy, one obtains an isoenergy surface identical to Cr₂AlC FS, and by shifting downwards by approximately 1.14 eV, one obtains the Ti_2AIC FS.

The band structures (BSs) demonstrate a similar trend (see Figs. 3 and 4): the V₂AlC BS is recovered when shifting the Cr₂AlC bands by roughly 0.6 eV downwards. It is worth noticing that despite their strong resemblance, some discrepancies between shifted Cr₂AlC and plain V₂AlC DFT BSs remain [Figs. 3(a) and 3(c)]. Some bands mismatch by a few meV, up to 160 meV for the camel-back structure centered on Γ . These differences actually correspond to what is observed between the ARPES BS of Cr₂AlC and DFT calculations [36]. This means that the shifted V₂AlC band structure would actually be a better fit to Cr₂AlC ARPES BS than the output of previously published Cr₂AlC DFT calculations. This is indeed what is



FIG. 2. Overall relations between M_2 AlC Fermi surfaces and isoenergy surfaces of V₂AlC. All energy shifts and isoenergy surfaces were computed by DFT calculations.

observed when directly comparing V₂AlC DFT BS shifted by 0.6 eV upward to Cr₂AlC ARPES BS mapping over Γ M and Γ K [Figs. 4(a) and 4(b)]. It also means that it is possible to navigate from a V₂AlC to Cr₂AlC electronic structure just by applying an appropriate energy shift of about 0.56–0.6 eV.

Let us now turn ourselves towards what is observed when we shift the V₂AlC spectra below the Fermi energy: For $E = E_F - 1.12$ eV, we get the ARPES mapping shown in Fig. 1(d), which is this time compared to the Ti₂AlC DFT FS. The two tubes centered on Γ (each of them actually stands for two different FSs that are almost degenerate) are electronlike while the platelike FSs centered on K are hole pockets. We obtain a similar level of matching between the Ti₂AlC DFT FS and shifted V₂AlC ARPES image as for Figs. 1(a) and 1(b). When shifted by 1.14 eV downwards, the V₂AlC DFT BS also happens to correspond to that of Ti₂AlC [Figs. 3(c) and 3(d)]. And once again, shifting the Ti₂AlC DFT BS by +1.16 eV accurately renders the ARPES BS map of V₂AlC over Γ M and Γ K [Figs. 4(c) and 4(d)]. The energy required to go from V₂AlC to Ti₂AlC lies between -1.12 and -1.16 eV.

These results clearly demonstrate that one can navigate across the electronic structure of the M_2 AlC phases just by applying an appropriate energy shift. Figures 1 and 4 thus constitute a direct experimental verification of the applicability of rigid band models to MAX phases. So far, the applicability of the rigid band model was only verified when navigating horizontally on the periodic table, going from Ti to Cr, and not horizontally. Figure 5 summarizes the similarities found between the BSs and FSs of V₂AlC and Nb₂AlC, all obtained from DFT calculations. (Our Nb₂AlC crystals are presently too small for being probed by conventional ARPES.) The band structures are plotted over ΓM [Fig. 5(a)], and the Nb₂AlC BS is renormalized to the volume of the V₂AlC BZ. Both show very similar features, but the Nb₂AlC band



FIG. 3. V_2AIC and -0.6 eV shifted Cr_2AIC band structures from DFT calculations, plotted together over ΓM (a) and ΓK (c). A 160-meV discrepancy is observed for the camel-back structure of Cr_2AIC near Γ , though the bands shape is nearly like V_2AIC . Similarly, Ti₂AIC band structure is plotted together with -1.16 eV shifted V_2AIC bands (b, d). For all figures, the Brillouin zones are scaled to that of V_2AIC .



FIG. 4. Cr_2AlC band structure from ARPES vs $V_2AlC + 0.6 \text{ eV}$ shifted band structure from DFT (red dotted lines) over ΓM (a) and ΓK (b). V_2AlC ARPES mapping over ΓM and ΓK is also compared with Ti₂AlC DFT BS, shifted by 1.16 eV. The energy shifts needed for the band structure to match are nearly the same as in Fig. 1.

structure seems to show sharper slopes than V₂AlC. It is almost as if one could obtain the V₂AlC BS from that of Nb₂AlC by simply dilating the energy axis and expanding the wave-vector axis. The topology of their bands at E_F seems quite similar [see Fig. 5(b)]. Nb₂AlC would then share a FS nearly identical to that of V₂AlC. This is reminiscent of the so-called jungle-gym Fermi surface [59] that describes the V, Nb, and Ta elemental metals. Horizontally varying the *M* atom of MAX phases would leave the FS unchanged but would homogeneously distort the bands.

IV. CHARGE TRANSFER AND RIGID ENERGY SHIFT

The energy shifts required to go from one M_2 AlC phase to another one are large: 0.6 eV for the shift between Cr₂AlC



FIG. 5. (a) The band structure of V_2AIC is compared to Nb_2AIC over ΓM . Their respective Fermi surfaces are given in (b).

and V₂AlC, and about 1.14 eV between V₂AlC and Ti₂AlC. Such shifts are quite large, as compared to the typical variation of the Fermi level that arises when doping a metal (adding a very high concentration of dopants would move E_F just by a few meV [60]) but of the same order of magnitude as those obtained between some elemental transition metals, when they can be described by the rigid band model [9]. If the origin of the changes in E_F is quite obvious for a doped metallic system [60], a slightly more involved explanation is needed to make sense of the energy shift values found in Sec. III for the M_2 AlC phases, and the corresponding analysis is described below.

In Fig. 6, the M atom partial densities of states (pDOS) of Cr₂AlC, V₂AlC, and Ti₂AlC are given. As expected from Sec. III, one can obtain one DOS from another by applying the same energy shifts as those required in Figs. 1–3. One can also integrate the pDOSs from the Fermi level of V₂AlC (Ti₂AlC) to Cr_2AlC (V₂AlC) and obtain quantities homogeneous to a charge per unit cell. Dividing the latter by the number of M atoms per unit cell (four), we obtain a quantity that would intuitively be considered as the charge variation on the Msite when going from one phase to another, which we will refer to as $\delta Q_{M^Z \to M^{Z+1}}^{\text{DOS}}$. To elaborate a proof of this identity, we also compute the charge variations on the M sites by another method involving the computation of Bader charges [61]. We first compute the Bader charge of the different atoms in the M_2 AlC unit cell. As a quick reminder, the Bader charge is defined as the integral of the charge density across the so-called "Bader atom area," which refers to the volume of space within the charge density basin, centered on a given nucleus [61]. Both the charge density basin and the Bader



FIG. 6. Various M_2 AlCM atom partial DOS, with M =Cr, V, Ti. DOSs are integrated from the Fermi level of V₂AlC (Ti₂AlC) to Cr₂AlC (V₂AlC) to get quantities homogenous to a charge per unit cell, which is later converted to a charge per M atom unit.

charge are calculated with the AIM code run in WIEN2K. The Bader charges of all the atoms considered are then subtracted from their respective atomic numbers in order to obtain a quantity that we call Bader charge transfer or ΔQ^{Bader} . For a given atom Ω , its Bader charge transfer is thus be given by the following expression:

$$\Delta Q_{\Omega}^{\text{Bader}} = Z_{\Omega} - \int_{\Omega} \rho(\mathbf{r}) d\mathbf{r}, \qquad (1)$$

where Z_{Ω} stands for the atomic number of Ω , and ρ is the electron density of the system that is being integrated over the charge density basin of atom Ω . We compile those values for the M_2 AlC (M = Ti, V, Cr, Nb) phases in Table I and Fig. 7. We observe that we conserve the overall charge neutrality when summing up ΔQ^{Bader} of all the elements within a phase unit cell. In Fig. 7(c), we plot the Pauling electronegativities of the *M* elements [62] against the ΔQ^{Bader} for those phases.

A roughly linear relationship is revealed, thus demonstrating the consistency of our charge-transfer analysis.

From the charge transfer on the M atom site, we can compute the local charge variation on the M site arising when changing the M element by one atomic number, given by the following expression:

$$\delta Q_{M^Z \to M^{Z+1}}^{\text{Bader}} = 1 + \left(\Delta Q_{M^{Z+1}}^{\text{Bader}} - \Delta Q_{M^Z}^{\text{Bader}} \right), \tag{2}$$

where M^{Z+1} and M^Z would, for example, stand for the vanadium and titanium atoms. All values of $\delta Q^{\text{Bader}}_{M^Z \to M^{Z+1}}$ are tabulated in Table I, together with ΔQ^{Bader} of the *M* elements and the $\delta Q_{M^Z \to M^{Z+1}}^{\text{DOS}}$ integrals of the pDOSs within the energy intervals of $\delta E_{Z \to Z+1}^{\text{DOS}}$. The $\delta Q_{M^Z \to M^{Z+1}}^{\text{Bader}}$ differs by less than 0.1 electrons/atom from $\delta Q_{M^Z \to M^{Z+1}}^{\text{DOS}}$ (see Table I). This means that the $\delta Q_{M^Z \to M^{Z+1}}^{\text{DOS}}$ integrals over the $\delta E_{Z \to Z+1}^{\text{DOS}}$ energy shift intervals can be associated to the charge transferred from the *M* atom site when going, for example, from Ti_2AIC to V_2AIC . The energy shifts experimentally determined in Sec. III can thus be understood both in terms of charge transfer and as the occupation of the states of the rigid electronic structure in the $\delta E_{Ti \rightarrow V}^{\text{DOS}}$ interval. This opens up the possibility of tuning the position of the Fermi level on the M_2 AlC BS over a wide energy range just by changing the nature of the atoms on the M sites. We note that the applicability of the rigid band model to M_2 AlC phases is far from obvious because of the implication of d orbitals in M_2 AlC's electronic structure. These could intuitively lead to non-negligible electronic correlations and to a dramatic failure of the rigid band model. But the success of the rigid band model at describing M_2 AlC phases strongly suggests that electronic correlations do not play a key role in the electronic structure of many 211 MAX phases around the Fermi energy value, as long as the atomic number of the Matom remains small enough (i.e., 211 phases avoiding, e.g., Ta, W, etc.) [12–14]. Here, an important word of caution must be offered to readers. In this work we did not need to account for magnetic ordering nor did we have to use a DFT+U approach for the DFT calculations in order to produce good fits of the band structure and FS as measured by ARPES (see, also, the results described in Sec. VI). However, it must be clear that for Cr-based compounds, a nonmagnetic configuration yields very inaccurate results for a range of other properties, notably, elastic (see, e.g., a review of such results in [22] and references therein). And in the case of strongly magnetic MAX phases, any property clearly requires taking magnetism in the DFT approach explicitly into account. As a consequence, the rigid band model approach can in no case be extended to other properties than band structure without a careful comparison of theory and experiment.

TABLE I. Tabulated in column 1 are the charge-transfer values from the Bader method for the *M* atoms of M_2 AlC phases (M = Cr, V, Ti). In column 2 are given the charge variations on the *M* site when going from one transition metal to another, also calculated with the Bader method. Column 3 stands for the integrals of the *M* atom partial DOSs over the energy intervals of column 4. These intervals are alternatively extracted from Fermi surface (column 5) or band structure rigid energy shifts (column 6).

	$\Delta Q^{\text{Bader}}(\text{e}/\text{atom})$	$\delta Q^{\text{Bader}}_{M^Z \to M^{Z+1}}(-e/\text{atom})$	$\delta Q^{\rm DOS}_{M^Z \to M^{Z+1}}(-{\rm e}/{\rm atom})$	$\delta E_{Z \to Z+1}^{\text{DOS}} (\text{eV})$	$\delta E^{FS}_{Z \to Z+1}$ (eV)	$\delta E_{Z \to Z+1}^{BS} (eV)$
Ti ₂ AIC	1.343	0.635	0.725	1.14	1.12	1.16
V ₂ AIC	0.979	0.575	0.635	0.60	0.60/0.56	0.60
Cr ₂ AIC	0.554					



FIG. 7. Charge transfer, or the difference between the electronic charge of atoms within MAX-phase unit cells (computed with the Bader method) and in vacuum, calculated for selected M_2 AlC (a), M_2 GaC (b), and Ti₂AC phases (d). In (c), a linear relationship is found between the *M* atom charge transfer for the Al 211 phases and the respective Pauling electronegativity of the *M* elements.

V. A RIGID BAND PICTURE OF MAX PHASES

Figure 8 is a summarizing picture of the rigid band model that describes M_2 AlC phases. The isoenergy surfaces that correspond to Cr₂AlC, V₂AlC (Nb₂AlC), and Ti₂AlC Fermi surfaces are appointed to their relative positions on the rigid band structure. All of them were computed with DFT. Note that several band crossings are observed in Fig. 8, notably at the V₂AlC Fermi level over Γ M (red line) and at the Ti₂AlC Fermi level over Γ K (green line); other crossing points also appear between these two energy positions. In [37], it has been predicted that the V₂AlC crossing at E_F is the signature of



FIG. 8. A summarizing picture of the rigid band model describing the M_2 AlC phase's electronic structure. Band crossings are observed at V₂AlC and Ti₂AlC Fermi levels. Crossings that might account for Dirac points or Dirac nodal lines are located in between those two energy levels.

a point with Dirac-like properties. It originates from a band inversion involving bands with a $d_{x^2-y^2} + d_{xy}$ and a $d_{xz} + d_{yz}$ orbital character, and some p orbital character from the Al bands. Similar Ti₂AlC band crossings occurring at E_F also exhibit Dirac-like properties, as well as some nodal lines which can be observed between the V2AlC and Ti2AlC Fermi levels. The bands involved in those band crossings exhibit a mixture of different M d orbitals, also with a significant weight of $p_x + p_y$ for some. Nodal lines are also present (see Fig. 8). In this paper, we do not want to give an exhaustive description all of those nodes, but in the next section we provide both detailed theoretical and experimental data to show the existence of two such features (a nodal line below E_F and a semi-Dirac-like band crossing at E_F) in the particular case of V₂AlC. If the rigid band approach is valid, alloying on the M site (with Ti or V) or controlling the vacancy concentration would allow one to navigate between several such band crossings by applying simple rigid band shifts. The applicability of the rigid band model could also guarantee that the bands would be conserved even if the M sites were randomly occupied by different transition-metal atoms [4]. One should note that synthesis of 211 phase solid solutions or ordered phases with several and differents Ms is already well described in the literature [26,63]. These results suggest that MAX phases could open up avenues for physicists to study gapped nodal lines and other Dirac-like band crossings, as the possibility to tune the Fermi-level position on the M_2 AlC rigid band structure would make a considerable number of band crossings experimentally accessible (see Fig. 8). Similar studies have been performed on doped semiconductors, where Dirac points were observed at higher energy [64,65].



FIG. 9. The band structure of several Ti₂AC phases (A = AI, Ga, Ge) over ΓM (a) and ΓK (b). The Fermi surfaces of these compounds are plotted in (c), (d), and (e).

The applicability of the rigid band model to M_2 AlCs brings up many directions for further research and could be generalized to other 211 phases with different atoms on the A site. In Fig. 9, the BS of Ti_2AC (A = Al, Ga, Ge) were computed over ΓM and ΓK [see Figs. 9(a) and 9(b)]. Ti₂AlC and Ti₂GaC BSs are very similar, sharing bands with the same features at all energies, and no shifts are required for them to match. A few minor discrepancies still remain, as some Ti₂GaC bands are locally displaced upwards or downwards from Ti₂AlC by a few tens of meV. After renormalization of the band structures to the Ti₂AlC BZ, almost no discrepancies in momentum seem to appear between Ti₂AlC and Ti₂GaC bands. Their FSs are also similar, with the same bands being involved at E_F . The main discrepancy appears in the hole pocket centered on K. For Ti₂GaC, it has the shape of a torus centered on K, whereas it is more of a plain triangular plate for Ti₂AlC. The Bader charge transfers were calculated for all atoms involved in Ga-based 211 phases [Fig. 7(b)], and they follow the same trend as the Al phases [Fig. 7(a)]. In contrast, Ti₂GeC BS diverges from its counterparts. No meaningful energy shift linking it to Ti₂AlC has been found. Even the number of bands involved in its FS is different, as is its overall FS topology. One should note that both Ga and Al belong to column IIIB of the periodic table, and their respective Ti₂AC phases are described by nearly identical BS and FS, while Ge belongs to column IVB and Ti2GeC show a BS very different from the two others. This implies that M_2 GaC and M_2 AlC phases will likely be described by a very similar rigid band model, while a very different one would be needed for any M_2 GeC phase. The following trends can then be intuited:

 M_2AX phases for which the *A* element belongs to a single column of the periodic table will be described by a single rigid band model, and keeping the *M* element constant while changing *A* over this column will not lead to any rigid energy

shift. Only five rigid band models, one for each A element column, should then be needed to describe all the existing 211 MAX phases [18]. The charge transfers for the Ti_2AC 's (A = Al,Ga,Ge,Sn) have been computed [Fig. 7(d)], and no significant difference in terms of charge transfer is observed between them.

VI. NODAL LINES AND OTHER TOPOLOGICAL NODES

In this section we wish to illustrate the interest of using the rigid band model for guiding Fermi-level tuning close to one of the particular topological features the model contains. We focus on two particular such points or lines because, being located at or close to E_F , they may be experimentally probed by ARPES in the case of V₂AlC. However, it is worth noticing that the rigid band model is not limited to those two points, as it contains other similar band crossings. V₂AlC is predicted to exhibit a crossing point at E_F (shown in Fig. 8 and hereafter designed as α) and a nodal line predicted by Fig. 8 to cross ΓM about 0.2 eV below E_F . Although the $P6_3/mmc$ space group is nonsymmorphic, this particular nodal line does not lie at a Brillouin zone boundary, so that is not symmetry protected against perturbations. This line is thus expected to be gapped by spin-orbit coupling [41,66]. For similar reasons, the crossing point with Dirac-like features is also expected to be split at the band crossing. Here we use DFT in order to estimate their value and assess whether they have a strong impact on the Dirac-like dispersions evidenced at those particular band crossings. Besides, those gaps are expected to depend on the element M involved in a particular phase, and below we give values corresponding to only M = V.

Let us first focus on the nodal line (labeled as β at its intersection with Γ M). It can be theoretically evidenced by plotting an isoenergy surface located slightly below the purple



FIG. 10. M_2 AlC nodal line features, as calculated from V₂AlC electronic structure, are plotted in (*E*, k_x , k_y) (a) and within V₂AlC isoenergy surfaces at $E = E_F - 0.29$ eV (b). A linear dispersion across the nodal line is found with GGA calculations and becomes 41.0 meV gapped when including spin-orbit coupling (SOC) (c). A V₂AlC Γ M-LA ARPES isoenergy surface mapping at around 0.21 eV below E_F reveals k_z broadened points in the Γ MK plane (d).

points observed in Fig. 8 along Γ M and Γ K. The resulting plot is shown in Fig. 10(b). In addition to conventional bands, one obtains a closed loop with a slightly varying diameter. The latter variation is due to the fact that although the nodal line lies exactly in the Γ plane, it slightly varies in energy in the k_x , k_y plane (see, e.g., its intersection points along Γ M and Γ K appearing in Fig. 8). It is therefore convenient to visualize it in the (k_x , k_y , E) space, as illustrated in Fig. 10(a). Such a variation is not an exceptional finding and is, e.g., already described in [44–46] for other materials. The line is located about 0.2–0.3 eV below E_F .

Before showing experimental evidence for the existence of this line using ARPES data, it is worth describing the band structure predicted by DFT, not only as a function of in-plane wave-vector coordinates k_x and k_y but also with k_z as a parameter. In a 2D system devoid of any dispersion with k_{z} , a given cut of the ARPES signal along a particular in-plane direction in reciprocal space is formed of "simple" lines which directly correspond to the band structure. However, for given k_x , k_y values, energy dispersion with k_z gives rise to a signal broadened in energy, the well-known " k_z -broadening" effect [67,68]. The signal is dispersed over an area in the cut which is limited by the dispersion in k_z over a Brillouin zone. Roughly speaking, a well-defined line indicates that the corresponding band is 2D, and a broad region is the sign that the band is 3D [67,68]. It is thus important when plotting the DFT band structure along a particular in-plane crystallographic direction, such as, e.g., ΓM , to plot a full set of dispersion lines corresponding to values of k_z ranging from 0 to a module equal to ΓA and not limited to, e.g., $k_z = 0$, as done in Fig. 8. Figure 11(a) shows such a set along ΓM and Fig. 11(c) along



FIG. 11. k_z projected band structure of V₂AlC along Γ M, from DFT (a) and ARPES (b). k_z broadening is considered from $k_z = 0$ to $k_z = \pi/c$ (red curves stand for extremal k_z values). The linear band crossing point at $E = E_F$ is labeled as α and that corresponding to the nodal line as β . The k_z projected band structure centered on α and perpendicular to Γ M from DFT and ARPES measurements is plotted in (c) and (d). In (b) and (d), full and dashed gray lines stand for the band structures in the Γ MK and ALH planes.

a line intercepting the crossing point α at E_F already indicated in Fig. 8 but with a cut direction parallel to k_y [Fig. 11(c)]. In those two figures, dispersion appearing as "bold" lines corresponds to quasi-2D bands (confined along z), and bands where k_z dispersion is appreciable now appear as defining domains. Those domains are bounded by the curves corresponding to $k_z = 0$ and $k_z = \pi/c$. Although photoionization cross-section effects should also be taken into account, Figs. 11(a) and 11(c) should reflect the overall appearance of ARPES images measured along the same cuts.

As expected from Fig. 11(a), the nodal line exhibits a strong dispersion in any direction perpendicular to the line. In particular, and as shown in Figs. 8 and 10(c), since around β the nodal line is parallel to k_y , it exhibits a linear dispersion both along k_x and k_z . This should result in the k_z -broadening



FIG. 12. (a) V₂AlC ARPES isoenergy surface mapping at $E = E_F - 0.21$ eV a few meV below β . (b) ARPES band structure is plotted vs DFT band structure along three directions parallel to Γ M and respectively crossing the nodal line at β , β_1 , and β_2 .

effect predicted by Fig. 11(a), defining an hourglass-shaped region below and above the line. Such an hourglass pattern is easily recognized in the ARPES image of Fig. 11(b). Welldefined lines are not observed around the nodal line, most probably due to k_z broadening. The blurred hourglass shape visible in the ARPES cut is also well bounded by the extremal dispersion lines predicted by DFT [located respectively in the Γ and A planes, and also shown in Fig. 11(a)].

To prove the existence of the line requires more than an ARPES cut, and we give additional evidence below. Figure 12(a) shows an isoenergy section at an energy value where most of the nodal line is expected to lie. We find the theoretically predicted hexagonal shape, and similarity between Figs. 12(a) and 10(b) is striking. Additional patterns appearing at the apices of the hexagon are due to the additional bands predicted in Fig. 10(b) and to the fact that the nodal line slightly varies in energy [see Fig. 10(a)], so that in those regions the isoenergy plane intersects the lower part of the "hourglass" instead of the crossing point. In order to prove that the hexagon seen in Fig. 12(a) does not simply represent the energy intercept of a regular band but corresponds to the intercept of the nodal line, we represent in Fig. 12(b) ARPES cuts parallel to k_r but intercepting points β , β_1 , or β_2 , defined in the zoomed part of Fig. 12(a). As is obvious from the three cuts of Fig. 12(b) and due to the fact that the nodal line runs parallel to k_v , the ARPES pattern remains almost unchanged-the "hourglass" is always present and lies at the same position. (Here we note that the ARPES line corresponding to the rising band going to α is also almost independent of k_v , and this is the reason why its location is also constant, as for the nodal line; this is discussed below in the section discussing the dispersion around α .) Dispersion in k_z is proved by the k_z broadening of Fig. 12(b), but it is also interesting to produce a direct k_z variation by varying the incident photon energy, as shown in Fig. 10(d). Location of the nodal line at $k_z = 0$ is compatible with the data shown in Fig. 10(d). What cannot be done experimentally is to get a quantitatively accurate estimation of the dispersion line around k_z , but combining the information given by Figs. 11 and 12 clearly demonstrates the experimental existence of the nodal line. DFT predicts a value of 41 meV for the gap in β [see Figs. 12(c) and 13]. Positioning E_F close to this line while maintaining its structure should result in spin polarization effects. From the DFT calculations, it is also worth noticing that in spite of the gap induced by spin-orbit coupling, dispersion becomes linear and "Dirac-like" roughly less than 2 meV away from the top of the band.

Let us now address the band topology around point α , which exhibits Dirac-like dispersions in various directions. k_z broadening not only affects the ARPES cuts of the nodal line but also the bands measured around α , as predicted by



FIG. 13. V₂AlC band structure near α across k_x , k_y , and k_z , with and without spin-orbit coupling.

Fig. 11(c). DFT predictions along various particular directions are given in Fig. 13. Three bands are present around α (bands 39, 40, and 41). When going from Γ to M and from bottom to top, these bands respectively form (i) a quasi-2D Dirac cone before α and linear dispersions along k_x and k_y but massive dispersion along k_z beyond α [see Fig. 11(a) and 13]; (ii) a quasi-1D line along k_x (i.e., large effective masses and almost flat dispersion along k_y and k_z [see Figs. 13(b) and 13(c)]); and (iii) a cone with Dirac-like dispersion along k_x [Fig. 13(a)] and mixed shapes along k_y and k_z [Figs. 13(b) and 13(c)]. The structure around α is thus quite complex (and is indeed much more involved than what we assumed in a previous work [37]). Below we describe in more detail the topology around this crossing point along with the experimental evidence that can be gained from ARPES.

Figure 11(a) shows the theoretical dispersion and predicted k_z broadening along k_x (i.e., along Γ M), and Fig. 11(c) shows the same features, but now along the line parallel to k_v intercepting α in reciprocal space. ARPES cuts are shown in Figs. 11(b) and 11(d), where extremal DFT lines are superimposed to the ARPES cut. All lines forming the Dirac-like point are distinctly recognized along k_x and k_y , respectively, taking into account effects already discussed for the nodal line. Let us first consider Fig. 11(b). The left ascending part is clearly visible as a line, because there is no predicted kz broadening in this part, and the band is quasi-2D with Dirac-like dispersions along k_x [Figs. 11(a) and 11(b)] and k_y [Figs. 11(c) and 11(d)] but at the top of the band, where the crossing point is split by spin-orbit coupling (see Fig. 11). In contrast, the right descending part appears as a blurred region, which is easily explained by two features. On the one hand, and in contrast to all other lines, the main orbital contribution of the "descending" part beyond α is $d_{xz} + d_{yz}$, and it turns out that the available angle range of our experiment makes the photoionization cross section of this part rather small. On the other hand, and most of all, beyond α [see Fig. 11(a)] there is a strong dispersion along k_z so that the ARPES cut is subject to the well-known k_z -broadening effect in that part [67,68]. (In fact, beyond α and going towards M, the upper band seen in Fig. 13(c) crosses E_F and goes down as k_x increases, so that it is responsible for the strong dispersion along k_z in that part.) Experimental dispersion is clearly visible along the line parallel to k_v [Fig. 11(d)]. It is thus clear from Fig. 11 that the crossing point is present where DFT predicts it to lie. The observed line broadening is explained by the low k_z dispersion, leading to k_z broadening, and is well circumscribed by the domain predicted by Fig. 11(c). [The extremal band lines defining the domain have also been superimposed in the ARPES cut of Fig. 11(d).] From the considerations above, the overall topology of the crossing point can be viewed as the complex result of the intersection of locally quasi-1D, quasi-2D, and 3D bands, respectively.

Due to k_z broadening, we could not accurately assess the experimental value of the spin-orbit splitting or the band curvature, and we did it using only DFT. We found a gap of 20.7 meV at α , to be compared, e.g., to the gap at around 70 meV found in the 3D Dirac semimetal Cd₃As₂ [69]. This small gap makes the dispersion become linear, e.g., Dirac-like, roughly less than 10 meV below the top of the band (see Fig. 13). This is indeed somewhat "better" than what is found

in an archetypal 3D material such as Cd₃As₂, where, due to crystal field splitting, 3D Dirac electrons are expected only around 100 meV below E_F [69]. Experimentally, the presence of, e.g., vacancies, could slightly empty the population of the lowest band or fill the upper one. Although this still remains speculative, the presence of a few holes in this valence band could then explain the fact that when measuring magnetoresistance (MR) in similar crystals, we never found a perfect parabolic dependence (V2AlC MR power exponent was around 1.4) [70]. In V_2AIC , this seemingly anomalous behavior could indeed be explained by the mixing of the parabolic contribution of the "conventional" bands at E_F with the linear contribution expected from a slightly populated band, as first theoretically considered in [71] and as observed later in many materials (see, e.g., [72]). In contrast, in the case of Cr_2AlC , which is devoid of such topological features at E_F , the MR was found to be almost perfectly parabolic [70].

VII. CONCLUSION

The applicability of the rigid band model to 211 MAX phases has been successfully assessed by means of ARPES analysis and DFT calculations. Changing the *M* atom leads to rigid shifts of the Fermi level that leave the bands almost unchanged. It also allows for a complete classification of 211 phases based on simple criteria: all those that can be modeled by the same rigid band model would belong to a given subfamily of 211 MAX phase, which leads to the typology of five subfamilies from the five *A* element columns from which one can build up known MAX phases. Such classification is compatible with others that were built upon a different criterion, i.e., bond stiffness [73]. It is also expected that a similar classification would describe the 312 and 413 phases.

One of the implications of a unified description of MAX phases by rigid band models is the possibility to navigate through their electronic structure by playing with a single parameter (e.g., a tunable atomic fraction of M,N elements in a given $(M_x N_{1-x})_2 AX$ solid solution or, still better, using totally ordered phases combining M,N elements [26]). The presence of band inversions (see Fig. 8) that lead to the existence of many crossings and topological nodes in the rigid band structure of M_2AC (A = Al, Ga, In, Tl) shows even greater promise. Tuning the atomic ratio of M elements in solid solutions could thus open the possibility for MAX phases to be established as a promising arena for metal physicists exploring topological properties of matter. To achieve this, one still has to prove that E_F can be tuned close to the existing topological nodes. As for other compound or elemental materials, those topological features happen in parallel with the contributions of more conventional bands (see, e.g., [46]) and thus differ from the few unique systems such as, e.g., Cd_3As_2 [69], which simply displays a Dirac-like point at E_F . But this does not preclude the observation of some specific effects usually associated with such nodes, e.g., the spin Hall effect or a linear MR component.

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