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Electronic correlation effects in Cr_2GeC $M_{n+1}AX_n$ -phase

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Abstract. The magnetic properties, electronic band structure and Fermi surfaces of the hexagonal Cr_2GeC system have been studied by means of both generalized gradient approximation (GGA) and the +U corrected method (GGA+U). The effective U value has been computed within the augmented plane-wave theoretical scheme by following the constrained density functional theory formalism of Anisimov *et al.* [1]. On the basis of our GGA+U calculations, a compensated anti-ferromagnetic spin ordering of Cr atoms has been found to be the ground state solution for this material, where a Ge-mediated super-exchange coupling is responsible for an opposite spin distribution between the ABA stacked in-plane Cr-C networks. Structural properties have also been tested and found to be in good agreement with the available experimental data. Topological analysis of Fermi surfaces have been used to qualitatively address the electronic transport properties of Cr_2GeC and found an important asymmetrical carrier-type distribution within the hexagonal crystal lattice. We conclude that an appropriate description of the strongly correlated Cr- d electrons is an essential issue for interpreting the material properties of this unusual Cr-based MAX -phase.

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1. Introduction

The $M_{n+1}AX_n$ or MAX phases are layered hexagonal solids with unusual and sometimes unique combination of properties [2]. They are made of an early transition metal M , an A -group element (group III , IV , V , or VI element), and by an X element that is either C or N. They have attracted much attention due to the peculiar combination of properties that are normally associated with either metals or ceramics. Just like metals, they are readily machinable, electrically and thermally conductive, not susceptible to thermal shock, plastic at high temperature and exceptionally damage tolerant. On the other hand, they are elastically rigid, lightweight, creep and fatigue resistant as ceramic materials. It is therefore not surprising that there has been a rapid increase of research activities on MAX phases by both experimental and theoretical works during recent years [2, 4, 5, 6]. A magnetic MAX phase that could potentially give rise to functional materials for spintronics applications [3] has also long been searched. However, to our knowledge, despite many attempts and efforts, none of the synthesized $M_{n+1}AX_n$ phases have been found to possess stable magnetic features.

Among the known $M_{n+1}AX_n$ phases, Cr_2GeC (Fig 1) is a relatively little studied member. It has the highest thermal expansion coefficient among all the present known MAX phases [7, 8, 9], high resistivity, a positive Seebeck coefficient both in- and out-of-plane [10], and a negative Hall coefficient. The calculated electronic density of states (DOS) at the Fermi level (E_F) is considerably underestimated [11] and there is a large and anisotropic electron-phonon coupling [12]. In general, Cr-containing $M_{n+1}AX_n$ -phases have unusually large DOS at the E_F stemming from the electronic d -states of the transition metal. In fact, for Cr_2GeC the DOS at E_F is by far the highest ($22 \text{ eV}^{-1}\cdot\text{cell}^{-1}$) measured among the $M_{n+1}AX_n$ -phases and for Cr_2AlC ($14.6 \text{ eV}^{-1}\cdot\text{cell}^{-1}$) it is the second highest. The carrier mobility is, however, rather limited in Cr-based MAX phases compared to Ti-containing ones, due to their strongly localized Cr d -states. The significantly correlated nature of the Cr d -electrons also make the magnetic coupling and ferromagnetic/anti-ferromagnetic ordering largely unknown and rather complicated to establish [8]. Moreover, there is some disagreement in the literature about the experimentally determined values for both bulk modulus and equilibrium volume [13, 14].

For all these reasons, a comprehensive theoretical study is needed to correctly address the material properties of this unusual MAX phase. Specifically, the aim of this work is to study the effect of correlation on the electronic structure and material properties of the Cr_2GeC MAX -phase. Particular attention has been given to the ground-state magnetic spin ordering, electro-structural correlations and transport properties. We observe that ferromagnetic Cr layers are anti-ferromagnetically coupled together via an interleaved Ge-atom, assembling a multilayer material that could, in principle, be tuned to provide thermodynamic stable magnetic MAX -phases.

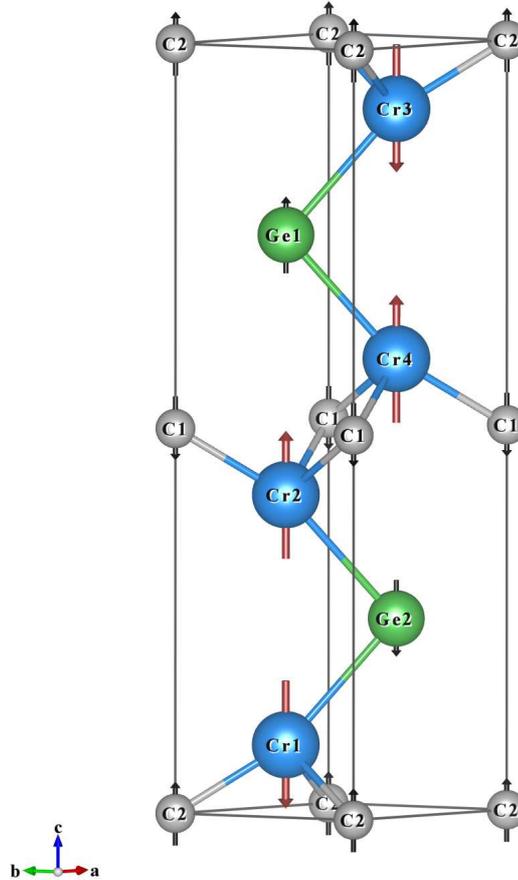


Figure 1. Atomic model of the hexagonal crystal structure of Cr_2GeC with space group $P3m1$ (156) and 8-atoms per unit-cell. Chromium (Cr), germanium (Ge), and carbon (C) atoms are depicted in blue (large spheres), green (medium spheres), and gray (small spheres), respectively. The large red arrows drawn at the $Cr_1 \cdots Cr_4$ atoms indicate the ground-state magnetic spin configuration inside the unit cell. Small black arrows represent the fractional magnetic spin moments localized at the Ge and C sites. The VESTA visualization software [15] was used to generate the present figure.

2. Computational details

2.1. First-principles calculations

The electronic structure of Cr_2GeC was computed within the WIEN2K code [16] employing the density-functional [17, 18] augmented plane wave plus local orbital (APW+lo) computational scheme. The APW+lo method expands the Kohn-Sham orbitals in atomic-like orbitals inside the muffin-tin (MT) atomic spheres and plane waves in the interstitial region. The Kohn-Sham equations were solved by means of the Wu-Cohen generalized gradient approximation (GGA^{WC}) [19, 20] for the exchange-

correlation (xc) potential. For a variety of materials it improves the equilibrium lattice constants and bulk moduli significantly over the local density approximation (LDA) [18], and performs pretty well for the Cr_2GeC material (see results in Table 2). The latter is the main reason that motivated our choice to adopt the Wu-Cohen approximation in studying this Cr-based MAX phase.

A plane-wave expansion with $R_{MT}\cdot K_{max}=10$ was used in the interstitial region, while the potential and the charge density were Fourier expanded up to $G_{max}=12$. The modified tetrahedron method [21] was applied to integrate inside the Brillouin zone (BZ), and a \mathbf{k} -point sampling with a $35\times 35\times 7$ Monkhorst-Pack [22] mesh in the full BZ (corresponding to 786 irreducible \mathbf{k} -points) was considered satisfactory for the hexagonal Cr_2GeC system. Magnetic ground-state properties and electronic band structure features were studied using the relaxed unit cell parameters. All the spin-polarized calculations were charge converged up to $10^{-4} e$.

Convergent and smooth Fermi surfaces (FSs) were achieved by sampling the whole BZ with 10000 \mathbf{k} -points along the $35\times 35\times 7$ Monkhorst-Pack grid. The presented FS plots were then generated with the help of the XCRYSDEN graphical user interface code [23] applying the tricubic spline interpolation with a degree of five.

2.2. Searching for an effective Hubbard U -value

Density functional theory (DFT) is an upright method for computing ground-state properties of solids with feeble electronic correlations. However, this method fails to describe systems with intermediate and strong electron correlations, such as transition-metal oxides, Kondo systems and rare earths. Such a short-coming description is due to the spurious self-interaction. Therefore, these materials are very often investigated by means of a phenomenological many-body Hamiltonian such as the Hubbard model [24], where the effective on-site Coulomb interaction is an empirical parameter (U) that permit to reproduce the experimental results of interest. Hence, by using this approach, the correct determination of U represents a critical issue because many properties, such as magnetism, can vary in MAX phases with the value of U .

When employing the local density approximation for the xc -part, then the LDA+U method indicates that an orbital-dependent field has been introduced to correct for self-interaction [25]. Particularly, a set of atomic-like orbitals is treated with an orbital-dependent potential with an associated on-site Coulomb (U) and exchange (J) interactions. Since in LDA, the electron-electron interactions have already been considered in a mean-field way, one has to identify the parts that occur twice and apply a double-counting (DC) correction. To overcome such a problem, in the non-spherical part of potential we used $U_{eff} = U - J$ [26], setting therefore $J=0$. Although several different ways of correcting for DC are existing [25, 1, 27, 28], we here use what has been referred to as the SIC method introduced by Anisimov *et al.* [25].

The physical meaning of the U parameter was defined by Anisimov and Gunnarsson [1], who described it as the Coulombic energy cost of placing two electrons on the same

Table 1. Calculated on-site Coulomb value (U_{eff} in eV) for different exchange-correlation functionals.

	<i>LDA</i>	<i>GGA^{WC}</i>	<i>GGA^{PBE}</i>
$U_{eff} (e_g)$	2.14	2.33	2.08
$U_{eff} (t_{2g})$	2.04	2.09	2.03

site. In an atom, U simply corresponds to the unscreened Slater-integrals, whereas in solids the U_{eff} is much smaller because of screening effects. The Hubbard U depends on the type of crystal structure, d electron number, d orbital filling and most generally on the degree of electronic localization.

Using the method of Anisimov and Gunnarsson (sometimes called *constrained DFT formalism*), the U -value has been calculated for the Cr atom in the hexagonal Cr_2GeC structure. Two kinds of calculations were performed on a $2 \times 2 \times 1$ supercell each with one impurity site forced to have the d -configuration as shown in eq. (1)

$$U_{eff} = \varepsilon_{3d\uparrow} \left(\frac{n+1}{2}, \frac{n}{2} \right) - \varepsilon_{3d\uparrow} \left(\frac{n+1}{2}, \frac{n}{2} - 1 \right) + \\ - E_F \left(\frac{n+1}{2}, \frac{n}{2} \right) + E_F \left(\frac{n+1}{2}, \frac{n}{2} - 1 \right) \quad (1)$$

where $\varepsilon_{3d\uparrow}$ is the spin-up $3d$ eigenvalue and E_F the Fermi energy. The d -character of the augmented plane waves at the chromium impurity sites was eliminated by setting the d -linearization energy far above the Fermi level [$E_{(\ell=2)}=20.30$ Ry]. Using eq. (1) we computed an U_{eff} value of 2.09 eV (t_{2g}) and 2.33 eV (e_g) for the chosen *GGA^{WC}* xc -functional. Table 1 shows the obtained Hubbard U parameter for various exchange-correlation potentials. In agreement with previous studies [29], the effective interaction between d electrons in e_g orbitals is larger than that in t_{2g} orbitals.

3. Results

3.1. Magnetic ground-state and equilibrium structural parameters

We have investigated several possible magnetic orders of the moments on the Cr atoms, either ferromagnetic (FM), antiferromagnetic (AFM), or with no magnetic moments (NM). As reported earlier, in the case of *GGA*, the ground state might correspond to either NM [30] or AFM [8], while for *GGA* + U the antiferromagnetic spin distribution of Cr atoms along the c -axis turns out to be the most stable solution [30]. In particular, using the *GGA^{WC}* functional (present study) we also found small amounts of localized Cr magnetic moments with an AFM spin ordering inside the in-plane Cr-C networks (i.e., $Cr_1^{(\uparrow)}=+0.012 \mu_B$, $Cr_2^{(\downarrow)}=-0.008 \mu_B$, $Cr_3^{(\downarrow)}=-0.012 \mu_B$, and $Cr_4^{(\uparrow)}=+0.008 \mu_B$). However, when using the $+U$ corrected functional (*GGA^{WC}* + U), the ground state magnetism turns out to be rather different, having an alternate FM spin distribution for the two Cr-C networks (Fig. 1). The computed magnetic moments for the Cr atoms that belong to the Cr-C network located at nearly half of the c -axis are $Cr_2^{(\uparrow)}=+0.011 \mu_B$

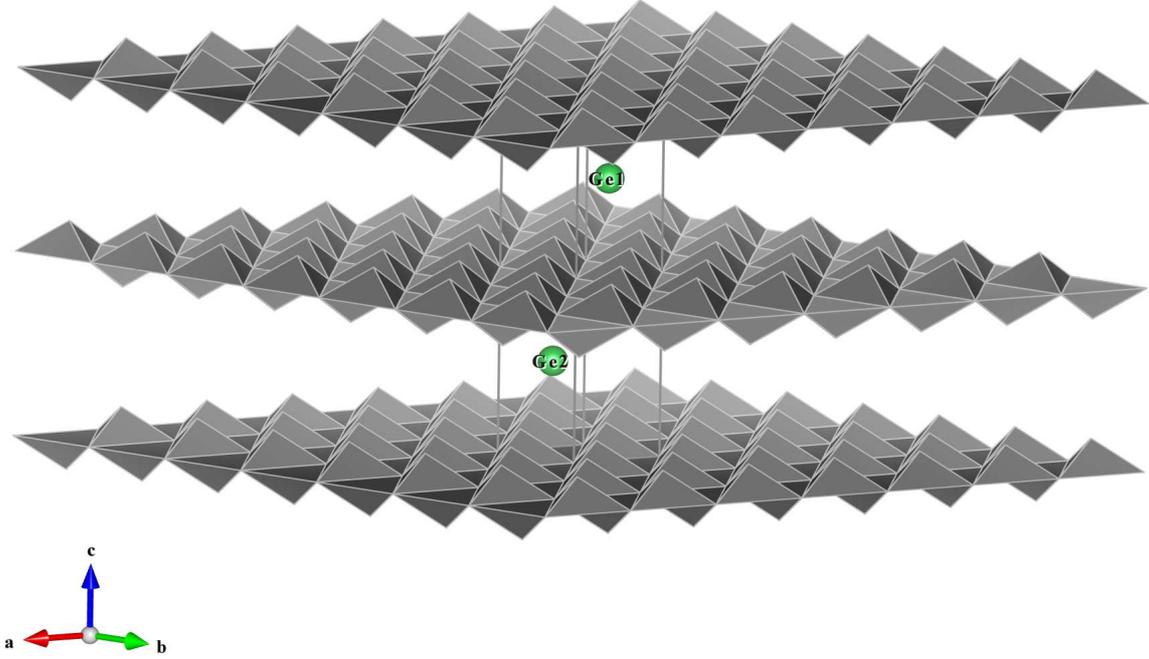


Figure 2. Polyhedral model for the Cr_2GeC phase showing the Cr-C layers (gray) that are propagating along the a - b crystal plane and the interleaved Cr atoms (green). Each polyhedral skeleton consists of three C atoms at the base and a Cr atom at the vertex. Note the alternating (up/down) vertex distribution within each layer that produce an ABA stacking order of layers along the c -axis. The Cr atom sitting on the polyhedral vertices of the middle (bottom-top) Cr-C network is Cr_4 (Cr_1) for the upward polyhedra and Cr_2 (Cr_3) for its downward counterpart.

and $\text{Cr}_4^{(\uparrow)} = +0.007 \mu_B$, whereas for those at the bottom/top of the hexagonal unit cell amount to $\text{Cr}_1^{(\downarrow)} = -0.007 \mu_B$ and $\text{Cr}_3^{(\downarrow)} = -0.011 \mu_B$. As shown in Fig. 1, the $+U$ corrected functional allows for a Ge-mediated super-exchange magnetic coupling [31] between Cr atoms belonging to different Cr-C networks (Fig. 2). This inter-layer interaction arises from the mixing of the Cr $3d$ and the Ge $4p$ states, which act along the 103° angle bend Cr-Ge-Cr three-point line. The computed unequal values for the Cr magnetic moments ($\text{Cr}_1 \neq \text{Cr}_2$ and $\text{Cr}_3 \neq \text{Cr}_4$) are ascribed to the small amount of $\text{Ge}_1 \rightarrow \text{Cr}_4$ and $\text{Ge}_2 \rightarrow \text{Cr}_1$ charge-transfer that is at the base of the super-exchange coupling mechanism [31]. This generates a very small spin polarization of the Ge atoms that sustains an antiferromagnetic spin coupling with the Cr atoms that are non directly involved in the

charge-transfer mechanism ($\text{Ge}_1^{(\uparrow)}\text{-Cr}_3^{(\downarrow)}$ and $\text{Ge}_2^{(\downarrow)}\text{-Cr}_2^{(\uparrow)}$). Also, when introducing the on-site Coulombic interaction the three C atoms, which constitute the first coordination shell of Cr ions, become slightly spin-polarized, thus stabilizing a FM in-plane Cr spin distribution ($\text{Cr}_{1,3}^{(\downarrow)}\text{-}3\times\text{C}_2^{(\uparrow)}$ and $\text{Cr}_{2,4}^{(\uparrow)}\text{-}3\times\text{C}_1^{(\downarrow)}$). It is worth noting that the total magnetic moment of the unit cell is still zero, as to indicate an almost perfect resulting AFM spin alignment inside the whole hexagonal lattice. Despite the tiny magnitude of Cr magnetism computed within the $GGA^{WC} + U$ scheme, the achieved results are clearly showing that Cr_2GeC has a considerably more complicated magnetic structure than believed earlier. Relativistic corrections in the electronic structure calculation have also been included in a second-variational procedure using scalar-relativistic wavefunctions [32]. Applying the spin-orbit coupling within the atomic spheres along the $[0\ 0\ 1]$ magnetization direction, leads to enhanced Cr magnetic moments while keeping exactly the same non-relativistic ground-state spin pattern.

The importance of the super-exchange coupling has been further underlined by $GGA^{WC} + U$ calculations performed on an iso-geometrical Ge-hollow unit cell. In this case, an AFM material is stabilized with exactly the same in-plane AFM spin arrangement of Cr atoms found within the GGA^{WC} method. Therefore, only an explicit description of the strongly correlated nature of the Cr 3d electrons is able to catch the super-exchange interaction, that maintain an in-plane FM Cr spin ordering. Preliminary experimental results seem to confirm this important finding [33], although the presence of small Cr magnetic moments might lead to a rather weak magnetic energy and therefore to a low Néel temperature.

Attention should also be paid to the nature of the interleaved non-magnetic A-atoms, that might play a crucial role in determining the overall magnetic properties of this MAX -phase. As a rule of thumb, the smaller the spin polarizability of the bridging A-atom is, the weaker the inter-layer super-exchange coupling will be [34]. Hence, smaller atoms having tightly bound valence electrons will then tend to weaken the super-exchange coupling, enhancing the FM behavior of the Cr_2GeC crystal phase. Formulated differently, this will translate into attempting to tune the Cr-A bonding type as to reduce its covalent character, thus rising up the observable Néel temperature.

In table 2, we report the volume, lattice parameters and bulk modulus within different correlation corrected xc -functionals. After including the $+U$ correction, the equilibrium volume considerably increases giving a good agreement with the experimental data of Phatak *et al.*[14], although the bulk modulus gets significantly lower. However, since the $GGA^{WC} + U$ is correctly treating the correlated nature of the Cr d -electrons, we believe that most likely this is the right value for the bulk modulus.

3.2. Electronic density of states and band structure

The DOS at the Fermi level is dominated by the Cr transition metal. Fig. 3 illustrates the calculated Cr- d total DOS for both GGA^{WC} and $GGA^{WC} + U$ methods. A bandwidth reduction of about 0.75 eV is found when including the on-site Coulombic interaction.

Table 2. Optimized cell parameters for the ground-state AFM spin configuration.

Property	GGA^{WC}	$GGA^{WC} + U$	$GGA^{PBE} + U^a$	exp. ^b	exp. ^c
V(Å ³)	86.24	92.71	91.21	91.10	92.82
a(Å)	2.899	2.981	2.97	2.950	2.958
c(Å)	11.875	12.044	12.16	12.086	12.249
c/a	4.097	4.040	4.094	4.097	4.141
B _o (GPa)	254.4	147.6	150	182	169

^a Using $U=1.95$ eV and $J=0.95$ eV (Ref.[30]).

^b From Ref.[13].

^c From Ref.[14].

The most distinct feature we observe is the shrinking of both valence and conduction bandwidths. The bottom of the valence band moves to higher energy by 0.25 eV and the top of the conduction band is reduced towards lower energies by 0.50 eV. The Cr d -electrons strongly hybridize with the Ge and C p -states and their relative energetic position determines the degree of hybridization and the width of the valence band. The Hubbard U correction has therefore a noticeable influence on the hybridization between localized and itinerant states. The top of the valence band and the bottom of the conduction band develop more C $2p$ and Ge $3p$ characters when including U and the Cr states hybridizes accordingly giving rise to smaller bandwidths. A similar behaviour of Ge states was found on the V_2GeC phase [35].

Since Cr_2GeC is a metallic system, the DOS at the Fermi level is a key quantity for stability purposes. The Cr_2GeC crystal has its E_F positioned exactly at a local minimum in the DOS, thus suggesting a higher level of intrinsic stability. As a matter of fact, local minimum at E_F is a good indicator of large structural stability as it represents a barrier for electrons below the Fermi-level to move into the unoccupied empty states. The $GGA^{WC} + U$ slightly increases the number of states at E_F (3.95 states/eV) with respect to GGA^{WC} calculations (3.85 states/eV), while keeping the same topological DOS. As such, band renormalization does not provide any remarkable effects concerning the total amount of electronic band filling of the occupied states.

Figure 4 shows the $GGA^{WC} + U$ calculated electronic band structure of Cr_2GeC . The dominant contribution to the electronic density of states at E_F derives from metallic bonding of the Cr d -electron orbitals in the Cr-Ge-C network. Several bands are formed that cross E_F , both electron- and hole-like, thus resulting in a multiband system dominated by Cr d -character. At the Fermi level, the bands that are crossing the Fermi energy are 44, 45, 46, 47 and 48, and their numbering follows exactly that of Fig. 4. Band 44 has the same $d_{xz}+d_{yz}$ orbital character contribution from all the Cr atoms ($\text{Cr}_1 \rightarrow \text{Cr}_4$), while in band 45 there is an important d_{z^2} weight from Cr_1 and Cr_2 and a $d_{x^2-y^2}+d_{xy}$ contribution from Cr_3 and Cr_4 . For band 46 all the Cr atoms contribute with the same amount of both d_{z^2} and $d_{x^2-y^2}+d_{xy}$ characters. The very similar bands 47 and 48 are mainly of $d_{x^2-y^2}+d_{xy}$ character from all the Cr atoms. Figure 4 also shows the hole- and electron-like character of the crossing bands. Specifically, hole-like

features are positioned at symmetry point M , midway the K - Γ symmetry line, and at L and H . On the contrary, an electron-like pocket can be seen at symmetry points Γ , A and K .

From band structure analysis, important information about electronic transport properties can be obtained. The Cr-containing MAX carbides are expected to show the highest resistivity along the series $\text{Ti}_2\text{GeC} \rightarrow \text{V}_2\text{GeC} \rightarrow \text{Cr}_2\text{GeC}$. As a matter of fact, the reported resistivity for Ti- and V-based MAX phases are in the range 15-30 $\mu\Omega\text{cm}$ compared to 53-67 $\mu\Omega\text{cm}$ for the Cr_2GeC material [5]. This is generally due to the reduced carrier mobilities in Cr-based systems, where strongly localized Cr d -states are present near the Fermi level [36]. In this regard, it is worth noting that the overall electronic band structure of Cr_2GeC is rather anisotropic, with bands crossing the E_F only along the symmetry lines of the basal xy -plane. Nevertheless, such an intrinsic band structure anisotropy is similar to that of typical hexagonal-close-packed materials [37], and therefore cannot be used to quantitatively explain the peculiar transport properties of Cr-containing MAX phases. In this respect, scattering processes and charge carrier-phonon coupling should be taken into account [38].

3.3. Fermi surfaces

In metals, the energy states that participate in determining most properties of a material lie in close proximity to the Fermi energy, that is, the level below which available energy states are filled. The Fermi surface thus separates the unfilled orbitals from the filled ones and represents a surface of constant energy ($E=E_F$) in \mathbf{k} -space. The electrical properties of metals are defined by the shape and size of the Fermi surface, as the current is due to changes in the occupancy of states, near the Fermi surface. Therefore, by observing the *fermiology* of the computed Fermi surfaces one can help addressing, from a qualitative point of view, the predominant role of each crossing band along either the z component or inside the xy plane.

Since the velocities of the electrons are perpendicular to the Fermi surface, then bands 45, 47 and 48 have large components within the basal plane, while bands 44 and 46 play an equally important role along the three k_x , k_y , and k_z axes. From band 44 a localized hole-like FS pocket emerges at the M -point (Fig. 6), defined as the \mathbf{k} -vector $(\frac{1}{2}, 0, 0)$ in the BZ of Fig. 5. The next band (45) has two hole-like band features, one centered at the symmetry point M and the other at L (Fig. 7). Band 46 has a mixture of characters, with hole-like features at M and L and an electron-like component at K . The Fermi surfaces of bands 47 and 48 have both very similar hole-like character along the point symmetries Γ - M , K - Γ , A - L and A - H . As with other transition metal-based materials, the introduced electronic correlation leads to a certain degree of electron renormalization of the band structure which, however, does not change the main topology of the Cr_2GeC Fermi surfaces.

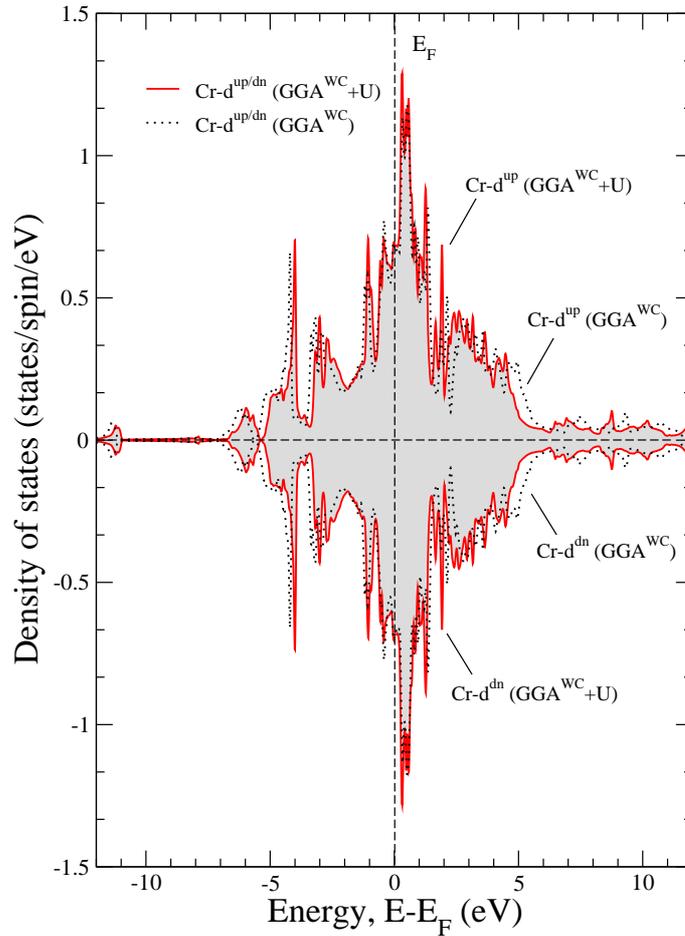


Figure 3. Density of states of AFM Cr_2GeC for spin-up (upper part) and spin-down (lower part) Cr- d electrons.

4. Discussion

It has been shown that an appropriate treatment of correlation effects in the Cr_2GeC MAX -phase leads to the discovery of a different magnetic spin pattern, where a super-exchange interaction operates through the non-magnetic Ge ions. The buckled Cr-C networks that are propagating parallel to the xy -plane of the crystal are thus showing a FM intra-layer spin distribution and an AFM inter-layer spin ordering. The FM layers are lined up in a perfect anti-ferromagnetic pattern giving a vanishing total magnetic moment inside the unit cell. This finding enables the possibility of tuning the exchange coupling between ferromagnetically ordered Cr-C layers so as to achieve stable magnetic MAX phases for electronic and spintronic applications. For instance, the inter-layer coupling could be varied by changing the inter-layer thickness [39], interface quality [40] or even by alloying with another M-element [41]. Further studies are being pursued in

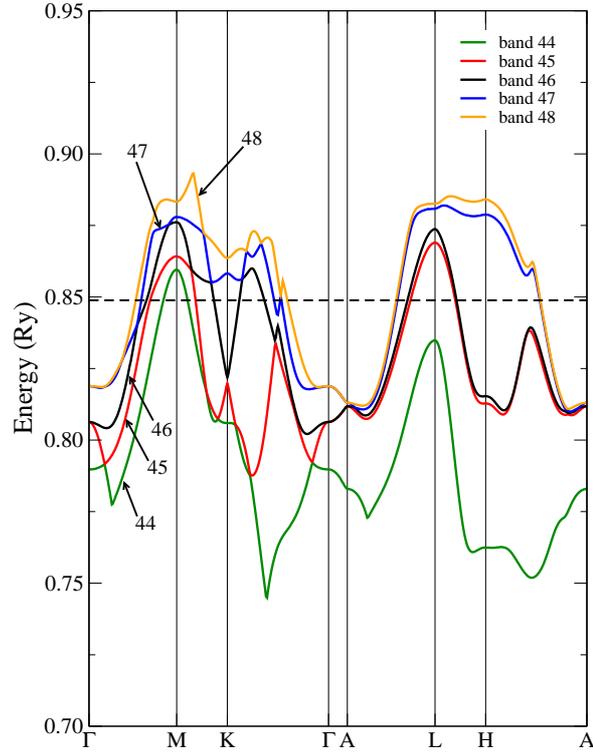


Figure 4. Energy band structure of Cr_2GeC for the spin-up configuration along high symmetry directions shown in Fig. 5. Only the electronic bands that are crossing the Fermi level are shown.

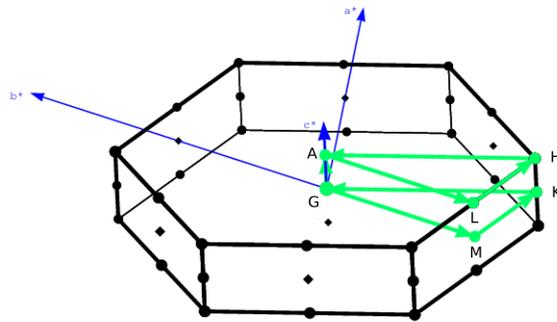


Figure 5. Primitive Brillouin zone of the hexagonal unit cell with the used symmetry points: Γ $(0,0,0)$, M $(\frac{1}{2},0,0)$, K $(\frac{2}{3},\frac{1}{3},0)$, A $(0,0,\frac{1}{2})$, L $(\frac{1}{2},0,\frac{1}{2})$ and H $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$. Reciprocal lattice vectors are also shown as a^* (k_x), b^* (k_y), and c^* (k_z).

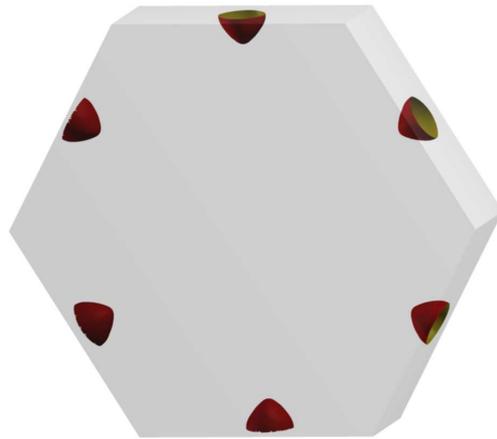


Figure 6. Constant energy surface for band 44 (spin-up) viewed along the k_x and k_y plane of the hexagonal Brillouin zone.

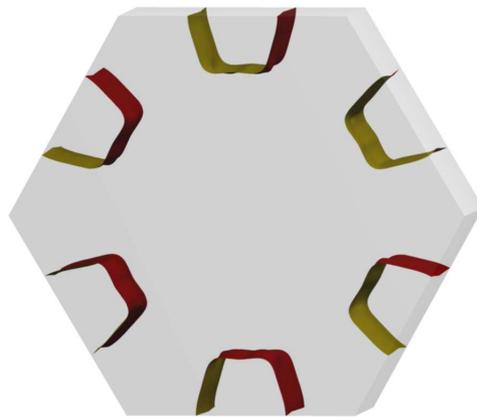


Figure 7. Fermi surface for band 45 (spin-up).

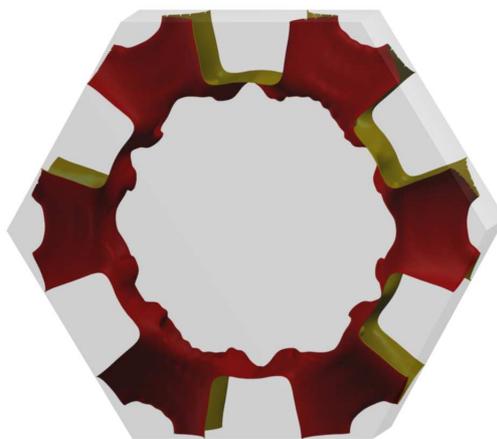


Figure 8. Fermi surface for band 46 (spin-up).

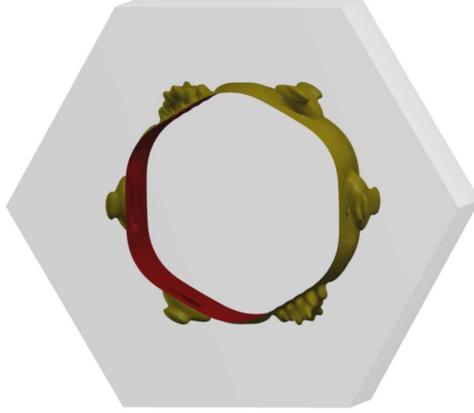


Figure 9. Fermi surface for band 47 (spin-up).

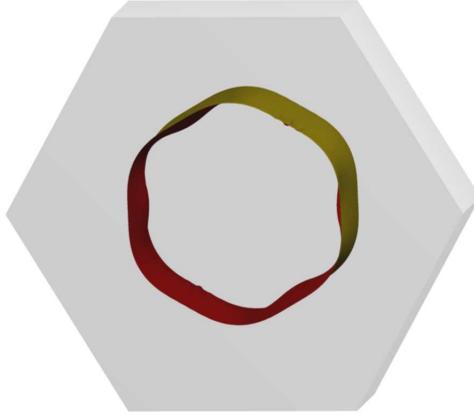


Figure 10. Fermi surface for band 48 (spin-up).

order to experimentally confirm such a magnetic pattern via a detailed XMCD analysis [33].

From the calculated Fermi surfaces we have seen that there is only one electron-like band (band 46) that shows a velocity component along the k_z axis. The other 4 Fermi surfaces are hole-like with large velocity contributions confined within the basal xy -plane. Therefore, Cr_2GeC appears to be a material characterized by a clear *carrier-type anisotropy*, being the positively hole charge carriers responsible for transport properties within the basal xy -plane, and the negatively electron charge carriers along the vertical z -axis. This qualitatively explains the reason why the experimentally determined Seebeck coefficients [33] along the [001] plane (i.e., the in-plane component) are generally larger than those along the [103] plane (i.e., the out-of-plane direction). Large and positive Seebeck coefficients indicate that Cr_2GeC behaves as a p -type material along the in-plane direction, having predominantly positive mobile charges (holes). On the contrary, the much lower magnitude of measured Seebeck coefficients along the [103]

plane points to an increased negative carrier concentration along the vertical direction of the hexagonal Cr_2GeC crystal. This may also be true in other Cr-based materials such as Cr_2AlC . As shown in this work, determining the super-exchange coupling will serve as an important method to predict which MAX phases are good candidates with stable magnetic features.

5. Conclusions

An *ad hoc* effective Hubbard U value has been computed for various exchange correlation functionals by using the constrained DFT formalism. We have shown that Cr_2GeC is a weak AFM material with a rather anisotropic electronic band structure. Most important, by properly accounting for Cr correlation effects we discovered the presence of a super-exchange coupling between different in-plane Cr-C networks of the Cr_2GeC unit cell. Therefore, the magnetic nature of the studied MAX phase is AFM (as proposed earlier) but with a substantially different electro-structural origin. The interleaved Ge-atoms stabilize the ferromagnetically ordered Cr layers that are exchange coupled together. If this kind of inter-layer coupling can be tailored, then very attractive layered magnetic materials can be proposed with a potential use for many electronics and spintronics applications.

Equilibrium structural parameters were also computed within the $\text{GGA}^{WC} + U$ and found to be in good agreements with the experimental data of Phatak *et al.*[14]. The topology of Fermi surfaces was studied to address the electric transport properties of the metallic Cr_2GeC material. The achieved results indicate that this Cr-containing MAX phase has a relevant asymmetrical carrier-type structure, where hole carriers dominate within the basal plane and electrons only contribute to carrier mobility along the z -axis.

Acknowledgments

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