Possible Nonactivated Conductivity of the Low-Dimensional Ternary Nitride Ca$_2$GeN$_2$

Josep M. Oliva and Enric Canadell*

Institut de Ciència de Materials de Barcelona (CSIC), Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

The electronic structure of the recently reported ternary nitride Ca$_2$GeN$_2$ has been studied by means of first-principles density functional calculations. The relatively short nonbonded Ge$\cdots$Ge contacts along the direction approximately perpendicular to the plane of the bent GeN$_2$ units confer a large dispersion to the energy bands based on the antibonding π-type level of GeN$_2$. This feature as well as the smaller but non-negligible interactions along the perpendicular directions suggests that this material, despite being built from discrete units, may exhibit a metallic behavior. This study suggests that the nature of the alkaline-earth atom has a crucial influence on the electrical conductivity of this type of phase.

Figure 1. Crystal structure of Ca$_2$GeN$_2$ viewed along the tetragonal axis (*c*-direction). The large and small filled circles represent the Ca and Ge atoms whereas the empty circles are the N atoms.

Despite the many technological applications of binary nitrides, synthetic difficulties and decomposition problems have been at the origin of a comparative lack of attention toward the in principle more versatile ternary nitrides. The situation has nevertheless completely changed during the past decade. The development of new synthetic strategies has resulted in a real flourishing of this field.[1-4] Ternary nitrides are interesting not only from a structural, synthetic, or physical viewpoint but also because of their electronic structure. As we have recently pointed out,[5] CaMN$_2$ (M = Nb, Ta) contain MN$_2$$^{2-}$ octahedral layers whose electronic structure resembles almost perfectly that of the isoelectronic TaS$_2$ layers of 1T-TaS$_2$. However the electronic structure of the trigonal prismatic MoN$_2$$^-$ layers of LiMoN$_2$[5,6] differs quite noticeably from that of the isoelectronic TaS$_2$ layers of 2H-TaS$_2$. There are a half-filled transition metal based band in the latter but two partially filled bands, one molybdenum-based and another mostly nitrogen-based, in the former so that the transition metal is formally d^1 in the latter but d^{1+x}
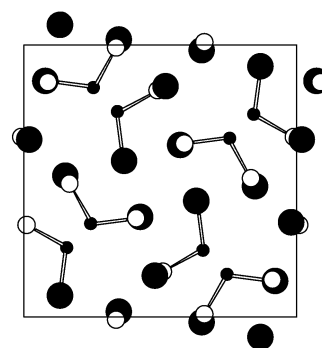
in the former. Careful analysis of the electronic structure of ternary nitrides can thus be very helpful in the search for correlations between crystal structure and physical properties in the very active field of ternary nitrides. Here we would like to report on the electronic structure of a potentially very interesting ternary nitride recently reported by DiSalvo et al.,[7] Ca$_2$GeN$_2$. Ca$_2$GeN$_2$ is a black solid isostructural to Sr$_2$GeN$_2$[8] which is built from GeN$_2$ triatomic units between which the Ca atoms reside (see Figure 1).

If the Ca atoms are considered to be Ca^{2+}, the triatomic units should be considered as GeN$_2$$^{4-}$, with 14 σ and 4 π valence electrons, thus being isoelectronic with SO$_2$ and explaining the bending of the triatomic units. This counting also suggests a closed-shell nature for the triatomic units and thus a semiconducting or insulating behavior for this phase. There are, however, some details in the crystal structure which indicate that the situation cannot be so clear-cut. For instance, the Ca atoms are between the N atoms of two successive GeN$_2$$^{4-}$ units along the *c*-direction and thus could well provide for some interconnection between the triatomic units. In addition, the Ge$\cdots$Ge contact between adjacent GeN$_2$$^{4-}$ units (2.894 Å), although not as short as a usual Ge–Ge bond (2.4–2.6 Å), is definitely shorter than what would be expected from a purely van der Waals interaction.[8]

* Author to whom correspondence should be addressed. E-mail: canadell@icmab.es.
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This distance is noticeably shorter than in the isostructural material Sr_2GeN_2 (3.112 Å), which in turn is reported to be dark blue. Even if the last observation could result from the presence of impurities, these observations prompted us to perform high-level first-principles calculations for Ca_2GeN_2.

The calculations were carried out using a numerical atomic orbitals density functional theory (DFT)[9,10] approach, which has been recently developed and designed for efficient calculations in large systems and implemented in the SIESTA code.[11-15] We have used the generalized gradient approximation to DFT and, in particular, the functional of Perdew, Burke, and Ernzerhof.[16] Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials[17] factorized in the Kleinman–Bylander form.[18] We have used a split-valence triple-ζ basis set including polarization orbitals for all atoms, as obtained with an energy shift of 125 meV.[14] The integrals of the self-consistent terms of the Kohn–Sham Hamiltonian are obtained with the help of a regular real space grid in which the electron density is projected. The grid spacing is determined by the maximum kinetic energy of the plane waves that can be represented in that grid. In the present work, we used a cutoff of 175 Ry, which yields to a spacing between the grid points of around 0.12 Å. The Brillouin zone (BZ) was sampled using a grid of ($3 \times 3 \times 20$) k-points.[19] We have checked that the results are well converged with respect to the real space grid, the BZ sampling, and the range of the atomic orbitals. The crystalline structure reported by DiSalvo et al.[7] has been used in the calculations.

The calculated band structure for Ca_2GeN_2 is reported in Figure 2a. The bottom part of a set of four highly dispersive bands along c^* (leading to the first, second, third, and fifth bands from the top at Γ) overlaps with the top of the valence bands, thus leading to a semimetallic type band overlap. The upper dispersive bands appear as a set of four bands because, as shown in Figure 1, the unit cell of this material contains four chains of double GeN_2 units along the c-direction. In fact, the upper part of the valence band also originates from a set of four bands (leading to the fourth, sixth, seventh, and eighth bands at Γ). The upper set originates from the upper antibonding π_3 level of the bent triatomic units. This level is strongly based on the p_z orbital of the less electronegative Ge atom and because of the relatively short Ge⋯Ge distance between adjacent tricenter units leads to the strongly dispersive set of four bands along $\Gamma \rightarrow Z$. The lower set of

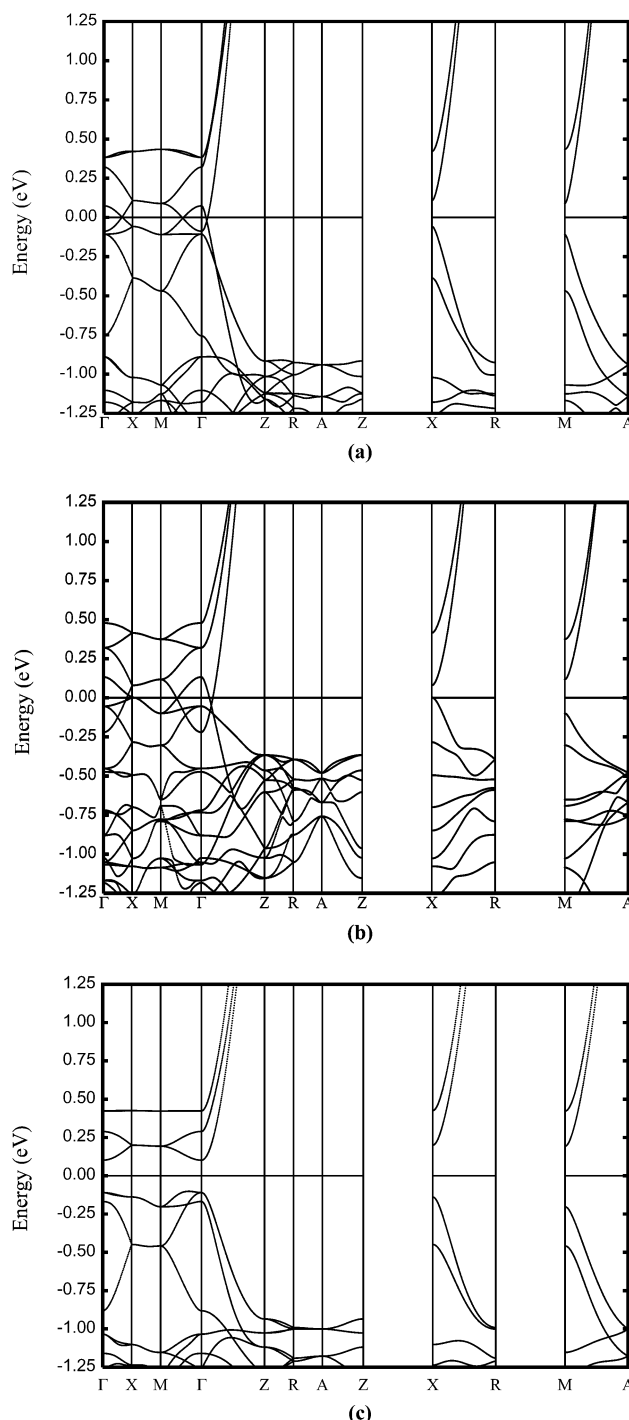(9) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, 864.
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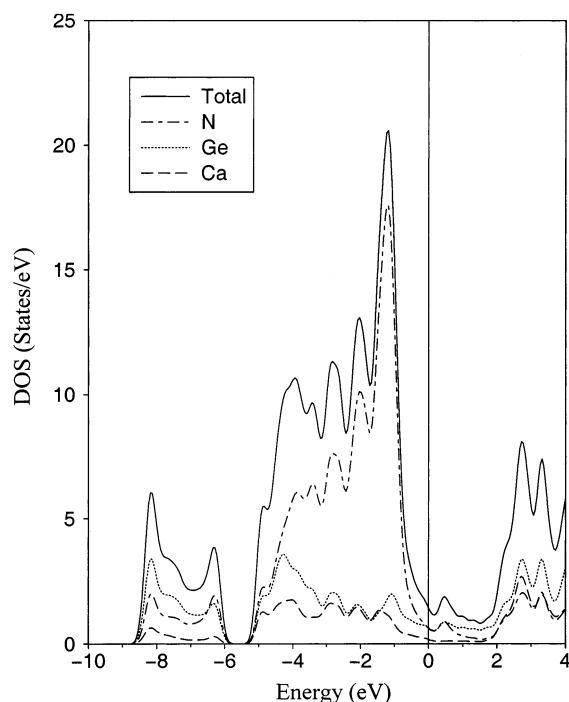
Figure 2. Calculated band structure for (a) Ca_2GeN_2, (b) $(\square^{2+})_2GeN_2^{4-}$, and (c) Sr_2GeN_2, where the solid line at $\epsilon = 0$ eV refers to the Fermi level. $\Gamma = (0, 0, 0)$, $X = (^1/_2, 0, 0)$, $M = (^1/_2, ^1/_2, 0)$, $Z = (0, 0, ^1/_2)$, $R = (^1/_2, 0, ^1/_2)$, and $A = (^1/_2, ^1/_2, ^1/_2)$ in units of the tetragonal reciprocal lattice vectors.

bands is of σ-type at Γ (i.e., based on orbitals symmetric with respect to the plane of the tricenter units and delocalized over the three atoms), but along the $\Gamma \rightarrow Z$ direction they can mix in π-type orbitals and due to the short Ge⋯Ge contacts along the zigzag chain they acquire considerable dispersion. If it were not for the existence of non-negligible interchain interactions, the sets of four bands would appear as almost superposed. As shown in Figure 2a, these interchain interactions are far from negligible, leading to a considerable

Figure 3. Total and atom-projected density of states of Ca_2GeN_2 projected onto the Ca, Ge, and N sites. Fermi level at $\epsilon = 0$ eV.

spread of the levels of the two types of bands (0.8 eV for the σ bands and 0.5 eV for the π bands). Thus, both intra- and interchain interactions cooperate in leading to the absence of a band gap at the Fermi level of this material.

At this point, the possible role of the Ca atoms in the making of the band overlap should be examined. As shown in Figure 1, the Ca atoms are almost on top of and below the N atoms of the tricenter units. Thus, it could be that at least part of the band dispersion along c^*, which after all is the main underlying cause of the band overlap, results from the fact that the antibonding π_3 levels of the GeN_2 units interact not only through the direct Ge $p_z \cdots$ Ge p_z overlap between adjacent tricenter units but also throughout the Ca orbitals bridging two translationally equivalent units along c. Shown in Figure 2b is the band structure calculated for $(\square^{2+})_2GeN_2^{4-}$ with exactly the same structure and number of electrons as in Ca_2GeN_2 except for the fact that the Ca positions are empty. As can be seen, the band overlap also occurs in Figure 2b so that the Ca atoms are not really essential in creating it. The Ca atoms have a non-negligible participation in the bonding levels of Ca_2GeN_2 (see the density of states of Figure 3), but this participation affects levels slightly lower in energy than those implicated in the band overlap. In fact the contribution of the Ca orbitals at the Fermi level is very small. The Ca levels considerably push down a significant part of the filled levels of the GeN_2

network (compare the lower parts of panels a and b of Figure 2). Consequently, the contribution of the Ca atoms to the stability of the structure must occur not only throughout the electrostatic interactions with the electronegative nitrogen atoms but also through some contribution to the covalent bonding. The strongly Ca 4s- and 4p-based bands remain in the empty band region (not shown in Figure 3) so that the formal description of this material as being built from GeN_2^{4-} and Ca^{2+} is still a reasonable one, although, as our analysis shows, this ionic description should not be overemphasized.

The present results suggest that Ca_2GeN_2 is a pseudo-one-dimensional material and could well show a nonactivated conductivity. In view of the rich physics exhibited by many low-dimensional conductors, Ca_2GeN_2 is thus a potentially very interesting material.[20] Since it is well-known that DFT underestimates the band gap energies in semiconductors, only a measurement of the conductivity of Ca_2GeN_2 can definitely prove our suggestion. However, let us note that Ca_2GeN_2 is black whereas the isostructural Sr_2GeN_2, in which the Ge$\cdots$Ge nonbonded distance is noticeably larger (3.112 Å), seems to be not. Even if it cannot be ruled out that the differences in color may arise from surface impurities or defects, this observation could be taken as suggestive of the appropriateness of the present view of the electronic structure of Ca_2GeN_2. The Ca atoms are certainly not essential in leading to the dispersion of the π-type bands through overlap interactions and, consequently, are not directly responsible for the band overlap. However, the Ca atoms are indirectly responsible for this overlap because the electrostatic and partially covalent interactions in which they are implicated lead to the short nonbonded Ge$\cdots$Ge contacts conferring a strong dispersion to these bands and thus preparing the band overlap ultimately brought about by the interchain inter-actions. The larger Sr^{2+} cations lead to a larger separation between the successive GeN_2^{4-} units, something which could result in the loss of the band overlap and nonactivated conductivity. Indeed, our first-principles calculations (see Figure 2c) prove that there is a band gap at the Fermi level for Sr_2GeN_2 and, consequently, this material is predicted to be a semiconductor. Thus, the nature of the alkaline-earth atom does not have strong structural consequences but, in an indirect way, can be essential in determining the transport properties of this type of material. In conclusion, the present study suggests that the recently reported Ca_2GeN_2 phase[7] is a potentially very interesting low-dimensional solid which certainly calls for detailed physical characterization.

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