Band Calculation for the Hexagonal and FCC Chalcogenide Ge$_2$Sb$_2$Te$_5$

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Abstract—The paper addresses the calculation of the band structure for different phases of the chalcogenide Ge$_2$Sb$_2$Te$_5$ compound, which is raising considerable interest in view of the applications to the nonvolatile-memory technology. The band structure is necessary for determining the charge- and heat-transport properties of the material. The band diagram of the face-centered cubic phase, which is the most important one for the operation of phase-change memories, is shown for the first time.

I. Introduction

Charge- and heat-transport properties of the chalcogenide Ge$_2$Sb$_2$Te$_5$ (GST) material, suitably modeled for describing phase-change memory devices, are presently the main focus of a number of research activities geared toward the application of this material in nonvolatile-memory technology. The principle of chalcogenide memory was first proposed in the late 1960s by Ovshinsky who reported the observation of a reversible memory switching in chalcogenide materials [1]. In the last years, semiconductor industries have considered the exploitation of the same concept for large-size, solid-state, non-volatile memories, which nowadays seem to be very promising in terms of both performance and scalability perspectives. More recent papers deal with the general principle of switching in view of the application to rewritable optical media [2], [3], or with possible conduction models in view of the applications to memories [4], [5]. GST may be found in either crystalline or amorphous phase. The crystalline phase of GST has two possible structures: a stable hexagonal (HEX) structure and a metastable face-centered cubic (FCC) structure. However, since the metastable phase crystallizes faster, during a fast phase-change switching event involving the crystalline structure GST is always in the FCC phase [6], even though real structures exhibit some distortion.

Chalcogenide materials can act as semiconductors. For the case of GST, the crystalline gap has been evaluated from optical-absorption measurements to be 0.5 eV [4]. This result is confirmed in [7], where partial density-of-state results are shown for the rock-salt-like crystalline and amorphous phases.
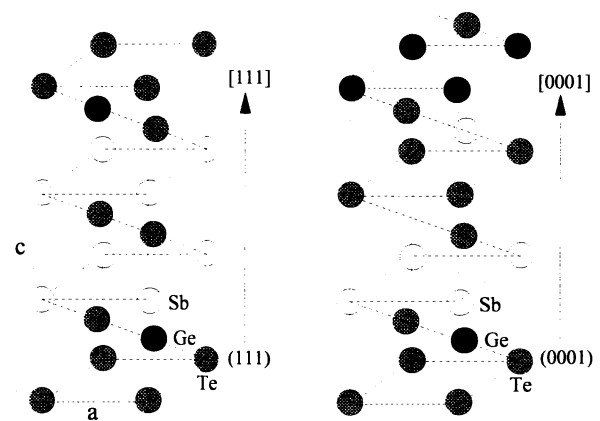

Fig. 1. Atomic arrangement of the hexagonal (left) and FCC (right) GST, showing the stacking sequence along the crystalline planes shown.

For investigating the transport properties of the material, including all the relevant scattering mechanisms, the information about the band structure is fundamental. So far, a few papers show detailed analyses of the band structure for the hexagonal GST (e.g., [8]). In contrast, no band diagrams for the FCC phase of GST have been published, at least in the authors' knowledge, despite the fact that such a phase is much more important for the device design, as mentioned above.

The calculation of the band structure of the FCC phase is substantially more complicated than that of the hexagonal phase because of the much larger number of atoms involved in the cubic stacking. The latter, in turn, is due to the movement of a sub unit of the hexagonal cell [9]. In this paper we address for the first time the calculation of the band structure of GST in the FCC phase.

II. Calculation Details

Most of the results shown in this paper have been calculated by means of the density-functional-theory (DFT) equations. The DFT calculations have been performed with the Quantum-ESPRESSO code [10] using the local-density approximation
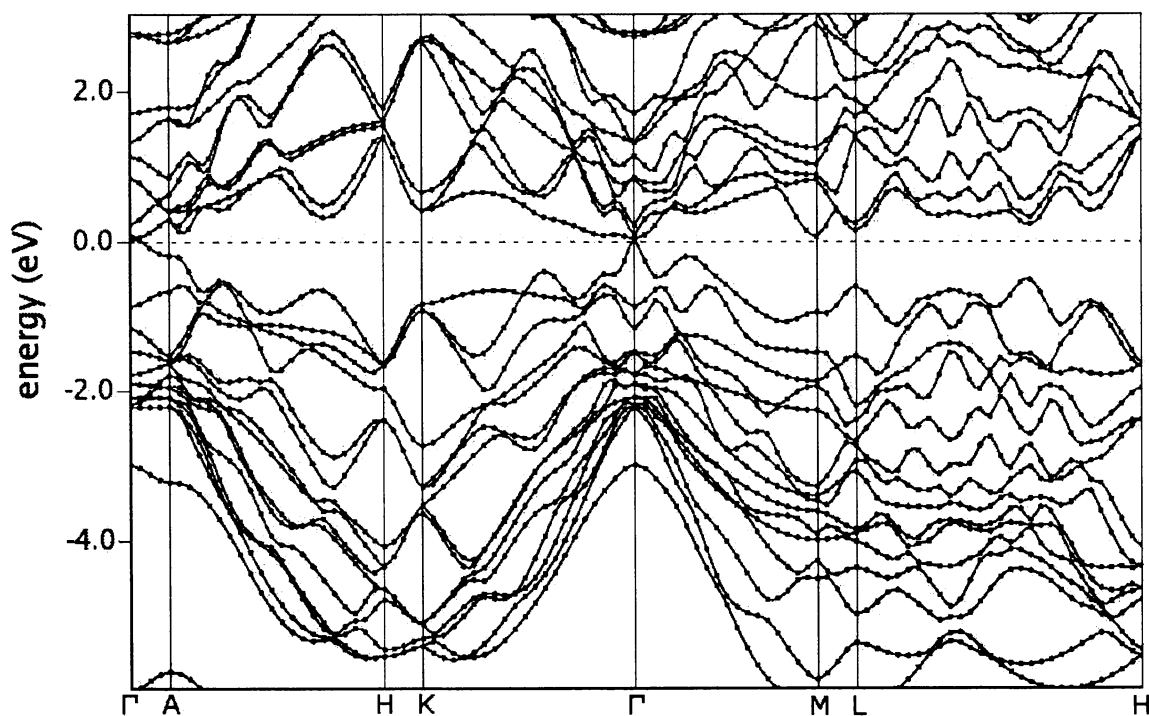
Fig. 2.   Band structure of the hexagonal phase in the first Brillouin zone for the top of the valence band and the bottom of the conduction band (the Fermi level is at 0 eV). The calculation has been carried out using the plane-wave basis set.

by Perdew and Zunger for the exchange-correlation energy functional. The electron-ion interaction is described by norm-conserving ionic Bachelet-Hamann-Schluter pseudopotentials available in public databases (e.g., [11] and references therein). The valence configurations are $4s^2 4p^2$, $5s^2 5p^3$, and $5s^2 5p^4$ for Ge, Sb, and Te, respectively. The scalar relativistic pseudopotentials are calculated without non-linear corrections.

In the plane-wave basis set used for the expansion of atomic orbitals, the cutoff in the kinetic energy was set to 80 Ry. In fact, this was a conservative choice: several preliminary tests showed that the changes in the results become irrelevant when the energy cutoff exceeds 40 Ry.

To check the consistency of the results a second approach has also been exploited, based on the Hartree-Fock method with a linear combination of atomic orbitals (LCAO). Specifically, Gaussian functions have been selected as basis set for the latter. These calculations have been carried out with CRYSTAL06 [12], featuring the restricted Hartree-Fock theory with LCAO. Periodic boundary conditions have been applied in both approaches.

Besides the need of checking consistency, another reason for using the Gaussian functions as basis set is that the computational load is expected to be smaller than in the plane-wave case.

III. RESULTS

A major issue concerning the band calculation is that of relaxation: the initial placement of the atoms within the unit
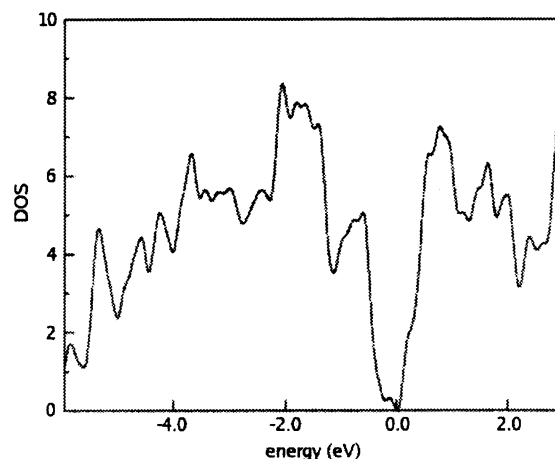

Fig. 3.   Density of states (DOS) calculated from the bands of Fig. 2.

cell, albeit taken from the available crystallographic data, does not coincide in general with the configuration of minimum energy of the structure. As a consequence, such a configuration must be sought by a preliminary calculation which is, typically, the most computationally demanding part of the analysis. On the other hand, if this step is skipped the calculated bands will not be realistic.

For checking purposes the calculations have been preliminarily been carried out on the hexagonal structure, using a unit

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cell with 9 atoms arranged in the same stacking sequence (Te − Ge − Te − Sb − Te − Te − Sb − Te − Ge) reported in [9] and shown in Fig. 1. After relaxation we have found a little shrinkage in the lattice parameters, $\Delta a \approx -1.5\%$, $\Delta c \approx -2.1\%$, consistently with the parametrization of the pseudopotentials used in the calculation. At the end of the relaxation stage, the internal planes of the unit cells are slightly shifted from their theoretical positions ($\Delta z < \pm 1\%$), still preserving their original space-group symmetry. The full calculation required one week on a 24-parallel processor Intel Xeon Linux cluster, most of it devoted to relaxation.

Figs. 2 and 3 show the band structure of the hexagonal phase in the first Brillouin zone, and the corresponding density of states, for the top of the valence band and the bottom of the conduction band (the Fermi level is at 0 eV). The actual calculation was performed over an energy interval larger than that shown. The results confirmed those of [8].

The LCAO method proved to be more efficient due to the smaller number of terms required to describe a localized system. On the other hand, the typical basis sets available from the software libraries were developed for the purpose of tackling single atoms or simple molecules, not crystals; hence they exhibit a number of Gaussian functions of the diffused type (namely, having a very large standard deviation). As a consequence, a direct introduction of such basis sets into an analysis code for band calculation does not provide realistic results, and in most cases prevents convergence as well.

The calculation for the case of interest was carried after a large number of numerical experiments, in which the diffused parts of the single-atom basis sets have been removed and the coefficients of the remaining parts have been optimized to reproduce the plane-wave results. The experiments were carried out by introducing the new basis sets into CRYSTAL06.

This part of the work eventually provided an LCAO basis set able to reproduce the band shape calculated with the plane waves. The dimensional variation of the unit cell from the experimental values is analogous to the one determined with the other method. Moreover, in contrast with the outcome of the plane-wave method, the output of the second calculation demonstrates the existence of a band gap for this material. This is in qualitative agreement with the optically-determined data of [13], even though band gaps determined by Hartree-Fock calculations tend to be overestimated (opposite to what is usually obtained by means of DFT equations [14]). The bands thus calculated are shown in Fig. 4; the corresponding density of states does not differ significantly with respect to that shown Fig. 3. The total calculation time was reduced to less than two days.

Finally, the same procedure depicted above has been repeated for the FCC phase. Following the findings of [9], the FCC structure can be built starting from the hexagonal phase by translating the Te − Sb − Te − Ge sub-unit along the [210] direction to create a vacancy site. As a consequence, the FCC cell is composed of 27 atoms and 3 vacancies, this resulting in a computational burden substantially larger than that of the hexagonal phase (about four times).
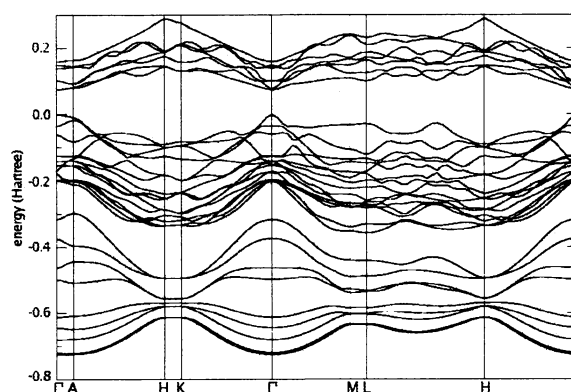

Fig. 4. Same bands as in Fig. 2 calculated using the Hartree-Fock method with LCAO.

After relaxation, the lattice is a distorted FCC cell with internal planes deviating from their theoretical positions. The amounts of the deviations and of the cell vectors are comparable with those of the hexagonal cell, never exceeding 2%.

Fig. 5 shows the density of states for the FCC phase calculated with the plane-wave method. The band structure in the first Brillouin zone is shown in Fig. 6. In the figures only the top of the valence band and the bottom of the conduction band are shown. As expected from the experimental findings of [13], an indirect gap of about 0.1 eV for the FCC phase is found. The transition from the hexagonal to the FCC phase implies the introduction of some degree of disorder in the lattice, e.g., a number of vacancy sites, making the band gap to increase. Even though DFT calculations fail in determining the exact value of the band gap, the method is reliable in reproducing trends like a band-gap increase or decrease. Such a trend is also consistent with the experimental value of the band gap of the amorphous phase of the same material, which is 0.7 eV instead of 0.5 eV as in the crystalline phases.

It is worth noting that, except for the above considerations about the band gap, the overall shape of the valence band found in the hexagonal phase is conserved in the FCC struc-
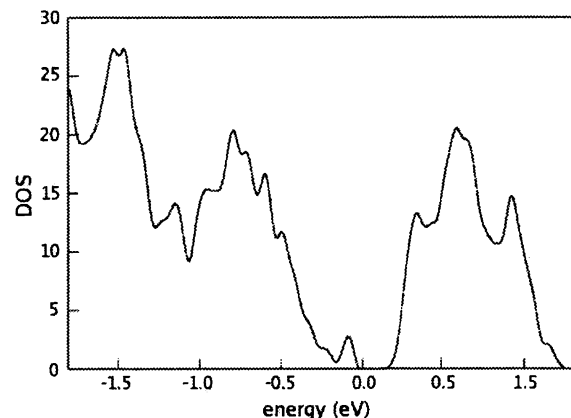

Fig. 5. Density of states (DOS) calculated from the bands of Fig. 6.
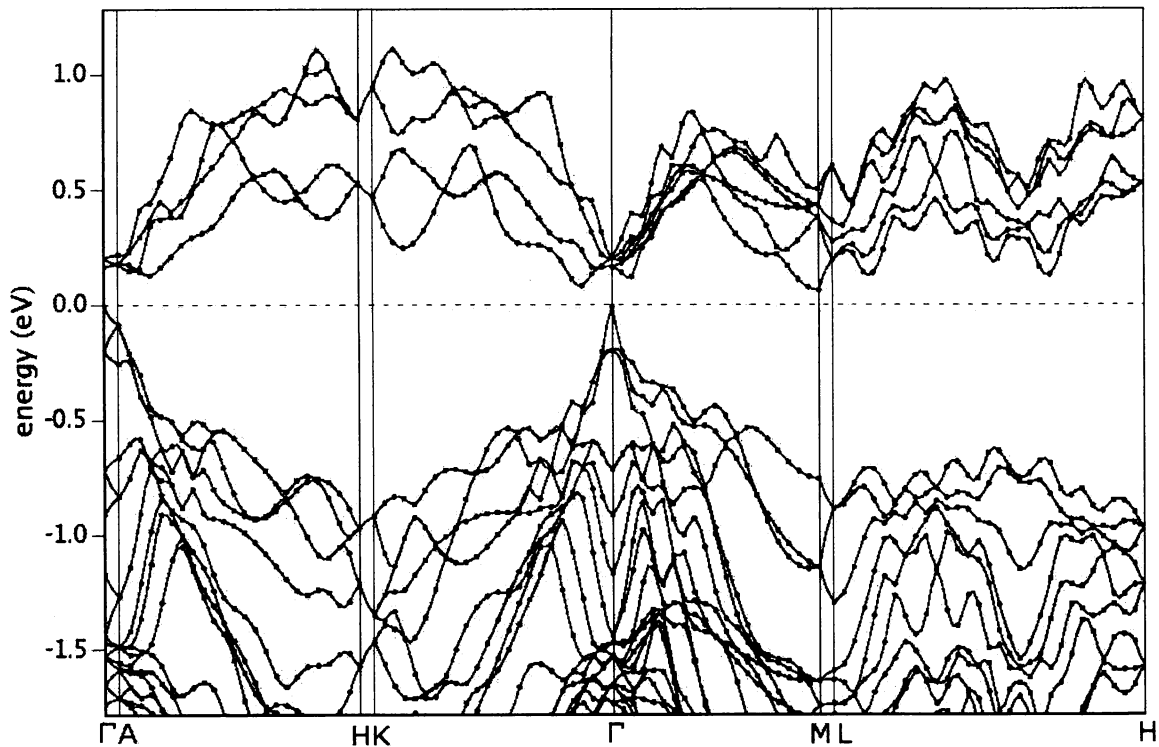
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Fig. 6. Band structure of the FCC phase in the first Brillouin zone for the top of the valence band and the bottom of the conduction band (the Fermi level is at 0 eV).

ture, as also shown by the comparison of the two densities of states. The same main peaks can be recognized in both plots; a more detailed inspection shows that the shape of the valence band in the FCC phase is broader than in the hexagonal phase, which, on the contrary, has sharper peaks and a more pronounced fall towards the core levels (this happens in an energy range not reported in Fig. 5).

In contrast to the case of the hexagonal cell, the use of the Hartree-Fock and LCAO methods, along with the basis set optimized in the previous case did not improve the calculations in a satisfactory way. The obtained band diagram qualitatively confirms the findings of the plane-wave method, but the details of the bands are poorer. Further calculations with a differently-optimized basis set, including a higher number of Gaussian functions, seems necessary to obtain a better representation. This, however, increases the computational burden significantly and prevents an overall speed-up of the simulation, whose duration becomes comparable with that of the plane-wave method.

IV. CONCLUSION

The band structure of the hexagonal and (for the first time) FCC phases of chalcogenide $Ge_2Sb_2Te_5$ have been calculated by means of the DFT method using plane waves. To implement the analogous calculation based on the LCAO method, which is expected to be computationally more efficient, a number of new basis sets (one for each chemical species involved)

have been derived and optimized. The procedure worked well for the hexagonal phase and the time needed to complete the computation was reduced to one third. The simulations carried out on the FCC case show that a different set of optimized Gaussian functions is necessary to achieve the same computational improvements. The band structure of the hexagonal and FCC phases of the chalcogenide $Ge_2Sb_2Te_5$ obtained from this investigation will constitute the basis for the analysis of the transport properties of the material.

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