JUGENE unravels Structures in Phase Change Materials

Phase change (PC) materials remain leading candidates for future computer Random Access Memory (RAM) and rewritable storage devices (CD-RW, DVD-RW, DVD-RAM, and Blu-ray Disc, BD). The battle to replace the de facto standard of optical recording materials, the Digital Versatile Disk (DVD), was decided in 2008 in favour of Blu-ray Disc, and the recording media of all BD products involve PC materials. Many readers will know that laser light is involved, but not all know how the information is recorded, read, and erased.

Information is stored in these devices in the form of microscopic bits (each less than 100 nanometers in size) in a thin layer of a polycrystalline alloy containing several elements. The bits can have a disordered (amorphous) or an ordered (crystalline) structure.

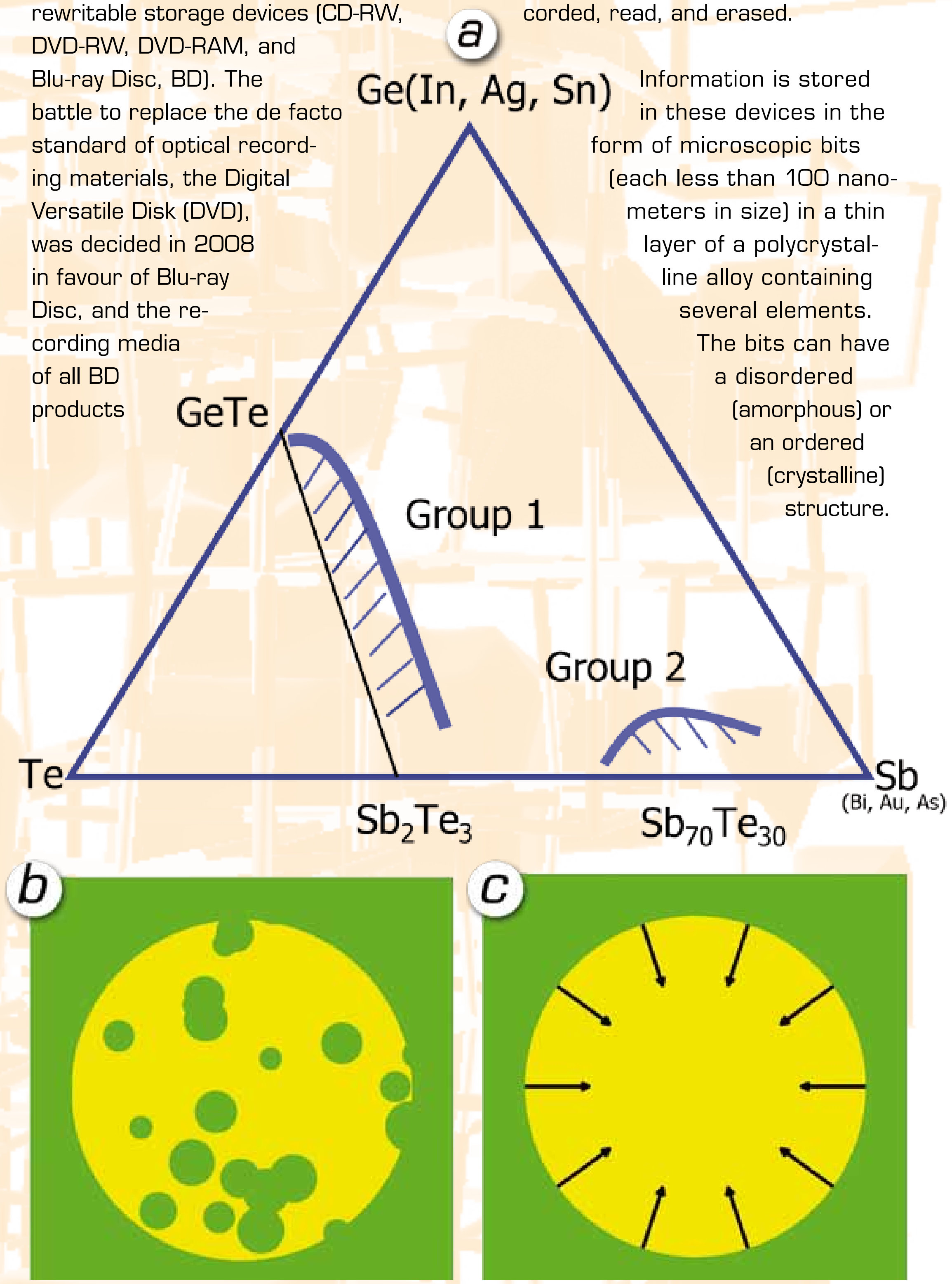


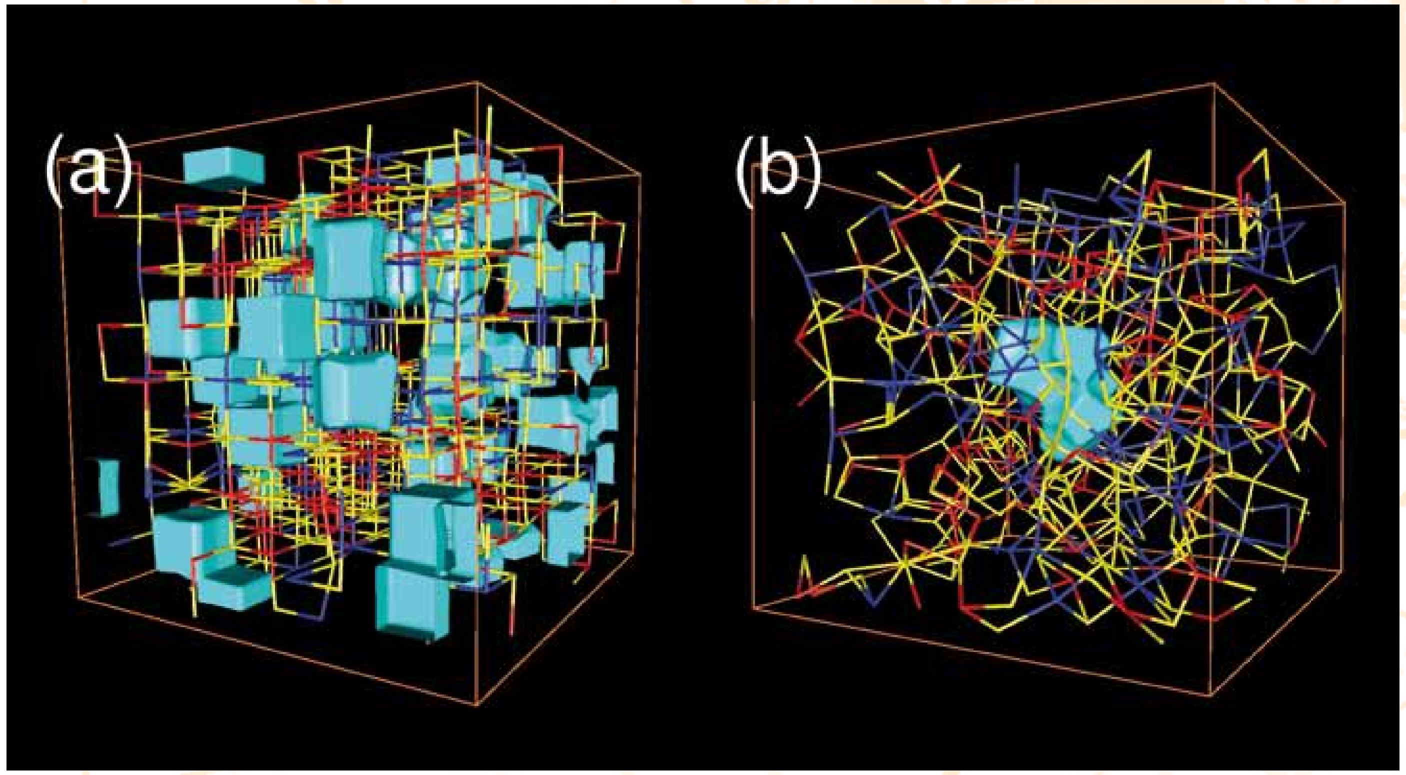
Figure 1: Phase diagram of PC materials and crystallization patterns. (a) The most commonly used materials for optical recording are in Groups 1 and 2, (b) Nucleation-dominated growth recrystallization (as in GST), (c) Growth-dominated recrystallization (as in AIST).

The transition between the two phases is not only extremely rapid (some tens of nanoseconds), but it is reversible. Amorphous bits are formed by quenching after a localized and short (~ 1 ns) pulse to above the melting temperature. Longer laser heating (of the order of 10 ns) to above the glass transition but below the melting point returns the bit to a metastable crystalline form. The state can be identified by monitoring the optical or electrical properties.

The physical requirements of PC materials, particularly the rapid crystallization, are satisfied by relatively few materials. The focus for some years now has been on alloys of three or four elements, many of which contain germanium (Ge), antimony (Sb) and tellurium (Te), and are referred to as "GST alloys" (Fig. 1a). Alloys along the line connecting GeTe and Sb_2Te_3 (Group 1) are common PC materials, particularly $Ge_2Sb_2Te_5$, which is used in DVD-RAM, and alloys near the GeTe end, which are favoured in BD applications. Also shown in Figure 1 are alloys near Sb (70%) and Te (30%) (Group 2). With small amounts of silver (Ag) and indium (In), "AIST" alloys are in widespread use in DVD-RW devices. Although both alloy families contain antimony and tellurium and appear to have much in common, the phase change mechanisms are very different. In GST materials, the amorphous bit crystallizes via nucleation, i.e. small crystallites formed in the interior grow rapidly until they cover the whole bit (Fig. 1b). The phase change in AIST alloys proceeds from the outside of the bit, where it adjoins the crystalline surroundings, towards its interior (Fig. 1c).

Materials in both groups have superior rewrite speeds and are stable at room temperature for long periods, indispensable characteristics of PC memories.

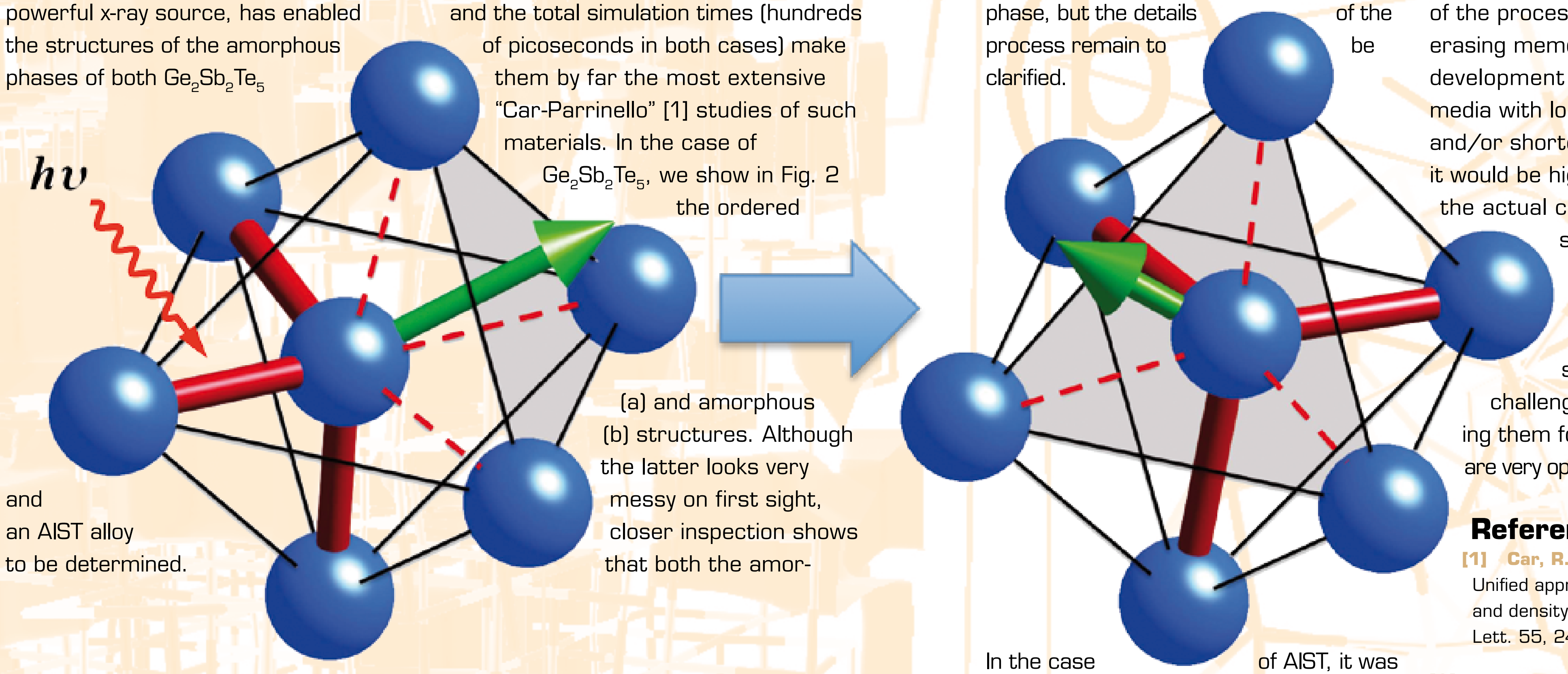
Figure 2: The simulation of 460 atoms and 52 vacancies in (a) crystalline GST and (b) amorphous GST. Red: Ge, blue: Sb, yellow: Te. Cavities are shown as light blue isosurfaces. A single large cavity is one of numerous cavities in a-GST.



Until recently, however, there was little understanding of the crucial - and rate-limiting - crystallization process and no convincing explanation for its astonishing rapidity. The combination of extensive simulations on the Jülich supercomputer JUGENE with new experimental data and x-ray spectra from the Japanese synchrotron SPring-8, the world's most powerful x-ray source, has enabled the structures of the amorphous phases of both $Ge_2Sb_2Te_5$ and an AIST alloy to be determined.

It has been possible in both cases to develop models that explain the rapid phase change.

The calculations involved density functional simulations of the cooling process from a high-temperature liquid down to room temperature, and the number of atoms in the unit cell (460 in GST, 640 in AIST) and the total simulation times (hundreds of picoseconds in both cases) make them by far the most extensive “Car-Parrinello” [1] studies of such materials. In the case of $Ge_2Sb_2Te_5$, we show in Fig. 2 the ordered (a) and amorphous (b) structures. Although the latter looks very messy on first sight, closer inspection shows that both the amorphous and crystalline phases contain the same structural units, “ABAB” rings. These four-membered rings contain two germanium or antimony atoms (A) and two tellurium atoms (B) and can rearrange in the available empty space without breaking many atomic bonds. This observation is consistent with the very rapid crystallization of the amorphous phase, but the details of the process remain to be clarified.



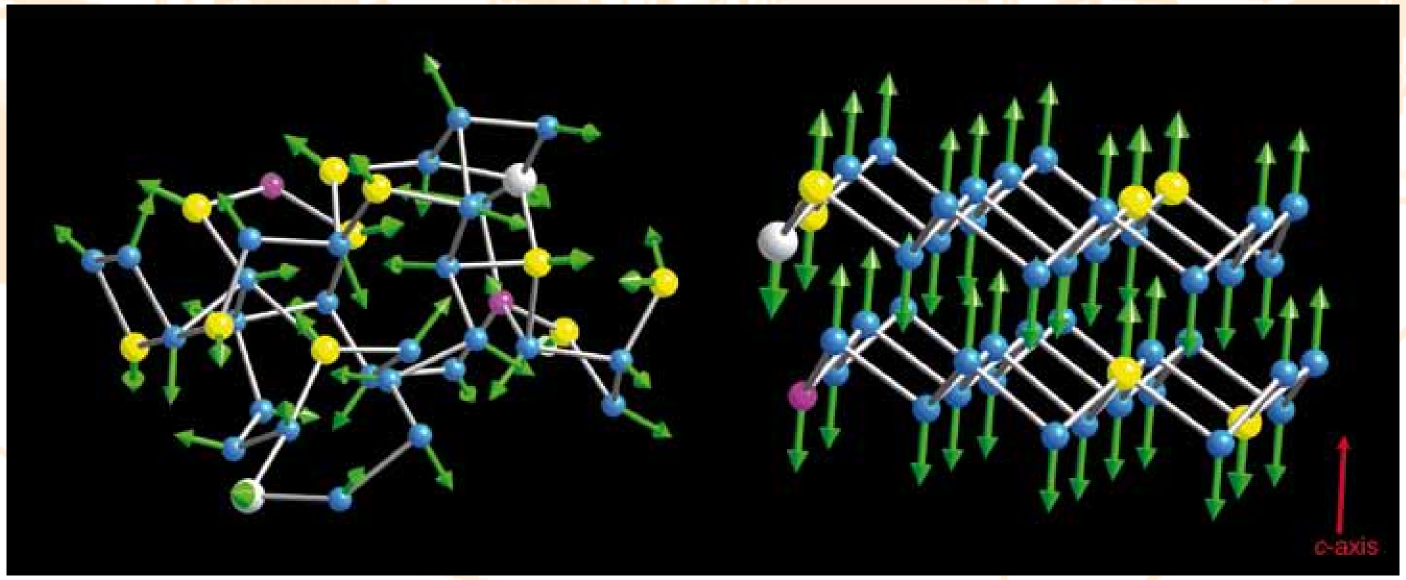


Figure 3: Model of crystallization of an AIST alloy. Upper left: a laser pulse (hv arrow) causes motion of the central antimony atom (left), which then exchanges its bonds to two neighbours. Upper right: The green vector sum of the three short red bonds changes.
Below: A sequence of such processes leads from the amorphous (left) to the crystalline form (right).

In the case of AIST, it was possible to determine a structure of the amorphous phase that reproduced the x-ray scattering data of our Japanese colleagues [3].

In conjunction with the known structure of the crystalline phase, this has again allowed us to propose a model for the crystallization process (Fig. 3). In this “bond exchange model”, the local environment in the amorphous bit is changed by small movements of an antimony atom (see Fig. 3, above) that result in the exchange of a short and a long bond. A sequence or avalanche of many such steps results in reorientation (crystallization), without requiring large atomic motions or the empty regions that were present in GST, but are absent here. The antimony atoms, stimulated by the laser pulse, have simply exchanged the strengths of the bonds to two neighbours.

The deeper theoretical understanding of the processes involved in writing and erasing memory devices should aid the development of phase change storage media with longer life, larger capacity, and/or shorter access times. Naturally it would be highly desirable to simulate the actual crystallization process and see whether these models are more than just plausible explanations. The time scale involved makes such calculations extremely challenging, but we are performing them for GST at the moment and are very optimistic about the prospects.

References

[1] Car, R., Parrinello, M.
Unified approach for molecular dynamics and density functional theory, Phys. Rev. Lett. 55, 2471 (1985)

[2] Akola, J., Jones, R. O., Kohara, S., Kimura, S., Kobayashi, K., Takata, M., Matsunaga, T., Kojima, R., Yamada, N.
Experimentally constrained density-functional calculations of the amorphous structure of the prototypical phase-change material $Ge_2Sb_2Te_5$, Phys. Rev. B 80, 020201(R) (2009)

[3] Matsunaga, T., Akola, J., Kohara, S., Honma, T., Kobayashi, K., Ikenaga, E., Jones, R. O., Yamada, N., Takata, M., Kojima, R.
From local structure to nanosecond recrystallization dynamics in AgInSbTe phase change materials, Nature Materials 10, 129 (2011)

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