

***Ab initio* molecular-dynamics (AIMD) simulations of homogeneous and heterogeneous crystallization in phase-change memory materials: *in silico* design?**

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Abstract

Existing phase-change (PC) materials, such as Ge-Sb-Te compounds, have so far been developed empirically. We present the first design, *in silico*, of a simulated new PC material, whose (cubic) crystal structure, and electrical-resistivity level, has been predetermined. Heterogeneous crystallization of PC memory cells has been reproduced by *ab initio* molecular-dynamics simulation for the first time. We show how an optimal choice of cell boundaries can drastically speed up crystallization and enhance resistivity contrast. This optimization method opens up a yet-unexplored dimension of the study of PC materials. The present computational approach offers a route for the efficient discovery of ultrafast PC memory materials that could even replace DRAM.

One possible replacement random-access memory (RAM) technology involves phase-change (PC) materials¹, which can reversibly and rapidly be transformed between high-resistance amorphous and low-resistance crystalline states by Joule heating via imposed current pulses, thereby recording binary bits of information. PC memory has the following advantages: sub-25nm size scalability, 10ns read/write speeds, 10⁸ cyclability, multilevel (e.g. 4-bit) memory-cell programming capability, low-power operation and radiation hardness. Unsolved scientific problems relating to PCRAM operation include: why is the crystallization so fast; what is the origin of the resistivity contrast between amorphous and crystalline states; what is the origin of the threshold-voltage switching effect needed to give enough Joule-heating current in the amorphous phase to crystallize it; what is the origin of the multilevel resistance states in the amorphous state (allowing multibit storage per cell); and is there a lower device-size scaling limit to efficient PC operation? In addition, several unsolved technological problems that can hinder further device optimization include: how can crystallization be speeded up even more; how can (chemical) phase separation be prevented from occurring on repeated cycling; and what is the origin of the temporal resistance drift in the amorphous state (limiting multilevel memory storage)?

Although the current crystallization speed of PC materials is fast enough (tens of ns) for them to be used as a replacement for NOR and/or NAND non-volatile flash-memory technology, such switch-ing times are not fast enough for them to replace volatile DRAM, where switching times of 1.5ns or less are needed². However, if ultrafast, non-volatile PCRAM could replace DRAM, this would open up possibilities of completely new computer architectures.

So far, PC-material development essentially has been an empirical process, involving the chance discovery of materials with promising behaviour, rather than systematic *de novo* materials design and synthesis, although a recent roadmap for materials optimization has been proposed³. Most PC memory materials investigated to date have been Ge-Sb-Te (GST) compounds, of which Ge₂Sb₂Te₅ (225) is probably the most studied. These materials crystallize into a metastable rocksalt structure (containing vacancies on the (Ge,Sb) sub-lattice) under the switching conditions pertaining to PCRAM operation^{4,5}. The

structural simplicity of this crystal phase (i.e. octahedral coordination of all atoms) facilitates the very rapid (~ns) crystallization observed in these materials, i.e. minimal atomic motion is needed to transform from the amorphous to the crystalline phase. Moreover, this (defective) octahedral local coordination of the metastable rocksalt structure has been associated with the resonant bonding (presumed to be absent in the amorphous phase) that has been proposed to be responsible for the low-resistance (metallic) state of the crystal⁶.

Although GST materials have been much studied for PCRAM applications, nevertheless there are problems with these materials, e.g. the desire to keep Te out of Si-CMOS fabrication lines used to make the supporting electronics or CPU circuitry^{7, 8}. Thus, IBM has been investigating the possibility of using Ge-Sb (GS) alloys for PCRAM applications^{7, 9}. However, GS behaves very differently from GST materials: crystal nucleation is heterogeneous (i.e. crystallization is growth-limited¹⁰), whereas nucleation in GST is homogeneous¹¹. Moreover, the GS crystallization product, formed even under rapid PCRAM device-switching conditions, is based on the stable rhombohedral A7 Sb structure⁷, not the metastable rocksalt phase characteristic of GST^{4, 5}. Finally, there is evidence for phase separation, into Sb and Ge crystalline products, upon repeated PC cycling in eutectic GS⁷ (and GST alloys), which so far has precluded the replacement of flash memory by PC technology.

It was recently reported that boundary effects and heterogeneous nucleation crucially influence device behaviour in nano-sized PC cells¹²⁻¹⁴. Although several computational studies¹⁵⁻²³ have been carried out in order to elucidate the microscopic mechanism involved in phase-change transformations, no study has yet investigated boundary effects or heterogeneous nucleation. Here, we present the first such atomistic simulation study and demonstrate the *in silico* design of a new type of interface boundary which dramatically enhances PCRAM device performance, i.e. crystallization speed and resistivity contrast.

In order to improve the PCRAM behaviour, e.g. of GS alloys, we have aimed to design new materials *in silico*, by directing the metastable crystallization product to a favourable form (e.g. the rocksalt structure), not normally produced under existing experimental conditions^{9, 12}, by means of an epitaxial templating procedure (changing the interface boundary around the PC cell). This demonstration has been achieved by performing *ab initio* molecular-dynamics (AIMD) simulations using the VASP code²⁴, in which the simulated crystallization of Sb and of the eutectic GS composition, Sb₈₅Ge₁₅, has been controlled by means of different crystal templates placed in the simulation box. Since the thickness of the simulated PC device (2 nm) and the smallest dimension of a real device (3 nm)⁹ are comparable, atomistic simulations become a reliable tool, which can predict the behaviour of newly designed PC materials and interfaces on time-scales comparable to experiment. Furthermore, MD simulations can give a deep microscopic insight into phase-change processes. In a simulation box with periodic boundary conditions (and no templates), simulated melts of Sb and the GS alloy were found *not* to crystallize at 600 K in 90-200 ps-long annealing runs. In simulations mimicking the growth-limited, heterogeneously-nucleated crystallization observed experimentally¹² in GS alloys, template layers, having the A7 rhombohedral structure, were placed in the simulation box. Melts of pure Sb, with one or two A7 template layers, crystallized to the A7 structure in 30-50 ps (Figs. 1a,b). A melt of eutectic GS, templated with 2 Sb A7 layers, also (partially) crystallized to the A7 structure on the same time-scale (Fig. 1c). There is some evidence, from the time-evolution plots (Figs. 1a,b)) of layer formation (in the $(x-y)$ plane parallel to the template layers), that another (cubic-like) layer spacing very rapidly forms before the model finally crystallizes into the A7 structure.

However, directed crystallization to a new metastable phase, not previously reported experimentally for GS, was achieved in a simulation in which a *cubic* template of Sb was placed in the simulation box. In this case, the GS melt crystallized to the rocksalt structure, in epitaxy with the template, with the Ge atoms being apparently distributed rather randomly (Fig. 2a). A cubic-templated melt of pure Sb similarly crystallized to the metastable rocksalt phase (Fig. 2b). In both cases, the time-scale of crystallization to the cubic phase was significantly *shorter* than to the equilibrium A7 phase, taking place in only about 10 ps for the eutectic GS alloy (Fig. 2a). Under normal experimental conditions, the cubic phase of Sb is only stable at high pressure²⁵, although there have been reports that metastable thin films of Sb can grow in the cubic phase under certain conditions^{26,27}.

Although this new rocksalt GS phase has very advantageous properties relative to the A7 phase, it would not be feasible experimentally to use this cubic phase itself as a templating layer in real PC-RAM devices: the template layer of GS would invariably be the stable A7 form, and anyway it would be likely to melt along with the PCRAM cell itself. However, materials other than GS, but with the rocksalt structure and a matching lattice spacing, could in principle also act as epitaxial crystallization templates. We have noted, for example, that the stable crystalline phases of SrS and SrSe have the rocksalt structure with almost the same lattice parameter ($a = 6.024 \text{ \AA}$ and 6.236 \AA , respectively²⁸) as twice that of the metastable rocksalt phase of pure Sb ($a = 3.07 \text{ \AA}$ ²⁶, 3.16 \AA ²⁷). These materials also have the advantage that they are extremely refractory, having melting points ($>2000^\circ\text{C}$ and 1600°C , respectively) greatly in excess of the eutectic temperature ($\sim 600^\circ\text{C}$ ²⁹) for $\text{Sb}_{85}\text{Ge}_{15}$; therefore epitaxial templates made of them should survive repeated PC cycling of the GS material, even via the GS melt.

It was found that, indeed, a template of SrSe in the simulation box also caused simulated crystallization of the eutectic GS melt to the rocksalt phase in a comparable time to that when cubic Sb was used as a template (Fig. 3). However, in this case, the crystallized GS rocksalt product does not grow in exact epitaxy with the SrSe template; instead, the atoms in the first crystallized GS layer are displaced by a small constant lateral amount from the Sr and Se atoms in the template (Fig. 3). Further simulation of the SrSe-GS crystal-liquid interface showed that, while the GS is melting, the SrSe crystal template remains intact, even at 1800 K. It is of interest to note that it has recently been shown that GaSb can act as a crystallization template to produce cubic GST³⁰. Since the lattice constants of cubic Sb^{26, 27} and cubic GST^{4, 5} are close (about 3% difference), it is not unreasonable to expect that GaSb could also be used as a template to produce cubic Sb/GS. However, since the melting point of GaSb is 709°C , only about 100K above that of GS, it is likely to be unsuitable as a template for PC cycling of GS (or Sb) between crystalline and amorphous states via the melt.

Estimates for the time scale for (templated) crystallization in these simulated models can be obtained more accurately by calculating the fraction of atoms closer to final crystalline lattice planes than a given distance (e.g. 0.4 \AA); this quantity is plotted in Fig. 4a as a function of time. This analysis clearly shows that, all other things being equal (viz number of template layers, size of models, annealing temperature = 600K), cubic GS (or Sb) crystallizes much faster (in about 10 ps) than the rhombohedral A7 structure. Moreover, there is a subtle difference in crystallization-ordering behaviour in layers parallel and perpendicular to the templating layers: perhaps not too surprisingly, Fourier analysis of the atomic positions shows that structural ordering in layers *parallel* to the template layer takes place more quickly than for layers *perpendicular* to the template, for crystallization to the cubic phase (Fig. 4b).

This new metastable, templated rocksalt structure for the GS alloy exhibits two significant improvements in PC behaviour with respect to the normal A7 phase. First, its crystallization speed from the melt is much faster. Simulated cubic crystallization of GS in a supercell of width ~ 20 Å (Figs. 2a, 3), templated on both sides, occurs in ~ 10 ps. Extrapolated to the case of crystallization of a 25 nm-width actual PCRAM cell⁹, (templated on both sides), the rocksalt crystallization time is predicted to be 0.125 ns, very significantly faster than current fastest experimental switching times⁹ of the order of tens of nanoseconds. Such an ultrafast crystallization speed would permit the replacement of DRAM memory by PC-memory technology.

Another important operational characteristic of PCRAM materials is the contrast in electrical resistance between amorphous and crystal phases: a large contrast in electrical conductivity allows for multilevel-memory operation. Fig. 5 shows the calculated electronic densities of states (EDOS) for Sb in the rocksalt and A7 rhombohedral phases. The EDOS curves for the quenched cubic and A7 phases of Sb are in very good agreement with those calculated by Kresse *et al.*²⁵. It can be seen that the rocksalt phase exhibits the largest EDOS at the Fermi level, $g(E_F)$, implying that the cubic phase would exhibit an even larger electronic conductivity than the A7 phase currently being studied experimentally^{9, 12}, since the electronic conductivity of metallic materials depends on $g(E_F)$. Such behaviour is commensurate with an expected increase in resonant bonding associated with the octahedral coordination characteristic of the rocksalt structure, compared with its reduction due to the Peierls distortion associated with the A7 structure and its assumed absence in the amorphous phase⁶.

In conclusion, we have demonstrated the first *in silico* design of a new, improved phase-change memory material, namely $Sb_{85}Ge_{15}$ and Sb having the metastable rocksalt structure. *Ab initio* molecular-dynamics simulations have shown that these materials crystallize to this new phase (having improved PC properties) when grown in contact with a suitable epitaxial template material, e.g. SrSe. It can be inferred that the reason why crystallization to the metastable cubic form is so much faster than to the A7 form in Sb or GS (Fig. 4a) is because the octahedral local bonding geometry, characteristic of the simple cubic structure, is already present in the amorphous phase. This generic simulational method for materials discovery can be extended to other systems in order to design phase-change materials with much improved behaviour (e.g. ultrafast crystallization), and opens the way for phase-change memory technology to replace even DRAM memory for non-volatile memory applications.

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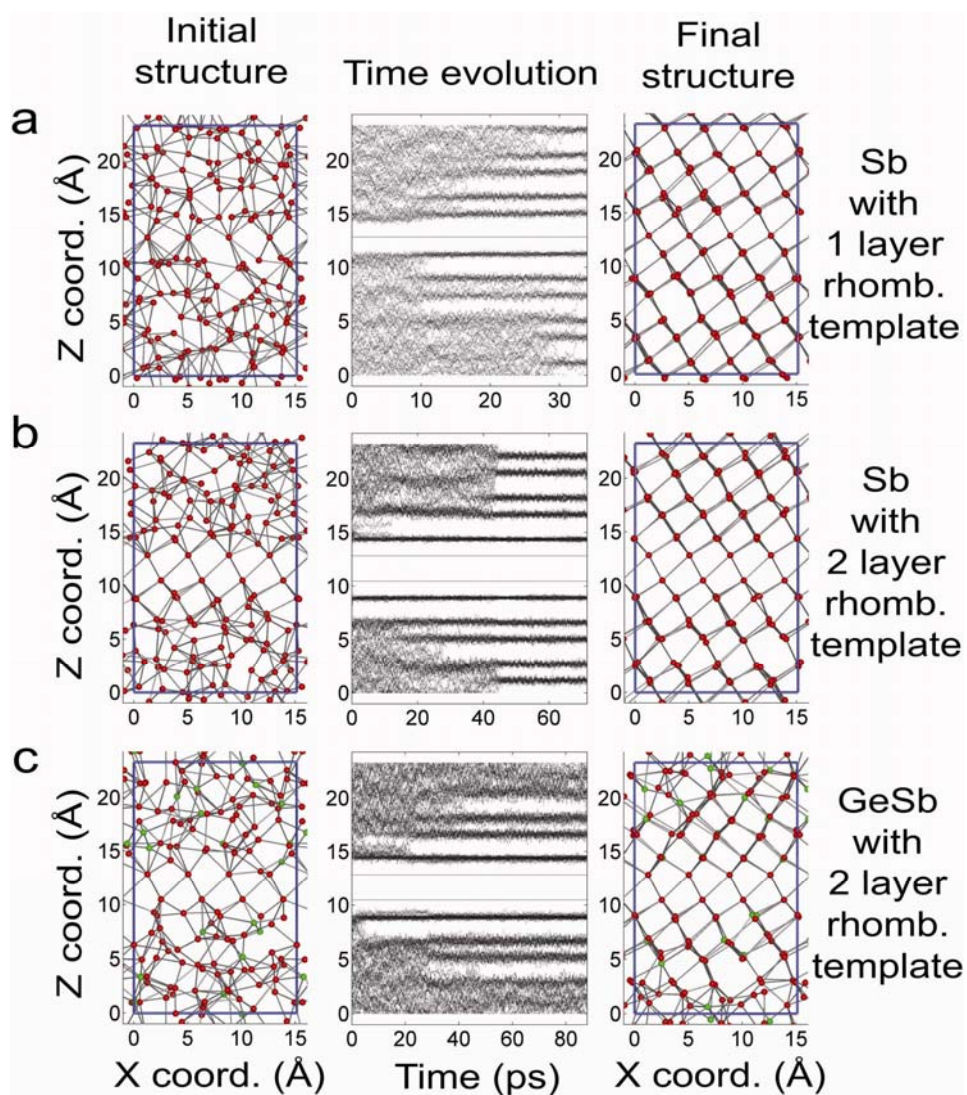


Fig. 1 Simulation of the templated crystallization to the A7 rhomb-ohedral Sb structure. Two 144-atom models of Sb with one (a) and two (b) template layers were used, and a third 144-atom model (c) with the composition $\text{Sb}_{85}\text{Ge}_{15}$. The left-hand panel is a projection of the model, onto the (x - z) plane, of the atomic coordinates of the starting configuration – a liquid equilibrated at $T > 2500$ K. At $t = 1$ ps, the temperature is lowered to 600 K, and the system evolves isothermally. The middle panel shows the time evolution of the z -coordinate of the atomic positions. The right-hand panel shows the final (crystalline) structure. The template is shown as a continuous line in the time-evolution plot. The template configurations were: (a) 1 Sb A7 layer; (b) 2 Sb A7 layers; (c) 2 Sb A7 layers. The GS melt (c) did not crystallize completely.

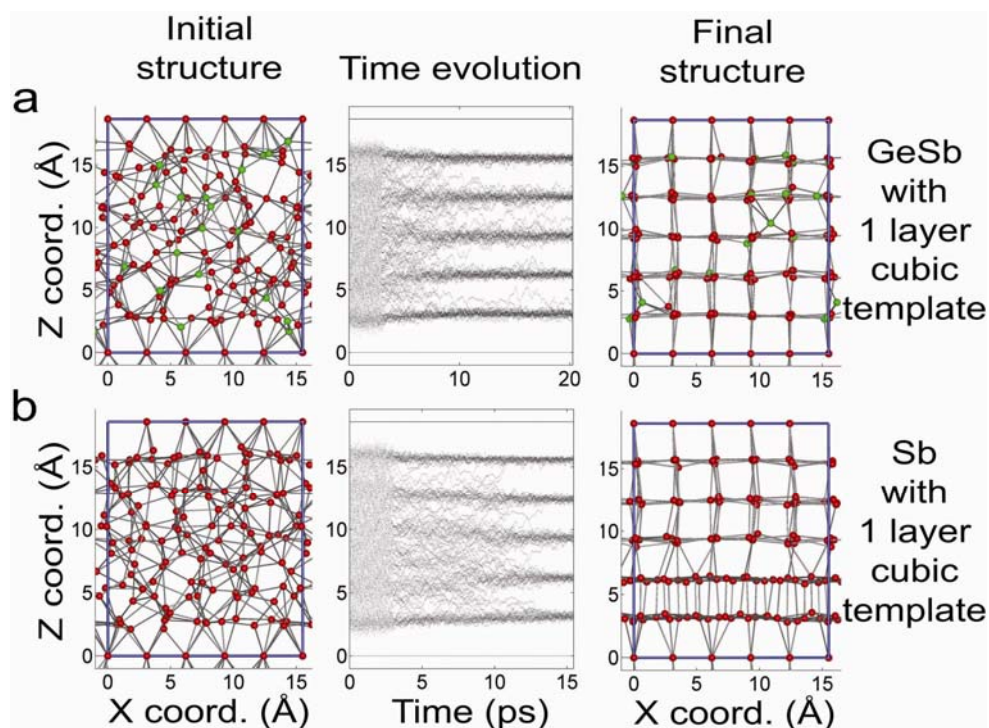


Fig. 2 Simulation of the templated crystallization to the metastable rocksalt structure. The models consist of 150 atoms of (a) $\text{Sb}_{85}\text{Ge}_{15}$ (Ge atoms in green) and (b) Sb. The 3 panels correspond to those in Fig. 1, and 1 cubic Sb template layer was used (at the edge of the simulation box, at $z=0$ Å). In (b), 2 crystal grains have grown, rotated about the z -axis. In the first 3 ps of the simulations, a liquid phase was equilibrated (> 2000 K) to randomize the atomic positions; the temperature was then lowered instantaneously to $T=600$ K.

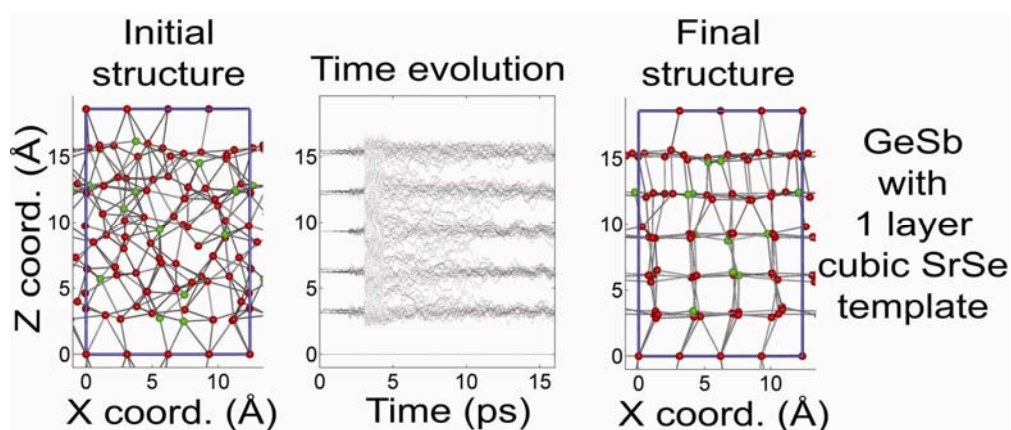


Figure 3 Simulation of the crystallization to the rocksalt structure of $\text{Sb}_{85}\text{Ge}_{15}$ using 1 template of SrSe. The 3 panels are as in Figs. 1 and 2. The SrSe template is placed at the edge of the simulation box, at $z=0$ Å. The starting configuration was the crystal phase (equilibrated at 50K for 2 ps, from $t=0$ to 2ps). This was then heated to 600 K for the next 1 ps. The crystal was then melted at 3600 K for 1.5 ps prior to being reduced to 600 K for the isothermal crystallization run. The left panel shows the atomic configuration just after annealing at 3600 K ($t=4.5$ ps).

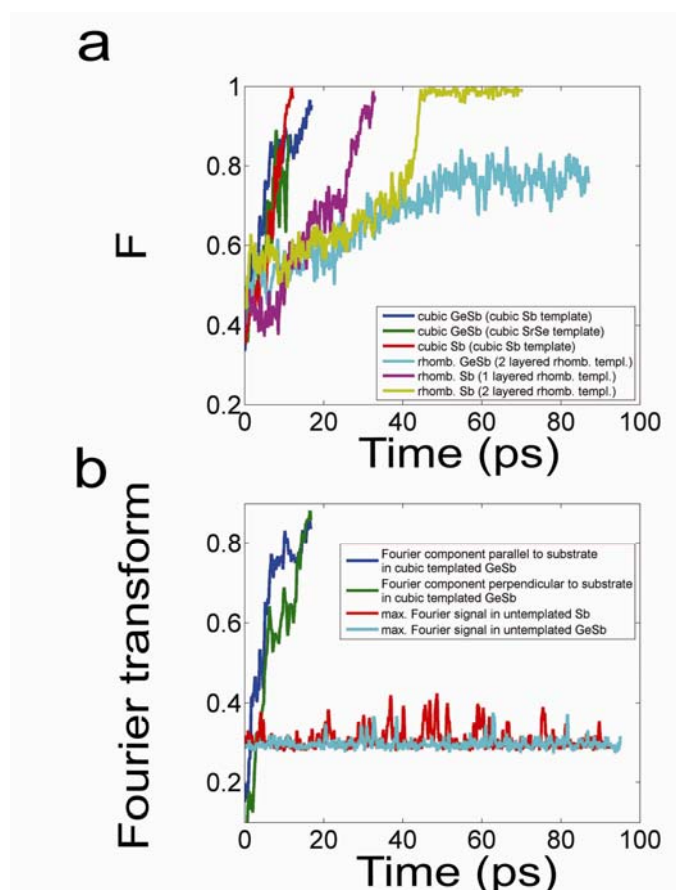


Fig. 4 Time evolution of crystallization of models of Sb and $\text{Sb}_{85}\text{Ge}_{15}$: **(a)** proportion, F , of atoms lying near lattice planes, showing that crystallization to the cubic form is considerably faster than to the A7 rhombohedral form; **(b)** 3D Fourier transforms of atomic positions; untemplated runs did not crystallize on times considerably longer than for cubic-templated models to crystallize.

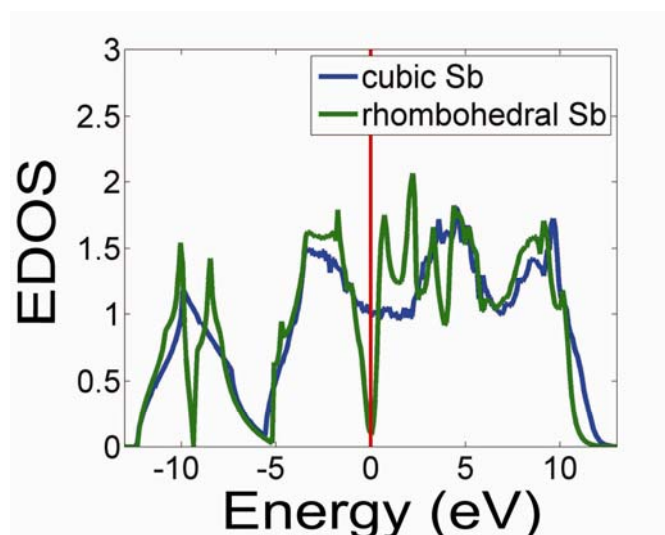


Fig. 5 Electronic densities of states for the cubic and A7 (rhombohedral) Sb structures. An increased conductivity of the cubic phase, as compared to that of the A7 phase, is predicted by the higher density of states at the Fermi level (red line).