Comment on "Formation of Large Voids in the Amorphous Phase-Change Memory $Ge_2Sb_2Te_5$ Alloy"

Sun *et al.* [1] have performed *ab initio* molecular dynamics simulations on amorphous and liquid $Ge_2Sb_2Te_5$ (GST) and proposed that very large voids play an important role in the fast reversible phase transition process in this material. Their structures are in sharp contradiction to information found in experiment [2–4] and in more extensive simulations of GST [5,6]. In [6] we suggested that (much smaller) vacancies are essential for the rapid phase transition in GST and in Ge/Te alloys [7].

The findings of [1] are artifacts of the details of the simulation, particularly the cooling rate and the shape of the simulation cell (the authors give no dimensions, but two appear to be $\lesssim$13 Å). Periodic boundary conditions (PBC) mean that the "void" shown is, in fact, a periodically repeated infinite "gap" in a layered structure. PBC combined with small cell parameters also rule out a description of the range of cavities (vacancies) found in [6], which showed that cavities (a) occur at 300 and 900 K, occasionally with volumes over 100 $Å^3$ (Fig. 9(b) of [6(a)]) and (b) prefer Te atoms as neighbors. The density used in [1] is ~4% less than the experimental value (Ref. [17] of [1]), and this may have contributed to the finding of unphysically large cavities.

The description of the cooling rate is imprecise. The authors report 6.6 K/ps from 1000 to 900 K, but this rate has obviously not been applied from the beginning (5000 K). Slow cooling is essential to describe the melt-quench process, particularly the number of homopolar bonds and *ABAB* squares (A = Ge, Sb, B = Te). This is demonstrated in Table I, where we compare partial coordination numbers of [1,6] with those obtained from a rapid quench to 0 K of a well-equilibrated sample at 900 K [9]. The numbers in [1] are generally higher than in the rapid quench and much higher than in [6], striking examples being Ge-Sb and Sb-Ge (it is unclear why these numbers differ in [1]) and Te-Te. The chemical short-range order parameters in [1] (or the binary mixture order parameters [6]) are much smaller than the corresponding values in [6], reflecting the large number of "wrong bonds" (bonds not present in crystalline GST) and less *AB* alternation in the structure of [1]. Reduced *AB* alternation leads to fewer "*ABAB* squares," the presence of which promotes the phase transition [6,10].

The calculated total coordination numbers in [1] (Ge, 5.25; Sb, 5.67; Te, 3.98) are vastly higher than those found in previous calculations [5,6] and in any experimental work on this material (x-ray diffraction, neutron diffraction, EXAFS) [2–4]. The authors neither compare with any of this work nor provide error estimates on their values. The significant contribution from triangular configurations (bond angles near 60°) is further evidence of flaws in the simulation.

TABLE I. Partial coordination numbers (as defined in Ref. [1]) and first minimum of PDF (r_1, used as integration cutoff).

	Sun *et al.*[a]	Akola and Jones[b]	Akola and Jones[c]	r_1 (Å) Akola and Jones[b]
Ge-Ge	0.68	0.36	0.48	3.2
Ge-Sb, Sb-Ge	0.72, 0.76	0.14	0.40	3.0
Sb-Sb	0.82	0.82	0.97	3.6
Te-Te	0.77	0.30	0.62	3.2

[a]Ref. [1]
[b]Ref. [6]
[c]Akola and Jones [8]

There are unclear points of detail, such as the meaning of a "[111] crystallographic direction" in an amorphous material, but we focus on the use of an elongated cell with two small dimensions in conjunction with PBC and on the quenching rate. More relevant results would have been obtained with the same number of atoms by using a cubic cell. The present structure is an unphysical, periodically repeated void of infinite extent, whose parameters bear no relationship to those found in more extensive simulations and experiments on the same material. The connections between cavities, Te atoms, and the phase transition in GST are not new [6].

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[1] Z. Sun, J. Zhou, A. Blomqvist, B. Johansson, and R. Ahuja, Phys. Rev. Lett. **102**, 075504 (2009).
[2] S. Kohara *et al.*, Appl. Phys. Lett. **89**, 201910 (2006).
[3] D. A. Baker *et al.*, Phys. Rev. Lett. **96**, 255501 (2006).
[4] P. Jóvári *et al.*, Phys. Rev. B **77**, 035202 (2008).
[5] S. Caravati *et al.*, Appl. Phys. Lett. **91**, 171906 (2007).
[6] (a) J. Akola and R. O. Jones, Phys. Rev. B **76**, 235201 (2007); (b) J. Akola and R. O. Jones, J. Phys. Condens. Matter **20**, 465103 (2008). The GST simulations were performed in a cubic cell containing 460 atoms.
[7] J. Akola and R. O. Jones, Phys. Rev. Lett. **100**, 205502 (2008).
[8] J. Akola and R. O. Jones (unpublished).
[9] The sample [6] was quenched after cooling from 3000 K to 900 K (42 ps) and data collection (21 ps).
[10] J. Hegedüs and S. R. Elliott, Nature Mater. **7**, 399 (2008).

