

MATERIALS SCIENCE

Breakdown of the Stokes-Einstein relation above the melting temperature in a liquid phase-change material

Shuai Wei^{1*}, Zach Evenson², Moritz Stolpe^{3,4}, Pierre Lucas⁵, C. Austen Angell^{6*}

The dynamic properties of liquid phase-change materials (PCMs), such as viscosity η and the atomic self-diffusion coefficient D , play an essential role in the ultrafast phase switching behavior of novel nonvolatile phase-change memory applications. To connect η to D , the Stokes-Einstein relation (SER) is commonly assumed to be valid at high temperatures near or above the melting temperature T_m and is often used for assessing liquid fragility (or crystal growth velocity) of technologically important PCMs. However, using quasi-elastic neutron scattering, we provide experimental evidence for a breakdown of the SER even at temperatures above T_m in the high-atomic mobility state of a PCM, $\text{Ge}_1\text{Sb}_2\text{Te}_4$. This implies that although viscosity may have strongly increased during cooling, diffusivity can remain high owing to early decoupling, being a favorable feature for the fast phase switching behavior of the high-fluidity PCM. We discuss the origin of the observation and propose the possible connection to a metal-semiconductor and fragile-strong transition hidden below T_m .

INTRODUCTION

Phase-change materials (PCMs) can be reversibly switched between their glassy and crystalline states by heating with a voltage or laser pulse (1). The strong optical/electrical contrast between these two states makes PCMs highly interesting for data storage applications (e.g., encoding “0” and “1”). An extremely fast phase switching on a time scale of nanoseconds is a requirement for high read/write speed. However, the fast atomic dynamics inherent to PCMs seems to be at odds with the concomitant requirement of good amorphous phase stability for data retention (1). Typical PCMs include the Ge-Sb-Te alloys, especially those along the $\text{GeTe-Sb}_2\text{Te}_3$ tie line, and doped Sb_2Te_3 alloys such as Ag-In-Sb-Te (1). Physical understanding of PCMs has been mainly centered around features of their crystalline states [e.g., bonding (2)], while the liquid-state behavior was considered “ordinary” or less explored, probably because a large portion of the (supercooled) liquid state is obscured by fast crystallization.

Requiring a critical cooling rate of $\sim 10^9 \text{ K s}^{-1}$ for vitrification, PCMs are generally recognized as poor glass formers. The amorphous phase is so prone to crystallization that no glass transition (T_g) can be observed in a differential scanning calorimeter (DSC) before crystallization sets in upon heating (3). Thus, the broad supercooled liquid regime, $\Delta T = T_m - T_x$, between the melting temperature (e.g., $T_m \sim 903 \text{ K}$ for $\text{Ge}_1\text{Sb}_2\text{Te}_4$) and the crystallization temperature upon heating (typically $T_x \sim 400 \text{ K}$ for $\text{GeTe-Sb}_2\text{Te}_3$ alloys) is experimentally inaccessible using standard techniques. For this reason, it has been a long-standing challenge to characterize the liquid-state behavior of PCMs—specifically, the liquid fragility that has been recently given much importance by Orava *et al.* (4). Fragility, defined as $m = d \log \eta / d(T_g/T)|_{T=T_g}$, where T_g is the “standard” value (where the viscosity η reaches the value $10^{12} \text{ Pa}\cdot\text{s}$) (5), describes the deviation of the temperature dependence of viscosity from the Arrhenius law.

Fragility has been recognized as a useful parameter for understanding crystallization kinetics and the stability of amorphous states (6).

The Stokes-Einstein relation (SER) is frequently used to calculate η from D (or vice versa) in technologically important PCMs at “sufficiently” high temperature

$$D \cdot \eta = (k_B \cdot T) / (6\pi r_H) \quad (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and r_H is the effective hydrodynamic radius. For instance, Orava *et al.* (4) assumed a valid SER at T_m for deriving the absolute values of crystal growth velocity of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ from the Kissinger-type analysis using ultrafast DSC data. Salinga *et al.* (7) used crystal growth velocity data from laser reflectivity measurements to determine the fragility of Ag-In-Sb-Te ($m \sim 190$), assuming a valid SER over a wide temperature range well below T_m . Schumacher *et al.* (8) compared the experimental viscosity data for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ at $T > T_m$ to the values derived from the SER based on simulated self-diffusion coefficients and observed a nonnegligible discrepancy.

In general, liquids at high temperature are expected to obey the SER, as they do not feel the energy landscape, and single-particle dynamics follow the same temperature dependence as the collective macroscopic stress relaxation processes. When the temperature approaches T_g on cooling, D progressively decouples from η in fragile liquids such as *o*-terphenyl (OTP), phenolphthaleine dimethyl ether (PDE), and salol, beginning at $\sim 1.2 T_g$ (9), supposedly due to the dynamic heterogeneity (9). A SER breakdown in PCM GeTe was also asserted by Sosso *et al.* (10) based on ab initio simulations, which occurs in the supercooled liquid attributed to dynamic heterogeneities. Such a breakdown in supercooled $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe nanoparticles was also taken into account by Chen *et al.* (11) and Orava *et al.* (4), where the necessity of using a fractional SER to describe the supercooled liquid was emphasized. Also, the crystal growth kinetic coefficient U_{kin} decouples from η following the Ediger *et al.* relation (6) $U_{\text{kin}} \propto \eta^{-\xi^*}$ ($\xi^* < 1$ depending on fragility). Detailed experimental studies of multicomponent bulk metallic glass-forming liquids with high atomic packing fractions (12) ($\phi \sim 0.51$ to 0.55) revealed a clear breakdown of the SER close to, or even well above, the critical temperature T_c of mode-coupling theory (13, 14). Liquid PCMs, on the other hand, represent *p*-electron bonded (15) fragile glass formers (4)

¹Institute of Physics (IA), RWTH Aachen University, Aachen, Germany. ²Heinz Maier-Leibnitz Zentrum (MLZ) and Physik Department, Technische Universität München, Lichtenbergstrasse 1, 85747 Garching, Germany. ³Heraeus Holding GmbH, Heraeusstr. 12-14, 63450 Hanau, Germany. ⁴Chair of Metallic Materials, Saarland University, Campus C6.3, 66123 Saarbrücken, Germany. ⁵Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85712, USA. ⁶School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA.

*Corresponding author. Email: austenangell@gmail.com (C.A.A.); shuai.wei@physik.rwth-aachen.de (S.W.)

with low atomic packing fractions ($\phi \sim 0.3$ to 0.4). There has been unexpectedly little interest in, or experimental data related to, the SER above T_m for PCMs. However, the recent discussion concerning the likely existence of liquid-liquid transitions (LLTs) in PCMs suggests the probability of complex dynamical behavior, including a breakdown of the SER in these liquids (16).

In this work, we probe the microscopic dynamics in the liquid state of a typical PCM $\text{Ge}_1\text{Sb}_2\text{Te}_4$ using quasi-elastic neutron scattering (QENS), which permits direct determination of both the structural α -relaxation time (proportional to shear viscosity η) and the self-diffusion coefficient D on the same sample under identical conditions. Our results question the validity of the commonly used SER in those technologically important PCMs, even well above T_m . We discuss the origin of the breakdown of SER and its relation to a possible metal-semiconductor (also fragile-strong liquid) transition hidden below T_m , which may play a critical role in speeding up crystallization kinetics, before restraining the atomic rearrangements through the fragile-strong transition. The fundamental importance of these phenomena to the technical performance of PCMs has been stressed elsewhere (16, 17).

RESULTS

α -Relaxation time

We obtain relaxation times from the decay of the intermediate scattering function (ISF) $S(q, t)$, which describes the decay of microscopic density fluctuations in the liquid and was obtained according to the procedure outlined in Materials and Methods. Figure 1A shows $S(q, t)$ taken at the first structure factor maximum $q_0 = 2.0 \text{ \AA}^{-1}$ of the liquid at different temperatures above $T_m = 903 \text{ K}$. The data are best fitted with a simple exponential function, $S(q, t)/S(q, 0) = f_q \exp(-t/\tau_q)$, where f_q is a constant accounting for atomic vibrations and τ_q is the structural relaxation time. In the case of $q_0 = 2.0 \text{ \AA}^{-1}$, that is, the position of the structure factor maximum, the fitting yields a collective structural relaxation time, or α -relaxation time τ_α , as shown in Fig. 1B, as the quasi-elastic signal at q_0 arises predominantly from the coherent scattering contribution. τ_α is associated with the shear viscosity η in the viscoelastic model of Maxwell, which establishes a proportional relation via $\eta = G_\infty \tau_\alpha$, where G_∞ is the infinite frequency shear modulus measured on time scales very short with respect to τ_α . This proportionality has been directly tested by combining QENS and viscosity measurements on various glass-forming melts (18).

Self-diffusivity

Self-diffusion coefficients were determined from the QENS signal in the low- q range, where the signal is dominated by the incoherent scattering of both Ge and Te atoms and reflects their single-particle dynamics on long length and time scales. Given the incoherent cross sections of each species and their relative concentration in the alloy melt, the measured self-diffusion coefficient of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ represents a mean value weighted by roughly $1/3$ Ge and $2/3$ Te (the incoherent scattering cross section of Sb is negligibly small). As shown in the inset of Fig. 2, the incoherent relaxation times τ^{inc} follow a $1/q^2$ dependence at low $q^2 \leq 0.6 \text{ \AA}^{-2}$, which is characteristic of long-range atomic diffusion in liquids in the hydrodynamic limit as $q \rightarrow 0 \text{ \AA}^{-1}$ (19). This thus allows us to derive a mean Ge/Te self-diffusion coefficient via $D_{\text{Ge/Te}} = 1/(\tau^{\text{inc}} q^2)$. In Fig. 2, the resulting $D_{\text{Ge/Te}}$ values are fitted with the Arrhenius law, yielding an activation energy $E_{a,D} = 26.41 \pm 0.89 \text{ kJ mol}^{-1}$ and a pre-exponent $D_0 = 1.4 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. To

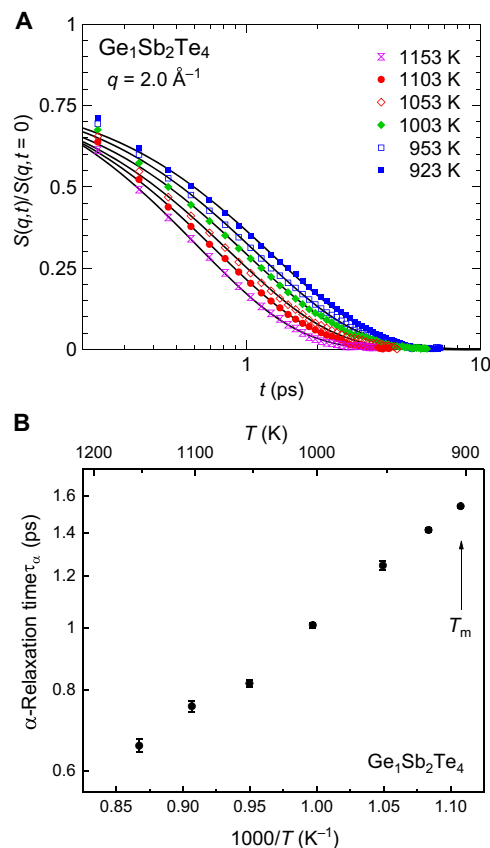


Fig. 1. Exponential decay of the ISF and the α -relaxation time τ_α for liquid $\text{Ge}_1\text{Sb}_2\text{Te}_4$ above T_m . (A) The decay of the ISF $S(q, t)$ of liquid $\text{Ge}_1\text{Sb}_2\text{Te}_4$ at the structure factor first maximum $q_0 = 2.0 \text{ \AA}^{-1}$ measured at temperatures above $T_m = 903 \text{ K}$. The data, typical of high-fluidity systems, are best fitted by simple exponential functions (solid lines), each yielding a single relaxation time τ_α (see the main text for details). Note that at a very short time ($< 0.65 \text{ ps}$), the data points correspond to phonons and fast processes that are not explicitly taken into account in the fitting. This is consistent with the analysis of the dynamic structure factor $S(q, \omega)$ in the energy transfer ($\hbar\omega$) domain (see fig. S1), where $S(q, \omega)$ is best described by a single Lorentzian form. (B) Arrhenius plot for the α -relaxation time τ_α above T_m .

our knowledge, there are no experimental diffusivity data available for liquid PCMs. Some partial atomic diffusion coefficients are available from ab initio computer simulations (20) $D_{\text{Ge}} = 4.04 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{Te}} = 4.06 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 1000 K for the same composition, which are close to our value ($D \approx 5.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) at 1003 K .

DISCUSSION

The breakdown of the SER

According to the SER, the product $(D\eta)/T$ and, hence, $(D\tau_\alpha)/T$ should remain constant as a function of T (Eq. 1). For the liquid PCM $\text{Ge}_1\text{Sb}_2\text{Te}_4$, this is evidently not the case, as highlighted in Fig. 3A. A marked deviation is observed at 1050 K on approaching T_m (903 K) during cooling, indicating a breakdown of the SER well above the melting point up to at least 1050 K , $\sim 1.16 T_m$. For $T > 1050 \text{ K}$, the SER seems to hold, although the limited temperature range does not allow for a conclusive assessment for even higher temperatures. Note that we take the SER in its form of $D \propto (\tau_\alpha/T)^{-1}$. If G_∞ in the Maxwell

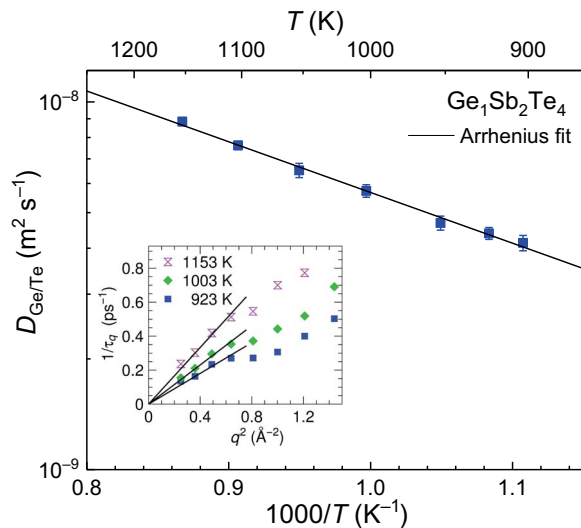


Fig. 2. Mean self-diffusion coefficient $D_{\text{Ge/Te}}$ of liquid $\text{Ge}_1\text{Sb}_2\text{Te}_4$ derived from incoherent scattering signal at low q . Inset: q^2 dependence of the inverse relaxation time $1/\tau_q$. At low q ($q^2 \leq 0.6 \text{ \AA}^{-2}$), $1/\tau_q$ follows a q^2 dependence (solid straight lines), as expected from hydrodynamic theory as $q \rightarrow 0 \text{ \AA}^{-1}$. For $q^2 > 0.6 \text{ \AA}^{-2}$, $1/\tau_q$ deviates from the q^2 dependence due to coherent scattering contributions from a prepeak of $S(q)$ at $\sim 1 \text{ \AA}^{-1}$ (see fig. S2).

relation is temperature dependent (as it certainly is for fragile liquids), then the temperature of SER breakdown, in its original form with viscosity, might differ somewhat from the breakdown temperature observed here. In either case, it should occur at relaxation times on the order of 1 ps (from Figs. 1 and 3B), far shorter than in any normal liquid where the breakdown only occurs at nanosecond relaxation times.

In Fig. 3B, by fitting the data with a fractional SER of the form (21)

$$D \propto (\tau_\alpha/T)^{-\xi} \quad (2)$$

where $0 < \xi \leq 1$, we see that the high-temperature liquid for $T \geq 1050 \text{ K}$ closely follows the SER with an exponent $\xi \approx 0.97 \pm 0.11$, while $\xi \approx 0.60 \pm 0.03$ is obtained for $T \leq 1050 \text{ K}$, indicating a strong deviation from the SER. The latter can be related to the decoupling of crystal growth coefficient U_{kin} and viscosity η for fragile liquids, which is described by the form $U_{\text{kin}} \propto \eta^{-\xi^*}$ given by Ediger *et al.* (6). $\xi^* = 0.67$ in a similar PCM $\text{Ge}_2\text{Sb}_2\text{Te}_5$, estimated by Orava *et al.* (4) from an empirical correlation with fragility, is close to our $\xi \approx 0.6$.

The breakdown of the SER at such high temperatures ($> T_m$), and short relaxation times, is an important observation because (i) the SER has provided the basis for calculating viscosity and fragility from simulated self-diffusion coefficients and/or crystal growth velocities (or vice versa) of PCMs near T_m (4, 7, 8); (ii) it occurs at temperatures where diffusivities are nearly four orders of magnitude higher ($\sim 5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) than where the SER breakdown is observed in conventional glass formers [for instance, for the typical fragile molecular liquid OTP, the SER remains valid down to the much lower diffusivity $D \approx 1.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ (22) where $\eta \approx 7.7 \text{ Pa}\cdot\text{s}$]; and (iii) it is a feature favorable for fast phase switching behavior required for PCM functions in memory devices.

For phase-change memory devices, the PCMs must have ultrafast crystallization kinetics to crystallize in a few nanoseconds. The early (high temperature) fractional SER behavior inevitably leads to a

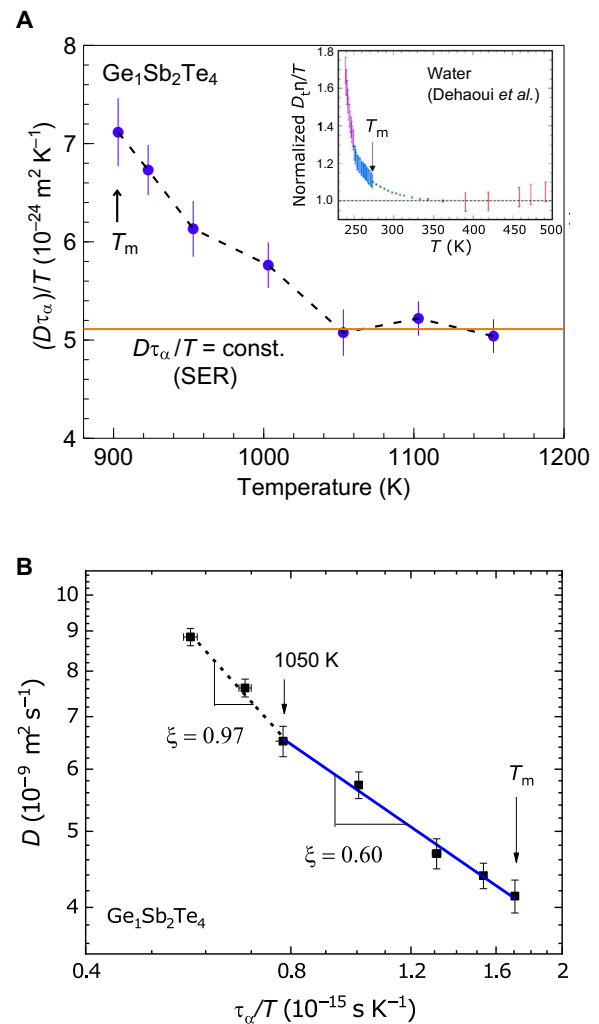


Fig. 3. The breakdown of the SER in liquid PCMs. (A) During cooling, $(D\tau_\alpha)/T$ initially has a constant value at $T \geq 1050 \text{ K}$ as expected from the SER but shows a marked positive deviation from the constant below 1050 K as $T_m = 903 \text{ K}$ is approached, indicating a breakdown of the SER at $T_{\text{SE}} = 1050 \text{ K}$. Inset: The SER breakdown in water occurs at around 340 K , which is about $1.25 T_m$ [adapted from Dehaoui *et al.* (28)]. (B) The data fitting with the fractional SER indicates $\xi \approx 0.60 \pm 0.03$ for $T_{\text{SE}} < 1050 \text{ K}$, indicating a strong deviation from the SER, as in (A), while a larger slope with $\xi \approx 0.97 \pm 0.11$ at higher temperature follows the SER ($\xi = 1$).

higher diffusivity than that expected from the SER. With decreasing temperature, this difference may develop up to a few orders of magnitude in the supercooled liquid. In other words, the viscous flow may have slowed down, while the atomic diffusion could remain much faster, which would facilitate the diffusion-controlled nucleation and growth process. Hence, this can be one of the favorable factors governing the fast phase switching at a moderate temperature when heated by a “set” electric pulse in the memory devices.

The origin of the SER violation and its related phenomenology

The origin of the breakdown is usually explained by dynamical heterogeneities for viscous liquids. In our work, we have been struck by the fact that the onset temperature for deviation from the SER occurs in a temperature domain where $S(q, t)$ is still exponential, with no

sign, even at temperatures very near the melting point, of the sort of shoulder usually associated with stretching of the exponential and the development of the dynamic heterogeneity [seen, for instance, in (23)]. Then, how can the observed SER breakdown be attributed to heterogeneity? Poole and coworkers (24) demonstrated the presence of dynamic and structural heterogeneity in a model molecular liquid in a single instantaneous configuration, where a two-step relaxation was not observable due to the loss of information during averaging over initial configurations. Moreover, our experiment, probing the short time scale (a few picoseconds), has a limited energy resolution, which does not allow us to resolve even shorter time scales. Note that the height of the plateau in the decay is less than 1, which might already signify the existence of the first-step relaxation (shoulder in the decay of ISF) even when not being undercooled. The molecular dynamics (MD) simulation study of the ISF shows the presence of dynamic heterogeneity in the supercooled GeTe (25), which, originating from structural heterogeneities due to chains of Ge–Ge homopolar bonds, may explain the breakdown of the SER in GeTe in the viscous regime below T_m (26). From our measurement, despite the observed exponential decay in ISF, the dynamic heterogeneity may still be present in the PCM above T_m . If it is the case, then the underlying structural signature and physical origin remain to be determined.

Our observation indicates that the SER is violated in the PCM well above T_m up to at least 1050 K. The limited temperature range of the data does not allow us to conclusively assert the validity of the SER at even higher temperatures. Whether the SER holds in any temperature in the PCM at all needs further experimental and, perhaps more helpful, simulation studies. Using MD simulations, Horbach and Kob (27) showed that the SER does not hold, even at very high temperatures above 3 T_m in the network glass-forming liquid silica. This raises the question whether the breakdown in the PCM is similar to the ones of directionally bonded, network glass-forming liquids. However, such a scenario is difficult to reconcile with the distinct characteristics of PCMs. PCMs have fast dynamics with a high fragility of $m = 90$ or higher (4, 7), whereas liquid silica has slow dynamics with a fragility of $m = 20$ near the strong liquid limit. The viscosity of PCMs is about ~ 2 mPa s at T_m , which is nine orders of magnitude lower than that of liquid silica ($\sim 10^6$ Pa s) at its T_m . PCMs are covalently bonded in the semiconducting solid amorphous phase but defy the description of a typical network structure by deviating from Zachariasen's glass picture (1, 2). Above the melting point, their liquid state becomes metallic (16). Thus, neither slow dynamics nor a typical network structure is a prerequisite for the breakdown of the SER in the PCM. We note that a simulation study of a similar PCM GeTe, computing viscosity with the Green-Kubo formula and self-diffusivity, shows that the SER holds well at high temperature (10).

The observation in $\text{Ge}_1\text{Sb}_2\text{Te}_4$ more resembles the case of the “most anomalous liquid”—supercooled water. For bulk water, the recent data of Dehaoui *et al.* (28) showed a crossover in the fractional SER behavior from $\xi \approx 1$ at high temperature to $\xi \approx 0.8$ at low temperature. The breakdown temperature T_{SE} of ~ 340 K, $\sim 1.25 T_m$, and the diffusivity $D \approx 5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at T_{SE} (where viscosity $\eta \approx 0.4$ mPa s) are comparable to those of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ (see Fig. 3A, inset). Note that the deviation from the SER in water appears well above other known anomalies such as density maximum (277 K), rapid C_p increase, and sharp viscosity rising (below T_m). As is much discussed, the anomalies of water are thought to be related to an LLT and possibly a nearby, but hidden, second critical point suggested by

some computational models (29). Errington and Debenedetti (30) showed that a “Russian doll” of nested kinetic and thermodynamic anomalies exists in water and the same has since been found for other water-like systems [e.g., Si (31)]. The breakdown of the SER appears to be the anomaly persisting to the highest temperature and a much more sensitive signaler of impending anomalous character than any of the other signals yet studied.

Given that “water-like” anomalies such as density maxima, and diverging (or peaked) heat capacities, occur in supercooled Te, Ge, and Si (32–34); in $\text{Ge}_{15}\text{Te}_{85}$ just above the eutectic temperature (35); and in As_2Te_3 somewhat above its T_m (36), we should expect the unusual behavior in the PCMs at lower temperatures (16). The thermodynamic response function maxima in the abovementioned chalcogenides are also associated with liquid metal-semiconductor transitions (16). Pressure-induced polyamorphic transitions between high- and low-density amorphous states (which are also metallic and semiconducting states) have been found in both $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (37, 38), and these closely parallel the polyamorphism in amorphous silicon (39) and vitreous ice (40)—except that the latter obviously does not have a semiconductor-metal transition. On the basis of all of the above, the proposed LLT scenario is illustrated in the pressure-temperature (P - T) diagram for liquid and metastable liquid states of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ in fig. S3, which shows a conjectured LLT regime, together with available literature data. Its analogy to that of water is provided by the inset. Tanaka's two-order-parameter model already predicts that a “V-shape” P - T phase diagram (as is the case for our PCM) is directly related to thermodynamic and dynamic anomalies similar to those of water (41). The fact that we observe the same sort of SER breakdown for the PCM as for water (see fig. S3) lends credence to the suggested phase diagram and its implication of a submerged LLT. An LLT scenario is consistent with the evidence of a fragile-strong crossover/transition found recently in a similar composition $\text{Ge}_2\text{Sb}_2\text{Te}_5$ below T_m , manifesting as a continuous crossover argued by Chen *et al.* (11) and as a singular temperature (792 K) argued by Flores-Ruiz *et al.* (42).

It is important that the phenomena described in this work are not confused with recent reports of SER breakdown above “ T_m ” (a ternary eutectic temperature) in certain glass-forming metallic mixtures, such as ZrCuAl , where the species Cu decouples from the Zr–Al matrix (43, 44). The latter phenomenon is more closely related to the case of Cu in amorphous silicon, where D_{Cu} can be four orders of magnitude greater than that of the host (Si) atoms (45). A related phenomenon, also quite different from our conjecture, is the superionicity of Cu (or Ag) cations in many superionic glass formers, where the mobile ion decoupling is observed well above any liquidus temperature (and also above 2 T_g), and the Stokes-Einstein discrepancy at T_g can reach 11 orders of magnitude (46).

SUMMARY

We have performed neutron scattering studies of diffusion and relaxation times in the PCM $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and identified a breakdown in the SER well above the T_m , which lies in a relaxation time domain 10^4 times shorter than that in normal liquids. The high-temperature deviation from the SER, characterized by a fractional SER with an exponent $\xi \approx 0.60 \pm 0.03$, implies a high diffusivity, which is favorable for fast phase switching for PCM functions. We link our finding to the behavior observed in liquid silicon, germanium, and water, where it is seen as a consequence of a submerged LLT, which provokes facile crystallization and fragile-strong transitions when ultrafast

cooling preserves the liquid state. The exploration of PCMs' anomalous liquid-state behavior will be an essential step toward understanding the fast phase switching behavior in this class of material.

MATERIALS AND METHODS

Sample preparation

$\text{Ge}_1\text{Sb}_2\text{Te}_4$ was prepared using the Ge, Sb, and Te elements with purities ranging from 99.999 to 99.9999 atomic %. The elements were sealed under vacuum (10^{-6} mbar) in a fused quartz tube with an internal diameter of 5 mm and synthesized in a rocking furnace for homogenization at 900°C for 15 hours.

QENS measurements and data analysis

The sample, sealed in the fused quartz tube, was loaded into a thin-walled Al_2O_3 container for the QENS measurements, which were carried out at the time-of-flight spectrometer TOFTOF at the Heinz Maier-Leibnitz neutron source (FRM II) in Munich (47, 48). Two incident neutron wavelengths $\lambda_i = 4.4$ and 7 Å were used to obtain a broad q and energy transfer range along with a high resolution of about 90 μeV (full width at half maximum).

Spectra were collected as a function of temperature in a high-vacuum, high-temperature Nb furnace. Raw time-of-flight data were normalized to a vanadium standard and interpolated to constant q to obtain the dynamic structure factor $S(q, \omega)$ using the FRIDA-1 software (see <http://sourceforge.net/projects/frida/> for source code). All spectra were found to be well described by a model composed of the quasi-elastic scattering from the alloy melt and a flat background to approximate the processes too fast to be accurately measured by the spectrometer. The $S(q, \omega)$ obtained in the measurements, where $\lambda_i = 7$ Å, was additionally modeled to include the elastic scattering from the container. In general, the model $S(q, \omega)$ reads

$$S(q, \omega) = R(q, \omega) \otimes N[A_0 \delta(\omega) + (1 - A_0)L(q, \omega)] + b(q, \omega)$$

where $R(q, \omega)$ is the instrumental resolution function, N is a normalization factor, A_0 is the magnitude of the elastic scattering, and $b(q, \omega)$ is a constant but q -dependent background. The symbol $\otimes$ denotes a numerical convolution. The quasi-elastic scattering was found to be best described with a single Lorentzian of the form (see fig. S1)

$$L(q, \omega) = \frac{1}{\pi} \frac{\Gamma(q)}{(\hbar\omega)^2 + \Gamma(q)^2}$$

where Γ is the half width at half maximum. Below $q^2 \sim 0.6 \text{ Å}^{-2}$, the incoherent scattering from Ge and Te dominates and the coherent contributions from thermal diffusion (Rayleigh line) and acoustic modes are effectively contained in the flat background of the observed quasi-elastic spectra (49). A mean Ge/Te self-diffusion coefficient was determined via

$$D_{\text{Ge/Te}} = \frac{\Gamma(q)}{\hbar q^2}$$

An analysis was also carried out in the time domain first by obtaining the ISF $S(q, t)$ (or density correlation function) via cosine Fourier transform of the measured $S(q, \omega)$ and normalizing to the

instrumental resolution function $R(q, t)$. In general, the data were then fitted with a simple exponential decay as

$$S(q, t)/S(q, 0) = f(q) \exp[-t/\tau(q)] + c$$

where $f(q)$ is the amplitude, τ is the structural relaxation time, and the constant c is an offset that takes care of any remaining elastic scattering. It should be noted that this is in line with the model used for $S(q, \omega)$, as the Fourier transform of a Lorentzian is a simple exponential. To ensure consistency of the analyses in both energy transfer and time domain, we restricted the fitting range in the energy transfer domain to $[-1, 1]$ meV and in the time domain to the data points after 0.65 ps. At higher energy transfers and shorter times, the spectra are dominated by phononic vibrations and fast relaxation processes. The self-diffusion coefficient was obtained from the time domain analysis via

$$D_{\text{Ge/Te}} = \tau(q)^{-1} q^{-2}$$

The values of $D_{\text{Ge/Te}}$ reported in the manuscript represent an average of the values obtained in both analyses.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/11/eaat8632/DC1>

Fig. S1. The dynamic structure factor $S(q, \omega)$ in the energy transfer domain ($\hbar\omega$) obtained from QENS.

Fig. S2. The "effective" diffusion coefficient D_q as a function of q derived at a given temperature of 1103 K using the relation $D_q = 1/(\tau_q q^2)$.

Fig. S3. P - T metastable liquid phase diagram conjectured for $\text{Ge}_1\text{Sb}_2\text{Te}_4$, in analogy to that of water (inset).

References (50–63)

REFERENCES AND NOTES

1. M. Wuttig, N. Yamada, Phase-change materials for rewriteable data storage. *Nat. Mater.* **6**, 824–832 (2007).
2. K. Shportko, S. Kremers, M. Woda, D. Lencer, J. Robertson, M. Wuttig, Resonant bonding in crystalline phase-change materials. *Nat. Mater.* **7**, 653–658 (2008).
3. J. A. Kalb, M. Wuttig, F. Spaepen, Calorimetric measurements of structural relaxation and glass transition temperatures in sputtered films of amorphous Te alloys used for phase change recording. *J. Mater. Res.* **22**, 748–754 (2007).
4. J. Orava, L. Greer, B. Gholipour, D. W. Hewak, C. E. Smith, Characterization of supercooled liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and its crystallization by ultrafast-heating calorimetry. *Nat. Mater.* **11**, 279–283 (2012).
5. C. A. Angell, Formation of glasses from liquids and biopolymers. *Science* **267**, 1924–1935 (1995).
6. M. D. Ediger, P. Harrowell, L. Yu, Crystal growth kinetics exhibit a fragility-dependent decoupling from viscosity. *J. Chem. Phys.* **128**, 034709 (2008).
7. M. Salinga, E. Carria, A. Kaldenbach, M. Bornhöft, J. Benke, J. Mayer, M. Wuttig, Measurement of crystal growth velocity in a melt-quenched phase-change material. *Nat. Commun.* **4**, 2371 (2013).
8. M. Schumacher, H. Weber, P. Jónvári, Y. Tsuchiya, T. G. A. Youngs, I. Kaban, R. Mazzarello, Structural, electronic and kinetic properties of the phase-change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$ in the liquid state. *Sci. Rep.* **6**, 27434 (2016).
9. I. Chang, H. Sillescu, Heterogeneity at the glass transition: Translational and rotational self-diffusion. *J. Phys. Chem. B* **101**, 8794–8801 (1997).
10. G. C. Sosso, J. Behler, M. Bernasconi, Breakdown of Stokes–Einstein relation in the supercooled liquid state of phase change materials. *Phys. Status Solidi B Basic Solid State Phys.* **249**, 1880–1885 (2012).
11. B. Chen, G. H. ten Brink, G. Palasantzas, B. J. Kooij, Crystallization kinetics of GeSbTe phase-change nanoparticles resolved by ultrafast calorimetry. *J. Phys. Chem. C* **121**, 8569–8578 (2017).
12. A. Meyer, Atomic transport in dense multicomponent metallic liquids. *Phys. Rev. B* **66**, 134205 (2002).

13. A. Bartsch, K. Rätzke, A. Meyer, F. Faupel, Dynamic arrest in multicomponent glass-forming alloys. *Phys. Rev. Lett.* **104**, 195901 (2010).
14. J. Brillo, A. I. Pommrich, A. Meyer, Relation between self-diffusion and viscosity in dense liquids: New experimental results from electrostatic levitation. *Phys. Rev. Lett.* **107**, 165902 (2011).
15. C. Bichara, M. Johnson, J. P. Gaspard, Octahedral structure of liquid GeSb₂Te₄ alloy: First-principles molecular dynamics study. *Phys. Rev. B* **75**, 060201 (2007).
16. S. Wei, G. J. Coleman, P. Lucas, C. A. Angell, Glass transitions, semiconductor-metal transitions, and fragilities in Ge-V-Te (V=As, Sb) liquid alloys: The difference one element can make. *Phys. Rev. Appl.* **7**, 034035 (2017).
17. J. Orava, D. W. Hewak, A. L. Greer, Fragile-to-strong crossover in supercooled liquid Ag-In-Sb-Te studied by ultrafast calorimetry. *Adv. Funct. Mater.* **25**, 4851–4858 (2015).
18. F. Yang, T. Unruh, A. Meyer, Coupled relaxation processes in a glass forming ZrTiNiCuBe liquid. *EPL* **107**, 26001 (2014).
19. J. P. Boon, S. Yip, *Molecular Hydrodynamics* (Courier Corporation, 1980).
20. Z. Sun, J. Zhou, A. Blomqvist, L. Xu, R. Ahuja, Local structure of liquid Ge₁Sb₂Te₄ for rewritable data storage use. *J. Phys. Condens. Matter* **20**, 205102 (2008).
21. S. R. Becker, P. H. Poole, F. W. Starr, Fractional Stokes-Einstein and Debye-Stokes-Einstein Relations in a network-forming liquid. *Phys. Rev. Lett.* **97**, 055901 (2006).
22. F. Fujara, B. Geil, H. Sillescu, G. Fleischer, Translational and rotational diffusion in supercooled orthoterphenyl close to the glass transition. *Z. Für Phys. B Condens. Matter* **88**, 195–204 (1992).
23. G. Sun, L. Xu, N. Giovambattista, Relationship between the potential energy landscape and the dynamic crossover in a water-like monatomic liquid with a liquid-liquid phase transition. *J. Chem. Phys.* **146**, 014503 (2017).
24. G. S. Matharoo, M. S. G. Razul, P. H. Poole, Structural and dynamical heterogeneity in a glass-forming liquid. *Phys. Rev. E* **74**, 050502 (2006).
25. G. C. Sossio, J. Colombo, J. Behler, E. Del Gado, M. Bernasconi, Dynamical heterogeneity in the supercooled liquid state of the phase change material GeTe. *J. Phys. Chem. B* **118**, 13621–13628 (2014).
26. S. Gabardi, S. Caravati, G. C. Sossio, J. Behler, M. Bernasconi, Microscopic origin of resistance drift in the amorphous state of the phase-change compound GeTe. *Phys. Rev. B* **92**, 054201 (2015).
27. J. Horbach, W. Kob, Relaxation dynamics of a viscous silica melt: The intermediate scattering functions. *Phys. Rev. E* **64**, 041503 (2001).
28. A. Dehaoui, B. Isenmann, F. Caupin, Viscosity of deeply supercooled water and its coupling to molecular diffusion. *Proc. Natl. Acad. Sci. U.S.A.* **112**, 12020–12025 (2015).
29. P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley, H. Tanaka, C. Vega, L. Xu, L. G. Pettersson, Water: A tale of two liquids. *Chem. Rev.* **116**, 7463–7500 (2016).
30. J. R. Errington, P. G. Debenedetti, Relationship between structural order and the anomalies of liquid water. *Nature* **409**, 318–321 (2001).
31. V. V. Vasisht, J. Mathew, S. Sengupta, S. Sastry, Nesting of thermodynamic, structural, and dynamic anomalies in liquid silicon. *J. Chem. Phys.* **141**, 124501 (2014).
32. H. Kanno, H. Yokoyama, Y. Yoshimura, A new interpretation of anomalous properties of water based on Stillinger's postulate. *J. Phys. Chem. B* **105**, 2019–2026 (2001).
33. M. H. Bhat, V. Molinero, E. Soignard, V. C. Solomon, S. Sastry, J. L. Yarger, C. A. Angell, Vitrification of a monatomic metallic liquid. *Nature* **448**, 787–790 (2007).
34. N. Jakse, A. Pasturel, S. Sastry, C. A. Angell, Response to "Comment on 'Dynamic aspects of the liquid-liquid phase transformation in silicon'" [*J. Chem. Phys.* **130**, 247102 (2009)]. *J. Chem. Phys.* **130**, 247103 (2009).
35. S. Wei, P. Lucas, C. A. Angell, Phase change alloy viscosities down to T_g using Adam-Gibbs-equation fittings to excess entropy data: A fragile-to-strong transition. *J. Appl. Phys.* **118**, 034903 (2015).
36. Y. S. Tver'yanovich, V. M. Ushakov, A. Tverjanovich, Heat of structural transformation at the semiconductor-metal transition in As₂Te₃ liquid. *J. Non Cryst. Solids* **197**, 235–237 (1996).
37. B. Kalkan, S. Sen, J.-Y. Cho, Y.-C. Joo, S. M. Clark, Observation of polymorphism in the phase change alloy Ge₁Sb₂Te₄. *Appl. Phys. Lett.* **101**, 151906 (2012).
38. Z. Sun, J. Zhou, Y. Pan, Z. Song, H.-K. Mao, R. Ahuja, Pressure-induced reversible amorphization and an amorphous–amorphous transition in Ge₂Sb₂Te₅ phase-change memory material. *Proc. Natl. Acad. Sci. U.S.A.* **108**, 10410–10414 (2011).
39. P. F. McMillan, M. Wilson, D. Daisenberger, D. Machon, A density-driven phase transition between semiconducting and metallic polyamorphs of silicon. *Nat. Mater.* **4**, 680–684 (2005).
40. O. Mishima, Reversible first-order transition between two H₂O amorphs at ~0.2 GPa and ~135 K. *J. Chem. Phys.* **100**, 5910–5912 (1994).
41. H. Tanaka, Simple view of waterlike anomalies of atomic liquids with directional bonding. *Phys. Rev. B* **66**, 064202 (2002).
42. H. Flores-Ruiz, M. Micoulaut, From elemental tellurium to Ge₂Sb₂Te₅ melts: High temperature dynamic and relaxation properties in relationship with the possible fragile to strong transition. *J. Chem. Phys.* **148**, 034502 (2018).
43. A. Jaiswal, T. Egami, Y. Zhang, Atomic-scale dynamics of a model glass-forming metallic liquid: Dynamical crossover, dynamical decoupling, and dynamical clustering. *Phys. Rev. B* **91**, 134204 (2015).
44. R. Soklaski, V. Tran, Z. Nussinov, K. F. Kelton, L. Yang, A locally preferred structure characterises all dynamical regimes of a supercooled liquid. *Philos. Mag.* **96**, 1212–1227 (2016).
45. H. Fritzsche, *Amorphous Silicon and Related Materials* (World Scientific, 1989), vol. 1 of *Advances in Disordered Semiconductors*.
46. C. A. Angell, Mobile ions in amorphous solids. *Annu. Rev. Phys. Chem.* **43**, 693–717 (1992).
47. T. Unruh, J. Neuhaus, W. Petry, The high-resolution time-of-flight spectrometer TOFTOF. *Nucl. Instrum. Methods Phys. Res. A* **580**, 1414–1422 (2007).
48. W. Lohstroh, Z. Evenson, TOFTOF: Cold neutron time-of-flight spectrometer. *J. Large Scale Res. Facilities JLSRF* **1**, 15 (2015).
49. A. Meyer, The measurement of self-diffusion coefficients in liquid metals with quasielastic neutron scattering. *EPJ Web Conf.* **83**, 01002 (2015).
50. B. Kalkan, S. Sen, B. G. Aitken, S. V. Raju, S. M. Clark, Negative P – T slopes characterize phase change processes: Case of the Ge₁Sb₂Te₄ phase change alloy. *Phys. Rev. B* **84**, 014202 (2011).
51. B. Kalkan, S. Sen, S. M. Clark, Nature of phase transitions in crystalline and amorphous GeTe-Sb₂Te₃ phase change materials. *J. Chem. Phys.* **135**, 124510 (2011).
52. C. Steimer, V. Coulet, W. Welnic, H. Dieker, R. Detemple, C. Bichara, B. Beuneu, J.-P. Gaspard, M. Wuttig, Characteristic ordering in liquid phase-change materials. *Adv. Mater.* **20**, 4535–4540 (2008).
53. C. Otjacques, J.-Y. Raty, J.-P. Gaspard, Y. Tsuchiya, C. Bichara, in *Collection SFN* (EDP Sciences, 2011), vol. 12, pp. 233–245.
54. S. Stishov, N. Tikhomirova, Maximum in the melting curve of antimony. *Sov. J. Exp. Theor. Phys.* **21**, 810 (1965).
55. V. V. Brazhkin, R. N. Voloshin, S. V. Popova, A. G. Umnov, Pressure-temperature phase diagram of solid and liquid Te under pressures up to 10 GPa. *J. Phys. Condens. Matter* **4**, 1419–1425 (1992).
56. P. R. ten Wolde, D. Frenkel, Enhancement of protein crystal nucleation by critical density fluctuations. *Science* **277**, 1975–1978 (1997).
57. Y. C. Shen, D. W. Oxtoby, Nucleation of Lennard-Jones fluids: A density functional approach. *J. Chem. Phys.* **105**, 6517–6524 (1996).
58. J. F. Lutsko, A dynamical theory of nucleation for colloids and macromolecules. *J. Chem. Phys.* **136**, 034509 (2012).
59. J. Russo, H. Tanaka, The microscopic pathway to crystallization in supercooled liquids. *Sci. Rep.* **2**, 505 (2012).
60. H. Kanno, C. A. Angell, Water: Anomalous compressibilities to 1.9 kbar and correlation with supercooling limits. *J. Chem. Phys.* **70**, 4008–4016 (1979).
61. T. Bartels-Rausch, V. Bergeron, J. H. E. Cartwright, R. Escibano, J. L. Finney, H. Grothe, P. J. Gutiérrez, J. Haapala, W. F. Kuhs, J. B. C. Pettersson, S. D. Price, C. Ignacio Sainz-Diaz, D. J. Stokes, G. Strazzulla, E. S. Thomson, H. Trinks, N. Uras-Aytemiz, Ice structures, patterns, and processes: A view across the icefields. *Rev. Mod. Phys.* **84**, 885–944 (2012).
62. G. Pallares, M. A. Gonzalez, J. L. F. Abascal, C. Valeriani, F. Caupin, Equation of state for water and its line of density maxima down to –120 MPa. *Phys. Chem. Chem. Phys.* **18**, 5896–5900 (2016).
63. V. Holten, M. A. Anisimov, Entropy-driven liquid–liquid separation in supercooled water. *Sci. Rep.* **2**, 713 (2012).

Acknowledgments: We acknowledge the beamtime at the TOFTOF instrument operated by FRM II at the Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany. **Funding:** We acknowledge financial support provided by FRM II to perform the QENS measurements. S.W. acknowledges support from Feodor Lynen Postdoctoral Research Fellowship of the Alexander von Humboldt Foundation, the Place-to-be RWTH Start-Up fund, and the DFG within SFB917. P.L. acknowledges financial support from NSF-EFRI award no. 1640860. C.A.A. acknowledges support from National Science Foundation Research grant no. CHE-1213265. **Author contributions:** C.A.A., P.L., Z.E., and S.W. initiated the project. M.S. and Z.E. performed experiments with samples contributed by S.W. and P.L. Z.E. and S.W. analyzed the data. S.W., C.A.A., and Z.E. wrote the manuscript with specific contributions from M.S. and P.L. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 15 April 2018

Accepted 26 October 2018

Published 30 November 2018

10.1126/sciadv.aat8632

Citation: S. Wei, Z. Evenson, M. Stolpe, P. Lucas, C. A. Angell, Breakdown of the Stokes-Einstein relation above the melting temperature in a liquid phase-change material. *Sci. Adv.* **4**, eaat8632 (2018).

Breakdown of the Stokes-Einstein relation above the melting temperature in a liquid phase-change material

Shuai Wei, Zach Evenson, Moritz Stolpe, Pierre Lucas and C. Austen Angell

Sci Adv 4 (11), eaat8632.
DOI: 10.1126/sciadv.aat8632

ARTICLE TOOLS

<http://advances.sciencemag.org/content/4/11/eaat8632>

SUPPLEMENTARY MATERIALS

<http://advances.sciencemag.org/content/suppl/2018/11/26/4.11.eaat8632.DC1>

REFERENCES

This article cites 60 articles, 4 of which you can access for free
<http://advances.sciencemag.org/content/4/11/eaat8632#BIBL>

PERMISSIONS

<http://www.sciencemag.org/help/reprints-and-permissions>

Use of this article is subject to the [Terms of Service](#)

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. 2017 © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. The title *Science Advances* is a registered trademark of AAAS.