Correlating ultrafast calorimetry, viscosity, and structural measurements in liquid GeTe and Ge₁₅Te₈₅

Hans Weber,¹ Jiri Orava,^{1,*} Ivan Kaban,^{1,†} Julian Pries,² and A. Lindsay Greer³

¹IFW Dresden, Institute for Complex Materials, Helmholtzstrasse 20, Dresden 01069, Germany

²I. Physikalisches Institut IA, RWTH Aachen, Sommerfeldstrasse 14, 52074 Aachen, Germany

³Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom

(Received 4 June 2018; published 21 September 2018)

Two distinct trends in the temperature dependence of viscosity, measured directly and inferred from calorimetry by analyzing crystallization kinetics, can be correlated with the temperature evolution of the height of the first peak of the x-ray total structure factor for liquid GeTe and Ge₁₅Te₈₅. The phase-change chalcogenide GeTe is a high-fragility liquid with the kinetic fragility value of 76, at the glass-transition temperature, being between those for liquid (Ag,In)-doped Sb₂Te and Ge₂Sb₂Te₅. The viscosity of the high-temperature liquid shows Arrhenius kinetics on cooling to the melting point, and the structure factor conforms to the fragile liquid. For liquid Ge₁₅Te₈₅, the temperature evolution of the structure factor suggests a transition in the temperature range of about 100 K above the melting. The crystallization shows a wide range of Arrhenius kinetics in the supercooled liquid region. This finding combined with the dynamic viscosity measurements is interpreted by invoking a weak fragile-to-strong crossover on cooling the liquid Ge₁₅Te₈₅. The differences in structures and dynamics of liquid GeTe and Ge₁₅Te₈₅ appear closely correlated to their distinctly different crystallization mechanisms.

DOI: [10.1103/PhysRevMaterials.2.093405](https://doi.org/10.1103/PhysRevMaterials.2.093405)

I. INTRODUCTION

Phase-change memory (PCM), based on chalcogenides such as Ge-Sb-Te and Ag-In-Sb-Te, is a resistive-type memory with Joule-heating-induced reversible glassy-to-crystalline transitions [1]. The phase change (PC) of interest is from the glass to the crystal via supercooled liquid. Change in this direction is the SET (writing) operation in PCM and crystallization, characterized by the crystal growth rate (U), is the rate-limiting step. The RESET operation (erasing) is via melting followed by rapid quenching with the range of critical cooling rates $\sim 10^8$ – 10^{12} K s^{−1} [2]. Two conflicting requirements must be met in PCM operation: the crystallization time must be short at elevated temperatures, preferably below ~ 1 ns [3–5] (typically < 100 ns), but the glass must be resistant to spontaneous crystallization at and to some extent above room temperature for data retention.

Chalcogenide Ge₂Sb₂Te₅ (GST) is the archetype of the PC supercooled liquid with a high kinetic fragility ($m \approx 90$) [6], where $m = [d(\log_{10}\eta)/d(T_g/T)]_{T=T_g}$ [7] just above the glass-transition temperature T_g , and high growth rate of

$\sim 10^0$ m s^{−1} spanning a remarkably wide temperature range of $(0.60\text{--}0.95)T_m$, (T_m = melting temperature). The breakdown in the Stokes-Einstein relation [8] can lead to almost $10^5 \times$ higher U around T_g [6] than would be predicted from the simple coupling relation between the kinetic coefficient of crystal growth U_{kin} and viscosity η : $U_{\text{kin}}(T) \propto \eta(T)^{-1}$ [9].

The focus here is on two compositions from the binary Ge-Te system: GeTe and Ge₁₅Te₈₅ (at. %). Liquid GeTe was reported to be a high-fragility liquid with $m \approx 131$ inferred from ultrafast differential scanning calorimetry (FDSC) [10], or $m \approx 104$ – 111 by molecular-dynamic (MD) simulations [8]. Such a high fragility does not conform well to the relatively lower activation energy for crystal growth $Q_G = 171$ kJ mol^{−1} [11] reported for GeTe in contrast to the value of $Q_G = 227$ kJ mol^{−1} for GST [12]. The breakdown in the Stokes-Einstein relation was also suggested by MD simulations in liquid GeTe, where a high atomic mobility is retained even at large supercooling ($\Delta T = T_m - T$) unlike what would be expected from the steep increase in viscosity [8]. Recent experimental work did not consider any important role of decoupling for GeTe [10].

The viscosity of supercooled liquid Ge₁₅Te₈₅ [13] does not fit to single-fragility models, but it can be described by invoking a *fragile-to-strong crossover*; the liquid is characterized by two distinct values of fragility m' (high-temperature end) and m (at T_g) on either side of the crossover. On cooling, such a liquid progressively changes from being fragile at high temperatures to moderately strong at T_g . The values of $m' \approx 90$ and $m \approx 50$ were reported for Ge₁₅Te₈₅ [13], and $m' \approx 74$ and $m \approx 37$ for AIST [14,15].

*Authors to whom correspondence should be addressed: j.orava@ifw-dresden.de

†i.kaban@ifw-dresden.de

Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

Although the liquid $\text{Ge}_{15}\text{Te}_{85}$ is not of interest as an active material for PCM because of the sluggish crystallization kinetics, the existence of a crossover similar to that for AIST, in contrast to PC liquid GeTe and $\text{Ge}_2\text{Sb}_2\text{Te}_5$, is of fundamental interest. The existence of a crossover means that fast crystallization can be maintained at high temperatures of the supercooled liquid, and longer incubation times and lower growth rates at larger ΔT [2,16], due to lower mobility, could help to improve the resistance against spontaneous crystallization. In the presence of a crossover there is no, or negligible, role of the decoupling between U_{kin} and η around T_g [9,14]. The shape of $\eta(T)$, especially at large ΔT , seems to underlie the experimentally observed difference in the crystallization mechanisms between two categories of PC chalcogenides [14]: *nucleation* dominated, represented by GST, and *growth* dominated, represented by AIST [17].

In this paper, an evaluation of $\eta(T)$ for liquid GeTe and $\text{Ge}_{15}\text{Te}_{85}$ is made by direct measurements of dynamic viscosity combined together with trends inferred from FDSC. The former system conforms to a highly fragile liquid with the experimental fragility being now between those for liquid AIST and GST. The presence of a crossover is confirmed in supercooled liquid $\text{Ge}_{15}\text{Te}_{85}$, revealing a wide range of Arrhenius kinetics at intermediate temperatures and resembling the crossover in liquid AIST. The evaluated liquid fragilities can be correlated with the temperature evolution of the x-ray structure factor.

II. MATERIALS AND METHODS

The bulk crystalline $\text{Ge}_{15}\text{Te}_{85}$ master alloy for viscosity and x-ray measurements was prepared from 5N purity elements in fused silica ampoules under Ar atmosphere of 2.5×10^4 Pa as described in Ref. [18]. The glass was prepared in a fused silica capillary, with inner diameter of 1.4 mm, with the alloy sealed under Ar atmosphere and then heated up to glowing and quenched in icy water.

Thin-film GeTe , with thickness of $d = 5.6 \mu\text{m}$, was deposited by magnetron sputtering using a background pressure of 3×10^{-4} Pa and an argon pressure of 0.6 Pa.

Calorimetric measurements were made on a Mettler Toledo Flash DSC 1. A sample ($d < 10 \mu\text{m}$, a length and a width of up to $50 \times 50 \mu\text{m}^2$, and a mass of < 75 ng) of the glassy $\text{Ge}_{15}\text{Te}_{85}$ and flakes peeled off the thin-film GeTe were used for the calorimetry.

Viscosity measurements of liquid $\text{Ge}_{15}\text{Te}_{85}$ were carried out with an oscillating-cup, described in Ref. [19]. A crucible was heated up to 1223 K at heating rate of $\Phi = 5 \text{ K min}^{-1}$ then equilibrated and subsequently measured on cooling at $\Phi = -1 \text{ K min}^{-1}$. The experimentally determined temperature-dependent density from Tsuchiya [20] was used for $\eta(T)$ calculations.

X-ray measurements were carried out at the beamline ID11 at the European Synchrotron Radiation Facility (ESRF, Grenoble) with 120-keV energy and in a fused silica capillary, an inner diameter of 1.9 mm, with similar conditions as in Ref. [18]. A commercial hot-gas blower (Cyberstar) heated the sample up to $T = 1116 \text{ K}$ followed by cooling to solidification at 658 K, with a dwell time of 3 min in between the heating and cooling, using a constant heating/cooling rate

FIG. 1. Kissinger plot of the increasing exothermic peak temperature T_p with increasing heating rate Φ in DSC. The full symbols, measured by FDSC, are for the present work on $\text{Ge}_{15}\text{Te}_{85}$ ($\Phi = 10$ – 2000 K s^{-1} , for which the inset shows the corresponding FDSC traces), and on GeTe ($\Phi = 50$ – $20\,000 \text{ K s}^{-1}$). The data of Chen *et al.* [10] are from as-deposited single-film GeTe (deposited on SiO_2/Si by magnetron sputtering, $d = 1.4 \mu\text{m}$) measured by FDSC ($\Phi = 20$ – $40\,000 \text{ K s}^{-1}$). The conventional DSC data from melt-spun ribbons of $\text{Ge}_{15}\text{Te}_{85}$ ($\Phi = 0.033$ – 0.667 K s^{-1}) are from Kaban *et al.* [25]—only the first crystallization peak is considered.

of $\Phi = \pm 5 \text{ K min}^{-1}$; the scattered intensities were measured with a FReLoN detector during cooling. Standard data treatment and corrections have been done as in Ref. [18].

III. RESULTS AND DISCUSSION

A. Ultrafast calorimetry

A Kissinger analysis [21] (Fig. 1) of the FDSC traces reveals non-Arrhenius kinetics of the thin-film GeTe crystallization (the traces are not shown) which is similar to that of Chen *et al.* [10]. Chen *et al.*'s data are taken for further calculations because of the wider temperature range than the present measurements. The curvature reflects the temperature-dependent $Q_G(T)$, therefore also $\eta(T)$, and it can be obtained by numerical modeling, described in Ref. [6]. The expression of Thompson and Spaepen [22] is used to approximate the driving force for crystallization with the thermodynamic parameters taken from Ref. [23] for GeTe and Ref. [13] for $\text{Ge}_{15}\text{Te}_{85}$.

The inset in Fig. 1 shows FDSC traces of the glassy $\text{Ge}_{15}\text{Te}_{85}$ with the endotherms representing T_g region, the exothermic crystallization peak temperature T_p used for the analysis, and the onset of melting (shown for the highest rate of $\Phi = 2000 \text{ K s}^{-1}$ only). The low eutectic-melting temperature $T_e = 658 \text{ K}$ of $\text{Ge}_{15}\text{Te}_{85}$ is used to evaluate a thermal lag in FDSC which is $\sim 5 \text{ K}$ and less. The crystallization overlaps with the melting at $\Phi > 2000 \text{ K s}^{-1}$ which makes the estimation of $Q_G(T)$ difficult [24].

The Kissinger analysis of $\text{Ge}_{15}\text{Te}_{85}$ shows Arrhenius kinetics, unlike in GeTe , with a single activation energy of $165 \pm 4 \text{ kJ mol}^{-1}$ (shown by the dashed line in Fig. 1—best

FIG. 2. Temperature-dependent dynamic viscosity $\eta(T)$ for $\text{Ge}_{15}\text{Te}_{85}$ (red open circles), solidifying around 637 K, the data of Herwig and Wobst [28] (grey open squares), and for GeTe [18] (blue open circles) on cooling ($\Phi = -1 \text{ K min}^{-1}$). The inset shows a logarithmic plot highlighting the temperature, $T_{\text{div}}^{\eta} \approx 750 \text{ K}$, at which $\eta(T)$ diverges from an Arrhenius dependence for $\text{Ge}_{15}\text{Te}_{85}$. The activation energy is $Q_{\eta} = 28 \text{ kJ mol}^{-1}$ for GeTe (taken over the full T range) and $Q_{\eta} = 18 \text{ kJ mol}^{-1}$ for $\text{Ge}_{15}\text{Te}_{85}$ at $T > T_{\text{div}}^{\eta}$.

fit to the combined measurements of conventional, only the first crystallization peak is considered, and ultrafast DSC) spanning a wide temperature range of $(0.70\text{--}0.91)T_e$. The crystallization shows a complex behavior at the conventional heating rates [25] which cannot be easily modeled using the simple numerical modeling from Refs. [6]. Therefore, only FDSC data are considered for inferring $\eta(T)$. The Arrhenius kinetics also indicates that maximum in crystal growth rate U_{max} has not been reached yet, which would be reflected by a greater apparent activation energy showing the opposite curvature to $U(T)$ in the Kissinger plot [24]. Orava *et al.* [14] (inferred from FDSC) and Salinga *et al.* [26] (optical reflectometry) showed similar Arrhenius kinetics in AIST in the intermediate temperature range of $(0.54\text{--}0.60)T_m$ and $(0.52\text{--}0.68)T_m$, respectively. Salinga *et al.* [26] argued that the Arrhenius kinetics cannot be explained by the decoupling, and Orava *et al.* [14] concluded that such Arrhenius dependence is the consequence of a weak fragile-to-strong crossover in the supercooled liquid.

B. Temperature dependence of viscosity

The dynamic viscosity $\eta(T)$ of $\text{Ge}_{15}\text{Te}_{85}$ measured in this work (tabulated data are shown in Table S1 of the Supplemental Material [27]) and that of GeTe taken from Weber *et al.* [18] are shown in Fig. 2. The uncertainty in $\eta(T)$ is below 10%. A supercooling of $\Delta T = 21 \text{ K}$ and 50 K could be achieved for $\text{Ge}_{15}\text{Te}_{85}$ and GeTe , respectively. The sharp decrease in the apparent viscosity below 637 K for $\text{Ge}_{15}\text{Te}_{85}$ is because the onset of crystallization reduces the viscous-flow-related damping in the sample. The crystallization in GeTe is very fast and the apparent viscosity goes virtually to zero within the time resolution of the measurement. The often-quoted data of Herwig and Wobst [28] for $\text{Ge}_{15}\text{Te}_{85}$ are

FIG. 3. Angell plot of $\eta(T)$ for liquid chalcogenides. The experimental values of $\eta(T)$ for the *single-fragility liquid* GeTe ($T_g = 423 \text{ K}$) are shown by the full diamonds—from Weber *et al.* [18]. The newly transposed $U_{\text{kin}}^{-1}(T)$ (open squares), the data are from Chen *et al.* [10], was obtained by numerical modeling [6] of the Kissinger plot (Fig. 1). The best fit of $\eta(T)$ to the MYEGA model [29] is shown by the blue solid curve giving $m = 76$. The shape of $\eta(T)$ derived by Chen *et al.* [10] is shown by the dashed curve giving $m = 131$. A *fragile-to-strong crossover* in $\text{Ge}_{15}\text{Te}_{85}$ ($T_g = 406 \text{ K}$) is represented by the red solid curve (the best fit to the generalized-MYEGA model [32]). The dynamic viscosity $\eta(T)$ (full circles) and the transposed $U_{\text{kin}}^{-1}(T)$ from FDSC (red open circles) are from the present work. A crossover prediction of Wei *et al.* [13] for $\text{Ge}_{15}\text{Te}_{85}$ is based on the Adam-Gibbs theory and the best fit to calorimetric measurements and viscosity data digitized from Neumann *et al.* [35]. The data of Herwig and Wobst [28] are shown by the black open circles. The viscosity of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [6] from Orava *et al.* and on the crossover in $\text{Ag}_{5.5}\text{In}_{6.5}\text{Sb}_{59}\text{Te}_{29}$ [15] are respectively from FDSC and from the combination of FDSC with $\eta(T)$ measurements.

shown in Fig. 2 for comparison. The present $\eta(T)$ and that of Herwig and Wobst strongly differ below $\approx 710 \text{ K}$ (see the inset plot). The Herwig and Wobst temperature dependence gives a sharper rise in $\eta(T)$ on cooling which is more pronounced on the Angell plot in Fig. 3 (discussed later). With the new high-temperature $\eta(T)$ established, its shape over the entire supercooled liquid region can be described.

For liquid GeTe , $\eta(T)$ can be modeled with a single value of fragility by using the MYEGA (Mauro-Yue-Ellison-Gupta-Allan) model [29]: $\log_{10}\eta(T) = \log_{10}\eta_{\infty} + (B/T)\exp(C/T)$, where η_{∞} is the high-temperature limit of viscosity, and B and C are adjustable parameters. The fit is constrained to contain the measured dynamic $\eta(T)$ (full diamonds) and the newly transposed $U_{\text{kin}}(T)^{-1}$ (open squares)—the shape is obtained by numerical modeling [6] from Chen *et al.* [10]. The best fit to the MYEGA model gives $\log_{10}\eta_{\infty} = -3.317 \pm 0.008 \text{ (Pa s)}$, $B = 126 \pm 3 \text{ K}$, and $C = 1666 \pm 8 \text{ K}$, with $R^2 = 0.9995$ (Fig. 3; the blue solid curve). The best fit defines a new value of $m \approx 76$, unlike $m \approx 131$ given by the dashed curve of Chen *et al.* [10] in Fig. 3. The viscosity suggested by Chen *et al.* [10] was derived by fitting transposed $U_{\text{kin}}(T)^{-1}$, obtained from FDSC, and high-temperature viscosity inferred from MD simulations by

Sosso *et al.* [23] to the MYEGA model. Taking the experimental $U_{\max} \approx 3.3 \text{ m s}^{-1}$ at $0.85T_m$ for as-deposited thin-film GeTe ($d = 30 \text{ nm}$), by Santala *et al.* [30] using dynamical transmission electron microscopy (TEM), the theoretical fragility can be estimated from the empirical relation presented by Orava and Greer [31] to be $m \approx 50\text{--}70$, i.e., between AIST ($m \approx 37$) and GST ($m \approx 90$) at T_g . Chen *et al.* [16] suggested the occurrence of a crossover in GeTe nanoparticles, with an average diameter of 10 nm, and they derived $m = 78$ by using a generalized-MYEGA model [32] which is surprisingly similar to the present value. It should be noted that viscosity of GST nanoparticles also shows a crossover with $m = 57\text{--}62$ [33], which is lower than that for the thin film ($m \approx 90$) [6]. Using a continuous normal crystal growth model [9], assuming no decoupling, the present calculated $U_{\max}$ is $\sim 0.8 \text{ m s}^{-1}$ at $0.89T_m$, which is close to the value reported by Santala *et al.* [30].

For liquid $\text{Ge}_{15}\text{Te}_{85}$, unlike for GeTe, it was suggested that $\eta(T)$ cannot be described with a single value of m [13,14]. For example, the best fit of the measured $\eta(T)$ (from Fig. 2) to the MYEGA model is not good, and gives $m = 98$ at T_g (the fit is shown in Fig. S1 of the Supplemental Material [27]), i.e., reiterating the ratio of $m'/m \approx 2$ for $\text{Ge}_{15}\text{Te}_{85}$ [13]. A fragile-to-strong crossover suggested by Wei *et al.* [13] is based on the Adams-Gibbs theory applied to calorimetric data and it is shown by the black dash-dotted line in Fig. 3, the strong end being characterized by $m = 50$ at T_g . Wei *et al.*'s fit accounts for the peak in the specific heat capacity around T_e , also known for liquid $\text{Te}_{80}\text{Ge}_{20-x}\text{Pb}_x$ [34], giving it its characteristic “double-kink” in $\eta(T)$. This may be further exaggerated because they considered the digitized high-temperature $\eta(T)$ taken from the work of Neumann *et al.* [35] in which the best fit of the Herwig and Wobst [28] data (black open circles in Fig. 3) to an exponential function is presented. A fragile-to-strong crossover can be described by the generalized-MYEGA model [32]: $\log_{10}\eta(T) = \log_{10}\eta_{\infty} + \{T[W_1\exp(-C_1/T) + W_2\exp(-C_2/T)]\}^{-1}$, where η_{∞} has the same meaning as in the MYEGA equation, and W_1 , C_1 , W_2 , and C_2 are fitting parameters. The fitting constraints are the dynamic $\eta(T)$ measured in this work, the transposed $U_{\text{kin}}(T)^{-1}$ from FDSC, and the kinetic fragility of 50 from Wei *et al.* [13]. The best fit to the generalized-MYEGA gives $\log_{10}\eta_{\infty} = -3.130 \pm 0.006$ (Pa s), $W_1 = (3.1 \pm 0.5) \times 10^{-4} \text{ K}^{-1}$, $C_1 = 330 \pm 60 \text{ K}$, $W_2 = 0.56 \pm 0.06 \text{ K}^{-1}$, and $C_2 = 4060 \pm 80 \text{ K}$, with $R^2 = 0.9996$, shown by the red solid curve in Fig. 3. A wide range of Arrhenius kinetics similar to that for AIST [14,15,26] can be distinguished (Fig. 3). Laser-induced crystallization experiments show that GeTe has the highest and $\text{Ge}_{15}\text{Te}_{85}$ has the lowest crystallization rate in the binary Ge-Te system [36]. The very sluggish kinetics in $\text{Ge}_{15}\text{Te}_{85}$ arises because of the strong behavior of the supercooled liquid in the range of $T_g/T = 0.75\text{--}1$, contrary to the fragile liquid GeTe.

C. Temperature evolution of the x-ray structure factor

The origin of a crossover in liquid chalcogenides remains unclear. It has been suggested that these are transitions between high-temperature metallic and low-temperature semiconducting liquids with directional covalent bonding [14].

FIG. 4. *Left-hand abscissa*: Temperature evolution of the height of the first peak $S(Q_1)$ of the x-ray structure factor for GeTe, $\text{Ge}_{15}\text{Te}_{85}$, and $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The data points of $\text{Ge}_{15}\text{Te}_{85}$ are vertically displaced by -0.2 for clarity. The data on the high-temperature liquid GeTe are taken from Weber *et al.* [18] on cooling ($\Phi = -5 \text{ K min}^{-1}$) and the room-temperature point is from Piarristeguy *et al.* [40] (as-deposited thin-film GeTe, $d = 1 - 3 \mu\text{m}$); extrapolated to T_g . The data on glassy (measured on heating, $\Phi = 20 \text{ K min}^{-1}$) and supercooled (measured on cooling, $\Phi = -20 \text{ K min}^{-1}$) $\text{Ge}_{15}\text{Te}_{85}$ are from Wei *et al.* [39] from measurements of bulk samples. The amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (as-deposited thin film, $d = 1\text{--}3 \mu\text{m}$) is from Jovari *et al.* [54], extrapolated to T_g using the temperature coefficient of $\text{Ge}_{15}\text{Te}_{85}$. The structural fragility index γ is highlighted by the vertical lines. Linear extrapolations of the high-temperature-liquids trends are shown by the corresponding dashed lines. *Right-hand abscissa*: Temperature dependence of mass density for liquid [20] and glassy [52] $\text{Ge}_{15}\text{Te}_{85}$.

Mauro *et al.* [37] demonstrated in several metallic-glass-forming liquids that the temperature evolution of the total structure factor $S(Q)$ can be correlated with kinetic fragility. A *structural fragility index* has been defined from the height of the first peak $S(Q_1)$ of the total structure factor as $\gamma = [(S(Q_1)_{\text{glass}} - S(Q_1)_{\text{extrapolated liquid}})/S(Q_1)_{\text{glass}}]100$ at T_g [37]; more details can be found in Refs. [37,38]. Though the chalcogenide semiconducting liquids and glasses are characterized by a short-range order (SRO) essentially different from that of liquid and glassy metals, the concept of the structural fragility seems to also provide a useful insight into structural evolution of liquid and glassy chalcogenides with temperature.

The temperature evolutions of the height of the first peak $S(Q_1)$ for $\text{Ge}_{15}\text{Te}_{85}$, GeTe (taken from Ref. [18]) and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are shown in Fig. 4. A three-dimensional view of the total x-ray structure factor for $\text{Ge}_{15}\text{Te}_{85}$ on cooling between 1116 and 657 K is shown in the Supplemental Material (Fig. S2) [27]. The $S(Q_1)$ for $\text{Ge}_{15}\text{Te}_{85}$ glass and the low-temperature liquid from Wei *et al.* [39] are also shown. We are not aware of any data for the temperature dependence of the $S(Q)$ for GeTe glass. Therefore $S(Q_1)$ of amorphous thin-film GeTe at room temperature reported by Piarristeguy *et al.* [40] and its extrapolation to T_g using the temperature coefficient of $\text{Ge}_{15}\text{Te}_{85}$ glass are plotted in Fig. 4.

For GeTe , $S(Q_1) - T$ follows linear dependence, above T_m , and $\gamma = 12.9$ (Fig. 4); the large discrepancy between the amorphous phase and the extrapolated liquid indicates a fragile liquid, which is in accordance with the viscosity (Fig. 3). A greater discrepancy between the extrapolations, $\gamma = 16.5$, can be seen for the phase-change chalcogenide $\text{Ge}_2\text{Sb}_2\text{Te}_5$ conforming to $m_{\text{Ge}_2\text{Sb}_2\text{Te}_5} = 90$ [6] vs $m_{\text{GeTe}} = 76$. The liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ was measured at the beamline ID11 at ESRF, Grenoble, using similar conditions as in Ref. [18].

For $\text{Ge}_{15}\text{Te}_{85}$, $S(Q_1) - T$ shows a remarkable deviation from the high-temperature linear dependence on cooling. The structural fragility of the extrapolated high-temperature liquid (the red dashed line in Fig. 4) is $\gamma = 8.2$. Taking the data of Wei *et al.* [39] only gives $\gamma = 10.2$, demonstrating that the eutectic composition is an apparently stronger liquid relative to GeTe . The divergence temperature $T_{\text{div}}^{S(Q_1)} \approx 750$ K (Fig. 4) corresponds to the value obtained by viscosity measurement $T_{\text{div}}^{\eta} \approx 750$ K (see the inset in Fig. 2). This temperature lies in the temperature range of ~ 600 – 800 K in which the anomalous behavior of several physical properties of liquid $\text{Ge}_{15}\text{Te}_{85}$ (e.g., molar volume, compressibility, sound velocity, specific heat capacity) was observed by Tsuchiya *et al.* [20,41–43]. Characterization of the $S(Q_1)$ evolution for the supercooled liquid region is hindered by the onset of crystallization around 592 K ($0.90T_m$) on cooling [39]. The Kissinger analysis shows a wide range of Arrhenius kinetics at $(0.70$ – $0.91)T_m$ (Fig. 1). This range coincides with the “no-man’s land” in the intermediate temperature range of the $S(Q_1)$ plot (Fig. 4), which could suggest a (nearly) Arrhenius trend (note the different activation energies).

As discussed by Angell and co-workers [13,39] there is a link between thermodynamic properties (represented, e.g., by an excess entropy), structure, and therefore $\eta(T)$ for $\text{Ge}_{15}\text{Te}_{85}$, and other liquids. Structural studies of $\text{Ge}_{15}\text{Te}_{85}$, e.g., Refs. [44–50], show that there is a transition from high-temperature to low-temperature liquid in the temperature range of about 100 K above T_m . Analysis of the partial atomic distributions in liquid $\text{Ge}_{15}\text{Te}_{85}$ [49] reveals developing tetrahedral local order in the low-temperature liquid, similar to that in the glassy state [51]. In particular, the first- and the second-coordination shells for Ge-Te and Te-Te correlations become very pronounced (distinctly separated) on cooling to the melting temperature. Wei *et al.* [39] analyzed the temperature dependencies of the total structure factors and pair distribution functions for $\text{Ge}_{15}\text{Te}_{85}$, particularly the ratio of the peak heights $S(Q_1)/S(Q_2)$ and the $S(Q_1)$ prepeak, and they also concluded that the crossover in liquid $\text{Ge}_{15}\text{Te}_{85}$ is related to the structural changes on SRO and on the medium-range (~ 8 Å) order (MRO) length scale.

A gradual structural change from the high-temperature to the low-temperature liquid $\text{Ge}_{15}\text{Te}_{85}$ between ≈ 750 K and T_m is seen in the temperature dependencies of $S(Q_1)$ in Fig. 4. Unfortunately, there are no data for the supercooled liquid between 461 and 592 K because of the occurrence of crystallization at the applied heating/cooling rates in the diffraction experiment [39]. Still, it is reasonable to suppose that after

formation of the low-temperature liquid with predominant tetrahedral order [49] around the eutectic temperature, this structure remains until freezing into the glass. This scenario is supported by the temperature dependency of the density of liquid [20] and glassy $\text{Ge}_{15}\text{Te}_{85}$ [52] presented in Fig. 4. The temperature evolution of $S(Q_2)$ (Fig. S3 of the Supplemental Material [27]), similar to that in Ref. [49] (see Fig. 3 in the reference), does not reflect so well the “anomalous” structural changes in liquid $\text{Ge}_{15}\text{Te}_{85}$ revealed by $S(Q_1) - T$.

For comparison we note that Georgarakis *et al.* [53] measured temperature-dependent $S(Q_1)$ in the entire supercooled region of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ with clear SRO and MRO evolution on cooling ($\Phi \approx -100$ K s $^{-1}$). Two structural fragility regimes, a fragile and a strong end, could be distinguished between the high- (above T_m) and the low-temperature (at large ΔT) liquid, respectively. The temperature of an “interplay” between the two γ ends, estimated by linear extrapolations, correlates with the temperature of a sharp increase in $\eta(T)$ hinting at a possible crossover in the liquid and demonstrating the correlation between $S(Q_1)$ and $\eta(T)$.

IV. CONCLUSIONS

The present work shows that the trends in the temperature-dependent viscosity, measured directly and inferred from calorimetry, can be correlated with the temperature evolution of the structure factor in the liquid chalcogenides. Two distinct temperature dependent behaviors of viscosity and structure factor are found between liquid GeTe and $\text{Ge}_{15}\text{Te}_{85}$. The chalcogenide GeTe conforms to a high-fragility liquid ($m = 76$) at T_g , and the high-temperature liquid, above T_m , shows Arrhenius kinetics in $\eta(T)$ and linear temperature evolution of $S(Q_1)$. For $\text{Ge}_{15}\text{Te}_{85}$, the temperature evolution of $S(Q_1)$ suggests a structural change from high-temperature metallic to low-temperature semiconducting liquid on cooling. The crystallization shows Arrhenius kinetics in the intermediate temperature range of the supercooled region because of the presence of the weak fragile-to-strong crossover on cooling. A tight correlation between the dynamic and the structural properties of the liquids studied explains the distinct crystallization mechanisms—the presence of a crossover and slow crystallization for $\text{Ge}_{15}\text{Te}_{85}$, and the absence of a crossover and fast crystallization for GeTe , which is important for phase-change memory applications and its performance.

ACKNOWLEDGMENTS

I.K. acknowledges the financial support by the German Research Foundation DFG (Contract No. Ka-3209/6-1). Professor M. Wuttig (RWTH Aachen) is greatly acknowledged for discussion. High-temperature x-ray diffraction measurements were done on the beamline ID11 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. We are grateful to Dr. J. Wright for the assistance with using the beamline and data treatment. We thank B. Opitz, B. Bartusch, and C. G. F. Blum for technical support. Dr. S. Wei is acknowledged for providing the XRD data for $\text{Ge}_{15}\text{Te}_{85}$ published in Ref. [39].

- [1] M. Wuttig and N. Yamada, *Nat. Mater.* **6**, 824 (2007).
- [2] J. Orava and A. L. Greer, *Acta Mater.* **139**, 226 (2017).
- [3] D. Loke, T. H. Lee, W. J. Wang, L. P. Shi, R. Zhao, Y. C. Yeo, T. C. Chong, and S. R. Elliott, *Science* **336**, 1566 (2012).
- [4] G. Bruns, P. Merkelbach, C. Schlockermann, M. Salinga, M. Wuttig, T. D. Happ, J. B. Philipp, and M. Kund, *Appl. Phys. Lett.* **95**, 043108 (2009).
- [5] F. Rao, K. Ding, Y. Zhou, Y. Zheng, M. Xia, S. Lv, Z. Song, S. Feng, I. Ronneberger, R. Mazzarello, W. Zhang, and E. Ma, *Science* **358**, 1423 (2017).
- [6] J. Orava, A. L. Greer, B. Gholipour, D. W. Hewak, and C. E. Smith, *Nat. Mater.* **11**, 279 (2012).
- [7] C. A. Angell, *Science* **267**, 1924 (1995).
- [8] G. C. Sosso, J. Behler, and M. Bernasconi, *Phys. Status Solidi B* **249**, 1880 (2012).
- [9] M. D. Ediger, P. Harrowell, and L. Yu, *J. Chem. Phys.* **128**, 034709 (2008).
- [10] Y. Chen, G. Wang, L. Song, X. Shen, J. Wang, J. Huo, R. Wang, T. Xu, S. Dai, and Q. Nie, *Cryst. Growth Des.* **17**, 3687 (2017).
- [11] Q. M. Lu and M. Libera, *J. Appl. Phys.* **77**, 517 (1995).
- [12] J. Kalb, F. Spaepen, and M. Wuttig, *Appl. Phys. Lett.* **84**, 5240 (2004).
- [13] S. Wei, P. Lucas, and C. A. Angell, *J. Appl. Phys.* **118**, 034903 (2015).
- [14] J. Orava, D. W. Hewak, and A. L. Greer, *Adv. Funct. Mater.* **25**, 4851 (2015).
- [15] J. Orava, H. Weber, I. Kaban, and A. L. Greer, *J. Chem. Phys.* **144**, 194503 (2016).
- [16] B. Chen, D. de Wal, G. H. ten Brink, G. Palasantzas, and B. J. Kooi, *Cryst. Growth Des.* **18**, 1041 (2018).
- [17] G.-F. Zhou, *Mater. Sci. Eng. A* **304–306**, 73 (2001).
- [18] H. Weber, M. Schumacher, P. Jvri, Y. Tsuchiya, W. Skrotzki, R. Mazzarello, and I. Kaban, *Phys. Rev. B* **96**, 054204 (2017).
- [19] S. Gruner, *J. Alloy Compds.* **480**, 629 (2009).
- [20] Y. Tsuchiya, *J. Non-Cryst. Solids* **312–314**, 212 (2002).
- [21] J. Orava and A. L. Greer, in *Handbook of Thermal Analysis and Calorimetry*, edited by S. Vyazovkin, N. Koba, and C. Schick (Elsevier, Amsterdam, 2018), Chap. 17, p. 685.
- [22] C. V. Thompson and F. Spaepen, *Acta Metall.* **27**, 1855 (1979).
- [23] G. C. Sosso, G. Miceli, S. Caravati, F. Giberti, J. Behler, and M. Bernasconi, *J. Phys. Chem. Lett.* **4**, 4241 (2013).
- [24] J. Orava and A. L. Greer, *Thermochim. Acta* **603**, 63 (2015).
- [25] I. Kaban, E. Dost, and W. Hoyer, *J. Alloy Compds.* **379**, 166 (2004).
- [26] M. Salinga, E. Carria, A. Kaldenbach, M. Bornfft, J. Benke, J. Mayer, and M. Wuttig, *Nat. Commun.* **4**, 2371 (2013).
- [27] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevMaterials.2.093405> for the dynamic viscosity (Table S1), the single-value fragility best fit (Fig. S1), the temperature evolution of the total structure factor for Ge₁₅Te₈₅ (Fig. S2), and the temperature dependence of $S(Q_2)$ (Fig. S3).
- [28] F. Herwig and M. Wobst, *Z. Metallkde.* **82**, 917 (1991).
- [29] J. C. Mauro, Y. Yue, A. J. Ellison, P. K. Gupta, and D. C. Allan, *Proc. Natl. Acad. Sci. USA* **106**, 19780 (2009).
- [30] M. K. Santala, B. W. Reed, S. Raoux, T. Topuria, T. LaGrange, and G. H. Campbell, *Appl. Phys. Lett.* **102**, 174105 (2013).
- [31] J. Orava and A. L. Greer, *J. Chem. Phys.* **140**, 214504 (2014).
- [32] C. Zhang, L. Hu, Y. Yue, and J. C. Mauro, *J. Chem. Phys.* **133**, 014508 (2010).
- [33] B. Chen, G. H. ten Brink, G. Palasantzas, and B. J. Kooi, *J. Phys. Chem. C* **121**, 8569 (2017).
- [34] L. Battezzati and A. L. Greer, *J. Mater. Res.* **3**, 570 (1988).
- [35] H. Neumann, F. Herwig, and W. Hoyer, *J. Non-Cryst. Solids* **205–207**, 438 (1996).
- [36] M. Chen, K. A. Rubin, and R. W. Barton, *Appl. Phys. Lett.* **49**, 502 (1986).
- [37] N. A. Mauro, M. Blodgett, M. L. Johnson, A. J. Vogt, and K. F. Kelton, *Nat. Commun.* **5**, 4616 (2014).
- [38] K. F. Kelton, *J. Phys.: Condens. Matter* **29**, 023002 (2017).
- [39] S. Wei, M. Stolpe, O. Gross, W. Hembree, S. Hechler, J. Bednarcik, R. Busch, and P. Lucas, *Acta Mater.* **129**, 259 (2017).
- [40] A. A. Piarristeguy, M. Micoulaut, R. Escalier, P. Jvri, I. Kaban, J. van Eijk, J. Luckas, S. Ravindren, P. Boolchand, and A. Pradel, *J. Chem. Phys.* **143**, 074502 (2015).
- [41] Y. Tsuchiya, *J. Phys. Soc. Jpn.* **60**, 227 (1991).
- [42] Y. Tsuchiya and H. Saitoh, *J. Phys. Soc. Jpn.* **62**, 1272 (1993).
- [43] Y. Tsuchiya, K. Saitoh, and F. Kakinuma, *Monatshefte fr Chem.* **136**, 1963 (2005).
- [44] H. Neumann, W. Hoyer, W. Matz, and M. Wobst, *J. Non-Cryst. Solids* **97–98**, 1251 (1987).
- [45] Y. Kameda, O. Uemura, and T. Usuki, *Mater. Trans., JIM* **37**, 1655 (1996).
- [46] S. Yoshioka, Y. Kawakita, M. Kanehira, and S. Takeda, *Jpn. J. Appl. Phys. Suppl.* **38**, 468 (1999).
- [47] C. Bichara, J. P. Gaspard, and J. R. Raty, *J. Non-Cryst. Solids* **312–314**, 341 (2002).
- [48] C. Bergman, C. Bichara, J. P. Gaspard, and Y. Tsuchiya, *Phys. Rev. B* **67**, 104202 (2003).
- [49] I. Kaban, P. Jvri, W. Hoyer, R. G. Delaplane, and A. Wannberg, *J. Phys.: Condens. Matter* **18**, 2749 (2006).
- [50] I. Kaban, W. Hoyer, A. Il'inskii, A. Shpak, and P. Jvri, *J. Non-Cryst. Solids* **353**, 1808 (2007).
- [51] P. Jvri, I. Kaban, W. Hoyer, R. G. Delaplane, and A. Wannberg, *J. Phys.: Condens. Matter* **17**, 1529 (2005).
- [52] I. Kaban, P. Jvri, W. Hoyer, and E. Welter, *J. Non-Cryst. Solids* **353**, 2474 (2007).
- [53] K. Georgarakis, L. Hennet, G. A. Evangelakis, J. Antonowicz, B. G. Bokas, V. Honkimaki, A. Bytchkov, M. W. Chen, and A. R. Yavari, *Acta Mater.* **87**, 174 (2015).
- [54] P. Jvri, I. Kaban, J. Steiner, B. Beuneu, A. Schps, and A. Webb, *J. Phys.: Condens. Matter* **19**, 335212 (2007).