Dynamics of the Negative Thermal Expansion in Tellurium Based Liquid Alloys

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Negative thermal expansion (NTE) in tellurium based liquid alloys ($GeTe_6$ and $GeTe_{12}$) is analyzed through the atomic vibrational properties. Using neutron inelastic scattering, we show that the structural evolution resulting in the NTE is due to a gain of vibrational entropy that cancels out the Peierls distortion. In the NTE temperature range, these competing effects give rise to noticeable changes in the vibrational density of states spectra. Additional first principles molecular dynamics simulations emphasize the role of the temperature dependance of the Ge atomic environment in this mechanism. For comparison, we extended our study to $Ge_2Sb_2Te_5$ and $Ge_1Sb_2Te_4$ phase-change materials.

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Not all materials expand when heated. The thermal expansion of condensed matter is the rule, due to the anharmonicity of the interatomic potential, but there are some exceptions, in solids and even in liquids, the most famous example being water in a 4 K range above its melting point [1]. As discussed by Barrera *et al.* [2], a negative thermal expansion (NTE) is observed in systems with different types of structures and bonding mechanisms: in alkali halides with rocksalt structure, in semiconductors with zinc blende structure, or in more complex structures made of rigid units bonded through bridging atoms. Some show a NTE over more than 1000 K [3]. This NTE behavior, often referred to as the "density anomaly," is also observed in some low coordinated liquid structures. Liquid compounds such as HgTe [4], In_2Te_3 [5], Ga_2Te_3 [5], As_2Te_3 [6] display a negative thermal expansion in a limited temperature range and the alloys Ge_xTe_{1-x} ($0 < x < 0.2$) [7] show the same behavior close to the melting point, either in the supercooled liquid (e.g. pure tellurium [8]) or in the thermodynamically stable liquid. In this latter case, the effect is most prominent around the eutectic concentration ($Ge_{15}Te_{85}$, referred to here as $GeTe_6$) between 633 and 733 K. It has been extensively studied by thermodynamic (density [7], specific heat [9]) and electrical resistivity measurements [10]. These anomalous variations in macroscopic properties have been related to structural changes, experimentally [11,12], or by first principles molecular dynamics (FPMD) [13]. These studies led to a picture of a p-bonded liquid in which atoms have an octahedral environment. This octahedral local structure is distorted at low temperature by a Peierls-like mechanism, leading to a larger atomic volume. At higher temperature, a more symmetric structure is recovered, together with a smaller volume because the longer bonds are more easily shortened than the shorter ones are elongated. This proposed mechanism displays some analogy with the $\alpha \rightleftharpoons \beta$ transition of the crystalline Ge-Te compound [14] that results from the disappearance of the Peierls distortion stabilizing the low temperature α-GeTe phase. However, no driving force for this gradual structural change in the liquid state could be clearly identified up to now and the first goal of the present work is to investigate this NTE via an analysis of the dynamical properties of liquid $GeTe_6$ and $GeTe_{12}$. Neutron inelastic scattering is the method of choice to measure the interatomic force constants as a function of the temperature around the NTE. We have extended our study to the dynamical structure of $Ge_2Sb_2Te_5$ and $Ge_1Sb_2Te_4$ liquid alloys. These are typical materials that form the active layer of phase change (PC) nonvolatile data storage devices. They do not exhibit any NTE in the stable liquid state, but adopt, like $GeTe_6$, a mostly octahedral local order, as evidenced by FPMD [15] and by an extensive set of neutron scattering measurements performed at various temperatures [16].

In this Letter we identify the driving force for the NTE: we demonstrate the role of the vibrational entropy by performing measurements of the vibrational densities of states (VDOS) of $GeTe_6$, $GeTe_{12}$, $Ge_1Sb_2Te_4$ and $Ge_2Sb_2Te_5$ at various temperatures by neutron inelastic scattering on the IN6 spectrometer at the ILL (Grenoble). For $GeTe_6$, measurements were performed at 673, 773 and 873 K. For $GeTe_{12}$ they were made at 643, 683, 693, 703, 763 and 873 K. For $Ge_1Sb_2Te_4$ and $Ge_2Sb_2Te_5$ the temperatures were 973, 1073, and 1173 K. The usual corrections were applied to the data: normalization of the spectra to identical values, subtraction of the quartz contribution and normalization to a reference spectrum of a 6 mm diameter vanadium cylinder. The data were corrected for the energy dependent detector efficiency and time-independent background. The time-of-flight data were converted into a dynamical structure factor $S(2\theta, \omega)$. An integration of $S(2\theta, \omega)$ over the 2θ range accessible to the experiment (10° to 115°) was performed in order to obtain the VDOS, $n(\omega)$ [17]. Finally, the experimental VDOS was normalized to unity. As the q-range available to the experiment is finite and correlated with the ω range, the $n(\omega)$ density is incomplete and slightly distorted. However, since the (q, ω) range is the same for all measurements, comparisons of $n(\omega)$ are reliable. The measured VDOS's are presented in Fig. 1. The error bars are estimated at $\pm 2\%$. The overall shapes are quite similar for the four systems studied, with noticeable contributions up to ~ 40 meV and a main broad peak around 10–20 meV. Close to zero energy transfer, the full contribution of the quasielastic neutron scattering (QENS) due to diffusion in the liquid could be removed, while it still contributes at higher energies. For this reason, the VDOS increase steeply (almost linearly) at low energies. This effect is steeper at higher temperature for GeTe_x and independent of T for PC materials. Accordingly, in the scattering function $S(q, \omega)$ (in which the QENS signal is most evident) GeTe_x materials show a significant temperature dependence of the width of the QENS signal, whereas the QENS signal of PC materials is essentially temperature independent. Moreover, these measurements produce contrasted results concerning the temperature dependence of the VDOS. The $\mathrm{Ge_1Sb_2Te_4}$ and $\mathrm{Ge_2Sb_2Te_5}$ VDOS's remain essentially unchanged in the 200 K range spanned. On the contrary $\mathrm{GeTe_6}$ and $\mathrm{GeTe_{12}}$ VDOS's show significant changes with temperature. Between 18 and 35 meV, the vibrational modes are shifted towards lower energies (or frequencies) when temperature is increased within the range of the NTE. This redshift is consequently related to the structural changes that are associated to the density anomaly. Since it appears in the medium to high frequency side of the VDOS, we may assume that it concerns mostly Ge-Te bonds (involving the lightest atoms, Ge). To quantify the shift of the vibrational modes to lower energies, we fitted the spectra with a sum of two Lorentzian functions, whose centers are indicated in Table I. We can see that the low energy part of the spectra remains roughly stable, for all the compounds, in the experimental temperature range. The center of the second Lorentzian, at higher energy, remains almost constant with temperature, within the accuracy of the experiments, in $\mathrm{Ge_2Sb_2Te_5}$ and $\mathrm{Ge_1Sb_2Te_4}$. On the contrary, in $\mathrm{GeTe_{12}}$ and $\mathrm{GeTe_6}$, the change of the vibrational modes is rather sharp: the second peak center shifts, respectively, by -23% and -24% while increasing temperature.

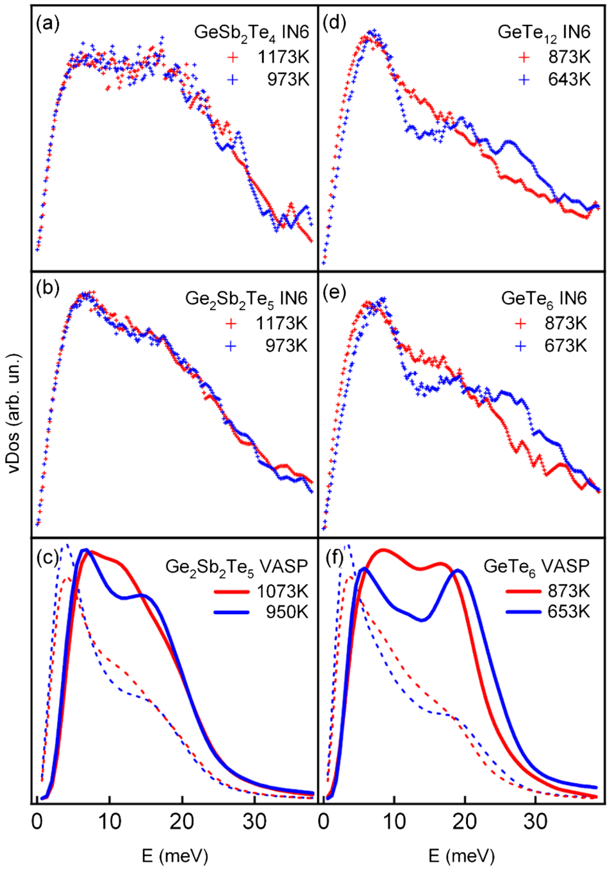

FIG. 1 (color online). Evolution of the VDOS with temperature for $\mathrm{Ge_1Sb_2Te_4}$ (a), $\mathrm{Ge_2Sb_2Te_5}$ (b), $\mathrm{GeTe_{12}}$ (d), and $\mathrm{GeTe_6}$ (e), obtained on IN6. Total VDOS obtained from $S(q, \omega)$ calculated on MD simulated $\mathrm{Ge_2Sb_2Te_5}$ and $\mathrm{GeTe_6}$ structures are plotted on (c) and (f) (dotted lines), jointly with the differences between VDOS and $\mathrm{VDOS_{sum_p}}$; see Eq. (4) (plain lines).

This analysis is coherent with the study of the VDOS's of liquid $\mathrm{GeTe_6}$ and $\mathrm{Ge_2Sb_2Te_5}$ that were calculated on atomic trajectories obtained using FPMD (VASP code) [18,22]. We calculated the total dynamical structure factor $S(q, \omega)$ and the partial dynamical structure factors $S_p(q, \omega)$ (for each type of element) on the molecular dynamic trajectories obtained for $\mathrm{GeTe_6}$ and $\mathrm{Ge_2Sb_2Te_5}$. We integrated the total and partial structure factors obtained from simulations over the same q range as accessible on the IN6 experiment, to obtain the total and partial vibrational densities of states

$$S(q, \omega) \rightarrow \mathrm{VDOS}, \tag{1}$$

$$S_p(q, \omega) \rightarrow \mathrm{VDOS}_p \quad \text{for Ge, Sb or Te atoms.} \tag{2}$$

The total VDOS are plotted (dashed lines) in Fig. 1(c) and 1(f). The FPMD results are in qualitative agreement with the experimental trends: in the case of $\mathrm{GeTe_6}$, we see a shift of the high frequency tail (which ranges from 18 to 30 meV) towards lower energies with increasing temperature and no evolution of this part of the spectra in the case of $\mathrm{Ge_2Sb_2Te_5}$. Nevertheless, in the simulations, the vibrational frequencies are about 30% lower than in the experiment, meaning that the calculated vibrational modes are too soft. This is in line with the observation that the

TABLE I. Centers (in meV) of the two peaks obtained by a fit of the experimental density of vibrational states with a sum of two Lorentzian curves (and the standard deviations), for every compound, at the different temperatures.

Composition	$Ge_1Sb_2Te_4$		$Ge_2Sb_2Te_5$		$GeTe_{12}$		$GeTe_6$	
Temperature	973 K	1173 K	973 K	1173 K	643 K	873 K	673 K	873 K
First peak	7.1(2)	6.4(1)	6.5(1)	6.4(1)	6.9(1)	6.7(1)	7.4(1)	6.3(1)
Second peak	18.8(3)	17.9(2)	17.6(2)	17.0(2)	20.4(4)	15.6(7)	22.4(2)	16.3(3)

computed local structure [13] is not distorted enough, leading to a too broad first neighbor peak in the pair correlation function and a too low second peak in the static structure factor as compared to the experiments [11]. However, the trends are reproduced and further analysis of the simulation results confirms that the high energy modes that appear between 18 and 30 meV in $GeTe_6$ at low temperature corresponds to Ge atoms contributions. Because of this general lowering of vibrational frequencies compared to the experiment, the diffusion contribution to the spectra (which arises at low energy) is dominating and partly obscuring the expected frequency shift. To remove the contribution of diffusion to the spectra, we proceeded as follows. We summed the partial VDOS_p obtained in Eq. (2), weighted by the concentration c of each element (Ge, Sb, or Te), and obtained, for $GeTe_6$ and $Ge_2Sb_2Te_5$, a $\mathrm{VDOS}_{\mathrm{sum}_p}$ that contains all the homopolar vibrational information, as well as the full diffusive part of the spectra

$$\mathrm{VDOS}_{\mathrm{sum}_p} = \sum_{el=\mathrm{Ge,Sb,Te}} c(el)\mathrm{VDOS}_p(el). \qquad (3)$$

The differences between the VDOS obtained from total $S(q, \omega)$ and the $\mathrm{VDOS}_{\mathrm{sum}_p}$ give $\mathrm{VDOS}_{\mathrm{dif}}$, which contains all interactions except the homopolar ones, and without the atomic diffusion

$$\mathrm{VDOS}_{\mathrm{dif}} = \mathrm{VDOS} - \mathrm{VDOS}_{\mathrm{sum}_p}. \qquad (4)$$

Finally, those differences, plotted in Fig. 1 for $Ge_2Sb_2Te_5$ (c) and $GeTe_6$ (f), were normalized to unity. This decomposition emphasizes the temperature evolution of the highest frequency modes in $GeTe_6$.

Actually, the observed redshift of the VDOS correlated with the volume contraction induced by a temperature increase in $Ge_xTe_{(1-x)}$ alloys ($0 \leq x \leq 0.20$) can be easily interpreted within the distorted octahedral liquid model briefly sketched in the introduction. Since the liquid is essentially chemically ordered in the temperature range of the NTE, Ge atoms reside inside distorted octahedral cages with six Te neighbors. Because of the Peierls instability, that has been shown to remain active also in disordered structures [23], the local environment is distorted at low temperatures: one Ge atom is more strongly bonded to some Te atoms (typically three or four) and more loosely bonded to the remaining ones. The shorter and stronger Ge-Te bonds correspond to higher vibrational frequencies. When temperature increases, as shown by combining neutron elastic scattering and EXAFS [12], the Ge and Te average coordination number *increases* (at variance with usual liquids) while the volume shrinks as sketched in Figs. 2(a) and 2(b). There is nevertheless an apparent paradox: the cage surrounding a Ge atom shrinks but at the same time the nearest neighbor distances elongate. This is also observed in the $\alpha \rightarrow \beta$ transition of the crystalline GeTe compound, and in pure Se and Te [24] alike. In GeTe the volume shrinks by $\simeq 1\%$ at the $\alpha \rightarrow \beta$ transition but at the same time the short interatomic distances increase by $+2.4\%$ (and simultaneously the long distances decrease by -2.8%) [25]. Our FPMD simulations on $GeTe_6$, performed at two different densities for low and high temperatures, reproduce this behavior. The three-body correlations for almost aligned triplets of atoms centered on Ge (bonds aligned within 15°) in $GeTe_6$, at 653 and

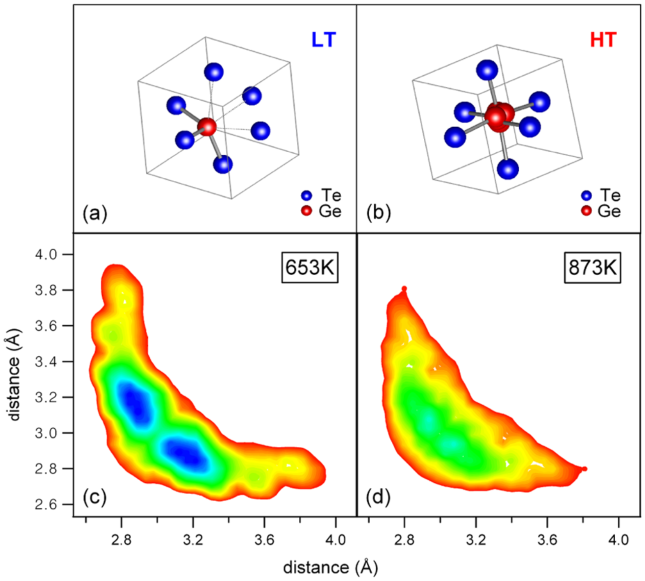

FIG. 2 (color online). (a) Sketch of the low temperature structure with a Ge atom in a larger volume distorted octahedral environment. (b) At higher temperature, the local environment of Ge atom inside the octahedral cage becomes more symmetric because vibrational entropy becomes larger. (c) and (d) Three-body correlation function for almost aligned triplets of atoms, centered on Ge atoms, calculated on simulated $GeTe_6$ structures, at 653 K (left panel) and 873 K (right panel). Almost aligned means that the bond angle between the two bonds is larger than 165°. Contours are drawn between 35% of the maximum value and maximum value of normalized correlation [from light grey to black (red to blue)].

873 K, are plotted in Figs. 2(c) and 2(d). The two distinct maxima observed at 653 K clearly indicate a tendency to alternate short r_s and long r_l almost aligned bonds, which is coherent with the distortion scheme presented in Fig. 2(a) at low temperature. At 873 K, the volume is smaller and the short and long bonds alternation around Ge atoms becomes much weaker, consistent with the symmetrization depicted in Fig. 2(b).

We can use the experimental VDOS to estimate the vibrational entropy of the system, S_{vib}, along the NTE [26]. In order to quantify its variation, ΔS_{vib}, for GeTe_6 between 673 and 873 K, we can approximate the contribution of the VDOS redshift to the vibrational entropy using [27]:

$$S_{\mathrm{vib}}(T) = 3R \int n(\omega)[\{(\hbar\omega/2kT)\coth(\hbar\omega/2kT)\} - \ln\{2\sinh(\hbar\omega/2kT)\}]d\omega. \quad (5)$$

Taking the value at 673 K as the reference, the vibrational entropy contribution between 673 K and 873 K, ΔS_{vib}, reaches 8.9 J/mol · K. Formula (5) is valid for harmonic normal modes and does not take into account the temperature derivative of the VDOS. The neglected contribution is estimated to 1.0 J/mol · K. The total entropy change, ΔS, between both temperatures, calculated by integrating the experimental C_p/T data [9], is equal to 14.3 J/mol · K. The ΔS is thus largely due (69%) to the vibrational contribution, that overcompensates the internal energy loss in the Gibbs energy balance.

The behavior is totally different for the PC-materials. Their VDOS and their structure factors $S(q)$ [28] are nearly independent of T above the melting temperature. From that we deduce that both the structure and the force constants are roughly temperature insensitive. This is related to the normal evolution of the atomic volume with respect to temperature.

Depending on the relative magnitude of the energy gained by the Peierls-like distortion (ΔE) and the vibrational entropy gained ($T\Delta S_{\mathrm{vib}}$) when the local symmetry is recovered, the NTE domain would correspond to $T\Delta S_{\mathrm{vib}} \approx \Delta E$. The heavier the p-bonded elements, the lower the Peierls distortion energy. For pure Te, the NTE occurs in the undercooled temperature range. An addition of Ge increases the Peierls distortion energy and a NTE is observed above the melting point because the melting temperature is lower. In conclusion, we have shown that, in rich-Te alloys, the gain of vibrational entropy is the driving force for the observed NTE. We may expect this mechanism to apply to all Peierls distorted p-bonded elements and alloys, provided that the melting temperature is smaller than the distortion energy.

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[1] P. G. Debenedetti, J. Phys. Condens. Matter **15**, R1669 (2003).
[2] G. D. Barrera *et al.*, J. Phys. Condens. Matter **17**, R217 (2005).
[3] T. A. Mary *et al.*, Science **272**, 90 (1996).
[4] D. Chandra and L. R. Holland, J. Vac. Sci. Technol. A **1**, 1620 (1983).
[5] V. M. Glazov *et al.*, *Liquid Semiconductors* (Plenum, New York, 1969).
[6] Y. Tsuchiya (private communication).
[7] Y. Tsuchiya, J. Phys. Soc. Jpn. **60**, 227 (1991).
[8] H. Thurn and J. Ruska, J. Non-Cryst. Solids **22**, 331 (1976).
[9] Y. Tsuchiya, J. Non-Cryst. Solids **312–314**, 212 (2002).
[10] Y. Tsuchiya and H. Saitoh, J. Phys. Soc. Jpn. **62**, 1272 (1993).
[11] C. Bergman *et al.*, Phys. Rev. B **67**, 104202 (2003).
[12] M.-V. Coulet *et al.*, Phys. Rev. B **72**, 174209 (2005).
[13] C. Bichara *et al.*, Phys. Rev. Lett. **95**, 267801 (2005); G. Zhao *et al.*, Phys. Rev. B **74**, 184202 (2006).
[14] A. Schlieper *et al.*, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **23**, 1 (1999).
[15] C. Bichara *et al.*, Phys. Rev. B **75**, 060201(R) (2007).
[16] C. Steimer *et al.*, Adv. Mater. **20**, 4535 (2008).
[17] LAMP, the Large Array Manipulation Program. http://wwwold.ill.fr/data_treat/lamp/lamp.html.
[18] Liquid GeTe_6 was obtained by calculations on a 216 atoms box (31 Ge, 185 Te) at the experimental liquid densities (0.0278 atom Å^{-3} at 653 K and 0.0287 atom Å^{-3} at 873 K) [19]. The liquid $\mathrm{Ge_2Sb_2Te_5}$ corresponds to calculations with 162 atoms (36 Ge, 36 Sb, 90 Te) at the experimental liquid density (0.0305 atom Å^{-3}). We used the PW91 exchange correlation functional [20], ultrasoft pseudopotentials [21], Ge ($4s$ and $4p$) and Sb and Te ($5s$ and $5p$) valence electrons and a planewave cutoff energy at 175 eV.
[19] Y. Tsuchiya, Thermochim. Acta **314**, 275 (1998).
[20] J. P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).
[21] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[22] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[23] J.-P. Gaspard *et al.*, Philos. Mag. A **119**, 000 (1986).
[24] R. H. Baughman *et al.*, Science **279**, 1522 (1998).
[25] C. Chattopadhyay *et al.*, J. Phys. C **20**, 1431 (1987).
[26] W. A. Phillips *et al.*, Phys. Rev. Lett. **63**, 2381 (1989).
[27] E. L. Gjersing *et al.*, J. Non-Cryst. Solids **355**, 748 (2009).
[28] M. Delheusy *et al.*, Physica (Amsterdam) **350B**, E1055 (2004).