PHYSICAL REVIEW B **67**, 104202 (2003)

Experimental investigation of the waterlike density anomaly in the liquid $Ge_{15}Te_{85}$ eutectic alloy

Claire Bergman
Laboratoire de Matériaux et Microélectronique de Provence, Faculté de Saint Jérôme, 13397 Marseille, France

Christophe Bichara
Centre de Recherche sur les Mécanismes de la Croissance Cristalline, CNRS, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France

Jean Pierre Gaspard
Physique de la Matière Condensée, Institut de Physique, B5, University of Liège, 4000 Sart-Tilman, Belgium

Yoshimi Tsuchiya
Department of Physics, Faculty of Science, Niigata University, Ikarashi 2-8050, Niigata 9502, Japan

(Received 29 October 2002; published 7 March 2003)

This paper presents an analysis of the structural changes undergone by liquid $Ge_{15}Te_{85}$ alloys in a 150 K temperature range above the eutectic temperature. This structural change is characterized by strong and anomalous variations of thermodynamic quantities among which are the density, the heat capacity, and the isothermal compressibility. The total structure factors were measured by neutron scattering on the D4B spectrometer at the ILL (Grenoble). The analysis of the thermodynamic and neutron scattering data suggests that the structural change undergone by the liquid mainly consists in a modification of the first-neighbor shell of the Ge atoms. With increasing temperature an increasingly large number of GeTe bonds become shorter, leading to a more compact local environment with a smaller atomic volume. The relation with the $\alpha \rightleftharpoons \beta$ transition of the solid GeTe compound is discussed.

DOI: 10.1103/PhysRevB.67.104202 PACS number(s): 61.25.Mv, 64.70.Ja, 65.20.+w

I. INTRODUCTION

Binary Ge-based chalcogenides are well known to present a good glass-forming ability. Less known are the unusual features encountered in their liquid state. In particular, the GeSe and GeTe compounds have been shown to remain semiconducting in the melt, with GeTe rapidly becoming metallic with increasing temperature.[1,2] Thermodynamic measurements[3] as well as neutron diffraction[4,5] showed the occurrence of a clear local order change upon melting characterized by a coordination number lower than that of the crystalline phase that melts and by a large volume expansion. These modifications are totally different from what is usually observed when melting semiconductors. Si, Ge, III-V, and the heavier II-VI compounds, for instance, have an increase of their coordination number as well as a volume contraction. *Ab initio* molecular dynamics calculations recently succeeded in providing the detailed atomic and electronic structure mechanisms that explain the large variations in conductivity in liquid GeSe and GeTe:[6–9]

(a) GeSe remains semiconducting in the liquid phase by recovering locally the atomic arrangement of its low-temperature crystalline α phase, the structure of which results from a Peierls distortion of the β phase that is stable at high temperature. The atomic volume expansion upon melting is 11%.

(b) GeTe behaves in the same way with a smaller volume expansion (7%) due to a smaller amplitude of the Peierls distortion.

Apart from the 50% compound concentration, the liquid alloys around the eutectic composition ($Ge_{0.15}Te_{0.85}$) exhibit a somewhat opposite behavior characterized, among others, by a contraction of the atomic volume[10] in the stable liquid state in a temperature range between 650 and 750 K, just above the eutectic temperature. This volume contraction (about -8%) is accompanied by a sharp maximum (at 680 K) in the constant pressure heat capacity[11–13] (C_p) and an increase of three orders of magnitude of the electrical conductivity in a 200 K temperature range.[14] Magnetic measurements[16] show also a very important minimum of the magnetic susceptibility at the eutectic composition, vanishing within 100 K above the eutectic temperature. In spite of this large number of experimental results, a recent thermodynamic assessment[17] of the germanium-tellurium system concludes that the liquid phase is not satisfactorily understood and cannot be described by the usual thermodynamic models, such as a regular associate model, especially around the eutectic composition. These anomalies on the thermodynamic quantities are indicative of a structural change at the microscopic level. Neutron diffraction measurements were performed on eutectic alloys by Nicotera *et al.*,[19] Neumann *et al.*,[20,21] and Bergman *et al.*[22] and published before the results of Tsuchiya and co-workers.[10,13,14] Combining neutron and x-ray diffraction measurements, Neumann *et al.* propose a scheme where α-GeTe-like areas and pure Te regions coexist in the low-temperature liquid. However, the small (q) range accessible to their neutron and x-ray diffraction experiments ($q \leqslant 10$ Å^{-1}) casts doubts on the interpretation of the pair correlation functions. These data were obtained from a

0163-1829/2003/67(10)/104202(5)/$20.00

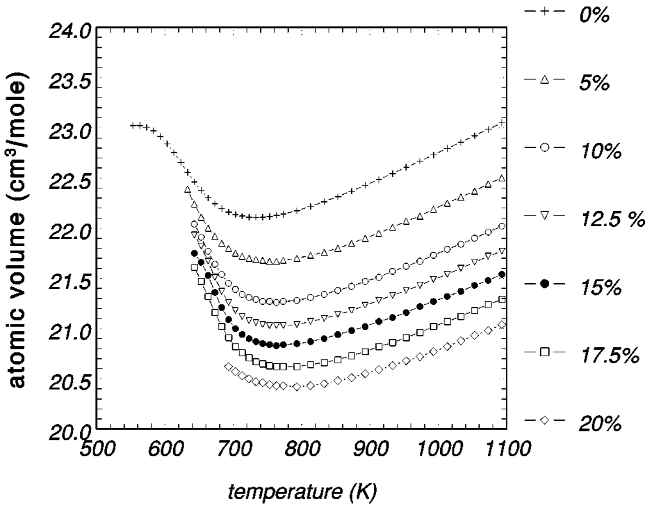

FIG. 1. Molar volume, V, of $Ge_xTe_{(1-x)}$ liquid alloys at $x=0.00$, 0.05, 0.10, 0.125, 0.15, 0.175, and 0.20 versus temperature.

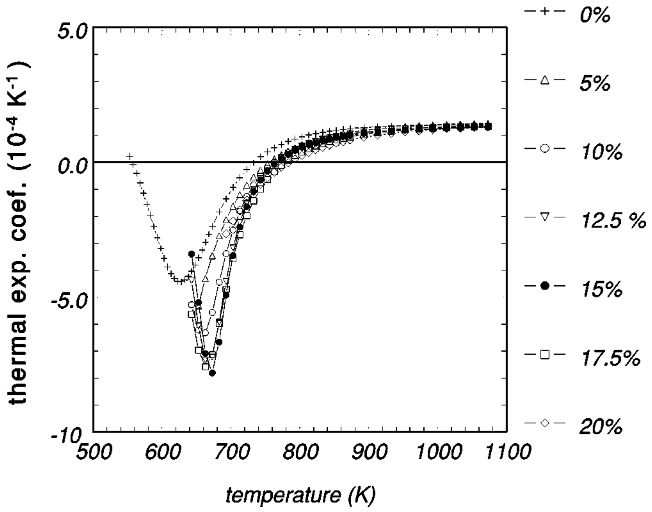

FIG. 2. Thermal expansion coefficient, α_P, of $Ge_xTe_{(1-x)}$ liquid alloys x = 0.00, 0.05, 0.10, 0.125, 0.15, 0.175, and 0.20 versus temperature.

Fourier transform of the structure factor and are then very sensitive to the width of the accessible q range. No clear picture of the mechanisms driving the structural change in liquid $Ge_{0.15}Te_{0.85}$ emerges from the cited literature, although phenomena that might be related to it are observed and understood in neighboring phases of the phase diagram. First, pure undercooled liquid tellurium undergoes a smoother structural change (see Ref. 15 and references therein) at a slightly lower temperature (maximum of C_p at 623 K). Second, the GeTe compound undergoes a second-order transition in the solid state[17,18] at 673 K on the Te-rich side and around 700 K on the Ge-rich one. The low temperature (α) form has a Peierls distorted structure ($R3m$) with three short and three long GeTe bonds ($r_1=2.81$ and $r_2=3.15$ Å at 295 K). The transition leads to a more symmetric (β) structure ($Fm3m$) with six equal GeTe bonds (2.98 Å at 716 K).

The aim of this paper is to analyze previouly published, but hardly available, neutron scattering data[22] in light of the thermodynamic measurements that are more recent and of the recent simulation results obtained on liquid $Ge_{15}Te_{85}$ alloys.[23] We first recall some thermodynamic properties of the liquid alloys around the eutectic composition, adding some recent data showing that the anomalies are maximal at the eutectic composition. We then present the neutron scattering results and propose an analysis of the data that provides a simple model for the structural change observed.

II. PHYSICOCHEMICAL PROPERTIES OF $Ge_{15}Te_{85}$ ALLOYS

A high-energy γ-ray attenuation method described in Ref. 24 was used to determine the molar volume. Figure 1 displays the variation of this quantity for pure Te and six different Ge_xTe_{1-x} alloys ($0.05 \leqslant x \leqslant 0.2$) (some of these data were already published in Ref. 10). A density anomaly can be observed since the molar volume, V, contracts in a narrow temperature range and reaches a minimum just below 773 K. Above this temperature the volume increases linearly as for a normal liquid. Consequently the thermal expansion coefficient, $\alpha_P=(1/V)(\partial V/\partial T)_P$ is negative and displays a sharp minimum. It can be seen on Fig. 2 that α_P decreases strongly from the eutectic temperature (648 K) to 673 K and then increases up to 773 K. Similar behaviors were observed on the adiabatic compressibility[10] and on the sound velocity.[25] The measurements of these quantities for different molar fractions around the eutectic show that the effect is maximum for $x=0.15$ which corresponds to the eutectic composition. In most binary systems, at constant temperature, the constant pressure heat capacity of the mixture is assumed to follow an additivity rule. Departures from this additivity rule[26] are directly indicative of structural modifications in the liquid. The determination of C_p obtained from drop calorimetry measurements[11] and by differential scanning calorimetry[12] indicates a significant deviation from additivity. This rapid variation, confirmed by modulation calorimetry[13] measurements, takes place in a temperature range of about 150 K above the eutectic point. The evolution of C_p with the molar fraction, presented in Fig. 3, shows that a maximum of the peak intensity and position is reached at the eutectic composition. By integrating C_p and C_p/T as a function of temperature one can estimate an order of magnitude for the changes of enthalpy and entropy caused by the structural change in the liquid. For $Ge_{15}Te_{85}$ one obtains $\Delta H=6.4(\pm 0.4)$ kJ mol^{-1} and $\Delta S=9.5$ (± 0.5) J mol^{-1} K^{-1}, whereas for pure undercooled tellurium, one obtains $\Delta H=4.7(\pm 0.3)$ kJ mol^{-1} and $\Delta S=7.5$ (± 0.5) J mol^{-1} K^{-1}. Although the difference in the composition of the liquids is only 15% germanium, the changes in ΔH and ΔS are about 1.3 times larger in the case of the eutectic alloy. In addition, we can see in Fig. 2 and Fig. 3 that they are also significantly sharper, since they take place in a narrower temperature range. This is an indication that the structural changes in the $Ge_{15}Te_{85}$ are not a simple extension in the dilute Ge range of the changes in pure Te. The changes are of a different kind or, more likely, concern different bonds, namely GeTe bonds in the alloy and TeTe bonds in pure tellurium. In order to analyze at an atomic

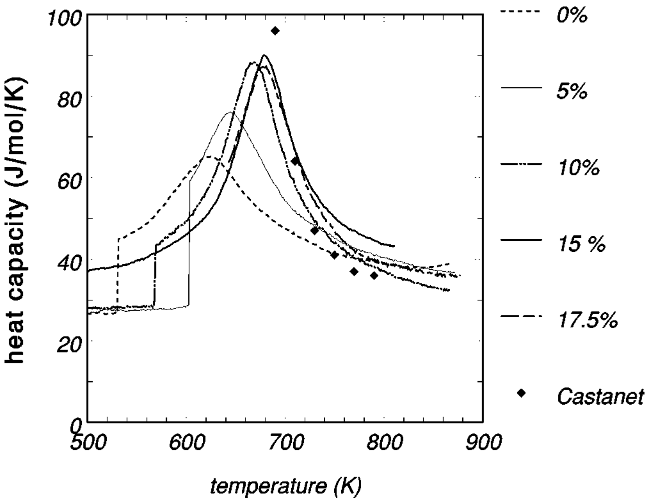

FIG. 3. Heat capacity, C_p, of $Ge_xTe_{(1-x)}$ liquid alloys at $x = 0.00$, 0.05, 0.10, 0.15, and 0.175 versus temperature given as lines. Values of Ref. 11 at $x = 0.15$ given as symbols.

level the numerous and coherent anomalies recorded above, we now turn to the diffraction measurements.

III. NEUTRON DIFFRACTION MEASUREMENTS

Our experiments were carried out on the D4B spectrometer located at the Institut Max Von Laue–Paul Langevin, Grenoble, operating at a wavelength $\lambda = 0.703$ Å with accessible q values from 0.3 to 16 Å^{-1}. The data were corrected for the 1.2 mm thick quartz container ($\phi \approx 5.9, 7.1$ mm), the 0.1 mm thick vanadium foil heater and the sample self-absorption in the usual way. The corrections for inelastic effects, multiple and incoherent scattering were made according to Eisenberg *et al.*[27] The experiments were performed on samples at the eutectic composition ($x = 0.15$) at four different temperatures $T = 633$, 673, 733, and 943 K. The measurements were carried out by decreasing the temperature in order to obtain a supercooled liquid (the eutectic temperature is 648 K). The experimental details concerning the preparation are reported in Ref. 22. The corresponding atomic densities measured by Tsuchiya are respectively 0.0276, 0.0281, 0.0287, and 0.0285 Å^{-3}. Figure 4 displays the structure factors at the four different temperatures and the values of the peak positions of $S(q)$ and $g(r)$ are given in Tables I and II. The structure factor $S(q)$ presents a prepeak, around $q_0 \approx 1.1$ Å^{-1}, which vanishes with increasing temperature. This indicates a pseudoperiodicity at distances around $2\pi/q_0 = 5.8$ Å. At larger q, the structure factor presents another five peaks denoted q_1 to q_5. By increasing the temperature, the positions of the peaks q_2 to q_5 slightly shift towards smaller q values. By contrast, q_0 and q_1 shift towards higher q values (Table I). The intensity and width of the peaks q_0 and q_2 more strongly depend on the temperature than the others. This indicates that the changes of q_0 and q_2 are not only caused by thermal damping but is caused by a structural modification of the liquid with increasing temperature. The $S(0)$ values that can be estimated from the measured isothermal compressibility[13] slightly increase with increasing temperature [$S(0) = 0.034, 0.069, 0.075$ and 0.092 at 633, 673, 733, and 943 K, respectively] but remain quite low. Such values of $S(0)$ indicate that no small-angle scattering is present and that the melt is homogenous. The four corresponding pair correlation functions $g(r)$ are reported on Fig. 5. The peak positions of the pair correlation functions $g(r)$ are given in Table II. Three main peaks are observed. The corresponding r_2 and r_3 values of the second and the third maximum are constant while $\mathbf{r}_1$ varies from 2.68 Å to 2.86 Å in the temperature range investigated. It is interesting to notice that this shift of the position of the maximum of the first peak coincides with the presence of a shoulder on its large $\mathbf{r}$ side that tends to fill the gap between the first and second peaks.

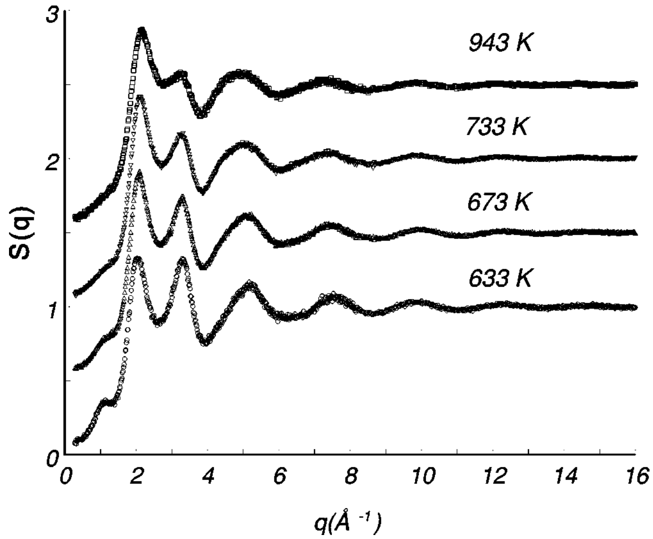

FIG. 4. Total structure factors $S(q)$ for $x = 0.15$ at $T = 633$, 673, 733, and 943 K.

TABLE I. Peak position q_i and width σ_i (in Å^{-1}) of the main peaks of the experimental $S(q)$ for the $Ge_{15}Te_{85}$ eutectic alloy at 633, 673, 733, and 943 K.

T (K)	q_0	σ_0	q_1	σ_1	q_2	σ_2	q_3	q_4	q_5
633	1.08	0.28	2.05	0.33	3.27	0.51	5.20	7.53	9.74
673	1.13	0.33	2.08	0.30	3.24	0.56	5.07	7.41	9.66
733	1.19	0.39	2.10	0.29	3.21	0.62	4.99	7.33	9.54
943			2.12	0.28	3.15	0.77	4.91	7.29	9.50

TABLE II. Peak positions (in Å) of the main peaks of the experimental $g(r)$ for the $Ge_{15}Te_{85}$ eutectic alloy at 633, 673, 733, and 943 K.

T (K)	r_1 (Å)	r_2 (Å)	r_3 (Å)
633	2.68	4.12	6.17
673	2.77	4.12	6.17
733	2.77	4.12	6.17
943	2.86	4.12	6.26

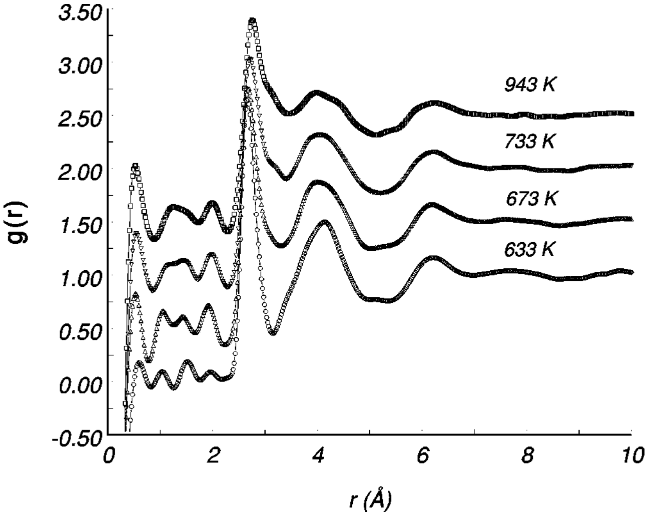

FIG. 5. Pair correlation functions $g(r)$ for $x=0.15$ at $T=633$, 673, 733, and 943 K.

IV. DISCUSSION

In order to analyze the results obtained by neutron diffraction in terms of real space structure and local environment, the determination of the partial quantities would be of great interest. The measurement of the partial structure factors can be achieved either by isotopic substitution and neutron scattering (hardly possible in this case because of the large molar fraction of Te, which displays no isotopes with significantly different scattering lengths) or by anomalous x-ray scattering. This has not been done yet, but we show below that reasonable assumptions on the structure can give us a better insight on the mechanisms involved in the structural change.

First, taking into account the differences in the scattering lengths of the two elements Ge and Te ($b_{\mathrm{Ge}}=8.2\times10^{-15}$ m, $b_{Te}=5.8\times10^{-15}$ m), the partial GeGe, GeTe, and Te Te contributions to the measured total structure factor are weighed by 0.04, 0.32, and 0.64, respectively. In a first approximation, the GeGe contribution to the total structure factor can then be neglected in the following analysis. Second, we can assume that the structural change undergone by the liquid mainly concerns the GeTe bonds. This assumption is supported by the analysis of the orders of magnitude of the variations of the enthalpy and entropy between 650 and 750 K given above, as well as by recent *ab initio* computer simulation of the liquid eutectic alloy[23] that shows that the GeTe partial structure factor is mostly affected by the density and temperature changes, whereas the TeTe partial structure factor remains essentially unaffected except for the usual damping effect due to the temperature increase. The second step is to calculate the average number of first neighbors $N_1(T)$ by integrating $N(r)=4\pi r^2 g(r)$. The integration range, $N_1(T)$, and the differences $\Delta N_{\mathrm{GeTe}}(T)=\Delta N_1/2x_{\mathrm{Ge}}x_{\mathrm{Te}}$ calculated under two different assumptions are given in Table III. Strictly speaking $N_1(T)$ has no physical meaning since we are dealing with a binary alloy with components having different scattering lengths. We can nevertheless see that $N_1(633\ \mathrm{K})$ is equal to 2.65, which is close to the value one would expect considering an "average atom" with a p band filling $\langle z\rangle$ equal to $\langle z\rangle=0.15z_{\mathrm{Ge}}+0.85z_{\mathrm{Te}}=3.7$. In such a case, following the octet rule one expects[28,29] an average coordination number $\langle N\rangle=8-(2+3.7)=2.3$. If we assume that the structural change mainly affects the GeTe partials we may go one step further by calculating the increase of the heteroatomic coordination number $\Delta N_{\mathrm{GeTe}}=\Delta N_1/2x_{\mathrm{Ge}}x_{\mathrm{Te}}$, taking the value at 633 K as a reference, with an upper integration bound located either at the first minimum of $N(r)$ or a fixed upper bound at 3.31 Å. These values, ranging from 1.18 to 2.85, are an upper bound since it is likely that a minority of bonds of different kind are also modified.

TABLE III. Upper integration bound, average number of first neighbors, and variation of the number of GeTe bonds as a function of temperature, using the integration range of column 2 or a fixed upper integration bound at 3.31 Å.

T (K)	r_{cut} (Å)	N_1	ΔN_{GeTe}	$\Delta' N_{\mathrm{GeTe}}$
633	3.17	2.65		
673	3.25	3.00	1.40	1.18
733	3.29	3.25	2.40	1.84
943	3.31	3.37	2.85	2.12

The above analysis assigns the structural change to an increase of the number of GeTe bonds but tells nothing about the structure of the liquid at the lowest temperature. As long as we have no quantitative data on the partial structure factors or partial coordination numbers obtained by a different method such as extended x-ray absorption fine structure, we cannot push further any quantitative analysis. We can, however, relate the observed density anomaly to two possible scenarios, depending on the characteristics of the bonding around Ge atoms. We can either think of sp^3 bonded germanium atoms with 4 Te neighbors, in which case the volume contraction, increase of coordination number, and semiconductor to metal transition observed would be similar to what is observed upon melting of silicon, except for the melting itself. Indeed, a gradual decrease of the coordination number with decreasing temperature has been observed in supercooled liquid Si,[30] but this decrease does not yield a fourfold coordinated liquid silicon. Furthermore, it has to be remembered that, contrary to the GeSe system for which fourfold coordinated Ge atoms exist in the $\mathrm{GeSe_2}$ compound, no stable $\mathrm{GeTe_2}$ compound exists in the stable phase diagram. Another possibility is to assume that a Peierls-like distortion of the local environment of Ge, analogous to the α-GeTe crystalline phase, is stabilized in the low-temperature liquid, with a coordination number around 3 for Ge atoms, corresponding to the short GeTe bonds, the longer GeTe bonds lying outside the first coordination shell defined by the first peak of $g(r)$. At higher temperature the shorter bonds become longer and the longer bonds become shorter as expected in a reduction of the Peierls distortion scheme, and a more symmetric local environment, with a coordination number closer to 6 for Ge atoms, is stabilized because the vibrational entropy favors this situation.

V. CONCLUSIONS

The results presented here show that the $\mathrm{Ge_{15}Te_{85}}$ liquid alloy presents significant changes of its thermodynamic, physical and structural properties in a range of 150 K above the eutectic temperature. The most striking effects are observed on the thermodynamic properties such as the density and heat capacity at the eutectic composition. High-precision measurements of the structure factors by neutron scattering at four different temperatures indicate that these changes in the macroscopic properties are accompanied by significant changes of the local order in the liquid. The analysis of the local order we propose relies on an assumption resulting from a quantitative analysis of the changes in ΔH and ΔS, which is confirmed by *ab initio* computer simulations. We assign the changes of $S(q)$ and $g(r)$ to a change of the local environment of Ge atoms and hence to an increase of the number of Te neighbors around Ge atoms since GeGe correlations are negligible and the melt is probably chemically ordered at least at low temperatures. Taking the experiment at 633 K as a reference, the (heteroatomic) coordination number of Ge is increased by 1.4 at 673 K, 2.5 at 733 K, and 2.85 at 943K. Although we cannot rule out a gradual change of the bonding of Ge from a fourfold sp^3 bonding to a sixfold p bonding, we suggest that the driving force for the structural change that explains the observed density anomaly might be the reduction of the Peierls distortion around the Ge atoms similar to the $\alpha \rightleftharpoons \beta$ transition in the solid GeTe compound. Both direct measurements of the partial structure factors and a complete computer simulation of the liquid state would be useful to confirm this interpretation.

[1] V. M. Glazov and O. D. Schelikov, Fiz. Tekh. Poluprovodn. **18** (4), 662 (1984) [Sov. Phys. Semicond. **18**, 411 (1984)].

[2] V. M. Glazov, S. N. Chizevskaya, and N. N. Glagoleva, *Liquid Semiconductors* (Plenum, New York, 1969).

[3] Y. Tsuchiya, J. Phys. Soc. Jpn. **60**, 227 (1991).

[4] I. Petry, P. S. Salmon, and H. E. Fisher, J. Phys.: Condens. Matter **11**, 7051 (1999).

[5] J.-Y. Raty, J.-P. Gaspard, M. Bionducci, R. Céolin, and R. Bellissent, J. Non-Cryst. Solids **250-252**, 277 (1999).

[6] F. H. M. van Roon, C. Massobrio, E. de Wolff, and S. W. dw Leeuw, J. Chem. Phys. **113**, 5425 (2000).

[7] J.-Y. Raty, V. V. Godlevsky, J.-P. Gaspard, C. Bichara, M. Bionducci, R. Bellissent, R. Céolin, J. R. Chelikowsky, and Ph. Ghosez, Phys. Rev. B **64**, 235209 (2001).

[8] J.-Y. Raty, V. V. Godlevsky, Ph. Ghosez, C. Bichara, J.-P. Gaspard, and J. R. Chelikowsky, Phys. Rev. Lett. **85**, 1950 (2000).

[9] J.-Y. Raty, V. V. Godlevsky, J.-P. Gaspard, C. Bichara, M. Bionducci, R. Bellissent, R. Céolin, J. R. Chelikowsky, and Ph. Ghosez, Phys. Rev. B **65**, 115205 (2001).

[10] Y. Tsuchiya, J. Phys. Soc. Jpn. **60**, 227 (1991).

[11] R. Castanet and C. Bergman, Phys. Chem. Liq. **14**, 219 (1985).

[12] J. P. de Neufville, J. Non-Cryst. Solids **8-10**, 85 (1972).

[13] Y. Tsuchiya, J. Non-Cryst. Solids **156-158**, 700 (1993).

[14] Y. Tsuchiya and H. Saitoh, J. Phys. Soc. Jpn. **62**, 1272 (1993).

[15] C. Bichara, J.-Y. Raty, and J.-P. Gaspard, Phys. Rev. B **53**, 206 (1996).

[16] P. Terzieff, K. L. Komarek, and E. Wachtel, Phys. Chem. Liq. **15**, 217 (1986).

[17] A. Schlieper, Y. Feutelais, S. G. Fries, B. Legendre, and R. Blachnik, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **23**, 1 (1999).

[18] T. Chattopadhyay, J. X. Boucherle, and H. G. von Schnering, J. Phys. C **20**, 1431 (1987).

[19] E. Nicotera, M. Corchia, G. De Giorgi, F. Villa, and M. Antonini, J. Non-Cryst. Solids **11**, 417 (1973).

[20] H. Neumann, W. Matz, W. Hoyer, and M. Wobst, Phys. Status Solidi A **90**, 489 (1985).

[21] H. Neumann, W. Hoyer, W. Matz, and M. Wobst, J. Non-Cryst. Solids **97-98**, 1251 (1987).

[22] C. Bergman, C. Bichara, R. Bellissent, R. Céolin, J. P. Gaspard, and P. Chieux, An. Fis. Ser. B **86**, 138 (1990).

[23] C. Bichara, J.-P. Gaspard, and J.-Y. Raty, J. Non-Cryst. Solids **312-314**, 341 (2002).

[24] Y. Tsuchiya, J. Phys. Soc. Jpn. **57**, 3851 (1988).

[25] Y. Tsuchiya, Scand. J. Metall. **30**, 345 (2001).

[26] C. Bergman and K. L. Komarek, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **9**, 1 (1985).

[27] S. Eisenberg, J. F. Jal, J. Dupuy, P. Chieux, and J. Goffart, Philos. Mag. A **46**, 195 (1982).

[28] J.-P. Gaspard and R. Céolin, Solid State Commun. **84**, 839 (1992).

[29] J.-P. Gaspard, A. Pellegatti, F. Marinelli, and C. Bichara, Philos. Mag. B **77**, 727 (1998).

[30] S. Ansell, S. Krishnan, J. J. Felten, and D. L. Price, J. Phys.: Condens. Matter **10**, L73 (1998).