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Review Paper

Low-temperature specific heat and thermal conductivity of ternary chalcogenide glasses

E. VATEVA*, B. TERZIYSKA, D. ARSOVA
Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

The main results from the investigated in the temperature range 3 - 300 K thermal properties, specific heat C_p and thermal conductivity k, of the $Ge_xAs_{40-x}S_{60}$ glasses are reviewed and concurrently analyzed. The nonmonotonic dependences of the parameters of the universal low-temperature features on the composition (defined by the average coordination number Z) are correlated with their degree of the thermodynamic fragility. The correlation is based on the prevalence of the excess of vibrational soft modes (SM) in the less fragile glasses. Some assumptions of the soft-potential model (SPM) are checked and new Z dependences have been found for the energetic parameter connected with the delocalization of the SM. This parameter is calculated in two ways: according to relations obtained in the SPM, using an evaluated characteristic energy W, or using only the macroscopic material parameters of the studied glasses. A relation between the crossover temperature for the soft-mode delocalization and the temperature dependence of the calculated thermal diffusivity D is found. The complete analysis of the thermal characteristics leads to new scaling laws and new insight into some implications of the SPM clarifying the peculiarities of the peak in the Cp/T^3 vs T plot and the plateau of $k(T)$.

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1. Introduction

It is well known that at low temperatures T or frequencies ν glassy materials exhibit certain universal properties [1]. Namely, at T<1 K the temperature dependence of the specific heat C_p is linear ($C_p \sim T$) in contrast to the cubic dependence ($C_p \sim T^3$) observed in crystals and explained by the Debye's theory. This linear dependence, as well as the quadratic dependence of the thermal conductivity k ($k \sim T^2$ instead of $k \sim T^3$ found in crystals) is understood in the framework of the tunneling model (TM), which postulates two-level systems (TLS) with almost constant density of the tunneling states [2]. At T>1 K the temperature dependences of C_p and k also deviate from Debye's dependences showing well-expressed features: a broad maximum in the C_p/T^3 vs T plot and a plateau in the k vs T dependence, both appearing in nearly the same temperature range.

The universal features of glasses are related to an excess in vibrational density of states $g(\nu)$, over the expected density for the crystalline materials in the Debye theory. This excess leads to a maximum in $g(\nu)/\nu^2$ in the THz frequency range, known as the boson peak (BP). In the low-frequency Raman scattering spectra the reduced boson-peak intensity differs from $g(\nu)/\nu^2$ only by the light-vibration coupling coefficient.

There are two main approaches for explaining the appearance of the maximum in C_p/T^3, the BP in the vibrational spectra and the plateau in k [1].

1. *Coexistence at low frequencies of Debye-like sound waves with excess vibrational excitations*. According to the soft-potential model (SPM) [3,4] the excess vibrational excitations are principally quasi-localized soft modes (SM) and the softening of the vibrations is disorder-related. The SPM, which is an extension of the TM, presumes that there are two mode types additional to the sound waves. The modes of the first type are anharmonic. They are described by soft double-well potentials with two-level states for tunneling at an energy difference lower than a characteristic energy W. The modes of the second type are quasi-harmonic or harmonic. They are described by soft single-well potentials with levels, which energy differences are higher than W. The density of states of the single-well quasi-harmonic excitations, i.e. of the quasi-localized soft modes, increases at E>2W proportionally to E^4, leading to the appearance of the mentioned universal features and being limited by the delocalization of the excitations.

2. *Dominance of hybrid modes*. It is due to the disorder in glasses, which could make the distinction between the extended and quasi-localized vibrations unsuitable in the range of the BP.

In our preliminary investigations of the ternary $Ge_xAs_{40-x}S_{60}$ system thermal characteristics, $C_p(T)$ and $k(T)$, were measured within the temperature range 3 – 300 K [5-7]. We demonstrated that despite the universality of the glassy low-temperature features the parameters of the (C_p/T^3) peak and of the plateau region of k depend on the composition (x) and the respective mean coordination number Z. Previous studies of binary chalcogenide glasses [8] also showed compositional dependences of these parameters and are in agreements with our findings. These observations pose two important questions. If the low-temperature features are conditioned by excess of

vibrational excitations, why does their availability lead to the nonmonotonic compositional changes of the parameters in the studied system? What is the temperature extent of the influence of the quasi-localized soft modes? To address the first question we have supposed [6] a correlation of the parameters of the low-temperature features with the fragility of the glasses. However, this correlation was questioned for some other materials [9] and, therefore, must be convincingly verified. The answer of the second question could be found by evaluating some of the parameters of the SPM.

In this work the previously published experimental data [5-7] for the specific heat and the thermal conductivity of the $Ge_xAs_{40-x}S_{60}$ system are completely analyzed. By checking the prediction of the SPM, some new insights into the model implications are revealed. The main results from the Z dependences of the low-temperature specific heat features are presented and compared with that of high-temperature specific heat features, thereby emphasizing their resemblance. The low-temperature scaling law is compared with a general relationship between the parameters of the (C_p/T^3) peak and the similarities and differences are emphasized. The concurrent analysis of the thermal conductivity and specific heat data leads to a new scaling law. New compositional and temperature dependences of parameters based on the SPM are established. The Z dependences of the energetic parameter connected with the delocalization of the harmonic excitations are found. On the basis of these evaluated in two ways Z dependences of the parameter of delocalization the problems connected with the temperature dependences of C_p/T^3 and k at various Z are discussed. New scaling relations in the thermal characteristics are found, as well as in the temperature dependence of the thermal diffusivity D calculated by C_p and k data.

2. Results

2.1. Specific heat

The nonmonotonic dependences of the parameters of the peaks in the C_p/T^3 vs T plot on the composition and the average structural coordination of the studied glasses have shown that the extremes in the height of the peaks, $(C_p/T^3)_{max}$, and its position, T_{max}, are just in the middle of the Z range of the $Ge_xAs_{40-x}S_{60}$ system. In order to confirm our supposition for a correlation with the fragility we shall clarify the connection of the low-temperature and high-temperature features of the specific heat.

The term fragility was proposed by Angell [10,11] to characterize the lack of resistance of the supercooled liquids to structural degradation as they approach the glass transition. Fragility is usually defined by the departure of the slope of the temperature dependence of the viscosity (or the relaxation time) from an Arrhenius law. The higher the departure from the Arrhenius viscosity behavior, the higher is the so defined kinetic fragility. A lower departure classifies the glass formers as stronger in the "strong" and "fragile" liquids classification [11,12]. The almost Arrhenius variation observed in structures resistant to thermal degradation reflects a small heat capacity jump ΔC_p at the glass transition temperature T_g [10,12]. For a wide set of substances it has been shown that the thermodynamic fragility, judged by ΔC_p at T_g, correlates with the kinetic fragility [13]. However, this correlation is violated in some liquids, and in particular in those with hydrogen bonding [13,14]. To our knowledge deviations from this correlation have not been seen in covalent chalcogenide glasses. It has been shown in Ref. 12 that for a Ge-As-Se glassy system the Z dependences of the activation energies for viscosity and enthalpy relaxation are parallel to that of ΔC_p at T_g, establishing a correlation between kinetic and thermodynamic fragility. We assume that this correlation could be valid in the $Ge_xAs_{40-x}S_{60}$ system. However, since this assumption is not directly proved, in this paper when we characterize the degree of fragility of the glasses from this system, we refer to their thermodynamic fragility.

Prior to investigating the low-temperature specific heat and thermal conductivity of the $Ge_xAs_{40-x}S_{60}$ glasses we have studied some of the thermal properties of three ternary Ge-As(Sb)-S systems in the glass transition region by differential scanning calorimetry and found that the specific heat capacity jump ΔC_p at T_g depends nonmonotonicly on Z in the investigated systems[15]. This means that the thermodynamic fragility of these systems depends nonmonotonicly on Z.

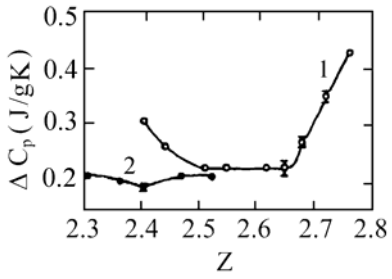

Fig. 1. Dependences of the specific heat capacity jump ΔC_p at the glass transition temperature T_g on the mean coordination number Z for glasses from the Ge_2S_3-As_2S_3 ($Ge_xAs_{40-x}S_{60}$) (1) and Ge_2As_3-AsS_3 (2) systems.

As can be seen from the plotted in Fig.1 data for the $Ge_xAs_{40-x}S_{60}$ system studied here the ΔC_p values at T_g increase to a large degree at Z>2.67. A small increase at Z<2.5 towards Z=2.4 can also be seen in this system (curve 1). The small ΔC_p at T_g in glasses with Z between 2.5 and 2.65 implies that the low fragile glass formers are in the middle Z range of this system and the respective glasses can be considered as “strong”. The abrupt change from the "strong" to "fragile" character of the glasses around Z=2.67 has been accepted in Ref. 15 as evidence for a structural 2D-3D transition [16]. The more fragile character of the stoichiometric glass with Z=2.4 ($As_{40}S_{60}$) in comparison with the non-stoichiometric glass with the

same Z value ($Ge_{11.2}As_{18}S_{70.8}$ from another Ge-As-S system, see Fig. 1, curve 2) is in accordance with the results for the selenide glasses studied in Ref. 12. The minimum of ΔC_p at T_g can be expected at the floppy to rigid transition at Z=2.4 [17] in cases when the chemical ordering effect does not dominate. The latter effect dominates in the compound As_2S_3, which explains the small increase of the fragility at Z between 2.5 and 2.4.

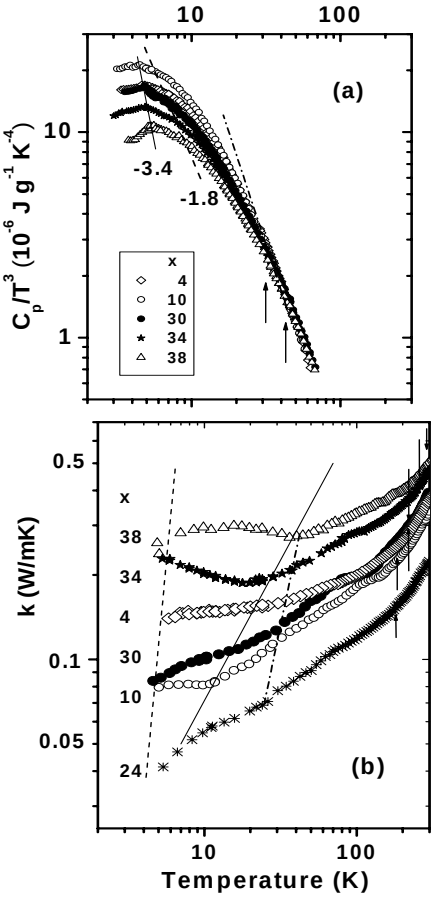

Fig. 2. Temperature dependences of low-temperature thermal properties of various $Ge_xAs_{40-x}S_{60}$ glasses: (a) specific heat plotted as C_p/T^3 vs T. The straight lines represent: experimental $(Cp/T^3)_{max}$ vs T_{max} (solid line), C_p/T^3 vs $E_c/4.93k_B$ relation according to a supposition of the SPM (dashed line) and C_p/T^3 vs E_c/k_B in the temperature range marked with arrows (dashed-dotted line); (b) thermal conductivity k. The dashed line at the onset of the plateau is drown through the k values at T_{max} of the C_p/T^3 peaks of the corresponding glasses; the solid line at the end of the plateau represents the experimental k_{min} vs T^k_{min} relation and the dashed-dotted line is drown through the k values at E_c/k_B. Arrows at the high temperature end mark the Debye temperatures.

As is known the thermal diffusivity D, defined by the relation $D=k/C_p\rho$, expresses the peculiarities of the specific heat C_p and the thermal conductivity k (ρ is the density). The Z dependence of D for Ge-As-S(Se) glasses obtained at 300 K by an optical beam deflection method in Ref. 18, also leads to the assumption that the lowest D values at the middle Z range of the $Ge_xAs_{40-x}S_{60}$ system are typical for the strongest glasses.

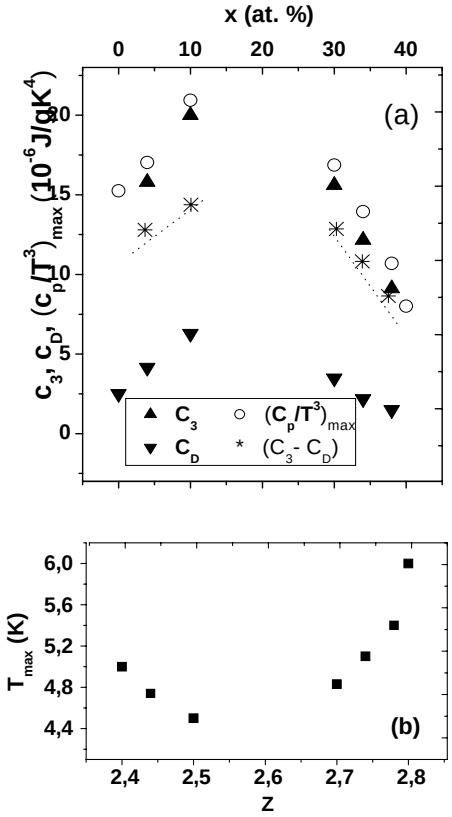

Fig. 3. Z dependences of the specific heat parameters: (a) $(C_p/T^3)_{max}$ - experimental values; C_3 - cubic coefficient in Eq. (1); C_D - true Debye coefficient in Eq. (2); $(C_3 - C_D)$ - difference reflecting the presence of SM; (b) T_{max} - the temperatures at which (C_p/T^3) values are maximal.

The low-temperature dependences of the specific heat in the C_p/T^3 vs T plot, taken from our preliminary results [5] for five compositions of the $Ge_xAs_{40-x}S_{60}$ system are presented in double logarithmic scale in Fig. 2*a*. In the temperature range from 3 K up to 70 K all curves exhibit peaks at the low-temperature end around 5 K and tend to a common curve above ~30 K. Most importantly, the maximal C_p/T^3 values depend nonmonotonicly on the coordination number Z. This dependence (included in Fig. 3*a* where evaluated parameters are plotted too) displays a decrease of $(C_p/T^3)_{max}$ with increasing fragility when Z increases from 2.7 to 2.8 or decreases from 2.5 to 2.4 (the data for the binary compounds added here are from Ref. 19 for Z=2.8 and from Ref. 20 for Z=2.4; in the last case we have taken the lowest $(C_p/T^3)_{max}$ values because our glasses are not quenched rapidly). The result that the $(C_p/T^3)_{max}$ values are highest for the strongest glasses of the studied system will be compared in Section 3 with corresponding results for some other groups of glasses [13,21,22].

The highest $(C_p/T^3)_{max}$ values are reached at the lowest temperatures T_{max} as observed in other materials [8]. The Z dependence of the temperatures at which the C_p/T^3 value is maximal is displayed in Fig. 3*b* to be compared with other Z dependences. It must be pointed that the parameter T_{max} has a Z dependence similar to that of the thermodynamic fragility of the studied system shown in Fig. 1, and is inverse to the Z dependence of $(C_p/T^3)_{max}$ and the other specific heat parameters in Fig.*3a*. However, all Z dependences have extremes in the same middle Z range of the studied system.

Fig. 2*a* shows the scaled $(C_p/T^3)_{max}$ vs T_{max} dependence. It is worth noting that our data (for $(C_p/T^3)_{max}$ at T_{max}) could be placed in a region near to the line with exponent (-1.6) in the more general scaling found in Ref. 22 for a wide set of glassy and crystalline materials. But all data for the investigated system are situated exactly on a line with exponent (-3.4). This line should cross the line with exponent (-1.6) at a point where the data for the studied here more fragile glasses should lie. Deviations from the general scaling are also found in other studies and are ascribed to the different nature of the low-energy vibrational spectra of glasses and crystalline solids [9]. It would be interesting to relate the problem for determining the unknown reason of these deviations to the predictions of the SPM. The dashed line with exponent (-1.8) in Fig. 2*a* will be discussed below in accordance with these predictions.

The compositional dependences of C_p at various temperatures around the appearance of the C_p/T^3 peak have been normalized and compared in Ref. 7. With the strongest glasses well-expressed maxima in $C_p(Z)$ have been seen from 4.5 to about 20 K. They nearly disappear at 55 K. Thereby, a question arises whether the highest C_p values of the strongest glasses are related to the highest SM contributions and the extent of the SM influence is limited in some degree at temperatures above 20 K. This will be clarified in latter sections.

2.2. Thermal conductivity

The temperature dependences of the thermal conductivity k taken from our preliminary results [6] are shown in Fig. 2 together with that of C_p/T^3 of the $Ge_xAs_{40-x}S_{60}$ glasses using the same temperature scale. The curves of the temperature dependence of k in the range from 4.5 to 300 K (Fig. 2*b*) exhibit the expected, more or less temperature independent plateau in $k(T)$. The well-defined parameters of the plateau are: the value of k at the high temperature end of the plateau region followed by an increased slope in $k(T)$, which is defined as k_{min} (in accordance with Ref. 8) and the temperature at this end of the plateau (where k_{min} is reached) defined as T^k_{min}. The main result is that the changes of k with the composition are also nonmonotonic. Moreover, k changes inversely and more strongly than C_p/T^3, as has been noticed before [6,9]. In fact, the k_{min} values are minimal for the strongest glasses and increase with increasing fragility in contrast to the $(C_p/T^3)_{max}$ vs Z dependence.

The Z dependences of k_{min} and of T^k_{min}, are included in Fig. 4 and 5, respectively. They are similar to the Z dependence of the thermodynamic fragility of the studied system.

The concurrent analysis of the temperature dependences of k and C_p yields a new scaling relation. In particular, comparison of Fig. 2*a* and Fig. 2*b* shows that the maximum in C_p/T^3 is not in the center of the plateau. It can be supposed that the T_{max} values are near to the values of the temperatures of the appearance of the plateau, T_{app}, where the k values are defined as k_{app}. The values of k for every composition at the temperature T_{max}, the temperature of the respective $(C_p/T^3)_{max}$, are connected with a straight line (Fig. 2*b*). This line crosses the $k(T)$ dependences at points coinciding well with k_{app} values for some of the compositions. Obviously, because of the lack of k data for low enough temperatures and because of the peculiarities in the plateau region, the parameters of the appearance of the plateau are ill defined. In our previous studies [6] an attempt has been made to evaluate the possible T_{app} values on the base of the calculated by Ramos and Buchenau [23] low-temperature dependence of k for glasses up to the plateau region. The plateau in $k(T)$ appears when the dimensionless variable u exceeds 2, i.e. when $u=Tk_B/W>2$, where k_B is the Boltzmann constant and W/k_B - the soft-potential parameter connected with the crossover from the temperature region where the tunneling dominates to the region where the main excitations are quasi-harmonic soft modes. We have previously evaluated [6] the values of the crossover energy W of the $Ge_xAs_{40-x}S_{60}$ glasses. In addition, via the well-defined value of T_{app} for one composition we estimated the respective value of u (by $u=T_{app}k_B/W$). We then accepted that the relation between T_{app} and W/k_B is the same in the other compositions, and used the calculated value of u to estimate the Z dependence of T_{app} [6].

Note that the k_{app} vs T_{app} dependence presented in Ref. 6 coincides with the scaling relation shown with a dashed line in Fig. 2*b*. This is due to the fact that the estimated values of T_{app} and the experimental values of T_{max} differ only by 0.1 to 1 K.

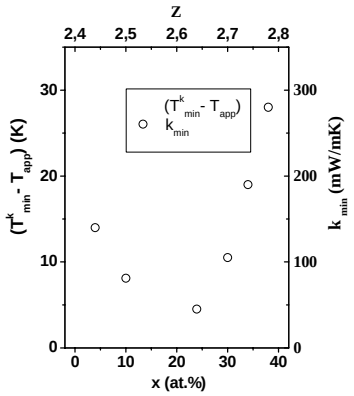

Fig. 4. Z dependence of the thermal conductivity plateau width (T^k_{min} - T_{app}), where $T_{app}\approx T_{max}$, compared with that of k_{min} - the experimental values of k at the high temperature end of the plateau.

The dashed line in Fig. 2*b* with an exponent ~ 3 together with the solid line through the k values at T^k_{min} with exponent ~ 1 (scaled in Ref. 6) shows narrowing of the plateau in the samples with lower k values at one and the same temperature. This has not been noticed for other systems and materials. The Z dependence of the plateau width presented in Fig. 4 shows a minimum for the strongest glasses. (Besides, the plateau regions can be extended to lower temperatures and limited by the expected $k \sim T^2$ dependence; narrowing of these regions could be also expected in the strongest glasses with lower k values.) According to Ref. 23, the plateau of k results from resonant scattering of sound waves from the localized vibrations. If the soft modes dominate in the strongest glasses, they will more strongly decrease the thermal conductivity in the plateau region of k, which is reflected in the $k_{min}(Z)$ dependence (Fig.4). It can be also pointed out that k values that are not nearly constant can also be seen in the plateau region. A decrease in k with increasing T is expressed at more fragile glasses (see data for x=34 and 38 in Fig. 2*b*). We accept the latter as a "negative thermal conductivity of *N*-type". It could be connected with the decrease of the average mean free path l with the temperature, which will be discussed bellow. According to the standard formula [23], k depends on T through C_p and l. The decrease of l may be compensated by the increase in C_p with T, which is higher in the stronger than in more fragile glasses, in such a way that k conditioned a plateau. However, when the increase in C_p in the more fragile glasses is not high enough, the decrease of l can lead to a negative *N*-type thermal conductivity.

The following peculiarities are apparent in Fig. 2*b*: (*i*) at temperatures above T^k_{min} the thermal conductivity increases with the temperature more strongly in the samples with the lowest k values; (*ii*) the exponent of $k(T)$ remains smaller than 0.5 up to the previously calculated [6] Debye temperatures θ_D, marked by arrows (the Z dependence of θ_D is governed by that of v_s - the average sound velocity and n - the number of atoms in unity volume, and depends on the fragility similarly to the parameters of k); (*iii*) above θ_D the thermal conductivity varies nearly linearly with T. Below, an insight into the reasons of the k increase just above T^k_{min} will be obtained on the base of the SPM.

2.3. Parameters defined by the soft potential model

The comparison of the Z dependences of the parameters of the low-temperature features of C_p and k with the Z dependence of ΔC_p at T_g shows well-expressed extremes (maximums and minimums) in the middle Z range of the $Ge_xAs_{40-x}S_{60}$ system. A correlation between the low-temperature properties and the thermodynamic fragility is proposed, based on the assumption for a higher contribution of the quasi-harmonic excitations, described with single-well soft potentials, in the strongest glasses in the middle Z range. This supposition will be evidenced on the base of the difference between the two frequently used equations for the specific heat [1,9], assigned here to the C_p/T^3 values.

One of the equations takes into account the linear contribution to C_p of the two-level states (C_1T) besides the cubic contribution (C_3T^3) related to the ordinary sound waves. The contributions to the C_p/T^3 values can be expressed as:

$$C_p/T^3 = C_1T^{-2} + C_3. \quad (1)$$

The other equation for C_p takes into account the single-level states as well, which, according to the soft potential model, give an additional contribution to C_p proportional to T^5 ($C_{SM}T^5$), besides the TLS ($C_{TLS}T$) and the Debye (C_DT^3) contributions. Hence, C_p/T^3 can be written as:

$$C_p/T^3 = C_{TLS}T^{-2} + C_D + C_{SM}T^2. \quad (2)$$

These two equations are valid (in accordance with the supposition for the equations for C_p [1,9]) up to a limiting temperature between T_{min} and T_{max} (where T_{min} is the temperature at which C_p/T^3 reaches a low-temperature minimum).

The values of C_3 at various Z were obtained from the experimental C_p data given in a C_p/T vs T^2 plot [6]. The Debye coefficient $C_D = (C_p)^D/T^3$ was also calculated in Ref. 6 by the well-known expression $(C_p)^D = 1.2\ 10^{11}T^3/\rho v_s^3$ (J/gK), using the data for ρ and v_s at 300 K, because of the lack of data at other temperatures (analogous extrapolation was used in similar studies of other chalcogenide glasses and a good coincidence between the calculated and experimental data was obtained [4]).

Because of the influence of the SM contribution, not taken into account in Eq. (1), the coefficient C_3 must be higher than the Debye coefficient C_D. The Z dependences of these coefficients are displayed in Fig. 3*a* (after estimating the C_3 data more precisely) and are compared with the Z dependence of the experimental data for $(C_p/T^3)_{max}$. The figure shows that all dependences of the specific heat parameters have maximums in the middle Z range. The differences (C_3-C_D), defined as $C_{SM}T^2$ in Eq. (2), determine the SM contributions to the C_p/T^3 values at the lowest temperatures reached by us. (Of course, the SM contributions increase up to T=T_{max}). The Z dependence of (C_3-C_D) confirms the supposition that there are more soft modes in the strongest glasses in the middle Z range. It can also be noted that the Debye contribution to C_p/T^3, defined with C_D in Eq. (2) and evaluated as described above, is also highest in the middle Z range. The C_D values are between 15 and 30% from the $(C_p/T^3)_{max}$ values in the studied system and the rest non-Debye contributions (between 85 and 70%) are predominantly the SM contributions conditioning the appearance of the specific heat peak. Indeed, the TLS contributions C_1T^{-2}, estimated from Eq. (1) for the lowest reached temperatures are around 1% (e.g. for the composition with x=34 at T=3 K it is 1.2%) and as C_1 or C_{TLS} are constants, these contributions decrease with the increase of the temperature. Therefore, using equations which are in accordance with the SPM assumptions, it can be concluded that the proposed correlation with the

thermodynamic fragility is based on the fact that there are more SM in the stronger than in the more fragile glasses. That is why in the strongest glasses the values of $(C_p/T^3)_{max}$ are the highest and the values of the parameters of the plateau of k are the lowest. The temperatures of the appearance of the peak and the plateau must be lower as well for the strongest glasses, where more excess vibrational excitations (more SM) are available.

To clarify the role and the temperature extent of the SM contribution to the features of $C_p(T)$ and $k(T)$ we note that the thermal conductivity at the lowest temperatures is connected with scattering of phonons by TLS [26] and at $T>W/k_B$, with their resonant scattering on the soft harmonic oscillators [23,4]. The modes with energy $E>W$ have a density of states proportional to E^4 (which leads to $C_p \sim T^5$) and their resonant phonon absorption induces a frequency dependent phonon mean free path, l. The strongly rising resonant scattering implies that at some energy E_d the decreasing mean free path becomes equal to the wavelength of the phonons. At $E>E_d$ the SM and the phonons cannot be regarded as independent. The quasi-localized SM are delocalized and the density of the harmonic (phonons and SM) excitations should change its energetic dependence to a weaker one. In this regard, it is important to clarify the correlation of the parameters of the low-temperature features with the temperature at which the quasi-harmonic excitations are delocalized. According to Ref. 27

$$E_d \approx 0.6 - 0.75\, W\, C^{-1/3}, \quad (3)$$

where C is a dimensionless parameter defined in the framework of the SPM.

Here we define E_d for the studied Ge-As-S system using the evaluated by us [6] W values as well as by calculating the values of the parameter C for different compositions according to the equation given by Parshin (Eq. (7.8) in Ref. 4)

$$C = \Psi(0)\hbar\rho^{1/3}v^{-1}\,\overline{M}^{-4/3}(\overline{M}/M)^{1/2} \quad (4)$$

Here,

- $\Psi(0)$ is the distribution function, whose acceptable order of magnitude is about 0.1, as estimated in Ref. 4;
- $\overline{M}$ is the average mass of atoms constituting the glass;
- M is the effective mass of the soft entity, most likely heavier than $\overline{M}$, as accepted in Ref. 1.

For the ratio $\overline{M}/M$ the values 1 and 0.1 have been proposed [27,4]. However for some chalcogenides the approximation $\overline{M}/M = 1$ leads to substantial deviations of the calculated W values from the experimentally determined W values and it has been concluded [4] that the most reasonable value is $\overline{M}/M = 0.1$. Our calculations using Eq. (7.10) from Ref. 4 where $W \sim (\overline{M}/M)^{2/3}$, show that for the studied system, the deviations of the calculated W values from the evaluated [6] ones also diminish using $\overline{M}/M$ values lower than 1. Therefore, we use the recommended in Ref. 4 value of 0.1 in all the calculations. We have to point out that this approximation is not too restrictive because the E_d/k_B values depend weakly on $\overline{M}/M$ as can be seen from Eq.(4).

The determined Z dependence of E_d/k_B for the studied ternary system is shown in Fig. 5. It is nonmonotonic as in the binary As_xSe_{1-x} system, where the same equation as Eq. (4) was used [27]. Besides, the smallest values of E_d are obtained for samples from the middle Z range. In Fig. 5 the Z dependences of the experimentally found parameter T^k_{min} and of the evaluated soft potential parameter W are also plotted. Comparison with the latter curves shows that E_d/k_B depends on Z in a similar manner.

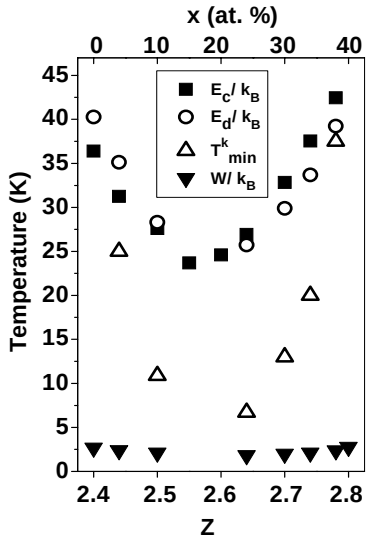

Fig. 5. Compositional dependences of the temperatures E_c/k_B and E_d/k_B corresponding to the calculated in two ways energy of delocalization of the SM. T^k_{min} and the temperature W/k_B corresponding to the crossover energy W are shown for comparison.

There is another possible way to define the crossover energy and the temperature above which the SM and phonons cannot be regarded as independent. In this approach we do not use the values of W evaluated before. Instead, the values of the crossover energy, marked as E_c, can be obtained on the basis of relations obtained in the framework of the SPM using only macroscopic material parameters: the density ρ, the averaged atomic mass $\overline{M}$ and the sound velocity v_s. According to Ref. 4 (Eqs. (4.43) and (1.8)) we find

$$E_c \approx (\rho\hbar^3 v_s^5)^{1/2}/\gamma. \quad (5)$$

The deformation potential $\gamma \approx E_o(\hbar^2/2Ma^2E_o)^{1/6}$ can be expressed (accepting $E_o = \overline{M}\, v_s^2$ and $a = (\overline{M}/\rho)^{1/3}$ in accordance with Ref.4) as

$$\gamma \approx \hbar^{2/6} 20^{-1/6}\, \overline{M}^{5/9} v_s^{10/6} \rho^{1/9} \quad (6)$$

Replacing (6) in (5) we obtain for E_c:

$$E_c = 20^{1/6}\,\hbar^{7/6}\,\overline{M}^{\,-5/9} v_s^{5/6}\rho^{7/18}. \qquad (7)$$

We use Eq. (7) to calculate the crossover energy E_c for 9 compositions from the $Ge_xAs_{40-x}S_{60}$ system. The so determined compositional dependence of E_c/k_B is plotted in Fig. 5, too. The compositional and/or Z dependences of E_d/k_B and E_c/k_B are very similar suggesting that the accepted approximation $\overline{M}/M = 0.1$ and our estimations of the W values given in Ref. 6 are reasonable.

3. Discussion

It will be useful to analyze the connection of the parameter of the soft mode delocalization E_c/k_B with the temperature dependences of the low-temperature thermal properties in order to check some predictions of the SPM.

As can be seen from the curves in Fig. 2*a* the C_p/T^3 values at temperatures corresponding to the E_c/k_B values of the investigated compositions define a line, which follows the C_p/T^3 vs T dependences in the temperature range from about 27 to 43 K, where the experimental curves nearly coincide for all compositions. In this range the C_p/T^3 values decrease more abruptly. It was suggested elsewhere [3,27] that the delocalization of the quasiharmonic excitations with increasing energy is responsible for the peak in C_p/T^3 at $T_{max}\approx E_c/5k_B$, because the harmonic oscillators with energy E have a maximum in C_p/T^3 at $k_BT=E/4.93$. In Fig. 2*a* we have plotted the C_p/T^3 values for the studied glasses at the corresponding $E_c/4.93k_B$ temperatures. The scaling relation marked with the dashed line differs from the experimental $(C_p/T^3)_{max}$ vs T_{max} relation (with exponent (-3.4)). Comparing the experimental values of T_{max} in the studied system with the evaluated values of $E_c(E_d)/4.93k_B$ at various Z we obtain deviations within ~20 to 38% for various glasses. The lowest deviations are for the strongest glasses, thereby confirming the established by us higher influence of the SM in the strongest glasses from the $Ge_xAs_{40-x}S_{60}$ system. The scaling law found here, on the base of the assumption of the SPM, has a slope about (-1.8). Its value is near to, but not exactly equal to the one found in the general scaling in Ref. 22 (-1.6). It should be pointed out that this assumption of the SPM does not take into account differences in the nature and degree of availability of the harmonic excitations.

It is worth noting that the fact that the SM contributions and the $(C_p/T^3)_{max}$ values are highest for the studied here glasses with the lowest thermodynamic fragility, is in accordance with the results for some other groups of glasses. For example, the maximums of C_p/T^3 are higher for the glasses As_2Se_3 and B_2O with lower thermodynamic fragility than that of SiO_2 [22], which has a higher thermodynamic fragility [13] (independent from the fact that it is kinetically stronger). Moreover, in systems like SiO_2 - Na_2OH the increase of the concentration of Na_2OH makes the system more kinetically fragile and this leads to a decrease in $(C_p/T^3)_{max}$ [21], similarly to the cases with thermodynamic fragility. However, considering the kinetic fragility, there are deviations from this correlation (as in some simple oxide glasses, including the cited above, which $(C_p/T^3)_{max}$ values are shown in Ref. 22 and the degree of kinetic fragility in Ref. 13) and one cannot conclude that the C_p/T^3 values are higher for all types of stronger glasses and for all chemically different groups of glasses. But it must be emphasized that our results for the studied covalent chalcogenide glasses establish undoubtedly that the C_p/T^3 values are the highest in the glass formers, which have the lowest thermodynamic fragility. The reasons for these deviations, the role of the chemical bonding and other factors, can be a mater of further debate.

The k values at temperatures corresponding to the calculated crossover energy E_c of the studied compositions define the dash-dotted line in Fig. 2*b*. One can see that the values of k at E_c/k_B are usually higher than that at T^k_{min} in one and the same composition. The k vs E_c/k_B dependence has an exponent of ~3 while k_{min} vs T^k_{min} (solid line in Fig. 2*b*) is nearly linear. The values of k at T^k_{min} and E_d/k_B nearly coincide only at the more fragile glasses. It was suggested before [4] that the loss of independence of the quasilocal harmonic excitations is responsible for the rise of the thermal conductivity above the plateau. In fact, the results established in Sec. 2.3 and reflected in the new scaling law show that the second rise in k appears at E_c/k_B, where the mean free path of phonons becomes equal to their wavelength [17,20] but only in the most fragile glasses (Fig. 2*b*). Therefore, in the strongest glasses the inequality, $T^k_{min}<E_c/k_B$, could be connected with the higher SM contribution to the phonons resonant scattering as well as with the competition between the C_p increase and the decrease of l, which may change after T^k_{min}. This competition (as noted in Sec.2.2) also governs the appearance of the negative N-type thermal conductivity in the more fragile glasses from the investigated system (with x=34 and 38). The found difference in the scaling laws reflects on the difference in the temperature dependences of the thermal diffusivity D up to E_c/k_B in the stronger and more fragile glasses. The latter difference is discussed below.

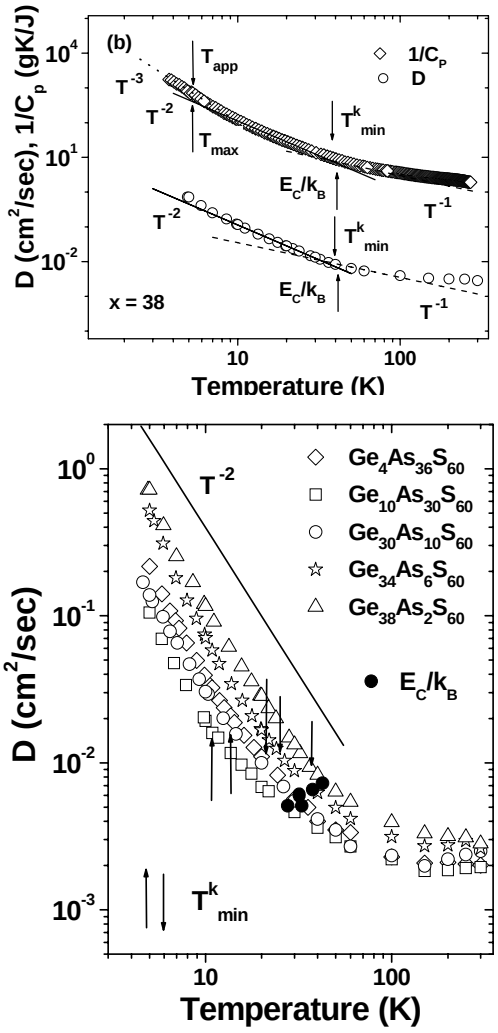

Fig. 6. Temperature dependences of the thermal diffusivity D evaluated for various compositions. Arrows and black points mark the temperatures T^k_{min} and E_c/k_B, respectively; a line of the temperature dependence with slope (-2) is also plotted.

The temperature dependences of D for various compositions determined by the experimental C_p and k data [7] are presented in more detail in Fig. 6, where the evaluated E_c/k_B values are also marked. The included new data for D confirm that the decrease of D is nearly proportional to T^{-2} up to temperatures near $T^k_{\min,}$ as has been accepted in Ref. 7, for the studied compositions and not to E_c/k_B, except for the more fragile glasses. Accepting that the temperature dependence of D in the plateau region in *k(T)* is governed primarily by the temperature dependence of $1/C_p$, we display the temperature dependence of $1/C_p$ for some samples, too. For comparison, in Fig. 7*a* and 7*b* the curves of $1/C_p(T)$ are presented together with that of *D(T)* for samples from a stronger and a more fragile glass with x=30 and 38, respectively.

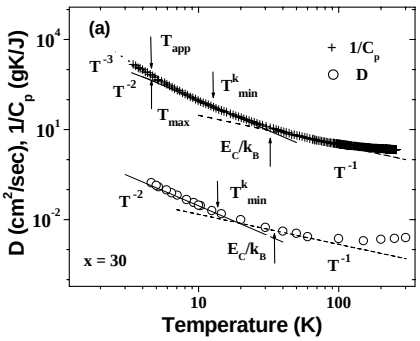

Fig. 7. Temperature dependences of $1/C_p$ and D for two compositions: (a) $Ge_{30}As_{10}S_{60}$ and (b) $Ge_{38}As_2S_{60}$. The characteristic parameters of the features of the specific heat, T_{max}, and of the plateau of the thermal conductivity, T_{app} and T^k_{min}, as well as the parameter E_c/k_B, are marked. The fitted dotted, solid, and dash lines with slopes (-3), (-2) and (-1), respectively, are also plotted.

Firstly, it can be mentioned that at the lowest temperature range $1/C_p$ decreases more abruptly than $1/C_p \sim T^{-2}$. The lines for temperature dependences with slope (-3) and (-2), fit well to $1/C_p(T)$, intersect at temperatures somewhat higher than $T_{\max}$ (the temperature at the maximal C_p/T^3 values) as well as than T_{app} (the evaluated [6] temperature of the appearance of the plateau of *k(T)*). It can be seen that in the lowest temperature range the *D(T)* curves deviate from the square decrease at this cross temperature (Fig. 7*b*) correlating with the change in the temperature behavior of $1/C_p(T)$. Secondly, while the lines for quadratic (T^{-2}) and linear (T^{-1}) temperature decrease fitted to $1/C_p(T)$ cross around E_c/k_B in both samples, the lines fitted to *D(T)* cross near $T^k_{\min}$, whose value coincides with E_c/k_B only for the fragile glasses. The tendency was confirmed by the other studied compositions. The abrupt change of the temperature dependence of the reciprocal value of the specific heat near E_c/k_B could be related to the reconstruction of the density of states of the harmonic excitation, which are not independent when the phonon wavelength becomes equal to the average distance between harmonic oscillators with energy $E>E_d$. The question whether the hybrid-mode model is applicable at temperatures $T>E_d/k_B$ can be addressed in the future. Finally, it should be noted that the nearly square temperature decrease of $1/C_p(T)$ reflects on *D(T)* only in the plateau region in *k(T)* where D is governed mainly by $1/C_p$. In the stronger glasses the slower (slower than T^{-2}) decrease of D between $T^k_{\min}$ and E_c/k_B (Figs.6 and 7) may be related to the higher rate of increase of k with T in this temperature range. According to our knowledge this has not been established until now.

4. Conclusions

It has been established (Fig. 3-5) that all parameters of the universal features of the low-temperature thermal properties of the $Ge_xAs_{40-x}S_{60}$ glasses, obtained

experimentally [$(C_p/T^3)_{max}$, T_{max}, k_{min}, T^k_{min}] or evaluated (C_3, C_D, θ_D, T_{min}, W/k_B, T_{app}, k_{app}), have Z dependences correlating with that of the thermodynamic fragility (Fig. 1). Based on calculations in the framework of the SPM, it has been concluded that the extremes in the Z dependences of the parameters and of the fragility of the glass formers are based on the higher excess of vibrational quasi-localized soft modes in the stronger glasses of the studied system. Accordingly, the higher SM contributions lead to higher C_p/T^3 peaks and inversely, to lower thermal conductivity in the plateau region and to lower temperatures of their appearance. It should be pointed out that the studied here correlation between the fragility and the properties of glasses is still a matter of interest. Indeed, the proposed correlation of fragility with elastic properties [28,14] is not accepted for all type of glasses or at all [29] and further studies of the subject are advisable. Our results could be useful for clarifying the rising problems of the correlation of various properties with fragility. The found Z dependences of the energetic parameter of delocalization of the SM, E_c (E_d), calculated in two ways according to relations based upon the SPM, correlate also with the Z dependence of the thermodynamic fragility. They are also related to the prevalence of the soft modes in the strongest $Ge_xAs_{40-x}S_{60}$ glasses. The novel scaling relations on the basis of this parameter and their comparison with the experimental scaling relations give new insights into the assumptions for the second rise of k above the plateau, the appearance of N-type thermal conductivity, the temperature dependences of the thermal diffusivity up to E_c/k_B, and their differences in the glasses with different degree of the thermodynamic fragility. So, it has been established how the low-temperature properties of the studied ternary chalcogenide glasses are influenced by their structural or chemical order.

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*Corresponding author: vateva@pronto.phys.bas.bg