Fragility and Boson Peak formation in a Supercooled Liquid

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ABSTRACT

We analyze results for the Boson Peak from the neutron time of flight spectroscopy data on Ge-As-Se, and Raman spectra data on m-TCP and OTP, using a recent mode coupling model that takes into account the coupling of density fluctuations with vibrational modes in presence of defects in the supercooled state. From the experimental results for different materials we observe that for more fragile systems characterized by increasing fragility parameter m, a slower relaxation of the defect-density correlation is needed to give rise to the observed peak in the spectra.

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The extra intensity observed in undercooled liquids in the neutron scattering [1, 2] as well as in Raman scattering [3, 4] at low frequencies, distinct from the quasi-elastic peak is usually referred to as the Boson peak in the literature. This characteristics feature of the supercooled liquid has been ascribed to the coupling between the relaxational and vibrational motions in the supercooled liquid in a recent work [5] with self consistent mode-coupling [6, 7] model. The mode coupling theory has a better agreement with dynamics in fragile glassy systems. The classification [8] used for glassy systems as strong and fragile depends on the ease with which structural degradation occur in those systems. A convenient measure for the fragility of the system [9] is computation of the slope m of the relaxation time τ curve against temperature T scaled with respect to the corresponding glass transition temperature T_g,

$$m = \frac{\mathrm{dlog} < \tau >}{\mathrm{d(T_g/T)}}|_{T=T_g} \tag{1}$$

In Ref. [5] we have described an extension of the simple mode coupling formalism to include the distinct vibrational modes that develop at low temperatures in the amorphous state for understanding the extra intensity appearing for the structure factor. The model follows from the equations of Nonlinear Fluctuating Hydrodynamics [5] extended to include the defect density in an amorphous solid like system which also sustains transverse sound modes. Here we have applied the model [5] to extensive data comparison to understand the underlying relationship between the fragility of the system and the Boson Peak formation. We fit the model with respect to the data of Russina et. al. from neutron time-of-flight-spectroscopy for Ge0.033 As0.033 Se0.934 glass, as well as the data for m-tricresyl phosphate (m-TCP) by Sokolov et. al. from Raman scattering. The present analysis demonstrates that the criteria for the appearance of the peak is crucially related to the dynamics of defect densities in the disordered system.

In studying the feedback effects on dynamics due to slowly decaying density fluctua-

tions at supercooled states, the memory function $H[\phi(t)]$ is obtained as a functional of the hydrodynamic correlation functions, in the following q independent form,

$$H(t) = c_1 F[\phi_L(t), \phi_T(t)]\psi(t) + c_2\psi^2(t) \tag{2}$$

where c_1 and c_2 are dimensionless constants determined in terms of the wave vector integrals due to the mode coupling vertex functions. ϕ_L and ϕ_T are the correlation functions for the longitudinal and transverse sound modes. The function $F(t)$ is expressed as [5],

$$F[\phi(t)] = e^{-\delta t} + f(\sigma)\phi_T(t) \tag{3}$$

where δ represents the time scale of very slowly decaying defect density and $f(\sigma) = (12 - 14\sigma)/9(1 - 2\sigma)$ with $\sigma = (3\lambda - 2\mu)/[2(3\lambda + \mu)]$ is the Poisson's ratio. For more details we refer to Ref. [5]. Following the procedure described there we have used this model to fit the data of Russina et. al. [10, 11] for Ge-As-Se. The central quasi-elastic peak is fitted a Lorentizian of width δ, and is equivalent to taking the time scales of relaxation of the defects to be same [12, 13] as that of the final time scale of relaxation of the density fluctuations. We show in Fig. 1a the dynamic structure factor as a function of frequency. The time scale for the decay of the defect density denoted by δ plays a central role in appearance of the peak on the shoulder of the quasi-elastic peak. This intermediate peak disappear in the shoulder of the quasi elastic peak as δ become large. This is shown by the fit of the data of Russina et. al. for a higher temperature in Figure 1b. We analyze the data for temperatures, T = 252, 334, 359, 402, 440 and 502 degree Kelvin, with suitable values of c_1 and c_2 in the expression (2) for the memory function. The parameter δ which gives the time scale of relaxation of defects is used here as the only adjustable parameter. It is considered in inverse units of the time τ_0 in terms of which the MCT equations are expressed in the dimension less form. τ_o can

be obtained in terms of the microscopic frequencies of the liquid state. To study the behavior of δ with the fragility parameter we have considered data on another material m-TCP with a different m, used by Sokolov et. al. [4] and done a similar fitting to the Boson peak at temperatures T = 205, 235, 262 and 287 degree Kelvin. In Fig. 2 the fit to the Boson Peak data [4] for m-TCP is shown. Variation of $\log(\delta)$ with the inverse temperature T_g/T is shown in Fig. 3, where T_g is the glass transition temperature of the corresponding material. The data points for m-TCP are shown by stars ($*$) and for OTP [14] by filled circles ($\bullet$). Variation of $log(\delta)$ with temperature for Ge-As-Se alloy is shown in the inset by squares ($\Box$). Solid lines show the straight line fit to the data points. For lower temperatures the quantity δ is small indicating that the defect densities are long lived and the Boson Peak appears to be more pronounced. The more fragile the system is, sharper is the fall of δ which represents the time scale of defect correlation. In all three cases δ shows an Arrhenius fall with temperature and a corresponding activation energy can be computed from the slope of the curve. In figure 4 we show the plot of activation energy A (in units of temperature T) for different systems with the corresponding fragility index m. With the systems of increasing fragility, more long lived defects are needed to give rise to the observed peak in the spectra.

We have approximated here through δ relaxation of the defect density by single exponential mode. The full wave vector dependence has to be considered to account the coupling of the structural relaxation to the vibrational modes. The explicit temperature dependence of the peak is not captured in the present model. This can be computed through proper input for the static or thermodynamic properties that appear in the mode coupling integrals. Figure 3, demonstrates the key result of this paper that for more fragile systems δ, inverse of which relates to the defect density correlation, shows a sharper fall with temperature. Also we like to point out here that the temperature range

covered for the materials in this paper actually correspond to the part where the fragile glasses starts showing a sharp increase of viscosity on the Angell plot[8] - more fragile the liquid is, more dramatic is the increase giving a higher value for the fragility index m [9, 15].

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Figure Captions

Figure 1

The neutron scattering data (in arb. units) of Ref. [10, 11] normalized with respect to the Bose factor $\omega[n(\omega)+1]$ (open circles) at (a) $T = 252^o$ K and (b) $T = 440^o$ K, Vs. the frequency in Mev. The solid line presents the result obtained from the present model for the normalized correlation function ψ.

Figure 2

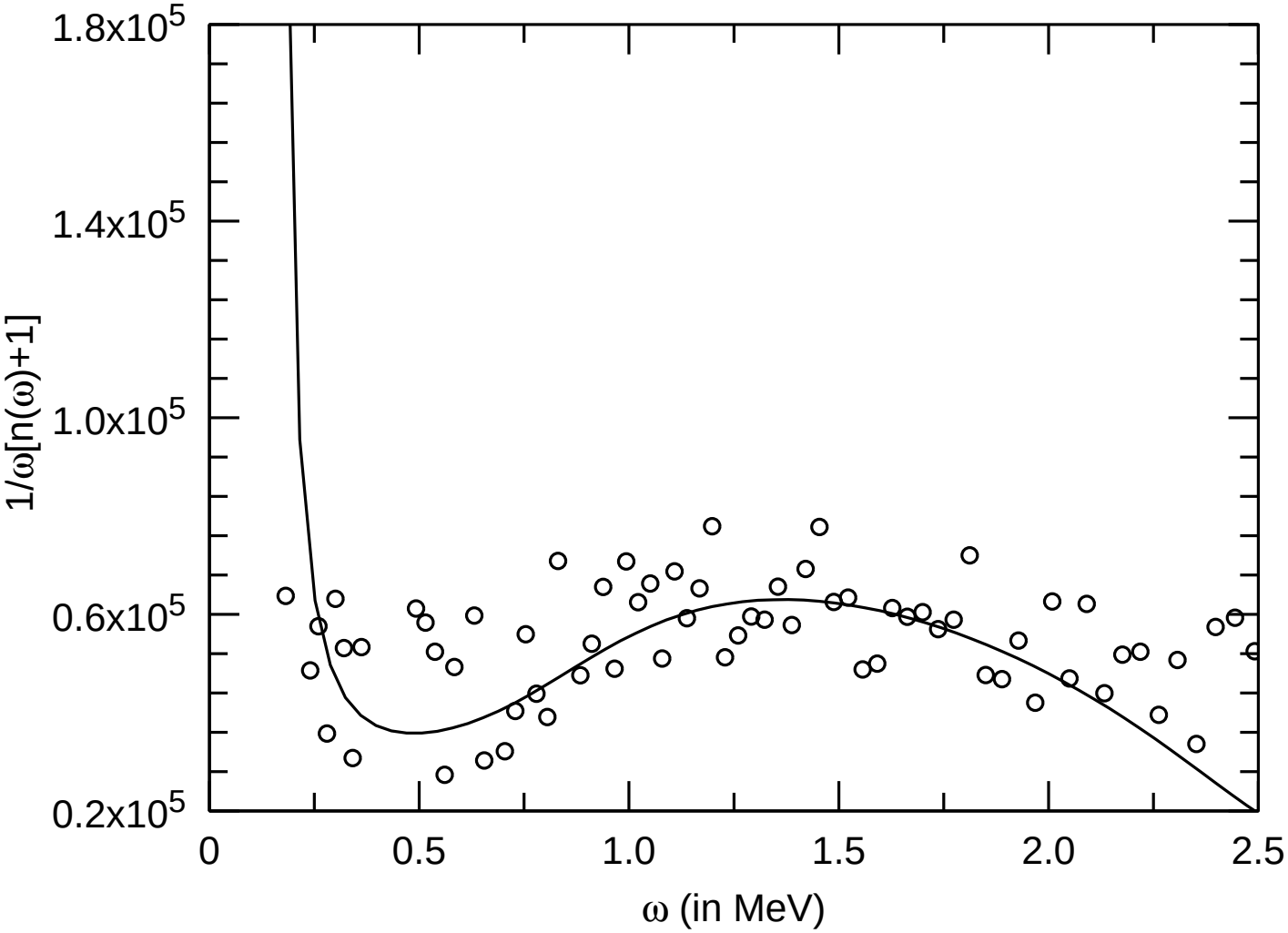
The Raman Spectra data (in arb. units) for TCP normalized with respect to the Bose factor $\omega[n(\omega)+1]$ (open circles) at $T = 205^o$ K, vs. the frequency in GHz. The solid line presents the result obtained from the present model for the normalized correlation function ψ.

Figure 3

$\log(\delta)$ as a function of temperature (T_g/T) for OTP ($\bullet$) and for m-TCP($*$). Inset: For Ge-As-Se alloy ($\Box$). The solid lines represent the straight line fit to the data points.

Figure 4

Slope for the δ-1/T curve, A (in unit of ^oK) Vs the fragility parameter [9] m.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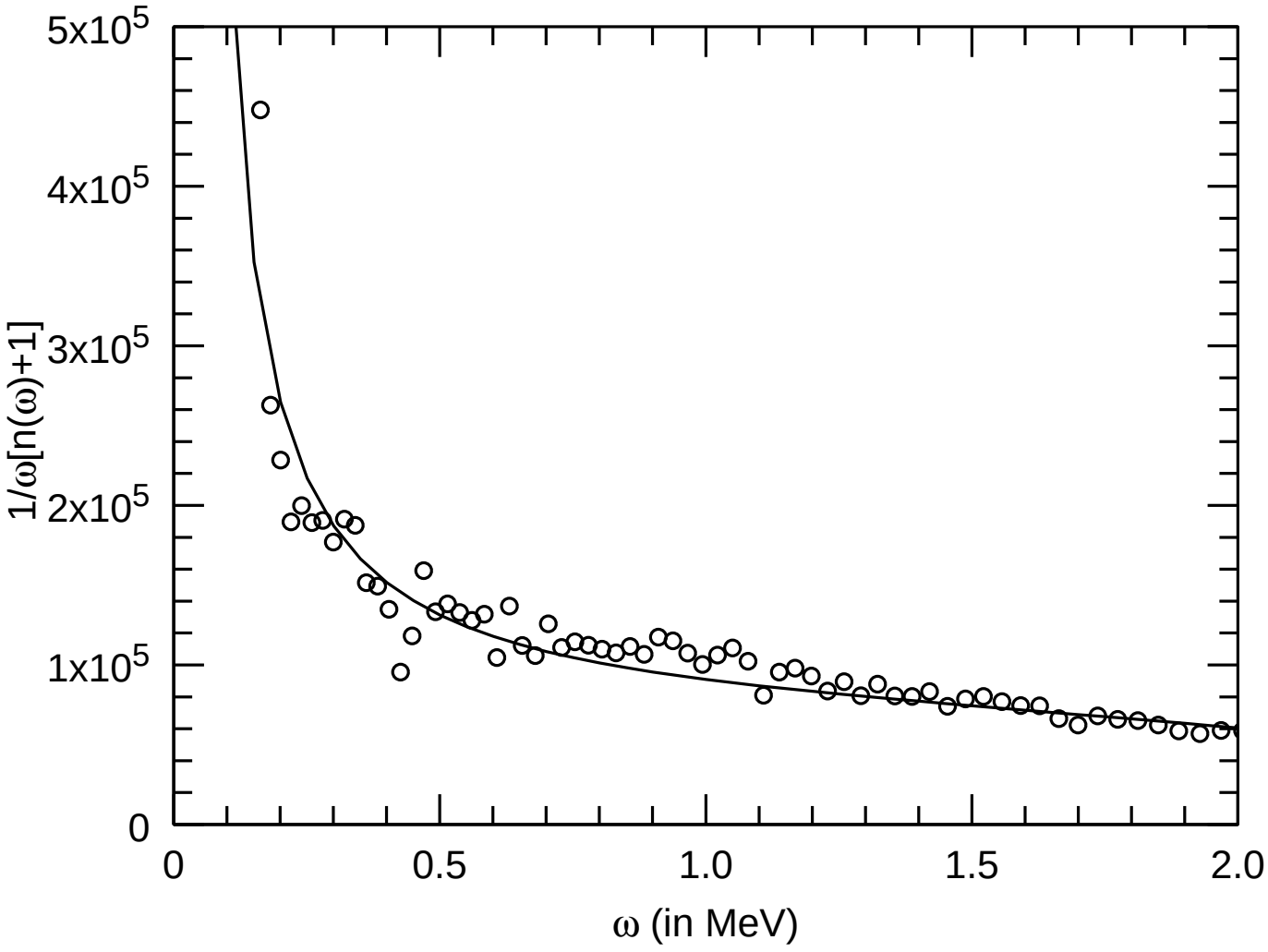
1.5
2.0
2.5
ω (in MeV)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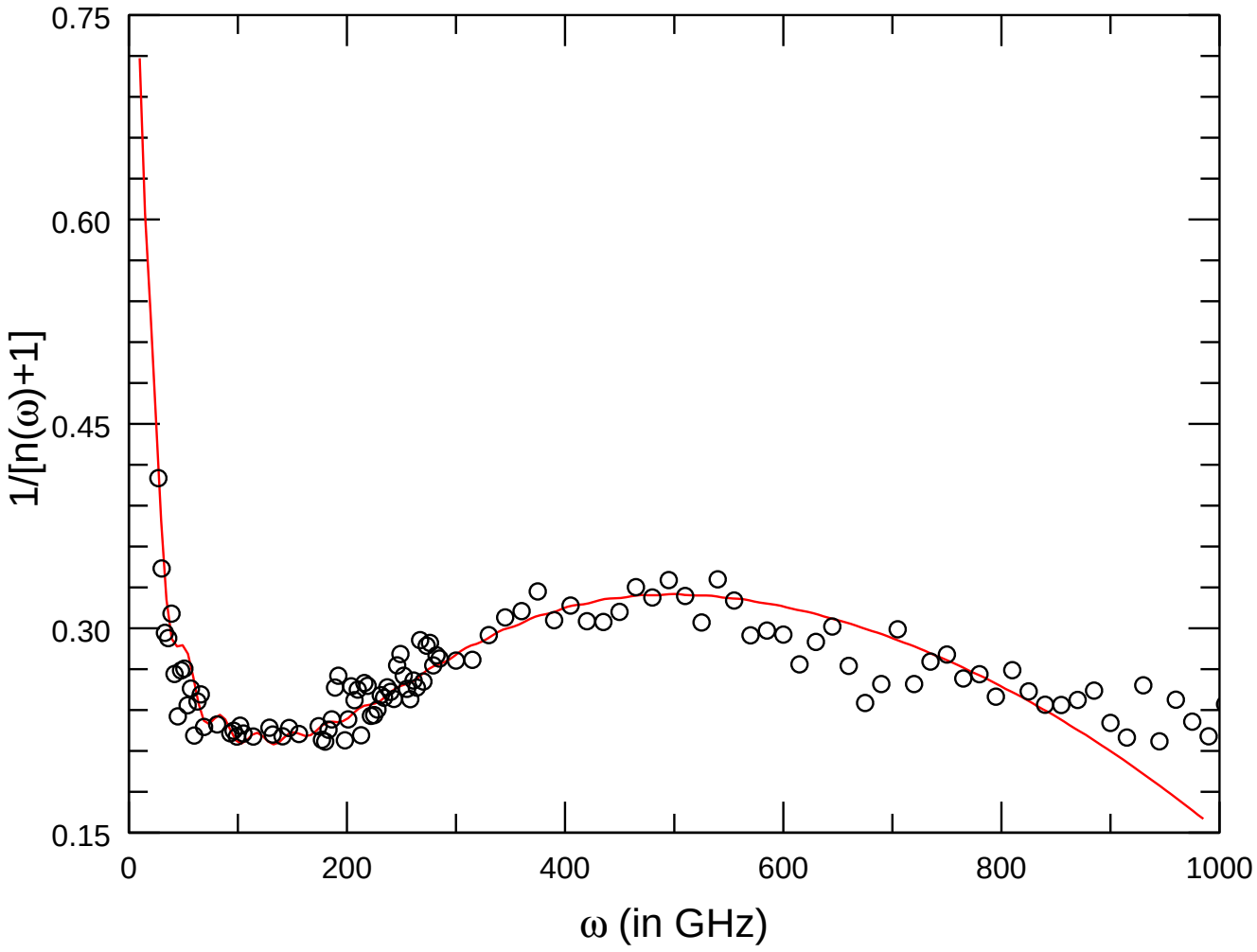
ω (in MeV)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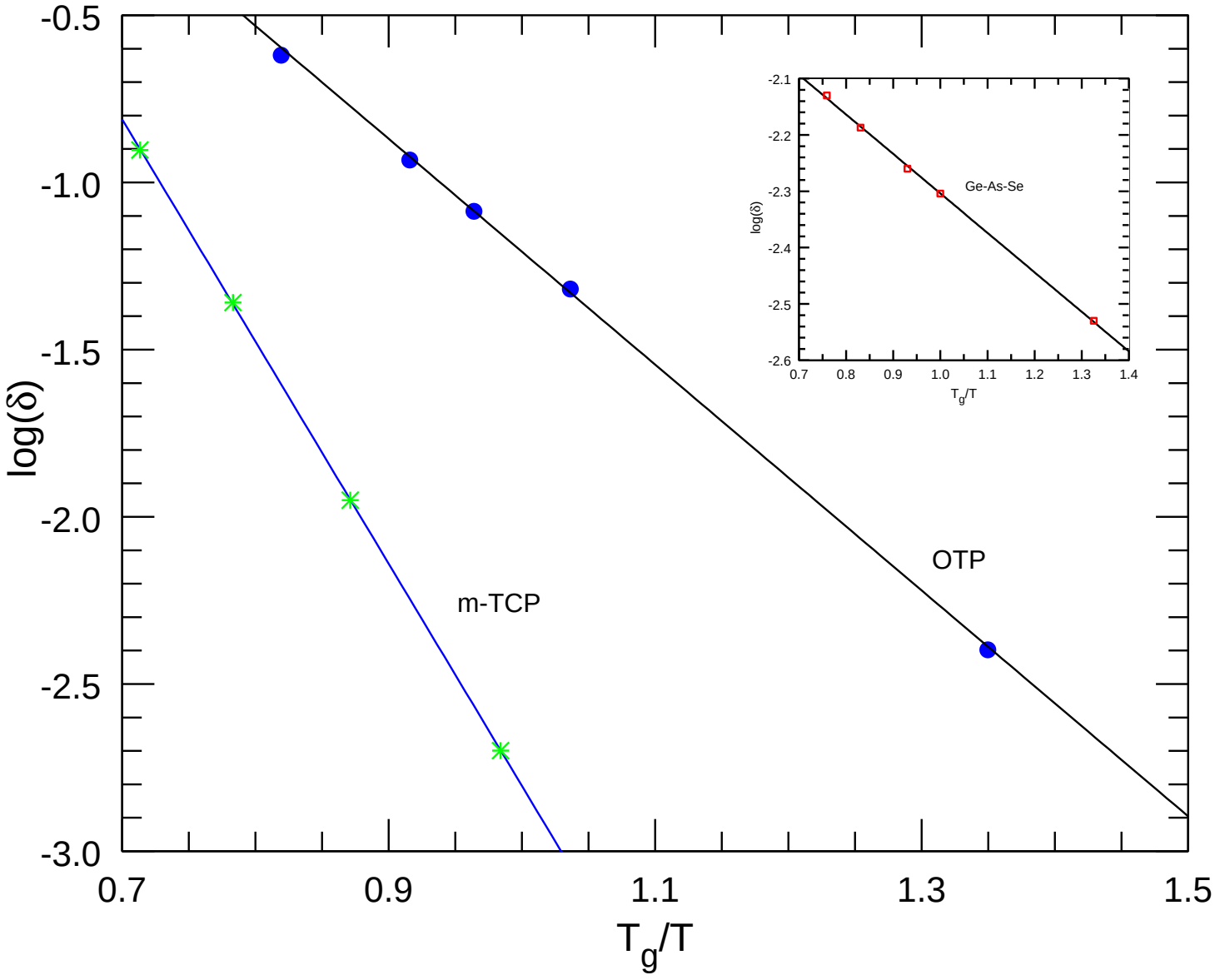
ω (in GHz)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-1.5
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-2.5
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0.9
1.1
1.3
1.5
T_g/T
OTP
m-TCP
Ge-As-Se
-2.1
-2.2
-2.3
-2.4
-2.5
-2.6
log(δ)
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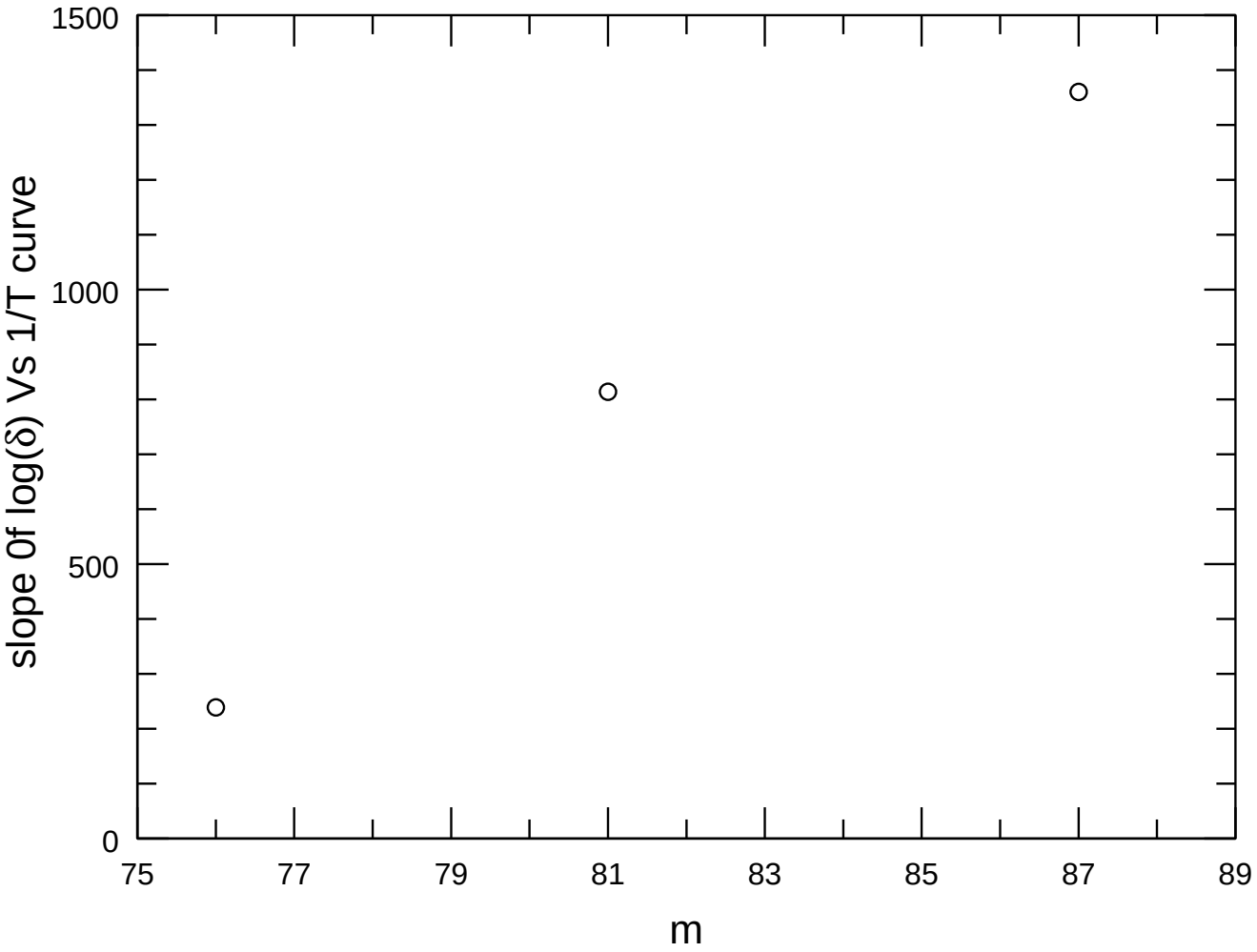
1.2
1.3
1.4
T_g/T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