Comment on "Structure of Covalently Bonded Glass-Forming Melts: A Full Partial-Structure-Factor Analysis of Liquid GeSe₂"

In this Letter [1], the full power of isotopic substitution and abundant neutron statistics is demonstrated in the context of the structure of glass-forming liquid $GeSe_2$. While there is little that can be added to this diffraction *tour de force*, we wish to comment here on the structural consequences of the occurrence of homopolar bonds in $GeSe_2$ that Penfold and Salmon [1] for the first time directly demonstrate from their diffraction experiments. Although the authors support the "outrigger raft model" which provides for such bonds at the edges of a crystal-like fragment [2], they rightly temper this bold conclusion with the reservation that "homopolar bonds will also occur in a defected chemically ordered continuous random network (COCRN) model in which well-defined layers need not be present."

Fortunately, the underlying reservation regarding homopolar bonds was addressed nearly a decade ago in related Mössbauer effect experiments [3] on Sn-doped Ge_xSe_{1-x} glasses, where it was shown that not only is there a finite concentration of Ge-Ge bond signature (site B) at $x = \frac{1}{3}$, but also that the rate γ at which the concentration of such bonds increases with x (near $x = \frac{1}{3}$) is substantially higher than the maximum permissible within bond statistics of a COCRN. Specifically, in Ref. [3] it was shown that the fractional integrated intensities of nontetrahedral Ge sites $[I_B/I = I_B/(I_A + I_B)]$ amount to 0.16 at $x = \frac{1}{3}$, and this translates into a Ge-Ge bond concentration of 0.02 for $GeSe_2$ glass. [The factor of 8 reduction from sites to bonds results since each Ge-Ge bond gives a pair of nontetrahedral Ge sites (labeled as B site) but four Ge-Se bonds are needed to form a tetrahedral Ge site (labeled A site).] In these Mössbauer-effect experiments, it was further found that the growth rate [3] γ of B sites near $x = \frac{1}{3}$ is $\gamma = 32(2)$, which is substantially higher than the value of $\gamma = 18$, the maximum value within a COCRN. This latter result unambiguously shows that the Ge-Ge bond signatures in $GeSe_2$ glass may not be identified as defects in a COCRN. Furthermore, recent [4] T-dependent Debye-Waller factors for the A and B sites lead to qualitatively different vibrational temperatures of these species, $\Theta_D^A/\Theta_D^B = 130(5)/100(5)$. This fact is hard to reconcile within a COCRN model since both sites (A, B) are then formed in a completely polymerized network and have four nearest neighbors of

almost the same mass ($Ge = 72.6$, $Se = 79$). On the other hand, if these sites are formed in two different types of clusters, the qualitative reduction in the vibrational temperature of the B sites in relation to A sites may be traced to an intercluster displacement of the smaller cluster as a whole in relation to the larger cluster.

In summary, the original Raman-scattering results [2], the Mössbauer-effect results on both the anion- [5] and cation-site [3] chemical order, and now the new neutron partial structure factors [1] on the $GeSe_2$ melt all provide a sound basis to visualize the molecular structure of this prototypical chalcogenide glass and melt in terms of phase separation into Ge-rich and Se-rich molecular fragments. Indeed, if the Se-rich clusters are layered, then when the glass is crystallized by laser irradiation with sample temperature far below the glass transition temperature, growth of the β phase (layered) will be favored. Moreover, growth of the α (β) phase can be promoted by annealing just above (below) the glass transition temperature [6]. Note that the (3D) α phase contains only corner-sharing tetrahedra.

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