THE VIBRATIONAL ISOCOORDINATE RULE IN SE-AS-GE GLASSES

Inorganic glasses are among the most widely used classes of materials, yet they remain poorly understood at the atomic level, because the lack of long-range atomic order makes it difficult to obtain detailed information. Drawing unifying concepts from data on many materials, and identifying exceptional cases that can have potential value to technology, are the goals of a neutron scattering program at the NCNR.

Chalcogens (S, Se or Te) combined with Column IVB or VB elements form a large variety of covalent systems which readily form glasses when quenched from the melt [1]. They offer a wide range of optical and electronic applications. For example, transmission bands in the infrared region of the spectrum permit applications such as fibers for IR laser surgery, cutting and welding, night-vision devices, etc. which are based on selecting materials to optimize transmission in a particularly useful IR band. Chalcogenide glasses are also used in extremely fast switching devices, in X-ray imaging, and in imagers for video cameras. In terms of basic physics, these materials present a fertile testing ground for studying the effect of network topology on glass properties.

In the Se-As-Ge system, Se atoms are almost always covalently bonded to two other atoms, while As and Ge are respectively almost always 3- and 4-coordinated. An isocoordinate rule is one that identifies a property of a multicomponent covalent network glass system that stays constant for all compositions which have the same average coordination number, <*r*>. There are several of these evident in ternary Se-based glass alloys. Examples are the glass transition temperature, softening temperature, elastic constants, measures of hardness, and Se-H spectral hole-burning relaxation. Most of these rules cover behavior that is nearly static and on a macroscopic length scale. Our neutron scattering experiments extend the range of times involved in these rules by many orders of magnitude. We have identified a simple feature in the dynamics of chalcogenide glasses, the vibrational isocoordinate rule (VIR), which states that *up to some frequency the vibrational density of states (VDOS) is the same for alloys having the same <r>[2]*. This observation extends the time scale for the operation of such rules to the picosecond regime and the length scale to a few bondlengths.

Figure 1 shows the Generalized Vibrational Density of States (GVDOS) measured by neutron TOF inelastic scattering for several Se-As-Ge glasses. Some data sets were measured at NCNR using the Fermi Chopper Spectrometer (FCS) and some at the IN4 TOF spectrometer at ILL. There are two or three curves for each value of <*r*> which correspond to the compositions indicated in the figure caption. The data at <*r*> = 2.4 are particularly remarkable in that they include As_2Se_3 having a nearly 2-D network and Ge_2Se_8 which has a network closer to 3-D in character. The energy bands below 20 meV are nearly identical. Near 25 meV the VIR breaks down since the tetrahedral breathing mode appears in the Ge glass but not in the As one, i.e. the short range order of the network matters for this

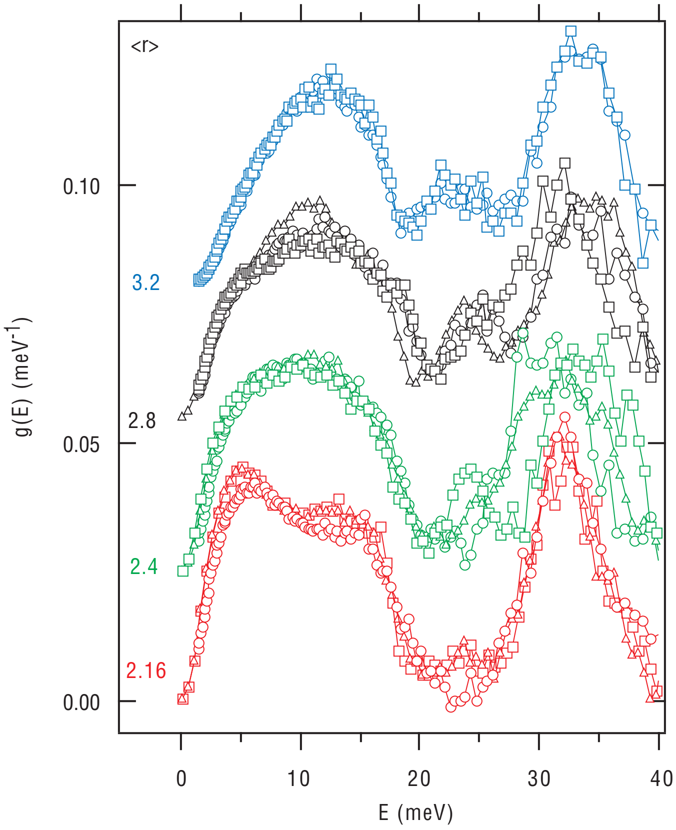

FIGURE 1. There are two or three experimentally-determined VDOS data sets for each of four coordination numbers <r>. VDOS for the same <r> have nearly identical shapes below 20 meV, illustrating the VIR. The Se/As/Ge compositions are: <r>=2.16: 92/0/8, 89/6/5, 84/16/0; <r>=2.4: 80/0/20, 68/25/7, 60/40/0; <r>=2.8: 51/18/31, 40/40/20, 30/60/10, and <r>=3.2: 25/30/45, 18/45/37. Data for increasing <r> have been successively displaced upward by 0.025 meV^{-1}.

R. L. Cappelletti and Birgit Effey
Condensed Matter and Surface Sciences Program
Department of Physics and Astronomy
Ohio University
Athens, OH 45701

W. A. Kamitakahara
NIST Center for Neutron Research
National Institute of Standards and Technology
Gaithersburg, MD 20899

mode. Apparently the VIR holds when *network connectivity and not short-range order* is important.

A clear departure from the VIR for <r> = 2.6 is shown in Fig. 2. The GVDOS of the lower curve, which clearly follows the trend of Fig. 1, is for $Se_{55}As_{30}Ge_{15}$. The upper curve displaying several sharp features is for glassy As_3Se_2. Surprisingly, these features are not evident in Raman scans in this glass. The origin of these features is not yet certain, but it is probable that they arise from a nanoscopic phase separation of isolated molecules within the glass that retain their well-defined molecular vibrational modes. Evidence supporting this view is that one can make several As_xSe_{1-x} glasses for $x \geqslant 0.5$ which display sharp features at the same frequencies, thus pointing to the same molecular species.

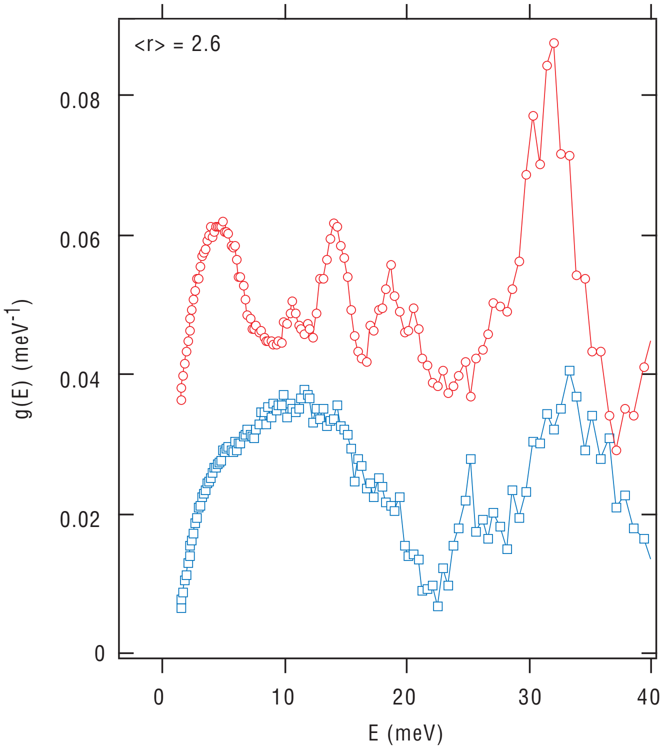

FIGURE 2. The bottom curve: $Se_{55}As_{30}Ge_{15}$ (FCS) follows the VIR. The top curve: As_3Se_2 (FCS) is an exception to the VIR. Both datasets are for <r> = 2.6. The top curve is shifted up by 0.030 units on the vertical scale.

The conclusions of this research are twofold: (1) The VIR is followed closely across the entire glass-forming region of the Se-As-Ge phase diagram, with the exception of a small region along and near the Se-As line for As-rich compositions. (2) Highly unusual behavior is observed for As_6Se_4, indicating the formation of molecular clusters or small structural units. The combination of (1) and (2) is intriguing, and may be relevant to unusual photocontractive effects that recently have been observed in As-Se thin films. Better understanding of the structural properties of the Se-As-Ge forms an improved basis for potential applications.

REFERENCES

[1] Valentina F. Kokorina, Glasses for Infrared Optics, CRC Press, Boca Raton (1996).

[2] Birgit Effey and R. L. Cappelletti, Phys. Rev. B, in press.