

## Chapter 12

### CONCLUDING REMARKS AND STATISTICS

We have now reviewed and analyzed a very wide range of measurements which explore the various nuclear, electronic, vibrational, and Zeeman levels accessible to glassy solids in the  $\gamma$ -ray, x-ray, ultraviolet, visible, infrared, and microwave regions of the electromagnetic spectrum. It will have become clear that the spectroscopic method provides not only the means of determining the energy levels of vitreous systems, but also, because of the dependence of these levels on atomic configurations, a powerful probe of the short-range order about atoms, ions, or electronic defects in these materials. The structural information available may be quite detailed for the first coordination shell for which average site symmetries, coordination numbers, oxidation state, bonding character, magnetic environment, hyperfine interaction, and motional dynamics may be defined. From the wealth of spectroscopic data revealed in the preceding chapters, it can be said that we have come a long way in understanding *qualitatively* the local structure of glasses. There is, however, a long way to go in unraveling glass structure *quantitatively* beyond the first two coordination shells about a central atom. At greater distances structural resolution similar to those by diffraction methods is also possible with EXAFS spectroscopy (Chap. 4). The ability of this technique to probe the structure around individual atomic species makes it particularly attractive and perhaps a unique tool for studying amorphous solids, especially multicomponent systems. With the availability of high intensity, continuous synchrotron radiation, at Stanford for instance, extensive applications of this spectroscopic technique are now being made to study the local structure of a variety of glassy solids.

Model-building helps to fill in this "quantitative" gap somewhat, and has been proven useful in structural calculations as well as property calculations such as electronic and vibrational density of states of simple systems like amorphous Si, Ge, and As.

It should be recognized that much of our present spectroscopy-derived understanding of structure in glasses is based on comparisons with parallel spectroscopic studies of crystals of known structure containing the spectroscopically active center or group. The outstanding example is perhaps that of vitreous  $\text{GeO}_2$ . In each spectral region, comparisons of glass spectra with the corresponding spectra of the quartz-like hexagonal polymorph (Ge 4-coordinated) and the rutile-like tetragonal polymorph (Ge 6-coordinated) have been used to show that the electronic structure and vibrational levels as well as defect centers characteristic of the vitreous material are without exception analogous to those of the 4-coordinated polymorph. The emphasis on glass-crystal comparisons in the literature is a reflection of the great difficulty of adequately formulating theoretical models for the energy levels of aperiodic structures. Currently, much attention is being given to this problem, and it is becoming apparent that the consequences to the predicted spectra of neglecting structure beyond the 2nd coordination shell of the active species are generally negligible. Thus, there is reason to expect that in the foreseeable future the current reliance on "fingerprint" techniques will be relaxed. The computer-simulation procedures currently being developed to synthesize EPR and NMR line-shapes observed in glassy solids (Chaps. 9 and 10) serve to indicate the potential which vitreous state spectral analysis is developing.

Spectroscopy also provides a very sensitive means of studying subtle changes in structure which occur in response to changes in the mode of preparation of the glass. For example, vitreous  $\text{SiO}_2$  prepared by chemical vapor-deposition (CVD) techniques at low temperatures ( $300^\circ\text{--}500^\circ\text{C}$ ) exhibits vibrational bands that are much broader than those of the normal bulk glass obtained by cooling the liquid, a clear indication of the greater spread of atomic configurations imposed on the system by preparation procedures which kinetically

exclude effective local energy minimization. Although significant differences in peak widths of the RDF derived from diffraction measurements are noted between the CVD material and ordinary silica glass (in that the rms deviations of atomic distances of the CVD film are much larger than those of thermal or bulk  $\text{SiO}_2$ ), the distinctions are less obvious than for the IR spectra.

Further to the above, the approach to minimum energy structures can be followed by spectroscopically monitoring the changes induced by heat-treating the material at temperatures above the deposition temperature. Such heat treatments produce progressive band narrowing and, in the case of  $\text{SiO}_2$ , the absorption bands of CVD and normal glass become identical after heat treatment above  $800^\circ\text{C}$ . Such observations establish a position for vibrational spectroscopy somewhat above diffraction methods in a hierarchy of structure-sensitive measurement techniques in which, however, absorption spectroscopy is by no means outstanding. The sensitivity limit for IR resolution of structural differences is, by the above observations, reached at the " $800^\circ\text{C}$  structure," since there are good reasons to suppose that this structure and the structure of the normal glass (which forms by loss of equilibrium at  $1200^\circ\text{C}$  during cooling) are not in fact identical. Whereas other absorption spectroscopy techniques have structure sensitivities similar to that of IR, a great improvement in structure-sensitivity may be obtained by passing to "relaxation spectroscopy" which has been treated in some detail in Chap. 11. In discussing the relation of relaxation spectroscopy to absorption/emission spectroscopy, it was emphasized that information on structure is not obtained directly in the former. On the other hand, its great sensitivity to structural alterations, particularly those taking place in the important glass transformation range, gives this type of spectroscopy a special place in glass science and ensures its increasing importance in the future.

Another point deserving final comment concerns the problem of spectroscopy in relation to microscopic structure which is coarse on the atomic scale. Specifically, we refer to the problem of microscopic phase separation which now proves to be so prevalent in

multicomponent glasses. Absorption spectroscopy, which explores only very short-range order, is clearly unable to determine whether or not the order it reveals is representative of the glassy medium as a whole or of only one type of microregion within it. This necessarily limits the type of statement which absorption spectroscopy can justify on the effect of composition changes on the distribution of spectroscopic centers (e.g. nonbridging oxygens) in the overall glass. A result is that spectroscopic studies by themselves cannot provide the basis for judging the merit of any type of continuous network theory of glass structure. This limitation again does not apply to relaxation spectroscopy in which the properties of a sample may depend critically on the continuity or otherwise of the structure.

There are, on the other hand, some developing applications of absorption spectroscopy in which the influence of the time-dependence of longer range processes (such as diffusion of species over distances which are macroscopic on the atomic scale) is the focus of attention. These studies may be based on lifetime broadening of spectral bands or simply on the time dependence of spectral intensities after perturbations of the glass from an equilibrium state. Such marriages of spectroscopic with relaxation techniques are likely to prove very beneficial in future work on glasses.

It will be useful, in conclusion, to examine on a comparative basis the types of systems to which each spectroscopic technique has been applied and the use made of each portion of the electromagnetic spectrum in the attempt to understand the vitreous state. The types of glass system studied, and the information derivable from each spectroscopic technique discussed in this monograph is given in Table I. Evidently, oxide glasses are by far the most commonly encountered systems in vitreous state spectroscopy. The novel class of glassy metal alloys mentioned in Chap. 2 is almost untouched experimentally by spectroscopists. The bar graph given in Fig. 1 shows the number of publications concerned with spectroscopic studies in glassy systems in the period 1960-1975 as referred in the present monograph. This again is presented in the order determined by the spectral energy region, for each of the areas of spectroscopy discussed in the

TABLE I  
Summary of the Types of Glass Systems Studied and the Information Obtainable from Each Spectroscopic Technique

Technique	Vitreous Systems Studied	Information
Mossbauer Effect	Borates, silicates, phosphates, FAS, <sup>a</sup> chalcogenides	CN, <sup>b</sup> site symmetry, valence, hyperfine interaction, diffusion kinetics, $T_g$
X-Ray Emission and EXAFS	Borates, silicates, phosphates, Se, Ge, GeO <sub>2</sub>	CN, bonding, effective charge, local order, RDF <sup>d</sup>
UV	Borates, silicates and phosphates, GeO <sub>2</sub> , chalcogenides, thin films	Bridging and nonbridging oxygens, oxidation state of impurity ions, band gaps, glass basicity, $T_g$
Visible	Color centers and radiation-induced defects in borates, silicates, phosphates, vitreous salts and FAS	CN and site symmetry of doped ions or defects, redox equilibrium, oxide ion activity, glass basicity.
IR, FIR, Raman	Borates, silicates, germanates, phosphates, arsenites, chalcogenides, vitreous salts, thin films	Vibrational dynamics, bonding, CN, IR transmission property, chemical composition, thermal history.
EPR	Paramagnetic impurities and radiation-induced defects in borates, silicates, phosphates, and chalcogenides	Local structure and CN of paramagnetic ions, nature of defect, induced vitrification and devitrification kinetics
NMR	Mainly borates; silicates, phosphates, chalcogenides, BeF <sub>2</sub>	Quadrupole coupling constants, CN of boron, bonding of modifying cations to anion network, diffusional motion of cations
Relaxation	All examples of vitreous and viscous liquid phases	Macroscopic structural equilibration times, electrical resistivities and losses, shear rigidities, relative mobilities of lattice elements, thermal history.

<sup>a</sup>FAS = frozen aqueous solutions; <sup>b</sup>CN = coordination number; <sup>c</sup> $T_g$  = glass transition temperature; <sup>d</sup>RDF = radial distribution function.

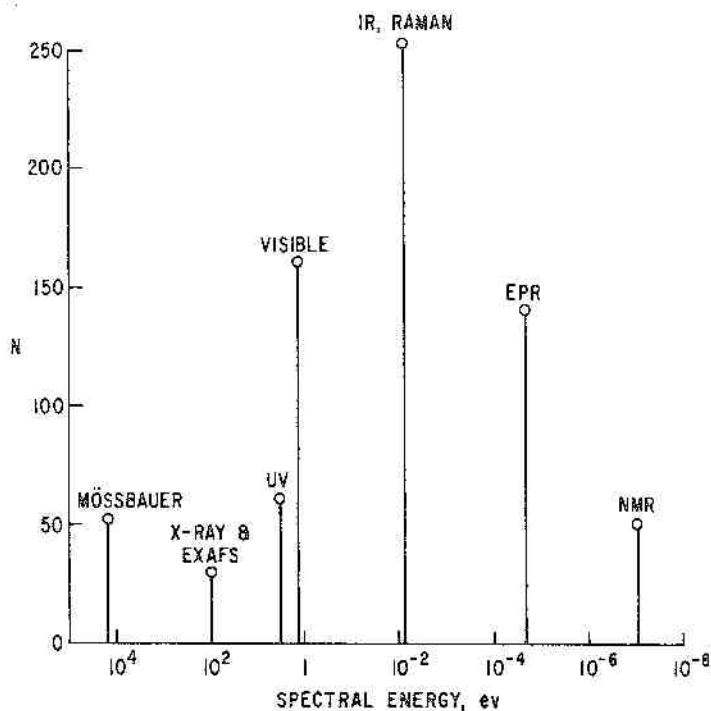


FIG. 1. The number of publications,  $N$ , dealing with spectroscopic studies in glassy systems in the period 1960-1975 as referred in the present monograph in various spectral regions.

preceding chapters. As can be seen, the greatest attention has been devoted to the vibrational spectroscopy of this class of solids. The diagram may serve as a useful statistical record for vitreous-state spectroscopists and may help influence the choice of energy regions for future investigations. One must bear in mind, however, that although each branch of spectroscopy probes a different aspect of the structure, eventually there should be a correlation among all spectroscopic properties of a given vitreous system.