Spying with spins on messy materials: 60 Years of glass structure elucidation by NMR spectroscopy

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Abstract
Glasses remain a focus of attraction to fundamental researchers and materials engineers alike. The desire of controlling physical property combinations by compositional design inspires the search for fundamental structural concepts describing the short- and medium-range order of the glassy state. From its early beginnings more than 60 years ago, solid-state nuclear magnetic resonance (NMR) spectroscopy has been making significant contributions toward this objective. Being element-selective, inherently quantitative as well as selective to the local environment, NMR in many ways presents an ideal experimental tool of structural investigation of glasses. Over the years, substantial NMR methods development, along with advances in the theoretical interpretation of NMR parameters, have significantly enhanced our fundamental knowledge of medium-range order and of composition-structure-function relationships. As we are approaching the 60th anniversary of the publication of the first article dealing with this topic (A.H. Silver and P.J. Bray, The Journal of Chemical Physics 1958, 29, 984), it is time to look back at the amazing scientific trajectory this field of investigation has taken, from the early beginnings to the present state of the art. As such, this overview does not strive to be comprehensive, but adopts a personal perspective, highlighting what in the view of the author have been influential developments and important insights obtained during the various phases of scientific inquiry in this research field.

KEYWORDS
characterization, electron spin resonance, medium-range order, nuclear magnetic resonance, structure elucidation

1 INTRODUCTION

Compared to crystalline solids, glasses present a formidable challenge to structure elucidation. Owing to the lack of translational symmetry in the glassy state, the concept of a “unit cell” is irrelevant, and structural models need to be cast in terms of interatomic distance statistics, the so-called pair correlation functions, which must be specified for each possible pair of atomic species occurring in the material. The details of such distance statistics very much depend on the type of glass system under consideration. The present contribution is about the most common (and technologically interesting) group of them, termed covalent network glasses, which are described by Zachariasen’s continuous random network model. They are built from polyvalent oxides, chalcogenides, and halides of the Group 13-16 elements (TxAy, T = B, Si, Ge, P, Te, A = O, S, Se), called network formers. In these T atoms are linked by two-coordinate bridging A atoms), establishing a seemingly random arrangement of corner-shared polyhedra. By
incorporating various types of oxides, chalcogenides and halides of mono- or divalent cations (termed network modifiers), the structure is transformed into a macro-anion typically containing nonbridging oxygen, sulfur, selenium, or halogen species. The negative charges associated with this macro-anion compensate the charges of the metal cations. Furthermore, some di- and many trivalent oxide species (intermediate oxides) can adopt the roles of both network former and network modifier species. The clear tendency toward forming directional chemical bonds leads to well-defined local structural geometries of the T atoms, whereas the environments of bridging A species (most notably the bridging oxygen atoms in oxide glasses) are significantly less well ordered and characterized by a relatively wide distribution of T–A–T bond angles. This disorder is a consequence of the multiple structural configurations within the complex energy landscape that are thermally accessible in the metastable supercooled liquid-state frozen in at the glass transition temperature. For developing a comprehensive view of glass structure, one needs to describe the loss of correlation as a function of distance. The relevant length scale domains include the following: (i) short-range order involving the first atomic coordination spheres (distance region 0.15-0.3 nm), (ii) intermediate-range order, comprising distance correlations in the second and third coordination spheres (0.3-0.5 nm), and (iii) medium-range order (0.5-1 nm and beyond) involving the formation of larger structural units such as clusters, chains, and rings. The latter aspect also includes nano-segregation phenomena that may occur in the liquid state due to incipient phase separation. With decreasing temperature of the melt, thermodynamic phase separation tendencies increase, while at the same time, the molecular dynamics and material transport kinetics promoting such structural evolution are slowed down. As a result, medium-range order on the nm distance scale depends on the thermal history of the materials. This structural aspect becomes particularly important when considering the transformation of glasses to glass ceramics, where incipient phase separation leading to nucleation and growth of crystals is continuously developed by controlled annealing experiments.

A comprehensive structural description of glasses needs to discuss all these aspects. From its early beginnings more than 60 years ago, solid-state nuclear magnetic resonance (NMR) spectroscopy has been one of the most important methods for obtaining structural information in this respect. As NMR spectra are rather sensitively influenced by the local environments of the nuclei, they offer structural information on the subnanometer scale, that is, exactly on that length scale domain, where the correlation loss differentiating glasses from crystals is observable. Owing to its inherently quantitative nature, NMR offers—in a manner unmatched by any other spectroscopic technique—a detailed numerical description in terms of coordination numbers and symmetries, bond connectivities, and interatomic distribution statistics averaged over the bulk material (see Figure 1). Finally, due to its element-selective character NMR spectra can give pertinent insights also on glasses that are compositionally complex and/or contain the species of interest in only low concentrations.

Solid-state NMR is based on the orientational quantization of nuclear magnetic moments, which gives rise to quantized energy levels in applied magnetic fields, $B_0$. By applying radio waves fulfilling the Bohr condition

![FIGURE 1](image-url)
transitions between these quantized energy levels can be
stimulated, producing the spectroscopic signal. Here, \( \gamma \), the
gyromagnetic ratio, characterizes the size of the nuclear
magnetic moment, and \( \omega \) denotes the resonance frequency.
In reality, the latter cannot be predicted by Equation (1),
but is further influenced by four physically distinct internal
interaction mechanisms, whose parameters reflect the
details of the local structural environment. These internal
interactions include (i) magnetic screening effects produced
by the electronic environment, (ii) nuclear electric
quadrupolar interactions between the quadrupole moment
of nuclei with spin quantum numbers \( > \frac{1}{2} \) and electrostatic
field gradients present at the nuclear origin, (iii) magnetic
dipole-dipole interactions of the nucleus under observation
with magnetic moments from other nuclei in their vicinity,
and (iv) spin-spin coupling via the polarization of electron
density within covalent bonds. The latter two mechanisms
may also include interactions between nuclear and elec-
tronic spins associated with unpaired electrons. For a more
detailed presentation of the theoretical foundations of solid-
state NMR and the specific manifestations of these interac-
tions upon the spectroscopic lineshapes, some excellent
introductory texts are available on its theory\(^{2a}\) and applica-
tion to inorganic materials.\(^{2b}\) All of the above-mentioned
internal interactions influencing the Zeeman energy levels
are anisotropic, and their simultaneous presence generally
results in poor spectroscopic resolution and featureless
lineshapes. In such cases, specific structural information is
available only if one of the above interactions is dominant.
If this is not the case, additional experimentation is neces-
sary, by means of which the complex Hamiltonian can be
simplified, using selective averaging strategies (see below).
As illustrated in Figure 2, nearly every element of the peri-
odic table offers a nuclear isotope with a magnetic
moment. About half of these (highlighted in red) are routi-
nely accessible with modern equipment. With regard to
their detection characteristics, relaxation behavior, and the
importance of certain internal interactions, each isotope has
its own, special spectroscopic personality. For example, for
those nuclei having a spin quantum number larger than \( \frac{1}{2} \)
and sizeable nuclear electric quadrupole moments (high-
lighted in purple in Figure 2), special techniques are often
necessary to separate the magnetic screening and dipolar
interactions from the nuclear electric quadrupolar interac-
tions. For other isotopes, applications are more limited
because of their small magnetic moments (orange entries),
extremely large quadrupole moments (blue entries) or low
natural abundances (yellow entries). Among the latter, the
\(^{17}\)O isotope, which is only 0.037% abundant and thus
always requires isotopic enrichment, is of special signifi-
cance for structural NMR studies of glasses.

Driven by the dynamic progress in the methodology of
experimental solid-state NMR and in computational chem-
istry alike, our fundamental understanding of glass structure
has enormously evolved over the past 30 years. We can

\[ \omega = \gamma B_0 \]  

FIGURE 2  Schematic of solid-state
NMR and its feasibility and limitations for
nuclei of the periodic table
identify three distinct, yet partially concurrent phases in this field, which have been leading us to the present state of the art. During the first 20 years (Phase I), solid-state NMR lineshapes were measured on electromagnets using mostly home-built spectrometers. Phase II started in the early 1980s with the advent of high-field, pulsed Fourier transform NMR techniques and the introduction of magic-angle spinning to this research area, supported by the widespread advent of commercial equipment. Phase III unfolded the full power of selective averaging methods, resulting in the cancellation, separation (and thence, selective study) of certain interactions via more advanced experimentation. At the current state of the art (which may be called Phase IV), such experiments are combined with increasingly sophisticated computational methods as an integral part of the experimental strategy, including (i) the definition of the problem and the formulation of work hypotheses, (ii) the data acquisition and processing steps, (iii) the “translation” of NMR data into structural information using quantum-chemical methods, (iv) the development of comprehensive, energy-minimized structures by molecular dynamics simulations and (v) the use of fundamental solid-state physics concepts relating structure to function.

The last comprehensive review article dealing with NMR studies of inorganic glasses appeared in 1992.5 Owing to the huge number of studies done since then and the increasing integration of theoretical methods into the experimental strategies, the goal of writing a comprehensive review on this subject appears nearly impossible today. The most recent attempts focus on oxide glasses, highlighting the contributions from modern experimental techniques,4 computational methods for the interpretation of NMR parameters,5 and the conceptual description of disorder in glasses.6 In this contribution, I will keep this focus on oxides and attempt to sketch the trajectory of NMR studies of glasses over the past ~60 years, highlighting some important milestones along the way.

2 | HISTORICAL DEVELOPMENT

2.1 | Phase I. Structural exploration by static continuous-wave field-sweep NMR methods

Early applications of NMR to glasses conducted during the 1960s and 1970s focused on the structural phenomenology of short-range order and their quantitative description in terms of local coordination polyhedra in glasses. The spectra were obtained by recording the nuclear induction signal obtained by monochromatic irradiation (continuous wave, cw) with variation (field sweep) of \( B_0 \). The equipment consisted of an electromagnet (with magnetic flux densities typically below 2 Tesla). While many laboratories used home-built equipment, a popular commercial spectrometer for such studies was the Varian 4200B unit, featuring a 2-16 MHz Hartley oscillator and two orthogonal coils for stimulating Zeeman transitions and detecting the nuclear induction signal. To improve signal-to-noise ratios, the field sweep was superimposed by a sinusoidal field modulation synchronized with lock-in detection. With this arrangement, the first derivative of the signal with respect to the magnetic field is detected. Using such equipment, Bray and his coworkers at Brown University were the first to develop \(^{11}\)B (later on also \(^{10}\)B) solid-state NMR spectroscopy for the structural analysis of borate glasses.7–9

The spectra of these nuclei are dominated by the interaction of the nuclear electric quadrupole moments \( eQ \) of these spin-3/2 nuclei with the local electric field gradients (EFG) tensor (components \( V_{xx} \), \( V_{yy} \), and \( V_{zz} \)) present at their sites. The effect of these interactions upon the NMR signals can be modeled by perturbation theory leading to lineshapes of the central \( m = 1/2 \) → \( m = -1/2 \) Zeeman transitions of the kind shown in Figure 3. These spectra reveal the 2 principal parameters characterizing this interaction: the nuclear electric quadrupolar coupling constant \( C_Q = eQV_{zz}/\hbar \) (i units of Hz), which is proportional to the size of the maximal EFG component, and the asymmetry parameter \( \eta_Q = (V_{xx} - V_{yy})/V_{zz} \), which characterizes its deviation from cylindrical symmetry.

As Figure 3 indicates, \(^{11}\)B NMR can differentiate between the various types of \( B^{(n)} \) environments very well because their EFG characteristics are very different. The triangular \( B^{(3)} \) units of glassy \( B_2O_3 \) experience a large, close to axially symmetric electric field gradient (\( \eta_Q = 0 \)) producing a characteristic lineshape displayed in Figure 3, middle. In alkali borate glasses, however, part of the boron atoms are four-coordinated where the \(^{11}\)B nuclei find themselves in a much more symmetric environment. For such moderately small electric field gradients, the central Zeeman transitions remain unaffected by the quadrupolar interaction, and a comparatively sharp signal is observed.

![FIGURE 3](image_url) The different types of local environments found in borate glasses corresponding to B(4), B(3), and B(2) units of Figure 1, and their static NMR lineshapes and electric field gradient parameters
Another part of the borate species feature three-coordinated environments containing a negatively charged nonbridging oxygen atom. In this case, the large field gradient is characterized by nonaxial symmetry, producing a lineshape shown in Figure 3, right.

By comparing their experimental spectra with computer simulations, Bray and coworkers obtained quantitative information on the boron speciation in a large number of binary and ternary borate glasses, providing a convincing structural rationale of the so-called borate anomaly (see Figure 4): Unlike the situation in silicate glasses, the presence of alkaline oxide does not depolymerize the glass network, but rather increases connectivity by converting three-into four-coordinated borate units. Up to an alkaline oxide/B$_2$O$_3$ ratio of $R = 0.5$, each oxide ion converts two neutral B(3) units into anionic B(4) units. At higher alkaline oxide content, the conversion is no longer quantitative and for $R > 0.7$, the fraction of four-coordinate boron decreases again, indicating that the anionic B(2) units become increasingly stable in the alkaline-rich composition range.

Müller-Warmuth and coworkers were able to extend Bray’s NMR approach to silicate glasses, showing that the different types Si(n) species (see Figure 1) can be similarly differentiated by their $^{29}$Si NMR chemical shift anisotropies. However, for most of the nuclear isotopes low-field continuous-wave NMR was hampered by its low intrinsic detection sensitivity, limiting its applications to glasses to the most receptive nuclei $^1$H, $^{19}$F, $^7$Li, $^{31}$P, and $^{205}$Tl. Moreover, as these wideline NMR spectra are usually influenced by multiple interactions simultaneously, their interpretation is difficult. Notable exceptions include the distinction between OH groups and molecular H$_2$O in glasses, based on the strong $^1$H-$^1$H magnetic dipole-dipole coupling in the latter species and the qualitative detection of ionic mobility by motional narrowing effects observed in the static spectra of $^7$Li and $^{19}$F. A comprehensive summary of all the work from this particular period up to 1982 has been given in reference. In a parallel universe, a separate community developed, measuring and interpreting electron spin resonance spectra of glasses, using paramagnetic dopants as spies for local structural information. This work was comprehensively summarized in a 1980 review article. Despite identical quantum mechanical backgrounds and similar measurement techniques, these two communities interacted very little with each other at the time. During the past decade, the two fields have been finally converging, owing to the increasing proliferation of pulsed electron spin resonance methods and the use of electron polarization transfer processes for measuring solid-state NMR spectra.

## 2.2 Phase II: Speciation and quantification of local environments by high-field high-resolution Fourier transform NMR

During the mid-1970s, solid-state NMR instrumentation was revolutionized by three concurrent developments: (i) the advent of superconducting high-field magnets

![Figure 4](image-url)
(B_0 = 4.65-11.7 T), enhancing the sensitivity of NMR detection (which scales roughly proportional to the square of the magnetic flux density), (ii) the integration of online computers for the programming of pulsed NMR experiments and the subsequent frequency analysis of time-domain signals (pulsed Fourier transform NMR), and (iii) the construction of reliable magic-angle spinning (MAS) probes, producing significantly enhanced spectroscopic resolution. These three developments, along with their widespread commercial dissemination, produced a dramatic breakthrough for the structural analysis of glasses.

As mentioned in the Introduction, the interactions of the nuclei with their surrounding magnetic and electronic environments (magnetic shielding, dipolar or quadrupolar couplings) are anisotropic. These interactions can be described in terms of second-rank tensors in symmetry adapted coordinate systems (principal axis systems) that have a fixed relation to the local nuclear structural environments. As a consequence, the resonance frequency \( \omega \) depends on the orientation of this coordinate system in the magnetic field. If the internal interaction tensor is axially symmetric and if the interaction is weak relative to the Zeeman interaction (first order perturbation), this relationship is given by the expression

\[
\omega = \omega_{\text{iso}} + \Delta \omega \times (3 \cos^2 \theta - 1)
\]  

(2)

where \( \omega_{\text{iso}} \) is the isotropic contribution (characterizing the average value of the interaction strength in all three dimensions), \( \Delta \omega \) describes the differences between interaction strengths in different directions, and \( \theta \) specifies the angle between the principal axis of the interaction tensor and the magnetic field direction. In polycrystalline and glassy samples, there is a statistical distribution of \( \theta \) values, leading to a distribution of resonance frequencies, which manifests itself in the broad NMR lineshapes usually observed in solids. Magic-angle spinning removes this kind of inhomogeneous broadening by mechanical sample rotation about an axis inclined by 54.7° (the magic angle) relative to the magnetic field direction.\(^{15}\) This operation makes \( \theta \) time dependent and thus modulates the resonance frequency (see Figure 5). Denoting the rotation angle by \( \beta \), we have the following:

\[
\omega = \omega_{\text{iso}} + \Delta \omega \times (3 \cos^2 \beta - 1) 
\]  

(3)

For sufficiently large rotation frequencies (\( \omega_r > \Delta \omega \)), the spins cannot sample the various individual orientations during the rotor cycle any more, but end up “seeing” only an average orientation. This average corresponds to the orientation \( \beta \) of the rotor axis itself, and for \( \beta = 54.7^\circ \), the zero point of Equation (2), the anisotropy is eliminated. In this way, MAS produces narrow spectra as the inhomogeneous broadening by anisotropic magnetic shielding, dipolar and quadrupolar interactions is cancelled, and only the isotropic magnetic shielding effect remains. The peak positions are characterized by \textit{isotropic chemical shifts}, defined by

\[
\delta_{\text{iso}} = (\omega_{\text{sample}} - \omega_{\text{ref}})/\omega_{\text{ref}}
\]  

(4)

as the normalized difference between the resonance frequency of the sample and that of a suitably chosen reference standard. As shown by three independent groups in 1984,\(^{16-18}\) the various Si\(^{\text{IV}}\) species occurring in alkali silicate glasses have different chemical shifts and can thus be identified and quantified from such MAS-NMR spectra. Figure 5 shows an early result from that period. Both the static and the MAS-NMR spectra showed, for the first time, that even “stoichiometric” alkali silicate glasses possess a distribution of Si\(^{\text{IV}}\) environments, providing impressive insights into the intrinsic disorder of the glassy state.\(^{19,20}\) In the same way, phosphate glasses have been analyzed by \(^{31}\)P MAS-NMR,\(^{21}\) where the corresponding P\(^{\text{VI}}\) distribution was found to be significantly more ordered. Important new insights were also obtained on the structural role of the intermediate oxide Al\(_2\)O\(_3\) in glasses\(^{22}\) as summarized in a review article from that period.\(^{23}\) Further scientific highlights were the detection and quantification of unusual coordination states (five- and six-coordinate Al and Si) in glasses prepared under high-pressure conditions\(^{24}\) and with special chemical compositions.\(^{25}\) To the present date, multinuclear MAS-NMR remains a standard part of glass structural characterization.

The late 1980s to mid-1990s were a period of particularly intense innovation in advanced solid-state NMR methods. Many new techniques were added to the NMR toolbox and explored for the structural characterization of glasses. As a common feature, they separate the different types of internal interactions into different dimensions of two- or three-dimensional data acquisition, thereby unfolding the full potential of selective averaging and correlation spectroscopy (Phase III). Concurrently, dramatic advances in computer hardware made computational methods an integral part of the planning, analysis, and interpretation of solid-state NMR experiments of glasses (Phase IV). Important advances include (i) the advent of freeware for the design of new NMR experiments and their detailed analysis, based on the concepts of density matrix and time-dependent perturbation theory,\(^{26}\) (ii) the use of quantum-chemical methods for the computation of NMR...
observables\(^6\) (https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solidstate_physics_software), and (iii) the integration of NMR results with molecular dynamics simulations for predicting energy-minimized structural arrangements\(^27,28\). As the advances on the sides of experimental\(^4\) and computational\(^5\) methodologies have been highly interdependent, a separate discussion of phases III and IV would seem artificial. In the following, I will highlight some of these advances, leading up to the current state of the art in this field.

### 3.1 Oxygen speciation by advanced quadrupolar NMR

While the static and MAS-NMR spectra of spin-1/2 nuclei are generally well described within the framework of Equations (2) and (3), the resonance frequencies of many spin > 1/2 nuclei show a more complicated orientational dependence if the quadrupolar interaction strength becomes comparable to the Zeeman interaction\(^29\) (this also applies to the \(^{11}B\) NMR lineshapes of the B(3) and B(2) species shown in Figures 3 and 4). As a consequence of this more complicated geometric dependence, line narrowing by magic-angle spinning is less effective.\(^30\) It was demonstrated, however, that the spectroscopic resolution of these quadrupolar nuclei can be enhanced when combining MAS with additional averaging in real space\(^31\) (dynamic angle spinning, DAS, double rotation, DOR) or by averaging in spin space\(^32\) (triple-quantum/single-quantum correlation). Figure 6 shows an impressive example: We see a \(^{11}B\) DAS-NMR spectrum of glassy boron oxide, revealing two distinct boron sites in a 3:1 ratio, which are assigned to B(3) units within sixfold boroxol rings and others that are not part of such rings.\(^33\) The \(^{11}B\) isotropic chemical shifts of these species differ by 3.5 ppm, as confirmed by subsequent magnetic shielding calculations.\(^34\) The DAS experiment confirmed Bray’s insightful analysis of the \(^{17}O\) NMR wideline spectrum recorded 17 years earlier.\(^35\) Even more information is available from \(^{17}O\) DOR-NMR in which three of the four distinct types of oxygen species can be resolved\(^36\): those that are part of boroxol rings (A), those linking two boroxol rings (B), those linking loose BO\(_3/2\) units (C), and those connecting such loose BO\(_3/2\) units with boroxol rings (D). Noteworthily, the latter species could not be observed, suggesting that boroxol rings and loose BO\(_3/2\) units form separate domains.\(^36\) Altogether, these studies put to rest the discussion about the existence or nonexistence of boroxol rings in borate glasses, which had lasted for several decades. Based on the NMR results, about 75 ± 5\% of the boron atoms in glassy B\(_2O_3\) are found in boroxol rings.

Advanced high-resolution techniques of this kind have had a profound impact upon the spectroscopy of the quadrupolar spin-5/2 \(^{17}O\) nuclei in many isotopically labeled glasses, allowing the distinction between bridging and nonbridging oxygen atoms, and of different types of bridging oxygen species in mixed-network former glasses. Figure 7 shows an illustrative example of a sodium aluminoborate glass, indicating various different bridging and nonbridging oxygen species.\(^37\) More results of this kind have been summarized in the most recent reviews of solid-state NMR spectroscopy of glasses.\(^4,5\)
3.2 | Bond angle distributions through ab-initio calculations of NMR parameters

The structure of glassy SiO₂ is based on tetrahedrally coordinated fully polymerized Si⁴ units that are linked via bridging oxygen atoms. As the potential \( V(\Omega) \) relating to the Si−O−Si bond angle \( \Omega \) is rather shallow, there are strong local variations in that particular bond angle, resulting in a distribution of Si−Si next-nearest neighbor distances \( r_{\text{Si-Si}} \) which allows such bond angle distribution functions to be extracted from diffraction data. Figure 8, left, shows a compilation\(^{38}\) of proposed distributions based on such analyses and on molecular dynamics simulations.\(^{39-43}\)

Early on NMR has been proposed and applied as an alternative method for extracting distribution functions of \( \Omega \) as the \(^{29}\)Si chemical shifts are also expected to be correlated with Si−O−Si bonding angles.\(^{44}\) The width of the \(^{29}\)Si MAS-NMR spectrum of glassy SiO₂ is given by a distribution of isotropic chemical shifts, which can be mapped into a distribution of Si−O−Si bond angles, using theory-based relations between both parameters. Assuming the contributions \( F_i(\Omega) \) of the four Si−O−Si bond angles involving a central Si atom to be independent, the chemical shift is given by

\[
\delta_{\text{iso}}^{(29}\text{Si}) = \left(\frac{1}{4}\right) \Sigma F_i(\Omega)
\]  

Using the empirical relation

\[
F(\Omega) = -102.36 - 6.95 \cos \Omega - 33.82 \cos 2\Omega
\]

which represents the best fit of ab-initio calculations from simulated structures excluding small ring structures, the analysis of the experimental spectrum of glassy SiO₂ produces \( <\Omega> = 148.4^\circ \) and \( \sigma_\Omega = 10.8^\circ \) (FWHM = 25.6°).\(^{45}\)

As a seemingly more direct access to the Si−O−Si bond angle distribution, solid-state \(^{17}\)O NMR can be used. The chief observables here are the electric field gradient tensor components at the \(^{17}\)O nucleus. Using two-dimensional dynamic spinning NMR on isotopically labeled samples, it is then possible to extract the distribution functions of \( C_Q \) and \( n_Q \) from such \(^{17}\)O NMR spectra. This was first elegantly demonstrated for a modified potassium silicate glass of composition K₂Si₄O₉ by analyzing the two-dimensional DAS-NMR spectrum.\(^{46}\) For glassy silica, this approach was revisited by the same group 10 years later, using refined
relations between $^{17}$O NMR quadrupolar coupling parameters, Si–O bond distances as well as Si–O–Si bond angles. Restricted Hartree-Fock calculations on (OH)$_3$Si–O–Si (OH)$_3$ clusters showed that the $^{17}$O quadrupolar coupling constant $C_Q(17O)$ is strongly dependent on both $\Omega$ and $r_{Si-O}$, whereas the asymmetry parameter $\eta_Q(17O)$ only depends on $\Omega$. Using the relations

$$C_Q(d_{TO}, \Omega) = a \left( \frac{1}{2} + \frac{\cos \Omega}{\cos \Omega - 1} \right)^x + m_d(d_{TO} - d_{TO}^0),$$

$$\eta_Q(\Omega) = b \left( \frac{1}{2} - \frac{\cos \Omega}{\cos \Omega - 1} \right)^\beta,$$  

(with $d_{TO} = r_{Si-O}$, $d_{TO}^0 = 165.4$ pm, and $a$, $b$, $\alpha$, and $\beta$ adjustable fit parameters). Clark et al.$^{48}$ had been able to map the quadrupolar coupling parameters into two-dimensional histograms, correlating $\theta_{Si-O-Si}$ with $r_{Si-O}$ and $r_{Si-Si}$ and also $r_{Si-O}$ with $r_{Si-Si}$. Based on these correlations, their analysis yields $<\Omega> = 146.6^\circ$ and $\sigma_{\Omega} = 3.8^\circ$ ($FWHM = 9^\circ$), suggesting a substantially narrower distribution than obtained from the diffraction analyses. A strong correlation between $\Omega_{Si-O-Si}$ and $r_{Si-O}$ was found, which was, however, opposite to experimental data on crystalline silica polymorphs.$^{48}$ Using a more sophisticated model-building approach of the SiO$_2$ network in conjunction with advanced DFT calculations of the NMR parameters, Charpentier et al.$^{45}$ found a much weaker correlation between $C_Q(17O)$ and $\eta_Q(17O)$ and hence a much weaker correlation between $\Omega_{Si-O-Si}$ and $r_{Si-O}$. Their resulting distribution is characterized by $<\Omega> = 147.1^\circ$ and $\sigma_{\Omega} = 11.2^\circ$ ($FWHM = 26^\circ$). A convincing advantage of the modeling approach described in Ref.$^{45}$ is the fact that the $^{17}$O NMR analysis when applied to the data of reference$^{48}$ and the $^{29}$Si MAS-NMR analyses using Equation (6) produced very consistent results. As mentioned in Ref.$^{45}$ there appear to be some variations in the experimental $^{29}$Si MAS-NMR line-shapes for glassy SiO$_2$ in the literature, which may be related to structural differences (defects, ring-size distributions) or differences in spin-lattice relaxation time distributions. Applying the analysis of reference$^{45}$ to some older $^{29}$Si NMR data,$^{49}$ produced $<\Omega>$ values and distributions in nearly perfect agreement with those deduced from neutron diffraction data.$^{42}$ Most recently, pressure effects on the bond angle distribution have been analyzed by $^{17}$O DAS-NMR. Densification shifts $<\Omega>$ to lower values and widens its distribution.$^{50}$

Finally, the possibility of measuring indirect $^2J$ ($^{29}$Si–$^{29}$Si) spin-spin coupling constants in silicate glasses by 2D-J-resolved NMR has been explored in wollastonite glass.$^{51}$ This method uses simple rotor-synchronized pulsed excitation schemes to separate magnetic shielding and indirect spin-spin couplings in two separate dimensions. Quantum-chemical computations done on calcium silicate glasses suggest a particularly simple relationship given by:

$$\Omega = 3.41J + 127$$  

and $\delta_{iso}(^{29}$Si) and $J$ are found to be linearly correlated. It would be interesting to see this method applied to glassy silica in the future.

FIGURE 8 Left: Compilation by Yuan and Cormack of different Si–O–Si bond angle distribution functions proposed in the literature for glassy SiO$_2$.$^{38}$ BKS: MD simulation based on the two-body potential of van Beest et al.$^{99}$ VSL: MD simulation based on the three-body potential of Vessal et al.$^{100}$ The curves 1, 2, 3, 4, and 5 originate from references,$^{39-43}$ respectively. Right: Bond angle distribution function derived in Ref.$^{45}$ from $^{29}$Si NMR spectra of Ref.$^{48}$ (solid curve), from Ref.$^{49}$ (dashed curve) and from neutron diffraction data (dashed-dotted curve), (Ref.$^{42}$)
3.3 Spatial cation distributions by dipolar spectroscopy

An important question to be addressed in the structural analysis of glasses concerns the spatial distribution of their constituents. Simple distribution scenarios include uniform, random, and clustered arrangements as sketched in Figure 9. The NMR parameter that differentiates most decisively between these different scenarios is the magnetic dipole-dipole coupling constant, because of its straightforward relationship with the internuclear distances involved. In multispin systems, the dipolar interactions are conveniently expressed in terms of average mean squared magnetic dipole-dipole coupling constants, called second moments $M_2$, which are proportional to the summed inverse sixth powers $\Sigma r_{ij}^{-6}$ of all internuclear distances involved. In a glass, of course an average over a sufficiently large number of nuclei has to be taken.

The proportionality factor between $M_2$ and $\Sigma r_{ij}^{-6}$ depends on the spin physics of the particular system considered, specifically on whether dipolar interactions between like nuclei (homonuclear case) or unlike nuclei (heteronuclear case) are analyzed. In addition, a different factor must be used for nuclei experiencing quadrupole interactions. An important question studied by this method is the spatial distribution of $\text{Na}^+$ ions in glassy solid electrolytes. The strength of the homonuclear $^{23}\text{Na}-^{23}\text{Na}$ magnetic dipole-dipole interaction can be measured by the simple selective averaging scheme shown in Figure 9. One records the amplitude of the spin echo generated by a $90^\circ-t_1-180^\circ-t_1$ pulse sequence as a function of the total evolution time $2t_1$. As the $180^\circ$ pulse reverses the spin evolution caused by magnetic shielding and heteronuclear dipolar interactions, the spin-echo amplitude at $2t_1$ is not affected by these interactions. In contrast, the signal continues to decay owing to the effect of homonuclear magnetic dipole-dipole couplings. For a multispin system, a Gaussian decay is expected (and observed),

$$\frac{I(2t_1)}{I_0} = \exp \left[ -\frac{M_2(\text{Na-Na})}{2} (2t_1)^2 \right]$$

affording a reliable measurement of the homonuclear van Vleck second moment $M_2^{(\text{Na-Na})}$. The theoretical expression for $M_2$ describing the homonuclear dipole-dipole coupling between the quadrupolar spin-$3/2$ $^{23}\text{Na}$ nuclei is given by

![Figure 9](attachment:image.png)
This relationship was verified by measurements on crystalline model compounds, for which $M_{2(\text{Na-Na})}$ can be calculated from the internuclear distances in the crystal structure. Thus, with the above two expressions we can test any spatial distribution model, for example, one produced from molecular dynamics simulations, against experimental data. As documented in Ref.52, subambient temperatures are generally required to suppress any potential influence of sodium ion dynamics. Figure 10 summarizes the $M_{2(\text{Na-Na})}$ values as a function of number density in sodium silicate and borate glasses.52–54 Note in particular the strikingly different compositional dependences observed. While in sodium borate glasses $M_2$ depends linearly on sodium concentration, consistent with a statistical spatial distribution, for the silicate glass system a more or less constant value is observed at Na concentrations below $2 \times 10^{28}$ m$^{-3}$. This behavior is consistent with a large degree of cation clustering or even phase separation. At higher Na concentrations, the curves for both systems seem to converge, suggesting similar ordering principles. A more detailed inspection of other types of sodium oxide containing glasses revealed that the clustering scenario as observed for alkali silicate glasses is the exception, whereas the behavior of sodium phosphate, germanate, and tellurite glasses resembles that of a statistical distribution of the network modifier species.54 The clustering behavior observed in sodium and lithium silicate glasses is consistent with their well-known incipient phase separation tendencies at low alkali contents (Figure 10).

Similar applications of spin-echo decay spectroscopy have been published concerning the spatial distribution of phosphorus atoms in various glass systems, based on the homonuclear second moments $M_{2(\text{P-P})}$ measured for the spin-1/2 nuclei $^{31}\text{P}$, as discussed in previous reviews.3,23 For example, the method has served to quantify the extent of P-P homonuclear bonds in phosphorus chalcogenide glasses.3 Also, a heteronuclear variant of this experiment, called spin-echo double resonance (SEOR), has been applied to study the relative distribution of unlike cations in mixed-alkali silicate, borate, and chalcogenide glasses.52–55 The results indicate close-to-random relative distributions of the unlike ions with respect to each other, and lend quantitative support to the dynamic structure model of Maass, Ingram, and Bunde,56 according to which the mixed-alkali effect is the natural consequence of a reduced probability of successful jumps between mismatched cation environments.

### 3.4 | Connectivity distribution in mixed-network glasses studied by MAS-NMR with dipolar recoupling

The informational content of dipolar spectroscopy can be significantly enhanced when combined with the high resolution afforded by magic-angle spinning. While MAS by
design eliminates magnetic dipole-dipole interactions, the latter can be re-introduced by means of special dipolar recoupling methods, which invert the sign of the dipolar coupling Hamiltonian during the rotor cycle (Figure 11).

In the rotational-echo double-resonance (REDOR) pulse sequence, the recoupling is accomplished by coherently applied 180° pulse trains during the MAS rotation period.\(^{57}\) In the most common variant, the inversion pulse trains are applied to the nonobserved I spins, while the S-spin signal is detected by a rotor-synchronized Hahn spin-echo sequence. One measures the normalized difference signal \(\Delta S/S_0 = (S_0 - S)/S_0\) in the absence (intensity \(S_0\)) and the presence (intensity \(S\)) of the recoupling pulses. A REDOR curve is then generated by plotting \(\Delta S/S_0\) as a function of dipolar evolution time \(N\tau\), that is, the duration of one rotor period multiplied by the number of rotor cycles. In the limit of short dipolar evolution times (\(\Delta S/S_0 < 0.2\)), the REDOR curve is found to be geometry-independent and can be approximated by:

\[
\frac{\Delta S}{S_0} = \frac{1}{2I + 1} \left( \sum_{m=-I}^{I} (2m)^2 \right) \frac{1}{\pi^2 (I + 1)!} (NT_r)^2 M_{2(I-S)} \tag{11}
\]

where the summation extends over the \(2I + 1\) quantum states with corresponding orientational quantum numbers \(m\). If the nonobserved nuclei are of the spin-1/2 kind, Equation (11) simplifies to\(^{58}\):

\[
\frac{\Delta S}{S_0} = \frac{4}{3\pi^2} (NT_r)^2 M_{2(1-S)} \tag{12}
\]

The average heteronuclear van-Vleck second moment \(M_{2(1-S)}\) can then be extracted from a simple parabolic fit of the experimental data. Using this method, a separate value can be specified for each signal resolved in the MAS-NMR spectrum. The heteronuclear second moment can be calculated theoretically using the expression\(^{59}\):

\[
M_{2(S-I)} = \frac{4}{15} \left( \frac{1}{4\pi} \right)^2 I(I+1) I_I^2 \sum \gamma_i^2 \tag{13}
\]

The combination of Equations (16) and (17) defines a successful strategy for the identification and quantification of heteroatomic connectivities in mixed-network glasses. Assuming that the average next-nearest neighbor distances \(r_{IS}\) dominate the second moment and assuming further that they are still reasonably well defined and comparable to those found in appropriate crystalline model compounds, the average number of I-O-S linkages \(<n_{IS-O-S}>\) can be estimated from experimental \(M_2\) values via equation (13). Aluminoborate glasses, containing \(\text{Al}^{(4)}, \text{Al}^{(5)}, \text{Al}^{(6)},\) as well as \(\text{B}^{(4)}, \text{B}^{(3)},\) and \(\text{B}^{(2)}\) units, were the first systems studied in detail by this method.\(^{53,60}\) Both \(\text{Al}^{(11\text{B})}\) and \(\text{B}^{(7\text{B})}\) REDOR measurements reveal, consistently, that the \(\text{B}^{(4)}\) units are much more remote from \(\text{Al}^{(4)}\) units than the \(\text{B}^{(3)}\) units. This apparent avoidance of \(\text{AlO}_{2\text{a}}-\text{BO}_{4\text{a}}\) linkages can be rationalized in terms of the mutual repulsion of these formally anionic centers. Altogether, the quantitative analysis revealed that the experimentally determined connectivity statistics are more consistent with a model assuming the avoidance of \(\text{B}^{(4)}-\text{B}^{(4)}\), \(\text{B}^{(4)}-\text{Al}^{(4)}\), and \(\text{Al}^{(4)}-\text{Al}^{(4)}\) linkages rather than with a statistical connectivity scenario (see Figure 12). These results conform with the old aluminum avoidance rule formulated for alkali aluminosilicate networks.\(^{61}\) Excellent quantitative agreement could be noted between the results of these REDOR analyses (Figure 12) and the spectroscopic deconvolutions of isotropic \(^{17}\text{O} \text{TQMAS-NMR spectra}^{37}\) (Figure 7).

Similar consistency between double-resonance NMR and \(^{17}\text{O} \text{NMR information was found for}^{37,62}\)
B₂O₃ glasses (see Figure 13). This system has been subject to considerable attention as it is known to contain a metastable region of immiscibility and phase separation tendency. While the ¹⁷O TQ-MAS-NMR studies differentiate clearly between bridging oxygen atoms within Si–O–Si linkages, Si–O–B linkages, and B–O–B linkages, the concentrations of the Si–O–B linkages are found to be lower than expected for statistical mixing.⁶² The data have been modeled in terms of the hypothetical reaction scheme Si–O–Si + B–O–B → 2 Si–O–B yielding good agreement with a positive mixing energy of 2W = 8 kJ/mol. The numerical value of this energy was independently predicted by ab-initio cluster calculations. The conclusions from ¹⁷O NMR are nicely compatible with results from ¹¹B and ²⁹Si NMR.⁶³ ²⁹Si{¹¹B} dipolar recoupling results indicate that the strength of the ²⁹Si–¹¹B magnetic dipole-dipole coupling attains a limiting value in glasses with B/Si near unity, corresponding to an average of about 2 Si–O–B linkages per Si⁴ species, and it does not increase upon further increase in the boron concentration. In glasses with B/Si > 1, high-resolution ¹¹B MAS-NMR spectra show substantial amounts of boron atoms within boroxol units, confirming the increased phase separation tendency in this compositional region. This effect can be understood on the basis of decreasing fictive temperatures and hence the increased importance of the positive mixing enthalpy term of boria rich as compared to silica-rich glasses.

Dipolar recoupling methods have also been used extensively to quantify homo- and heteroatomic connectivities in many other mixed-network former glasses, including those

**FIGURE 12** Left: Plot of moles of Al–O–B linkages per mole of network former species vs the fractional contribution xₐl of aluminum to the overall network (total Al + B content) in a series of sodium aluminoborate glasses. Data from ¹⁷O NMR are compared with those from ¹¹B {²⁷Al} and ²⁷Al{¹¹B} dipolar NMR spectroscopy. Solid and dashed lines show predictions based on a model assuming the avoidance of B(4)–B(4), B(4)–Al(4), and Al(4)–Al(4) linkages and a statistical connectivity (random mixing) scenario, respectively. Right: structural cartoon representing the dominant Al–O–B connectivities present in sodium aluminum borate glasses. For further details, see Refs⁷⁷,⁶⁰

**FIGURE 13** Solid-state NMR results on B₂O₃–SiO₂ glasses as a function of glass composition: Left: isotropic projection of ¹⁷O TQMAS-NMR data and corresponding peak assignments for three glasses with different Si/B ratios listed to the left of each trace.⁶² For Si/B = 0.75, fits of the projections to three individual Gaussians for quantification purposes are shown at the bottom. Right: ²⁹Si{¹¹B} REDOR results and comparison with simulations: solid curve: ²⁹Si–¹¹B two-spin system, dashed curve: ²⁹Si–²¹B two-spin system. Dotted curve: statistical distribution of connectivities expected at a B/Si ratio of unity⁶³
containing the intermediate oxide Al₂O₃ as summarized in various contributions⁶⁴,⁶⁵ and reviews.⁶⁶–⁶⁸ Alongside, they have been used to explore distance relations between network former and network modifier species offering insights into spatial distributions of the network modifiers and the mechanisms of local charge compensation.⁵²,⁶⁶–⁶⁸ In particular, these methods have provided unique insights into the structural origins of network former mixing effects upon thermal and mechanical stabilities and ionic conductivities in many ion-conducting systems. A comprehensive summary of these applications to glassy solid electrolytes has been recently published.⁶⁹

It must be emphasized that the quantification of connectivities as approached by Equation (12) is based on the assumption that the dipolar coupling between the nuclei involved in the T–O–T' bonds makes the dominant contribution to the magnetic dipole-dipole interaction. There are, however, expected contributions from more distant spatial correlations in higher coordination spheres that make (smaller) contributions to M(2J). A physically distinct and more rigorous approach for detecting network former connectivities is based on the measurement of indirect spin-spin couplings, for which bond connectivity is a prerequisite. The method relies on the selective excitation (and detection) of joint spin flips involving either nuclei of the same kind (homonuclear DQ-coherences) or of different kinds (heteronuclear DQ-coherences) that are effected by the indirect spin-spin interaction mechanism. As the latter mechanism requires the existence of covalent bonds linking the nuclei involved, the detection of such DQ-coherences is definitive evidence of such connectivities. Applications of such J-based connectivity studies were initially reported for phosphate glasses,⁷⁰ benefitting from the highly sensitive and abundant ³¹P spin-1/2 nuclei. More recently, promising extensions to homo- and heteronuclear connectivity studies involving the quadrupolar nuclei ¹¹B and ²⁷Al in glasses have also been reported,⁴,⁷¹,⁷² making this method potentially useful for analyzing connectivity distributions in a wide range of oxide glasses.

3.5 Rare-earth environments in photonic glasses studied by correlated NMR and EPR spectroscopies

Rare-earth (RE) ion-doped transparent glasses and glass ceramics are well-established materials for the design of new-generation lasers and other photonic devices. They are frequently based on phosphate, borate, tellurite, and fluoride network former components, which serve to dissolve and disperse large concentrations of luminescent rare-earth ions. Oxyfluoride glasses are particularly good host materials, combining mechanical strength and high emission intensities. To optimize these properties, the design goal is a framework structure dominated by bridging oxygen links between the network formers, resulting in high mechanical stability, while, at the same time, creating a fluoride-dominated low-phonon energy local environment for the luminescent ions, which favors high fluorescence quantum efficiencies and long excited-state lifetimes. Testing this design concept requires detailed information upon the local environments of the luminescent ions. To NMR spectroscopists, this is a considerable challenge, however, as the ⁴P-paramagnetism of the emitter species broadens their NMR signals beyond detectability. To overcome these problems, we have developed a three-pronged strategy, involving (i) NMR studies on trivalent diamagnetic mimics, (ii) NMR studies of constituent glass framework species (³¹P, ²⁷Al, ¹⁹F) interacting with the paramagnetic dopant ions, and (iii) pulsed EPR studies of the paramagnetic rare-earth ions themselves, probing direct ligation and/or spatial proximity to nuclear spins in their vicinity. In the following, most recent progress from our laboratory will be shortly summarized.

Diamagnetic mimic studies (approach i) have largely focused on MAS-NMR of ⁴⁵Sc and ⁸⁹Y dopants, which can be considered surrogates for small and mid-sized RE species, respectively. While some information can be obtained from chemical shift trends, particularly in the case of ⁸⁹Y NMR,⁷⁵ the most promising applications come from dipolar recoupling studies of the type reviewed in the previous Section. Most recent results focus on rare-earth-doped fluoride phosphate matrices, where the fractions of fluoride and phosphate ions in the first coordination sphere of the rare-earth species have been quantified by ⁴⁵Sc{¹⁹F} and ⁴⁵Sc{³¹P} REDOR experiments.⁷³ In principle, the rare-earth ion species ¹³⁹La can also be considered (to serve as a mimic for larger RE species); however, its spectroscopy (like that of the ¹⁷⁵Lu isotope) is rather limited owing to very strong quadrupolar interactions. This situation may change in the near future, however, as new excitation schemes for ultra-wide NMR spectra become increasingly available.⁷⁴

Paramagnetically perturbed NMR (approach ii) has been recently applied to study the crystallization of glasses in the Y₂O₃–Al₂O₃–B₂O₃ system containing Yb³⁺ dopants. Through careful analysis of the paramagnetic line broadening effects upon the ¹¹B, ²⁷Al, and ⁸⁹Y NMR spectra and the spin-lattice relaxation times of the resulting crystalline phases, it was possible to analyze the partitioning of the rare-earth ions between the different phases (YBO₃, YAl₁(BO₃)₄, and vitreous B₂O₃) obtained during the ceramization process.⁷⁶

Finally, the application of pulsed EPR methods (approach iii) represents a promising approach to this research area. Suitable EPR-active dopant species are ions with an odd number of unpaired electrons, for example,
Ce$^{3+}$(4f$^1$), Nd$^{3+}$(4f$^3$), Sm$^{3+}$(4f$^1$), Gd$^{3+}$/Eu$^{2+}$(4f$^7$), Dy$^{3+}$(4f$^8$), Er$^{3+}$(4f$^{11}$), and Yb$^{3+}$(4f$^{13}$). For recording the EPR spectra of these ions, the best results are obtained using pulsed excitation methods at cryogenic temperatures. Figure 14 illustrates the principle of the electron spin-echo envelope modulation (ESEEM) technique, which has been particularly instrumental for the study of luminescent glasses. In this method, the amplitude of a stimulated echo generated by applying a 3-pulse sequence to a selected set of spins resonating at a fixed magnetic field strength is measured as a function of the pulse spacing $T$. While it is expected that this signal decays exponentially as a function of $T$ owing to spin-spin relaxation, these decays contain additional information if the electron spins experience magnetic hyperfine couplings or dipolar interactions with nearby nuclear magnetic moments. In such cases, the decay is modulated by characteristic frequencies reflecting the nuclear Zeeman frequencies and the electron-nuclear hyperfine coupling constants. By Fourier transformation of this time-domain signal, the modulation frequencies can be obtained and compared with simulations. ESEEM and its two-dimensional version (hyperfine sublevel correlation spectroscopy, HYSCORE) have been rarely used for structural studies of glasses, and to date, no reviews are available. Defects created in gamma-irradiated glassy B$_2$O$_3$ and alkali borate glasses have been examined in some detail, giving evidence of magnetic hyperfine coupling between the unpaired electrons and the $^{10}$B and $^{11}$B nuclei. In addition, pulsed EPR methods revealed important information on the association of the unpaired electrons of rare-earth dopants in various pure network former glasses.

The above pulsed EPR methods present a new approach to rare-earth-doped luminescent glasses. Figure 15 shows results for a series of 25BaF$_2$–25SrF$_2$–(30–x)Al(PO$_3$)$_3$–xAlF$_3$–19.75YF$_3$–0.25YbF$_3$ glasses. Here, the electron spins associated with the paramagnetic Yb$^{3+}$ ions serve as the spies of their electronic and nuclear environments. Note that the static EPR lineshape, recorded with the echo-detected field-sweep (EDFS) method, is highly sensitive to the sample composition: The signal shifts successively toward higher field strengths, as the F/P batch ratio of these glasses increases with increasing AlF$_3$ content. These results suggest that the rare-earth ions have a mixed fluoride/phosphate ligand environment, which changes monotonically with increasing AlF$_3$ content. In the HYSCORE spectrum shown on the right, direct Yb-F covalent bonding manifests itself in off-diagonal resonances due to isotropic super-hyperfine coupling of the unpaired 4f electrons with the $^{19}$F nuclei. In addition, all the nuclei interacting with these unpaired electrons via through-space dipolar coupling over longer distances are identified by their corresponding Zeeman frequencies. These resonances
(due to $^{89}\text{Y}$, $^{27}\text{Al}$, and $^{31}\text{P}$) are found along the diagonal. Owing to the stronger magnetic moment of the unpaired electrons, the relevant distance range for probing these interactions is significantly larger than with NMR spectroscopy, making EPR a useful tool for detecting spatial proximities into the nanoscale. Figure 16 illustrates this complementarity of the NMR and EPR approaches. While standard MAS-NMR is most informative on the first coordination sphere, dipolar methods such as REDOR are sensitive over the 0.2-0.5 nm distance range, comprising primarily the second and third coordination spheres. In contrast, the EPR lineshape is most sensitive to the electronic structure of the atom carrying the electron spin itself and further influenced by the electronic interactions (magnetic super-hyperfine couplings) with nuclei in the first coordination sphere. On the other hand, electron-nuclear dipolar couplings detected by pulsed EPR methods extend to distance ranges much longer than possible via NMR spectroscopy. Of course, probing the structural organization of glasses by magnetic resonance techniques is at its best, when all of these techniques are applied jointly, and together with vibrational and electronic spectroscopic methods.

3.6 | From glasses to glass ceramics. Magnetic resonance strategies for studies on extended length scales

As mentioned in the introduction, nano-segregation and phase separation are important issues to be addressed when...
discussing the structure of glasses on the nanometer scale. The above-discussed dipolar NMR techniques have been used successfully to characterize those systems, using selective detection (such as cross-polarization) of species at nanodomain interfaces for an estimation of domain sizes based on the dipolar coupling strength measured, or by using double-quantum coherence excitation spectroscopy to estimate the extent of clustering. Phase separation effects are also an important issue in relation to the crystallization of glasses into glass ceramics. Martel et al. have studied the gradual phase separation preceding the ceramation of a sodium silicate glass containing 15 mole% Na$_2$O by carefully monitoring the Si(4)–Si(4), Si(3)–Si(4), and Si(3)–Si(3) connectivity distributions, and 29Si–29Si correlation spectra of isotopically enriched glasses subjected to a series of heat treatments. Interesting insights in relation to the nucleation mechanism can also be obtained by comparing local structural environments before and after crystallization. While the vast majority of glass-forming substances only undergo surface (heterogeneous) nucleation when sufficiently heated, a few systems also show the thermodynamically less favorable case of internal (homogeneous) nucleation on laboratory time/length scales. For such glass systems, various macroscopic properties, such as densities, configurational entropies, and frozen-in birefringence, have suggested that the structure in the glassy state shows a closer resemblance to the structure of the phase formed upon crystallization than in the case of glass systems only undergoing heterogeneous nucleation. This result has been supported by solid-state NMR techniques on some important benchmark alkali silicate and borate glasses. This work suggested in particular that dipolar second moments quantifying network modifier-network modifier and network modifier-network former interactions might form a particularly useful measure for probing structural resemblance or distinction between crystalline and glassy phases in the context of homogeneous nucleation ability. For example, $^{11}$B{6Li} and $^{11}$B{23Na} rotational-echo double-resonance (REDOR) experiments indicate much smaller $\Delta M_2$ values for lithium diborate (homogeneous nucleation) than for sodium diborate (heterogeneous nucleation). This hypothesis was subsequently tested by a review of all the relevant data presently in the literature on homogeneously and heterogeneously crystallizing stoichiometric glass systems. Figure 17 summarizes the relative deviations defined by $\Delta M_2 = (M_2 - M_{2c})/M_{2c}$. These deviations can be positive or negative. Note that for glasses that are able to nucleate homogeneously, $\Delta M_2$ values are generally small, suggesting that there is a rather close correspondence between the network modifier cation structural arrangements in the crystalline and in the glassy states. In contrast in glasses that only nucleate at the surface, the relative deviations $\Delta M_2$ are significantly larger. Overall, these observations corroborate the existence of a definite correlation between structural similarity at both the short and intermediate length scales, and nucleation mechanism, at least as far as the cation arrangements are concerned.

### 4 CONCLUSIONS AND OUTLOOK

Ever since the ground-breaking paper by W. H. Zachariasen on the atomic arrangements in glass, our fundamental insight into the vitreous state, and its ordering stages at different length scale domains, has advanced considerably. These advances include a convergent picture of the bond angle distributions and ring size statistics of simple network glasses, knowledge about the structural arrangements and spatial distributions of network modifier cations in simple binary oxide glass systems, and the quantification of chemical ordering effects in glasses having more than one network former species. NMR spectroscopy has played no small part in this progress, due to the dramatic evolution of its theoretical concepts and experimental methodology that has characterized this field during the past 25 years. In parallel, the availability of increasingly sophisticated molecular dynamics modeling techniques, aided by first-principles calculations, has been opening new opportunities for probing more deeply into medium-range ordering processes in disordered materials. Although these advances form all the elements of an integrated experimental/theoretical strategy combining all of these methods, such a comprehensive strategy has not yet been formulated for glasses, even though the idea was proposed many years ago.
the structural analysis of highly disordered crystalline compounds, this development is indeed just happening and called NMR crystallography. NMR crystallographers solve crystal structures based on Rietveld refinements of XRD powder patterns, which are constrained by input from NMR spectroscopic observables, and cross-checked against DFT calculations. In principle, various elements of NMR crystallography are transferable from crystalline compounds to glasses and amorphous materials. One may anticipate that with a considerably enhanced role of molecular dynamics simulations and DFT-based modeling approaches, significant further advances can be made toward our knowledge of medium-range order in glasses.

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REFERENCES

70. Fayon F, Saout G, Emsley L, Massiot D. Through-bond phosphorus-phosphorus connectivities in crystalline and disordered


100. Vossel B, Amini M, Fincham D, Catlow CRA. Water-like melting behavior of silica investigated by the molecular dynamics simulation techniques. Philos Mag B. 1989;60:753-775.

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