Structural assignments of NMR chemical shifts in Ge$_x$Se$_{1-x}$ glasses via first-principles calculations for GeSe$_2$, Ge$_4$Se$_9$, and GeSe crystals

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Structural assignments are determined for $^{77}$Se and $^{73}$Ge chemical shifts through density-functional NMR calculations for GeSe$_2$, Ge$_4$Se$_9$, and GeSe crystals. In particular, a very good agreement between calculated and measured $^{77}$Se isotropic chemical shifts and anisotropies is found for the GeSe$_2$ crystal, for which experimental data are available. These assignments provide a consistent interpretation of experimental $^{77}$Se spectra of Ge$_x$Se$_{1-x}$ glasses, indicating that the contribution from Ge-Se-Se linkages overlaps with that from Ge-Se-Ge linkages in corner-sharing tetrahedral arrangements, thereby dismissing the occurrence of a bimodal phase.

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Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photoinduced effects. These properties show potential for numerous applications in active and passive optics. Thus, chalcogenide Ge$_x$Se$_{1-x}$ glasses are currently under intense experimental and theoretical investigations to elucidate their structural arrangement. For Ge$_x$Se$_{1-x}$ glasses, conventional diffraction probes are not sufficient for providing a complete determination of the short-range order, which include corner-sharing (CS) and edge-sharing (ES) tetrahedral arrangements, undercoordinated and overcoordinated atoms, and homopolar bonds. Raman spectroscopy can also act as a structural probe for instance indications about the relative populations of corner-sharing and edge-sharing tetrahedra but relies on theoretical estimates of coupling factors.

Recently, the short-range structure in Ge$_x$Se$_{1-x}$ glasses has been studied by solid state nuclear magnetic resonance (NMR). The measured $^{77}$Se NMR spectra mainly consist of two different peaks but conflicting conclusions have been reached about their interpretation. One of the invoked models is based on the occurrence of a bimodal phase in which the two phases only bond weakly and are characterized by Se-Se-Se and Ge-Se-Ge sites, respectively. The other interpretation scheme relies on NMR measurements for crystalline GeSe$_2$ and assumes that the structure is fully bonded with intermediate configurations giving rise to overlapping contributions. The latter scheme is also supported by ab initio molecular-dynamics simulations on Ge-Se (Refs. 6 and 7) and Ge-Te (Ref. 11) systems. This situation highlights the need for a reliable assignment scheme to relate $^{77}$Se chemical shifts to bonding configurations.

In this work, we provide structural assignments for $^{77}$Se NMR chemical shifts based on density-functional calculations of NMR parameters of GeSe$_2$, Ge$_4$Se$_9$, and GeSe crystals. The reliability of our calculated results is demonstrated for the GeSe$_2$ crystal, for which experimental data are available. The proposed assignments support an interpretation of experimental $^{77}$Se spectra of Ge$_x$Se$_{1-x}$ glasses based on overlapping contributions from various bonding configurations and do not support the occurrence of a bimodal phase.

Magnetic shielding and electric field gradient (EFG) tensors were calculated for crystal GeSe$_2$, Ge$_4$Se$_9$, and GeSe (Ref. 14) structures using the gauge including projector augmented wave approach implemented in the CASTEP code. This approach uses periodic boundary conditions, which makes it applicable to crystalline systems. The CASTEP code uses a plane-wave-basis implementation of the density-functional theory. All calculations were carried out using ultrasoft pseudopotentials with the Perdew-Burke-Ernzerhof exchange-correlation functional and a maximum plane-wave energy of 500 eV. The Brillouin zone was sampled using a Monkhorst-Pack grid with a maximum density of up to $14 \times 18 \times 18$ k points. These parameters were chosen to converge the results to within 1 ppm for $^{77}$Se and $^{73}$Ge shieldings and within 0.1 MHz for $^{73}$Ge quadrupole coupling constants. Isotropic shieldings $\sigma_{\text{iso}}$ were calculated for each atom in the considered models. Experiment provides the isotropic chemical shift $\delta_{\text{iso}}$ which is defined relative to a reference shielding $\sigma_{\text{ref}}$ such that $\delta_{\text{iso}} = (\sigma_{\text{iso}} - \sigma_{\text{ref}})$. We used $\sigma_{\text{ref}} = 1494$ ppm for $^{77}$Se and $\sigma_{\text{ref}} = 1215$ ppm for $^{73}$Ge. The reference value for $^{77}$Se ensures that the average calculated shieldings for the GeSe$_2$ crystal coincide with that of the measured ones. The validity of this reference value was independently confirmed for the Se crystal (Ref. 21), for which we calculated a $^{77}$Se chemical shift of 824 ppm with the same reference, in excellent agreement with the experimental value of 809 ppm (Ref. 22). For $^{73}$Ge, the reference value was chosen to reproduce the experimental value of the shielding in $\alpha$ quartz GeO$_2$, $\delta_{\text{iso}} = -110$ ppm (Ref. 23), in accord with a previous NMR study on GeO$_2$. The chemical shift anisotropy $\Delta_{\text{cs}}$ was obtained from the calculated chemical shielding tensor using $\Delta_{\text{cs}} = (\sigma_{33} - \sigma_{\text{iso}})$, where the principal components of the chemical shielding tensor $\sigma_{11}$, $\sigma_{22}$, and $\sigma_{33}$ were ordered such that
obtained the quadrupole coupling constant $C_Q$ of the EFG tensor, 25 by taking the value of 19.60 meV. Measured isotropic shifts agree within the experimental accuracy, indicating a good connection between the calculated and measured results. The asterisk indicates one data point obtained through sign inversion of the measured anisotropy. The labeling is taken from Ref. 12.

$$|\sigma_{33} - \sigma_{11}| \geq |\sigma_{11} - \sigma_{22}| \geq |\sigma_{22} - \sigma_{33}|.$$  

We note that $\Delta_{cs}$ does not depend on the choice of $\sigma_{ref}$. We obtained the quadrupole coupling constant $C_Q$ for $^{75}$Ge from the EFG tensor, 25 by taking the value of $19.60 \times 10^{-30}$ m$^2$ (Ref. 26) for the quadrupole moment.

We first addressed isotropic chemical shifts for each Se site in the GeSe$_2$ crystal, 12 for which experimental NMR spectra were recently obtained. 10 The horizontal axis in Fig. 1 allows one to compare calculated isotropic chemical shift $\delta_{iso}$ with the experimental data of Ref. 10. The calculated and measured shifts agree within the experimental accuracy, leading to a straightforward assignment (Fig. 1). The comparison with experiment could be extended to the chemical shift anisotropy $\Delta_{cs}$ (vertical axis in Fig. 1). For this quantity, the agreement between theory and experiment is also very good, except for a single data point. However, we observe that if the sign of the anisotropy of this data point is inverted a good agreement is recovered with the calculated value for Se site 6 (cf. labeling of Ref. 12). Hence, we suggest that the experimental determination of the sign of this data point might have suffered from the noise in the spinning sidebands. 10

In the adopted assignment, the Se sites 2 and 3, which are involved in ES tetrahedra, correspond to the isotropic shifts at 644 and 600 ppm, i.e., at higher shift values than all the other Se atoms which are involved in CS arrangements. This correspondence differs from the assignment proposed in Ref. 10, where it was argued that the ES shifts should occur on the opposite side of the range of measured chemical shifts. As can be inferred from the structural parameters reported in Table I, the chemical shift is found to be very sensitive to the mean Se-Ge distance and less so to the Ge-Se-Ge angle.

The structure of Ge$_2$Se$_9$ forms a layered structure similar to that of the GeSe$_2$ crystal. 13 It only contains CS tetrahedra without any ES tetrahedra. However, one finds a Ge(3)-Se(6)-Se(7)-Ge(4) linkage, where the labeling corresponds to that of Ref. 13. In Fig. 2, the calculated results pertaining to each Se nucleus of the Ge$_2$Se$_9$ crystal are reported within the range plots showing the chemical shift anisotropy $\Delta_{cs}$ vs the isotropic chemical shift $\delta_{iso}$ and compared to those of the GeSe$_2$ crystal. All the isotropic shifts of Ge$_2$Se$_9$ fall within the range 0-50 ppm.

TABLE I. Calculated isotropic chemical shift $\delta_{iso}$ (ppm) and chemical shift anisotropy $\Delta_{cs}$ (ppm) are given for each Se nucleus in GeSe$_2$, Ge$_2$Se$_9$, GeSe, and Se crystals, successively. For GeSe$_2$ and Ge$_2$Se$_9$, we adopt the labeling given in Refs. 12 and 13, respectively. Structural parameters such as the Ge-Se-Ge angle and the mean Se-Ge distance (in Å) are given. For GeSe$_2$ and Se, the experimental results are from Refs. 10 and 22, respectively. The asterisk indicates that the sign of the experimental anisotropy has been inverted.

<table>
<thead>
<tr>
<th>Site</th>
<th>Theory $\Delta_{cs}$</th>
<th>Experiment $\delta_{iso}$</th>
<th>Structure $\angle$ Se-Se-Ge (deg)</th>
<th>Se-Ge distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(1)</td>
<td>542</td>
<td>−400</td>
<td>585</td>
<td>−366</td>
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<tr>
<td>Se(2)</td>
<td>644</td>
<td>−550</td>
<td>685</td>
<td>−555</td>
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<td>Se(3)</td>
<td>600</td>
<td>−350</td>
<td>625</td>
<td>−437</td>
</tr>
<tr>
<td>Se(4)</td>
<td>389</td>
<td>500</td>
<td>370</td>
<td>469</td>
</tr>
<tr>
<td>Se(5)</td>
<td>208</td>
<td>−350</td>
<td>133</td>
<td>−291</td>
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<td>Se(6)</td>
<td>224</td>
<td>470*</td>
<td>143</td>
<td>375</td>
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<td>Se(7)</td>
<td>396</td>
<td>500</td>
<td>413</td>
<td>526</td>
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<td>Se(8)</td>
<td>515</td>
<td>−450</td>
<td>560</td>
<td>−347</td>
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<td>Se(9)</td>
<td>382</td>
<td>348</td>
<td>97.3</td>
<td>2.354</td>
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<td>Se(10)</td>
<td>203</td>
<td>−538</td>
<td>94.7</td>
<td>2.357</td>
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<td>Se(11)</td>
<td>154</td>
<td>253</td>
<td>101.8</td>
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<td>Se(12)</td>
<td>235</td>
<td>−431</td>
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<td>Se(13)</td>
<td>447</td>
<td>343</td>
<td>97.4</td>
<td>2.356</td>
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<tr>
<td>Se(14)</td>
<td>453</td>
<td>417</td>
<td>91.3*</td>
<td>2.362b</td>
</tr>
<tr>
<td>Se(15)</td>
<td>536</td>
<td>425</td>
<td>91.1*</td>
<td>2.367b</td>
</tr>
<tr>
<td>Se(16)</td>
<td>247</td>
<td>416</td>
<td>96.4</td>
<td>2.353</td>
</tr>
<tr>
<td>Se(17)</td>
<td>221</td>
<td>−338</td>
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<td>2.357</td>
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<tr>
<td>Se(18)</td>
<td>176</td>
<td>372</td>
<td>96.2</td>
<td>103.5</td>
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<tr>
<td>Se(19)</td>
<td>809</td>
<td>824</td>
<td>391</td>
<td></td>
</tr>
</tbody>
</table>

$a$: Mean of Se-Se and Se-Se distances.

$b$: Mean of Se-Ge and Se-Se distances.
TABLE II. Mean and range of $^{77}\text{Se}$ isotropic chemical shifts $\delta_{iso}$ (ppm) as found in the present calculations for $\text{GeSe}_2$, $\text{Ge}_4\text{Se}_9$, $\text{GeSe}$, and $\text{Se}$ crystals. Five sites are distinguished.

<table>
<thead>
<tr>
<th>Se site</th>
<th>Mean $\delta_{iso}$</th>
<th>Range of $\delta_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se-Se-Se}$</td>
<td>824</td>
<td>824</td>
</tr>
<tr>
<td>$\text{Ge-Se-Ge (ES)}$</td>
<td>655</td>
<td>625–685</td>
</tr>
<tr>
<td>$\text{Se-Ge}$</td>
<td>495</td>
<td>453–536</td>
</tr>
<tr>
<td>$\text{Ge-Se-Ge (CS)}$</td>
<td>315</td>
<td>133–585</td>
</tr>
<tr>
<td>Threefold $\text{Se}$</td>
<td>176</td>
<td>176</td>
</tr>
</tbody>
</table>

of shifts corresponding to CS arrangements in the $\text{GeSe}_2$ crystal. This property also holds for the Se nuclei 6 and 7 belonging to $\text{Se-Se-Ge}$ linkages, which are found at 453 and 536 ppm. Hence, this indicates that the contributions from CS and $\text{Se-Se-Ge}$ arrangements overlap.

The atomic structure of the $\text{GeSe}$ crystal consists of threefold $\text{Ge}$ and threefold $\text{Se}$ atoms. By symmetry, this structure only shows one inequivalent site for both $\text{Se}$ and $\text{Ge}$. The corresponding calculated results have been added in the $\Delta_{cs}$-$\delta_{iso}$ plot in Fig. 2. This chemical shift lies at 176 ppm, suggesting that threefold coordinated Se sites contribute to the low-value side of the range of chemical shifts originating from CS arrangements.

Our calculations for the $\text{GeSe}_2$, $\text{Ge}_4\text{Se}_9$, $\text{GeSe}$, and $\text{Se}$ crystals give important indications for the interpretation of experimental $^{77}\text{Se}$ spectra of $\text{GeSe}_2$, $\text{Ge}_4\text{Se}_9$, glasses, leading to a globally consistent interpretation. Our assignments to $\text{Se-Se-Ge}$ linkages and $\text{Ge-Se-Ge}$ linkages in ES arrangements fall in correspondence of the two dominating peaks at $\sim 800$ ppm and $\sim 400$ ppm, respectively, consistent with previous interpretations. Our study indicates that $\text{Se-Se-Ge}$ linkages also contribute to the high-shift side of the peak at $\sim 400$ ppm, thereby giving overlapping contributions with those from $\text{Ge-Se-Ge}$ linkages in CS arrangements. Hence, the location of the $\text{Se-Se-Ge}$ contributions is in accord with the intuitive expectation that this line should lie in between those resulting from $\text{Se-Se-Ge}$ and $\text{Ge-Se-Ge}$ linkages. The shoulder observed at $\sim 650$ ppm in Fig. 3(a) also lies in this intermediate range and closely corresponds to our description to ES arrangements. The present assignment of the ES line differs from that adopted in Ref. 10, where this line was situated on the low-shift side of the main peak. Finally, the contributions from threefold coordinated Se atoms are found on the low-shift side of the peak at $\sim 400$ ppm, in close correspondence of one of the Gaussian lines introduced in the experimental analysis of Ref. 10.

From the fit of the $\text{GeSe}_2$ spectrum in Ref. 10, one infers that 16% of the Se atoms contribute to the Gaussian line centered at 587 ppm. When this value is taken as an estimate for the fraction of Se atoms in ES arrangements, one finds consistency with the fraction of ES tetrahedra inferred from neutron-diffraction measurements (34%), which corre-

FIG. 3. (Color online) Average (vertical lines) and range (horizontal bar) of $^{77}\text{Se}$ isotropic chemical shifts for various Se sites as found from the present calculations (Table II), superposed to experimental results for $\text{GeSe}_{2-x}$ glasses from (a) Ref. 10 and (b) Ref. 9. Five kinds of sites are distinguished: $\text{Se-Se-Se}$ linkages (pink), $\text{Ge-Se-Ge}$ linkages in ES arrangements (orange), $\text{Se-Se-Ge}$ linkages (red), $\text{Ge-Se-Ge}$ linkages in CS arrangements (blue), and threefold coordinated Se sites (green).
shifts for all 73Ge nuclei of the considered crystals, calculating the quadrupole coupling constant and chemical shifts assigned to ES and Se-Ge contributions are concerned, one notices that they fall in a region of the Ge$_x$Se$_{1-x}$ spectra where considerable intensity is observed. For GeSe$_2$, this intensity could well account for the fraction of 20% of Se atoms involved in Se-Se bonds, which has been derived from neutron-diffraction measurements. As the Ge concentration in Ge$_x$Se$_{1-x}$ glasses drops, the intensity in the experimental spectra shifts from the peak at $\sim$400 ppm (Ge-Ge-Se, CS) to the peak at $\sim$800 ppm (Se-Ge-Se) but the intensity corresponding to the lines assigned to ES and Se-Ge-Se arrangements remains sizable.

In anticipation of experiment, we complete this study by calculating the quadrupole coupling constant and chemical shifts for all $^{73}$Ge nuclei of the considered crystals (Table III). We distinguish four kinds of Ge atoms. Following Ref. 27, the first two types correspond to tetrahedral arrangements, either CS or ES, with average chemical shifts of 132 ppm and 101 ppm, respectively. The third type corresponds to Ge sites belonging to Ge-Se-Se linkages as found in the Ge$_x$Se$_2$ crystal, with an average chemical shift of 159 ppm. The last identified type is the threefold coordinated Ge, which has a chemical shift of $\sim$82 ppm in the GeSe crystal.

In conclusion, density-functional calculations of NMR parameters in various Ge$_x$Se$_{1-x}$ crystals were used for developing an assignment scheme relating chemical shifts to the underlying structure. Applied to $^{77}$Se spectra of Ge$_x$Se$_{1-x}$ glasses, our assignment scheme provides an interpretation of the experimental data which is consistent with the occurrence of Ge-Se-Se linkages and does not require the notion of a bimodal phase.

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