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Structural ordering in Cd$_x$Pb$_{1-x}$F$_2$ alloys: A combined molecular dynamics and solid state NMR study

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Molecular dynamics (MD) simulations of binary Cd$_x$Pb$_{1-x}$F$_2$ alloys have been carried out, using a two-body Buckingham interaction potential, leading to a correct description of structural properties as a function of composition and pointing towards an understanding of the eutectic phenomenon. The simulation data can be analyzed in terms of five local fluorine environments $Q(n)$ ($4 \equiv n \equiv 0$), where $n$ is the number of Pb nearest-neighbor environments. The results suggest a highly nonstatistical population distribution, suggesting an intrinsic phase segregation tendency in the undercooled melt, during the cooling process. This prediction has been tested experimentally for six representative compositions ($0.2 \leq x \leq 0.7$) on the basis of high-resolution $^{19}$F solid state NMR data, revealing important similarities between theory and experiment. While the NMR data confirm that the population distribution is, indeed, nonstatistical for all compositions, the results are only found to be consistent with an intrinsic segregation tendency of PbF$_2$-rich domains. This tendency manifests itself in substatistical populations of $Q(3)$ units, resulting in preferred $Q(2)$ and $Q(4)$ formations. © 2008 American Institute of Physics. [DOI: 10.1063/1.2938090]

I. INTRODUCTION

Solid solutions in the system Cd$_x$Pb$_{1-x}$F$_2$, which crystallizes in the fluorite lattice, are of considerable interest because of their high ionic conductivity. Specific heat measurements point towards a superionic phase transition, the temperature of which depends on the compositional parameter $x$ in a nonlinear fashion. At the eutectic composition near $x=0.35$, the transition temperature is minimized while the ionic conductivity is maximized. Similar trends are visible in the ionic mobilities, which have been characterized by detailed variable temperature $^{19}$F solid state NMR. In an effort to understanding the nonlinear dependence of the ionic conductivity on composition, the structure of these solids has been examined by a number of diffraction and spectroscopic techniques. The lattice parameters follow a simple Vegard’s law and extended x-ray-absorption fine structure (EXAFS) studies carried out at the Pb edge indicate increasing Pb–Cd interactions in the second coordination shell. Both of these results are in support of a random distribution of the cations on the cationic sublattice. Maximum disorder and maximum Debye–Waller factors are observed at the eutectic composition. Recently, molecular dynamics (MD) simulations have been employed to provide further insight into the structure of these materials. Using a standard rigid-ion potential model of the Buckingham form, Netshisaulu et al. were able to broadly reproduce the experimentally observed compositional dependence of the anion sublattice dynamics: a maximum diffusion coefficient is predicted near the eutectic composition.

Computational simulation as a prediction tool for structural characteristics of materials can be a powerful ally to the materials scientist for perfecting known properties as well as for developing new materials. Thus, an ideal interparticle interaction model is one which is accurately capable of fitting a large set of experimental data. Moreover, the analytic potential energy function must have transferability property for different structures and compositions in addition to reasonable computational efficiency. Hence, this consideration makes finding an ideal potential function a very difficult task. On the other hand, a comparison of the theoretical prediction with experimental data can serve to validate the proposed models. In the present study, we have used an interparticle interaction model, which can be included in this classification of effective potential energy function, to explain the melting properties of Cd$_x$Pb$_{1-x}$F$_2$ solid solutions, giving rise to the eutectic phenomenon. Furthermore, the structural characteristics of supercooled Cd$_x$Pb$_{1-x}$F$_2$ melts ($T < T < T_m$), predicted theoretically, are examined using a suitable experimental sample. High-resolution solid state nuclear magnetic resonance appears to be an ideal method for this purpose as it is element selective and particularly sensitive to variations in the nearest-neighbor environment. The ability of $^{19}$F magic angle spinning NMR (MAS-NMR) to differentiate between different structural environments has been documented by a number of insightful applications to
crystalline fluoride ion conductors, \textsuperscript{8,9} nanoparticles, \textsuperscript{10} and other relevant crystalline systems. \textsuperscript{11–15} In the present system, the tetrahedral fluoride sites in the fluorite lattice give rise to five distinct local fluorine environments \( Q^{m} \), corresponding to fluorine surrounded by \( n \) Pb and \( 4-n \) Cd neighbors \((0 \leq n \leq 4)\), respectively, which are expected to differ in their isotropic chemical shifts. While previous low-resolution \( \textsuperscript{19}F \) NMR work turned out to be unable to resolve between these different \( Q^{m} \) sites in \( \text{Cd}_x\text{Pb}_{1-x}\text{F}_2 \) alloys\textsuperscript{8} and related fluoride materials,\textsuperscript{16–18} the application of MAS is expected to result in a dramatic improvement in the spectroscopic resolution and should thus be able to give new insight into the quantitative distribution of site populations in these solid solutions.

II. SIMULATION APPROACH

Classical molecular dynamic simulations were carried out using the DL_POLY package,\textsuperscript{19} in the NPT ensemble (constant number of particles, pressure, and temperature), using the two-body Buckingham potential as follows:

\[
V(r) = \frac{Z_i Z_j}{4 \pi \varepsilon_0 r} + A_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6}.
\]

The parameters \( A, \rho, \) and \( C \) were adjusted to reproduce structural and dynamical properties in the entire \( \text{Cd}_x\text{Pb}_{1-x}\text{F}_2 \) compositional range.\textsuperscript{7} The same set of interatomic potential parameters was used in the simulation of all compositions. The simulations were conducted with 1728 anions and 864 cations, at experimental density, and periodic boundary condition was applied in order to avoid surface influences. The equations of motion were integrated using the Verlet leapfrog algorithm, with a time step of 0.001 ps. The initial solid solutions were obtained by random replacement of lead by cadmium atoms in the cationic positions of a fluorite \( \beta\)-\text{PbF}_2 structure and thermalized for 100 ps at 50 K. Melting processes of the initial solid solutions were attained using a heating rate of \( q=+0.2 \text{ K/ps} \) up to the time that the high temperature liquid state is reached at 3500 K. Melted systems were kept at 3500 K, during a 100 ps simulation run for thermalization, and subsequently were submitted to two different cooling regimes, \( q=-0.2 \text{ and } -1.0 \text{ K/ps}. \)

III. EXPERIMENTAL METHODS

Samples were prepared by rapid melt-cooling using the roller-quenching technique previously described for these materials.\textsuperscript{4} The structural characteristics of some samples had been previously studied by means of x-ray diffraction and EXAFS measurements.\textsuperscript{4} \( \textsuperscript{19}F \) solid state NMR spectra were obtained at 188.15 MHz on a Bruker DSX-400 MHz instrument, interfaced with a 4.65 T magnet, using a 2.5 mm probe operated at a spinning frequency of 25 kHz and at a sample temperature of 200 K. This temperature was found sufficiently low for obtaining spectra that are unaffected by site exchange phenomena caused by fluorine ionic motion. Spectra were acquired as rotor synchronized echoes, using 90° pulses of 2.2 \( \mu \text{s} \) length and a relaxation delay of 7 s. Peak deconvolutions were carried out using the DMFIT software.\textsuperscript{20} Chemical shifts are reported relative to CFCl\textsubscript{3}, using a solid AlF\textsubscript{3} sample as a secondary standard.

IV. RESULTS AND DISCUSSION

Figure 1 shows the pair radial distribution function \( g_{\text{Pb-F}}(r) \) curves for the Pb–F pairs of several \( \text{Cd}_x\text{Pb}_{1-x}\text{F}_2 \) initial crystalline solid solutions, from which the relative height \( h \) of the peaks were collected and grouped in the \( h \) vs \( x \) plot in the inset, where, for the sake of simplicity, only the values related to the second \( g_{\text{Pb-F}}(r) \) peaks are shown. In fact, to give the same qualitative result, any atomic pair and coordination shell could be used in the present analysis: an inverse cupola, indicating the variation of the peaks’ height with composition, with a minimum at around \( x=0.35 \). The height of the peak of a \( g_{\text{Pb-F}}(r) \) curve is strongly related to the degree of disorder on the respective coordination shell: larger disorder leads to a lower and broader \( g_{\text{Pb-F}}(r) \) peak due to a broader distribution of distances. This behavior is closely related to the eutectic composition on the solid-liquid phase diagram: melting is an endothermic process; therefore, it is accompanied by an increase in the system’s entropy. It must be ex-

function liquid phase transition where a volume discontinuity is observed during the solid-liquid phase transitions of cadmium fluoride. Figure 2 shows the volume variation distributed cations and anions, which is characteristic of a solid-liquid phase change of cadmium fluoride. The agreement of this simulated property with the experimental observations of the eutectic composition gives credence to our proposed model. It correctly predicts the entropy of fusion and the respective coordination number functions [integral of the $g_{ab}(r)$ curves, which provides the coordination number as a function of distance from the central atom], $c_{ab}(r)$, for the crystalline [Figs. 3(a) and 3(b)] and glassy [Figs. 3(c) and 3(d)] $\text{Cd}_{0.5}\text{Pb}_{0.5}\text{F}_2$ systems, which are obtained after cooling from the melt from 3500 to 50 K, at rates of $q=−0.2$ K/ps and $q=−1.0$ K/ps, respectively. The crystalline character of the system cooled at $q=−0.2$ K/ps is evident in this figure, where well defined peaks are observed, reflecting the consecutive coordination shells of the respective atomic pair. On the other hand, the curves obtained at $q=−1.0$ K/ps attest to the amorphous structure of the glass.

An analysis of the atomic coordinates, as shown in Fig. 4, provides important information concerning structural characteristics of these systems. This figure shows that, during cooling processes of the system, phase segregation takes place. As stated above, the liquid systems at equilibrium ($T>T_m$) are homogeneous. When the temperature decreases, using these cooling rates, the homogeneity of the systems is destroyed and a separation into two liquid phases occurs in expected that decreasing the difference between the entropy of the solid and liquid phases (the entropy of fusion) leads to a lower melting temperature. In our case, the system with higher internal disorder is the eutectic composition, with $x=0.35$. In the inset of Fig. 1 shown, for the sake of comparison, together with the $g_{ab}(r)$ peak height, are the melting temperatures $T_m$ simulated for various compositions, following the above cited behavior of the solid-liquid phase diagram. The agreement of this simulated property with the experimental observations of the eutectic composition gives credence to our proposed model. It correctly predicts phase changes of $\text{Cd}_{x}\text{Pb}_{1−x}\text{F}_2$ solid solutions, in addition to providing an insight on the nature of the eutectic phenomenon.

In the melt phase, all compositions display randomly distributed cations and anions, which is characteristic of a homogeneous liquid. Figure 2 shows the volume variation during the heating and cooling processes from the melt with $x=0.5$. The melting process is identified in Fig. 2 (curve A), where a volume discontinuity is observed during the solid-liquid phase transition (1330 K). Different cooling processes from the melt were simulated. Figure 2 shows the volume contraction during the cooling processes from the melt, at rates of $q=−0.2$ K/ps (curve B) and $−1.0$ K/ps (curve C). By using the cooling at $q=−0.2$ K/ps (curve B), a large volume contraction is observed during the phase transition of crystalline solidification. A faster cooling rate, i.e., $q=−1.0$ K/ps (curve C) leads to a vitreous solidification, with a change occurring on the thermal contraction curve, around the glass transition temperature $T_g$ (477 K).

Figure 3 depicts the partial pair radial distribution functions and the respective coordination number functions [integral of the $g_{ab}(r)$ curves, which provides the coordination number as a function of distance from the central atom], $c_{ab}(r)$, for the crystalline [Figs. 3(a) and 3(b)] and glassy [Figs. 3(c) and 3(d)] $\text{Cd}_{0.5}\text{Pb}_{0.5}\text{F}_2$ systems, which are obtained after cooling from the melt from 3500 to 50 K, at rates of $q=−0.2$ K/ps and $q=−1.0$ K/ps, respectively. The crystalline character of the system cooled at $q=−0.2$ K/ps is evident in this figure, where well defined peaks are observed, reflecting the consecutive coordination shells of the respective atomic pair. On the other hand, the curves obtained at $q=−1.0$ K/ps attest to the amorphous structure of the glass.

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the supercooled melt ($T_c < T < T_m$, in the case of a subsequent crystallization of the melt, where $T_c$ is the crystallization temperature, or $T_c < T < T_m$, in the case of melt vitrification). PbF$_2$- and CdF$_2$-rich regions are clearly visible in the snapshots shown in Fig. 4.

Moreover, an analysis of the structural parameters obtained by $g_{ag}(r)$ analysis indicates that the two separated phases possess structures close to those of crystalline PbF$_2$ and CdF$_2$. In the initial Cd$_{0.5}$Pb$_{0.5}$F$_2$ solid solution, the first-neighbor Pb–Pb distance was measured as 4.05 Å. In the phase-separated recrystallized material, this distance is larger (4.22 Å). Concurrently, while the first-neighbor Cd–Cd distance for the initial crystalline Cd$_{0.5}$Pb$_{0.5}$F$_2$ solid solution is 3.94 Å, for the phase-separated recrystallized material, this distance is shorter (3.78 Å). This behavior is expected due to the nature of the solid solution lattice parameter, which lies linearly between the lattice parameter of the pure fluorides. When the phase separation takes place, the interatomic distances tend to approach the ones observed for the respective crystalline form, $\beta$-PbF$_2$ ($r_{Pb-Pb}=4.20$ Å) and CdF$_2$ ($r_{Cd-Cd}=3.81$ Å).

In the present system, the tetrahedral fluoride sites in the fluorite lattice give rise to five distinct local fluoride environments $Q^{(n)}$, corresponding to fluorine surrounded by $n$ Pb and $4-n$ Cd neighbors ($0 \leq n \leq 4$), respectively. Figure 5 shows the comparison of the $Q^{(n)}$ population distributions predicted from the MD simulations, using the random substitution model of the initial solid solution (ISS) and the crystalline phase obtained from slow cooling of the melt (CM). The homogeneous initial solid solutions clearly display a purely statistical $Q^{(n)}$ population distribution according to its composition. In contrast, phase separation is observed in the material slowly crystallized from the liquid phase, where $Q^{(0)}$ and $Q^{(4)}$ units become dominant entities on the solid solution structures. Whether $Q^{(0)}$ or $Q^{(4)}$ unit is present in a larger proportion on the phase-separated system depends on the cadmium content, with the $x=0.5$ composition having nearly equal quantities of both.

Obviously, the phase separation tendency, detected by our MD model, must be interpreted, in real systems, in terms of small-scale composition fluctuations, leading to subnanometric phase-separated regions. On the experimental side, however, x-ray diffraction results have shown that the experimental lattice parameters follow Vegard’s law, and EXAFS data have also been interpreted in terms of random solid solutions. It should be borne in mind, however, that these techniques are only able to provide spatially averaged information and may not be sufficiently sensitive to local compositional fluctuations. In contrast, such information is principally available from more local probes, such as high-resolution $^{19}$F NMR spectroscopy.

Considering the five distinct local fluoride environments $Q^{(n)}$, corresponding to the number of Pb surrounding the fluorine atoms ($0 \leq n \leq 4$), and the fact that the isotropic $^{19}$F chemical shifts of the bordering crystalline phases are very different ($\beta$-PbF$_2$: −45 ppm; CdF$_2$: −195 ppm), we also expect NMR to differentiate between the various local environments corresponding to different $n$ in the alloys. As NMR spectroscopy is also inherently quantitative, a detailed line-shape analysis should be able to reveal the quantitative site distribution in these alloys. Figure 6 shows an overview of the spectra obtained on several alloy samples. Clearly, all of the samples show multiple resonances, indicating the presence of differentiable fluoride environments. The individual peak deconvolutions to Gauss–Lorentz components are shown in Figs. 7(a)–7(f). The analysis, summarized in Table 1, reveals that the isotropic chemical shift for a given site does not depend strongly on the composition $x$, allowing straightforward peak assignments to be made. Based on these deconvolutions, the actual sample compositions were back-calculated from the fractional peak areas $f_n$ using the formula

![FIG. 5. Comparison of the $Q^{(n)}$ population distributions predicted from the MD simulations, using the random substitution model of the ISS (black bars) and the crystalline phase obtained from slow CM (white bars).](image)

![FIG. 6. Overview of the $^{19}$F MAS-NMR spectra obtained on PbF$_2$–CdF$_2$ alloys. Proposed site assignments are indicated by vertical dotted lines.](image)
\[ x = \Sigma_n (4-n)f_n/4, \] producing satisfactory agreement with the nominal sample compositions in all cases (see Table I). Table II summarizes the fractional peak area contributions of the different \( Q^{(n)} \) sites and compares them to those predicted from a statistical substitution model for each of the samples investigated.

The spectrum of the \( x=0.2 \) sample [Fig. 7(a)] suggests a significant amount of nonstatistical ordering, which is indicative of either phase separation or at least nanoscopic segregation: a major lineshape contribution arises from a well-resolved five-peak pattern, centered at \(-37.5 \) ppm, which reflects different \( Q^{(4)} \) type isotopomers split by indirect spin-

\[ \text{TABLE I.} \] \[ Q^{(n)} \text{ chemical shifts and experimental compositions extracted from } ^{19}\text{F MAS-NMR data in } \text{Cd}_{x}\text{Pb}_{1-x}F_2 \text{ solid solutions.} \]

<table>
<thead>
<tr>
<th>Nominal composition ((x))</th>
<th>(Q^{(4)}) (\delta \text{ (ppm)})</th>
<th>(Q^{(3)}) (\delta \text{ (ppm)})</th>
<th>(Q^{(2)}) (\delta \text{ (ppm)})</th>
<th>(Q^{(1)}) (\delta \text{ (ppm)})</th>
<th>(Q^{(0)}) (\delta \text{ (ppm)})</th>
<th>Estimated composition ((x))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>(-37.8)</td>
<td>(-58.9)</td>
<td>(-76.2)</td>
<td>(-92.3)</td>
<td>(\cdots)</td>
<td>0.15</td>
</tr>
<tr>
<td>0.3</td>
<td>(-35.3)</td>
<td>(-57.8)</td>
<td>(-78.0)</td>
<td>(-130.7)</td>
<td>(-179)</td>
<td>0.31</td>
</tr>
<tr>
<td>0.4</td>
<td>(-35.9)</td>
<td>(-54.8)</td>
<td>(-78.6)</td>
<td>(-125)</td>
<td>(-187)</td>
<td>0.41</td>
</tr>
<tr>
<td>0.5</td>
<td>(-38.2)</td>
<td>(-54.1)</td>
<td>(-82.6)</td>
<td>(-128.8)</td>
<td>(-190)</td>
<td>0.51</td>
</tr>
<tr>
<td>0.6</td>
<td>(-38.2)</td>
<td>(-55)</td>
<td>(-83.8)</td>
<td>(-129.4)</td>
<td>(-187.5)</td>
<td>0.57</td>
</tr>
<tr>
<td>0.7</td>
<td>(-36.7)</td>
<td>(-57.8)</td>
<td>(-84.9)</td>
<td>(-131.8)</td>
<td>(-190.9)</td>
<td>0.72</td>
</tr>
</tbody>
</table>
spin interactions with zero, one, and two $^{207}$Pb nuclei, respectively ($J \sim 1250$ Hz). The rather narrow linewidth reflects the existence of well-ordered domains of $Q^{(4)}$ units, consistent with the idea of nanophase segregation. A further lineshape contribution appearing in the same chemical shift region can be assigned to a second type of $Q^{(3)}$ units, which occurs in less well-ordered domains. For this component, excessive line broadening precludes the observation of spin-spin coupling multiplets. Finally, two additional broad lineshape contributions are observable, which are easily assigned $Q^{(3)}$ and $Q^{(2)}$ units in the solid solutions; again, the indirect spin-spin coupling with the $^{207}$Pb nuclei is not resolved in these individual components due to strong line broadening effects. Clear deviations from a purely statistical $Q^{(x)}$ population distribution are also observed for the other samples. Thus, for $x=0.3$ and 0.4, the populations of the $Q^{(4)}$ sites are favored, while those of the $Q^{(3)}$ sites are disfavored to a significant extent. At intermediate compositions ($x=0.4$, 0.5, and 0.6), the concentrations of $Q^{(2)}$ units are higher than expected based on a statistical population distribution. Finally, in the region of high Cd contents ($x \geq 0.6$), the formations of $Q^{(0)}$ sites seem to be disfavored to a certain degree, resulting in $Q^{(1)}$ site concentrations that are much higher than predicted on a statistical basis. Overall, the NMR results confirm the MD prediction that the local site population distributions in PbF$_2$-CdF$_2$ alloys are, indeed, nonstatistical. Of course, the simulation results must be interpreted as a qualitative indication of phase segregation that occurs during the fast cooling of the melt in the supercooled region. Experimentally, the supercooled melt state is very difficult to attain, and crystals are obtained even with the use of the roller-quenching technique. In the present simulations, due to the characteristics of the computational treatment, mainly the size of the system and the velocity scales employed (cooling rates in the order of K/ps), the supercooling region is very extended (see Fig. 2) and the system has a lot more time to separate than in the experimental conditions. This results in a phase-separated system with PbF$_2$- and CdF$_2$-rich domains, not observed experimentally, whereas a segregation tendency of PbF$_2$-rich domains only was observed experimentally. In this case, the qualitative predictions made by the MD simulations were corroborated by the NMR studies, which also provided a quantitative insight on the site population distributions.

V. CONCLUSIONS

Summarizing, we have found that the eutectic phenomenon in the Cd$_x$Pb$_{1-x}$F$_2$ solid solution system is related to the internal disorder induced by the inclusion of cadmium atoms on the face centered cubic lattice of lead fluoride. MD simulations were used to successfully suggest that the composition with $x=0.35$ is the one that has a minimum entropy of fusion, due to the higher intrinsic disorder in the crystalline state, hence, explaining the occurrence of the eutectic composition. On the other hand, the MD simulations and the high-resolution $^{19}$F solid state NMR results produce certain similarities concerning the structure at the microscopic level, mainly the phase separation trends observed in the simulations and in fast quenched samples. Phase separation and/or segregation effects play a major role at the Pb-rich end of the composition range ($x \leq 0.4$), and the site population distribution has been found to be certainly nonstatistical. NMR results provided a quantitative insight into these distributions, corroborating the qualitative MD predictions.

ACKNOWLEDGMENTS

The authors wish to acknowledge Professor J. Schneider and C. J. Magon for valuable discussions. The financial support of CNPq, FAPESP, and FAPEMIG (Brazil) are gratefully acknowledged. This work is part of a joint program PRONEX/FAPESP/CNPq (Grant No. 03/09859-2).


### Table II. Quantitative $Q^{(x)}$ site populations predicted from statistical distribution and the experimental values determined by $^{19}$F MAS-NMR.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$Q^{(0)}$</th>
<th>$Q^{(1)}$</th>
<th>$Q^{(2)}$</th>
<th>$Q^{(3)}$</th>
<th>$Q^{(4)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>Statistical distribution</td>
<td>0.2</td>
<td>2.6</td>
<td>15.4</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>NMR</td>
<td>0</td>
<td>0</td>
<td>11.2</td>
<td>34.4</td>
</tr>
<tr>
<td>0.3</td>
<td>Statistical distribution</td>
<td>0.8</td>
<td>7.6</td>
<td>26.5</td>
<td>41.2</td>
</tr>
<tr>
<td></td>
<td>NMR</td>
<td>1.0</td>
<td>7.1</td>
<td>38.4</td>
<td>20.8</td>
</tr>
<tr>
<td>0.4</td>
<td>Statistical distribution</td>
<td>2.6</td>
<td>15.4</td>
<td>34.6</td>
<td>34.6</td>
</tr>
<tr>
<td></td>
<td>NMR</td>
<td>0.2</td>
<td>18.9</td>
<td>47.5</td>
<td>12.3</td>
</tr>
<tr>
<td>0.5</td>
<td>Statistical distribution</td>
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<td>25</td>
<td>37.5</td>
<td>25</td>
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<tr>
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<td>32.2</td>
<td>48.8</td>
<td>8.1</td>
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<td>0.6</td>
<td>Statistical distribution</td>
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<td>34.6</td>
<td>15.4</td>
</tr>
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<td>3.0</td>
<td>41.0</td>
<td>43.5</td>
<td>6.3</td>
</tr>
<tr>
<td>0.7</td>
<td>Statistical distribution</td>
<td>24.0</td>
<td>41.2</td>
<td>26.5</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>NMR</td>
<td>15.5</td>
<td>59.7</td>
<td>18.3</td>
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</table>
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