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NMR Selection of Space Groups in Structural Analysis of Ag_7PSe_6

Etienne Gaudin,[†,‡] Florent Boucher,[‡] Michel Evain,[‡] and Francis Taulelle*,[†]

RMN et Chimie du Solide, UMR 7510 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France, and Laboratoire de Chimie des Solides, I.M.N.; UMR C6502 CNRS, Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

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Ag_7PSe_6 is an archetype of the argyrodite family. It undergoes one phase transition at 453 K, and both phase structures have been recently determined by X-ray diffraction on single crystals. Argyrodites twin frequently when undergoing their phase transitions and solving the structures by diffraction may become difficult or even impossible. It is shown in this paper that solid-state NMR provides enough structural information to restrict the number of possible space groups to a small subset. In the case of Ag_7PSe_6 at room temperature, a restriction to three space groups is thus obtained, one of them being the space group of the structure determined by diffraction. The method to obtain the necessary NMR information to perform restriction of the subset of compatible space groups is explained and evaluated on this compound.

Introduction

Ag_7PSe_6 has been synthesized for the first time by Kuhs et al.[1] This compound exhibits an order−disorder phase transition at 453 K due to vacancies in the cationic network.[2−5] The structural resolution of these two polymorphs showed off a strong delocalization of Ag^+ within the $[PSe_6]$ framework at high temperature for the γ-phase (space group $F\bar{4}3m$).[5] The phase transition from high to low temperature form lowers the symmetry of the framework to $P2_13$ space group[5] with localization of the Ag^+ ions in the framework in tetrahedral, triangular, and linear coordination. This framework, in its high-temperature form, consists of a cubic face centered close packing array of Se^{2-} anions with tetrahedral sites alternatively occupied by Se^{2-} anions and $[PSe_4]^{3-}$ tetrahedra (Figure 1). The selenium atoms can occupy three types of sites: the sites Se1 belonging to $[PSe_4]^{3-}$ tetrahedron, and two sites named Se2 and Se3, corresponding to the Se^{2-} ions. When undergoing the phase transition, from high to low temperature, the framework slightly distorts.

In the high temperature form, the $[PSe_4]$ tetrahedron has site symmetry $\bar{4}3m$ (T_d) and the four selenium atoms around P are equivalent as Se1 (Figure 2a). Silver atoms electronic density around Se2 and Se3 is distributed with $\bar{4}3m$ (T_d) symmetry. For the low-temperature form β-Ag_7PSe_6, the symmetry of P, Se2, and Se3 sites lowers from $\bar{4}3m$ (T_d) to 3 (C_3). Selenium atoms of $[PSe_4]$ become therefore inequivalent with relative multiplicity of 3 to 1 for Se1x and Se1 (Figure 2b). Silver distributions around Se2 and Se3 are displayed on Figure 2c and 2d.

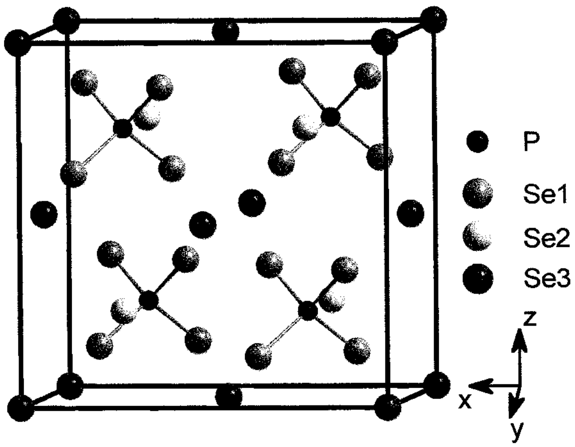

Figure 1. The cubic $[PSe_6]$ framework of γ-Ag_7PSe_6.

This compound has favorable NMR nuclei, namely ^{31}P and ^{77}Se. Hitherto, the only NMR study ever done, has been limited to room temperature β-Ag_7PSe_6 phase.[6] It reports two MAS ^{77}Se spectra with and without ^{31}P decoupling and one MAS ^{31}P. The authors observed the different selenium sites of the structure. However, they could not assign the sites, the crystallographic structure was not solved at that time.

Ag_7PSe_6 is an archetype of the argyrodite family.[7−8] Most members of the family undergo one or two phase

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[*] To whom correspondence should be addressed.

[†] Université Louis Pasteur.

[‡] Université de Nantes.

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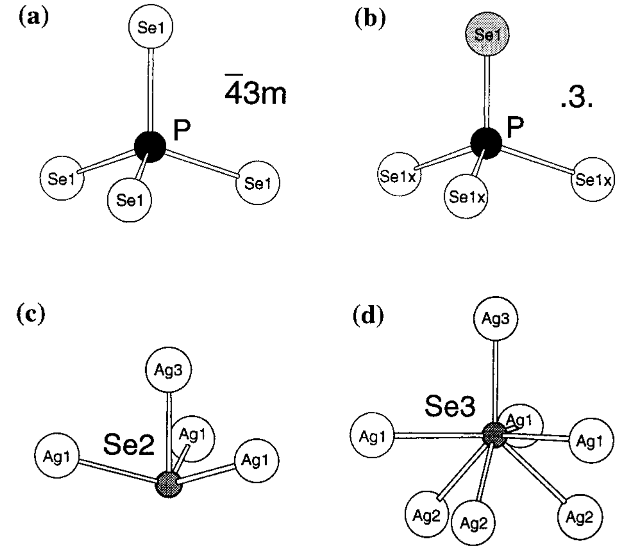

Figure 2. Tetrahedron [PSe_4] with indication of the phosphorus Wyckoff position symmetry which corresponds to the symmetry of the tetrahedron for (a) γ-Ag_7PSe_6 at 473 K and (b) β-Ag_7PSe_6 at 293 K. Silver atoms surrounding at room temperature (β-Ag_7PSe_6) of (c) Se2 and (d) Se3. All these information are taken from ref 5.

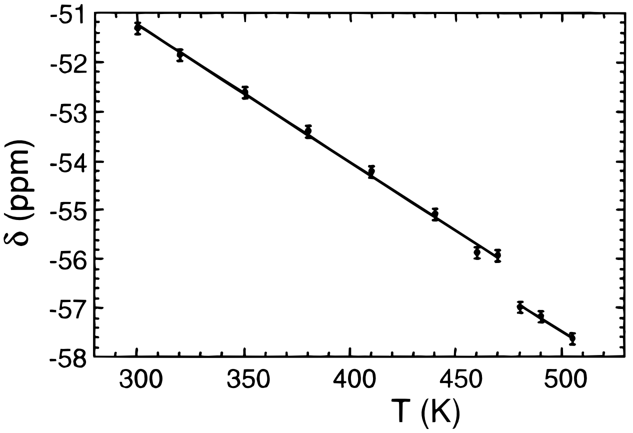

Figure 3. ^{31}P chemical shift variation as a function of temperature. At the transition at 470 K, a discontinuity is observed between the two linear regions.

transitions. When two phase transitions occur, the phases are labeled, to keep up with usual notations, by increasing temperature, i.e., α, β, and γ for the low-, medium-, and high-temperature phases. As $F\bar{4}3m$ is the most common space group of copper- and silver-based argyrodites at high temperature, the high-temperature form is always called γ. The low-temperature form of this silver argyrodite, for which only one phase transition occurs, is called β.

When going through the transitions $\gamma \rightarrow \beta$ or $\beta \rightarrow \alpha$, twinning of the crystals frequently complicates the structure determination. This is the case for the two polymorphs of Cu_7PSe_6, α and β, for which it has not been possible to solve the structures by XRD only. NMR has provided the necessary information to complete the structure determination.[9-10]

Ag_7PSe_6, for which the structure has been recently determined by single-crystal XRD for γ and β phases,[5] is considered here to establish a general methodology to use NMR information in the process of structure elucidation. The method relies on limiting the number of space groups compatible with XRD to the subensemble compatible also with NMR sites symmetry. Any other non-NMR information can be included in addition, like the chemical formula or known chemical environments of atoms, when they help to constrain sites symmetry.

This study unfolds into two stages. In the first, the agreement between NMR data and XRD structural data of the two polymorphic forms of Ag_7PSe_6 is checked. During the second stage, a strategy is set up allowing the establishment of an accurate structural information by a refined analysis of the NMR data, complemented by the powder XRD. At this stage, we will not consider that Ag_7PSe_6 structure has already been established.

Experimental Section

NMR experiments have been run on a DSX 500 Bruker spectrometer operating at 11.7 T. A Bruker 4 mm MAS probe has been used. Chemical shift referencing has been done versus H_3PO_4 85% for ^{31}P and $(CH_3)_2Se$ for ^{77}Se. H_2SeO_3 has also been used as a secondary reference for ^{77}Se with a chemical shift at 1282 ppm versus $(CH_3)_2Se$. The chemical shift of CdSe has been determined as being at -492 ppm versus $(CH_3)_2Se$ to compare our results with the ones from Maxwell et al. (CdSe was used as their primary reference).

^{31}P spectra have been recorded with recycle times between 20 and 10 s depending on temperature and 16 FIDs were accumulated. ^{77}Se spectra required long accumulation time (12−24 h) due to a very long T_1, a low natural abundance (7.5%). Recycle times have been set to 5 min for room temperature and 10 s at 505 K, with 7200 and 162 accumulated FIDs, respectively. Ag_7PSe_6 decomposes rapidly at high temperature; accumulation cannot therefore be too long. Single pulse excitation was used for both nuclei with pulse length of 4.6 μs for ^{31}P and 4.5 μs for ^{77}Se. Resonating frequencies were 202.416 and 95.344 MHz for ^{31}P and ^{77}Se, respectively. The respective sweep widths were 60 kHz and 500 kHz. MAS frequencies were between 0 and 8 kHz.

Results

^{31}P MAS NMR. The ^{31}P chemical shift variation is displayed in Figure 3. It varies linearly with temperature for each of the polymorphs. At the phase transition (470 K), a discontinuity is observed between the two linear regions. The first-order character of the transition is clearly confirmed by the coexistence of the two phases at the transition.

At room temperature, the spectral resolution of ^{31}P allows the observation of two indirect coupling constants J^1_{P-Se}. Their values are 515 and 430 Hz (Figure 4a). The relative areas of these lines are in a 3:1 ratio. Maxwell et al.[6] have observed J couplings of 524 and 430 Hz, values in very close agreement with ours. These coupling constants remain almost constant with the temperature increase up to the transition. At transition, both coupling constants coalesce into a single one of 475 Hz (Figure 4b). For ^{31}P high-temperature measurements, decomposition of the powder occurred, leading

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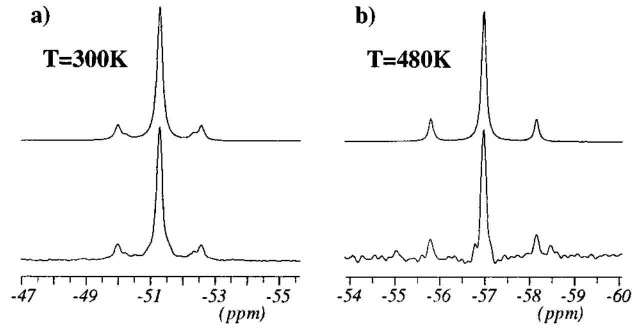

Figure 4. ^{31}P MAS NMR spectra with spinning frequency of 8 kHz of (a) β-Ag_7PSe_6 (300 K) and (b) γ-Ag_7PSe_6 (480 K). "Anafor" processed signal[16] is presented above the two spectra.

to limited acquisitions time and poor signal-to-noise ratio. These results confirm the site symmetry of phosphorus in both structures. At room temperature, in the β phase, phosphorus occupies a Wyckoff position .3.. It has therefore a 3:1 multiplicity for its selenium neighbors (Figure 2b). For the γ-phase, the phosphorus site has a $\bar{4}3m$ site symmetry with a multiplicity of 4 for surrounding selenium atoms (Figure 2a). A single type of selenium connects phosphorus and a unique coupling constant is clearly detected.

At low MAS frequency (1500 Hz), an anisotropic chemical shift tensor for ^{31}P is observed. The β-Ag_7PSe_6 (300 K) and γ-Ag_7PSe_6 (505 K) forms have, for phosphorus, respectively the following chemical shift tensor sets: $\delta_{iso} = -51.2$ ppm, $\delta_{aniso} = -13.4$ ppm and $\eta_{csa} = 0.5$ for β phase and $\delta_{iso} = -57.6$ ppm, $\delta_{aniso} = -6.5$ ppm and $\eta_{csa} = 0$ for the γ phase.

The δ_{aniso} and η_{csa} values remain almost constant at different temperatures for one given polymorphic form. One would expect for the γ form no anisotropy at all, due to the $\bar{4}3m$ (T_d) site symmetry. This is not strictly the case, although the anisotropy is small. However, the atomic displacement parameter (ADP) of XRD refinement has large values for the γ form.[5] This indicates a positional disorder that spatially averages PSe_4 to a perfect $\bar{4}3m$ symmetry. The very low anisotropy of the ^{31}P chemical shift tensor (with $\eta_{csa} = 0$) indicates a small difference in the site symmetry observed by NMR and deduced from the XRD analysis. NMR, in this case, does not time average the anisotropy of ^{31}P because of a too long period of motion compared to acquisition of signal. XRD however does space average the same anisotropy. This apparent symmetry difference is therefore consistent with both types of measurements.

^{77}Se MAS NMR. In Figure 5a, the γ-Ag_7PSe_6 form has a ^{77}Se spectrum with three types of selenium sites. This NMR observation agrees with the three inequivalent selenium atoms of the framework. At high frequency with a chemical shift at 751 ppm and a very large anisotropy of about −650 ppm (estimated due to the low signal-to-noise ratio) the ^{77}Se signal can therefore be easily assigned to $[PSe_4]$ types because of the J_{P-Se} coupling.

For the two sites at −881.8 and −1169.8 ppm, no anisotropy is observed; they correspond to Se^{2-} sites surrounded by Ag^+ ions. The unobserved anisotropy indicates that their environment is highly symmetric due to the geometric disposition of the silver ions around them. The symmetry can also be due to the motion of silver ion around these selenide ions. To assign the two selenide sites we may consider the first coordination sphere. By XRD the β-Ag_7PSe_6 phase presents two different repartitions of silver ions between Se2 and Se3 (see Figure 2c and 2d). Se2 site has a strongly anisotropic distribution of ions. At room temperature, Figure 5b, the site at −817.2 shows a well-defined spinning sideband pattern at 8 kHz MAS frequency ($\delta_{aniso} = 319$ ppm) although the site at −1273.9 ppm does not show any spinning sidebands for this spinning speed. Se2 can therefore be assigned to the −817.2 ppm site and Se3 to the −1273.9 ppm one. Se2 is more deshielded than Se3. This is consistent with electronic transfer from s orbital of silver to p orbitals of selenium and leads to a correlation between the number of silver surrounding selenium and the shielding of selenium. For selenium sites belonging to $[PSe_4]$, a splitting occurs at room temperature as expected, with two sites Se1 and Se1x with respective multiplicity 1 and 3. The chemical shift tensor values are for Se1, $\delta_{iso} = 618.6$ ppm, $\delta_{aniso} = -730$ ppm and $\eta_{csa} = 0.3$ and for Se1x $\delta_{iso} = 610.2$ ppm, $\delta_{aniso} = -738$ ppm and $\eta_{csa} = 0.25$ (see Table 1).

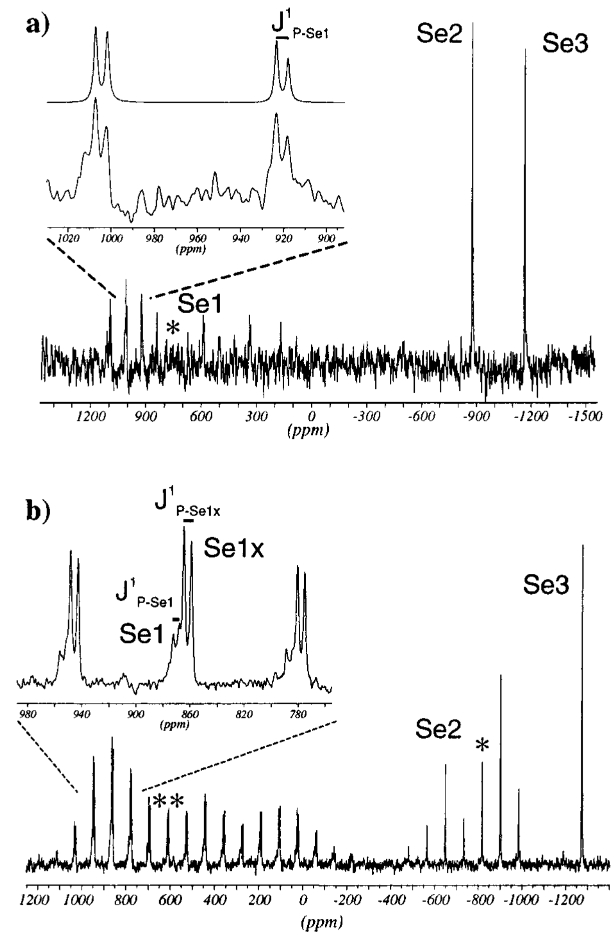

Figure 5. ^{77}Se MAS NMR spectra with spinning frequency of 8 kHz of (a) γ-Ag_7PSe_6 (505 K) and (b) β-Ag_7PSe_6 (300 K). The different sites are assigned to the crystallographic sites. The isotropic peaks are labeled by an asterisk. "Anafor" processed signal[16] is presented above the zoom of two spinning sidebands for (a) γ-Ag_7PSe_6.

Discussion

For argyrodites, twinning often obscures the structure determination. It would therefore be useful to know to

Table 1. CSA Tensor Parameters of the Selenium Sites Deduced from ^{77}Se MAS NMR with MAS Frequency of 8000 Hz for Both Ag_7PSe_6 Polymorphs[a]

	Se1	Se1x	Se2	Se3
	β-Ag_7PSe_6 (293K)			
δ_{iso} (ppm)	618.6	610.2	−817.2	−1273.9
δ_{iso} (ppm)(from [6])	612		−818	−1271
δ_{aniso} (ppm)	−730	−738	319	
η_{csa}	0.3	0.25	0.20	
	γ-Ag_7PSe_6 (500K)			
δ_{iso} (ppm)	751		−881.8	−1169.8
δ_{aniso} (ppm)	−650			
η_{csa}	0.3			

[a] In the case of γ-Ag_7PSe_6 the Se1 CSA tensors parameters have been approximately determined. All chemical shifts are referenced to $(CH_3)_2Se$.

Table 2. Relations between the Central Atom Site Symmetry and the Number of Symmetry-Related Ligands with Their Minimum Site Symmetries for a Tetrahedral Coordination

central atom site symmetry	X^y, minimum site symmetries (X) and multiplicities of the ligands (^{y})
$\bar{4}3m$ (T_d)	$3m^4$
23 (T)	3^4
$\bar{4}2m$ (D_{2d})	m^4
$\bar{3}m$ (C_{3v})	$3m + m^3$
$\bar{4}$ (S_4)	1^4
222 (D_2)	1^4
$mm2$ (C_{2v})	$m^2 + m^2$
3 (C_3)	$3 + 1^3$
$2m$ (C_2)	$1^2 + 1^2$
m (C_{1h})	$m + m + 1^2$
1 (C_1)	$1 + 1 + 1 + 1$

which extent NMR can provide information to solve the structure. For Ag_7PSe_6, we have been able to solve the structure[5] of the γ as well as the β forms. It is then a good test case for establishing how much structural information is contained in the NMR results and how to use this information. We will describe in a first part how to relate the site symmetry of the different sites to compatible space groups. In a second part, discussion of NMR parameters will be carried out from the point of view of determining the site symmetry of each observable site. From this collection of information, a compatible space group subset will be determined and eventually compared to the actually determined space group.

Actually, Ag_7PSe_6 crystallizes for its γ form in $F\bar{4}3m$ space group. Maxwell and al.[6] have only collected XRD powder data, lacking a single crystal of a sufficient size. They relied on NMR to solve, at room temperature the β form structure of Ag_7PSe_6. They have well shown off by NMR that the phosphorus site was a $[PSe_4]$ unit with a 3-fold axis of symmetry and that two other selenium sites were present in the unit cell surrounded by silver only. But they did not deduce any further constraints that could have allowed them to solve the structure.

NMR to Structure Relations. *General Aspects.* Brown[11] has deduced crystallographic constraints from the enumeration of all occupied sites and their point group symmetry. For a given space group, each atomic site has a local symmetry associated with the symmetry of the Wyckoff position of the site. Furthermore, the site symmetry must be compatible with the coordination polyhedron surrounding the atom of interest, and the coordinated atoms must fulfill the relative multiplicities fixed by the site symmetry.

From such general considerations, a search of crystallographic information from NMR is proposed. The first step of this strategy consists of identification of the different polyhedra occurring in the structure. The polyhedron symmetry corresponds to the symmetry of the central atom considered.[11] This argument should be rigorously limited to tetrahedra, octahedra, and cubes, the platonician polyhedra. This study stays within this limitation, for only tetrahedral site symmetry will be considered. To efficiently reduce the number of compatible space groups, let us consider the polyhedra of highest symmetry. For example, $\bar{4}3m$ is the site symmetry of the phosphorus position in γ-Ag_7PSe_6. It corresponds to a perfectly regular tetrahedron $[PSe_4]$. This site symmetry exists only in cubic space groups. Any NMR property that may experience this site symmetry can be used to select the highest symmetrical polyhedra. Chemical shift anisotropy and *J* couplings may very well be used too.[12] However the easiest way to access the central atom site symmetry of a polyhedron by NMR is to consider the multiplicities of the ligands. Brown has tabulated for each coordination type the relations between the central atom symmetry and the multiplicities of the surrounding coordinated atoms. In the case of tetrahedral symmetry, which concerns particularly this structure, these relations are summarized in Table 2. Compatible space groups must allow room for Wyckoff positions having the selected symmetry for central atom site, and the proper multiplicity of ligands atoms. These constraints are the more efficient the higher the symmetry of the polyhedron, because this allows elimination of more space groups.

The number of chemical formula units per unit cell *Z* permits the multiplicity of Wyckoff positions, instead of their ratio, to be established. This information can be easily obtained by the XRD powder diffractogram. It further constrains the subset of compatible space groups.

Structure Elucidation of β-Ag_7PSe_6. From ^{31}P and ^{77}Se MAS NMR, central atoms of highest symmetry polyhedra can be identified. In γ form, the three sites of highest symmetry are P, Se2, and Se3 as they exhibit very small chemical shift anisotropy. The indirect coupling constant $^1J_{P-Se}$ observed for Se1 and Se1x for the β form, respectively 430 and 515 Hz, or Se1 for the γ form (475 Hz), indicate first that a covalent bonding exists between P and Se1. The coupling pattern on the ^{31}P spectrum reveals also a 1:3 ratio with a $^{31}P-^{78}Se$ line of 72% and a $^{31}P-^{77}Se$ one of 28%.

This establishes the $[PSe_4]$ stoichiometry of the phosphorus unit. In ^{77}Se NMR, the β form exhibits signals at −618.6 ppm and −610.2 ppm, with a very strong anisotropy and a $^1J_{Se-P}$ coupling identical to $^1J_{P-Se}$. They are therefore assigned to Se1 and Se1x and have, as already revealed in ^{31}P NMR, a 1:3 ratio. In addition, two other signals at −817.2 ppm and −1273.9 ppm are assigned to Se2 and Se3. They do not exhibit any indirect coupling and have their anisotropies de-

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pendent on temperature. They are therefore likely to be the Se^{2-} entities expected in the argyrodite framework.

The relative ratio of Se1, Se1x, Se2, and Se3 are respectively 1:3:1:1. Therefore, the crystal formula can be written as follows: Z $(Ag_7)[P1(Se1)_1(Se1x)_3](Se2)_1(Se3)_1$.

Se2 and Se3 are only surrounded by silver atoms and are of quite high symmetry due to their small chemical shift anisotropy. Silver NMR has not been observed for lack of an appropriate probe, but motion and positional disorder of silver would have led to difficulties in extracting polyhedra multiplicity around Se2 and Se3 as already described in an Ag_9GaSe_6 NMR study of ^{107}Ag and ^{109}Ag.[13] Furthermore, the anionic framework elucidation might be sufficient to obtain a good start for the diffraction analysis and refinement. The phase can be sufficiently well approximated from the anionic framework to determine Ag^+ positions from Fourier difference analysis and density maxima of silver electronic density obtained on the high temperature form. In the γ form, Ag_7PSe_6 exhibits $^{77}Se2$ and $^{77}Se3$ signals without anisotropy. The ionic conductivity of the γ form indicates a silver motion. The lack of chemical shift anisotropy of $^{77}Se2$ and $^{77}Se3$ signals is therefore due to the motional averaging of the symmetry around them by silver atoms.

Polyhedra identification is quite easy in this case, and has been done already by Maxwell et al. from analysis of the couplings constants between P and Se in $[PSe_4]$.

Thus, in the case of this study, we considered polyhedra $[PSe_4]$, $[Se2Ag_x]$, $[Se3Ag_y]$, respectively centered on P (tetrahedral coordination), Se2, and Se3 positions.

Only $[PSe_4]$ tetrahedron symmetry is accessible due to the measured Se ligand multiplicities. For Se2 and Se3, the two other central atoms considered, it is however still possible to observe their symmetry lowering when undergoing the γ to β phase transition. This is revealed by the anisotropy that appears at constant (8 kHz) spinning speed when the temperature is lowered below the phase transition. For $[PSe_4]$ the symmetry lowering is revealed by the splitting of Se1 into two types of selenium, Se1 and Se1x in a 3:1 ratio.

From Table 2 this ligand multiplicity corresponds to a site of symmetry 3 or 3m for phosphorus. The compatible space groups should contain at least one Wyckoff position of symmetry 3 or 3m for P with the possibility of locating the three other selenium atoms in such a way that all these multiplicities are equal (P, Se1, Se2, and Se3). For Se1x a Wyckoff position of triple multiplicity should exist.

The compatible space groups can only belong to trigonal, hexagonal, and cubic crystalline systems, as only those contain positions of 3 and $3m$ Wyckoff symmetry. This is the majority of the space groups of these three crystalline systems. Furthermore, for all these space groups the 3 and $3m$ Wyckoff positions have axes at their loci, allowing four atoms of identical multiplicity P, Se1, Se2, and Se3 to be located. For Se1x a position of triple multiplicity is also available.

As this subensemble of space groups is too large, a restriction must be applied. The knowledge of Z, the number of formula unit in the unit cell allows the multiplicity of the different sites in the unit cell to be determined. The cell dimension, $a = 10.768$ Å[6] leads to a number of formula per unit cell of 4 by comparison with the well-known argyrodite structures determined by X-ray diffraction.[14,15] It is, of course always possible to determine Z by a classical measurement of density using the formula $Z = dV/M$. The expected compatible space groups must therefore contain four Wyckoff positions with symmetry $3m$ or 3. It should also house a Se1 with a multiplicity of 4 and one site of multiplicity 12 for Se1x. Nineteen space groups fulfill these conditions. At room temperature the unit cell is cubic. One may therefore assume a cubic crystalline system. If this assumption holds, only three cubic space groups fulfill the conditions enumerated, $P\bar{4}3m$, $P2_13$, and $P23$. Considering information on the powder diffractogram can further eliminate none of them. It is noticeable that $F\bar{4}3m$ space group proposed by Maxwell et al. does not allow a proper indexation of the XRD diagram. Moreover, the only Wyckoff position available in $F\bar{4}3m$ for locating phosphorus on a Wyckoff position of symmetry 3 or $3m$ is $16e$ (symmetry $3m$, multiplicity 16), in contradiction with the expected multiplicity of 4.

This combined XRD/NMR analysis shows that only three space groups are possible to refine the structure, $P23$, $P2_13$, and $P\bar{4}3m$. For the single-crystal considered in our structure determination,[5] $P2_13$ is selected by considering extinction conditions. However, in the case of twinning this simplicity would not hold, and all three NMR compatible space groups should be considered for a refinement. Only three, however, in this case, instead of a full indetermination without the NMR approach. The described strategy selecting a subensemble of compatible space groups by using NMR and XRD constraints seems therefore efficient and may allow compounds for which structural determination is still problematic to be studied. This will be applied in a forthcoming study to β and α forms of Cu_7PSe_6. For these examples, Ag_7PSe_6 and Cu_7PSe_6, NMR only does not allow obtaining all the information on the structure. This is due to the lack of sensitivity of ^{77}Se. For more sensitive NMR nuclei, polyhedra analysis could be obtained in more detail for other atoms. Selection of compatible space groups can be furthered in such favorable cases.

Conclusion

In this study all the NMR observables in ^{31}P and ^{77}Se show a phase transition of first-order kind. Using Brown's concepts, it has been shown also that determination of the sites' symmetries, by the multiplicity of the ligands when considering $[PSe_4]$, or more qualitatively using the anisotropic interactions, introduces constraints on the choice of space groups. This method evaluated on the β form of Ag_7PSe_6 will be used more

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extensively in the analysis of structures which cannot be solved by diffraction only. This is often the case in argyrodites and points toward a systematic joint XRD-NMR structure resolution method. It will probably benefit to structure solutions difficult to find. In this rich family of compounds, Cu_7PSe_6[9,10] will be the first example of such a strategy.

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