

## Isotropic and anisotropic chemical shift in $^{207}\text{Pb}$ NMR of inorganic solids

F. Fayon<sup>1,\*</sup>, C. Bessada<sup>1</sup>, D. Massiot<sup>1</sup>,  
I. Farnan<sup>2</sup> and J.-P. Coutures<sup>1</sup>

<sup>1</sup> *Centre de Recherche sur la Physique des Hautes Températures, CNRS,  
45071 Orléans cedex 2, France*

<sup>2</sup> *Department of Earth Science, University of Cambridge, Downing Street,  
Cambridge CB2 3EQ, U.K.*

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\* *Correspondence and reprints.*

### RÉSUMÉ

Nous avons récemment développé des corrélations empiriques entre déplacement chimique de  $^{207}\text{Pb}$  (état d'oxydation +2) et structure dans les solides (Fayon et al.). Dans cet article, nous nous proposons de comparer ces corrélations à de nouvelles données expérimentales de RMN obtenues pour des aluminates de plomb et silicates de plomb cristallins.

**Mots Clés :** RMN/ $^{207}\text{Pb}$ /déplacement chimique/corrélation

### ABSTRACT

We have recently described empirical correlations between  $^{207}\text{Pb}$  NMR chemical shift (oxidation state 2+) and structure in solids (Fayon et al.) that should allow the use of  $^{207}\text{Pb}$  NMR as a structural probe in disordered solids of complex composition. These empirical correlations are compared to new experimental NMR data in crystalline lead aluminates and lead silicates.

**Keywords :** NMR/ $^{207}\text{Pb}$ /chemical shift/correlation

For many spin  $\frac{1}{2}$  nuclei (like  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ), high resolution Magic Angle Spinning NMR has proved to be a very useful tool for the investigation of crystalline and amorphous solids. However, in the case of  $^{207}\text{Pb}$  (spin  $\frac{1}{2}$  nucleus with the highest atomic number) the NMR literature is not very exhaustive for inorganic lead compounds (Pb oxidation state 2+). This is because  $^{207}\text{Pb}$  NMR suffers some experimental difficulties that come from a wide  $^{207}\text{Pb}$  chemical shift range [1-2]

(7000-8000 ppm) and strong chemical shift anisotropy [2,4,5]. In a recent work, using  $^{207}\text{Pb}$  MAS NMR we have resolved and assigned different lead sites in crystalline lead oxides and lead silicates [5]. The very large chemical shift anisotropies (CSA) were also obtained from a spinning sidebands analysis. We apply here the same experimental protocol to determine the  $^{207}\text{Pb}$  chemical shift tensors in lead aluminates and silicates. The experimental spectra of  $\text{PbAl}_2\text{O}_4$ ,  $\text{PbAl}_{12}\text{O}_{19}$  and  $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$  are shown on figure 1. As these three compounds contain a single Pb site, the attribution of the isotropic bands is made unambiguously from the comparison of spectra at different spinning speed. The CSA values determined from spinning sidebands intensities [6] are given in table 1 (expressed with the convention of [7]).

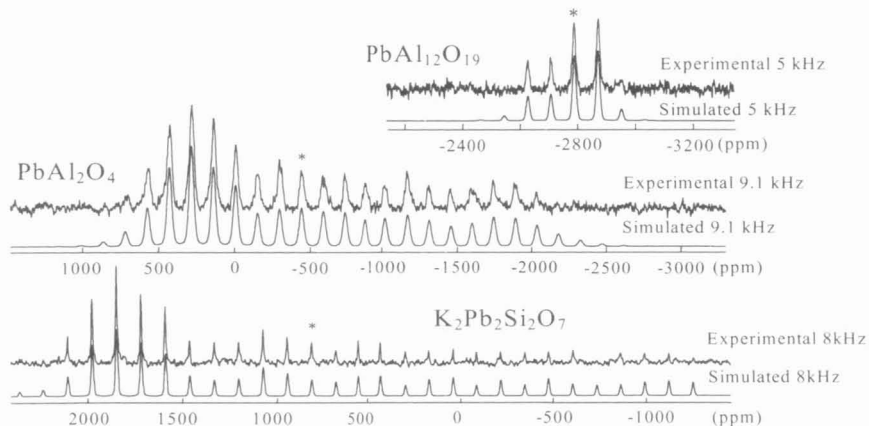


Figure 1 : Experimental MAS NMR spectra of  $\text{PbAl}_{12}\text{O}_{19}$ ,  $\text{PbAl}_2\text{O}_4$  and  $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$ , recorded on a Bruker DSX 300 spectrometer (operating at 62.6 MHz) using single pulse ( $\pi/9$ ) acquisition (asterisk marks isotropic lines).

Table I :  $^{207}\text{Pb}$  NMR chemical shifts for  $\text{PbAl}_2\text{O}_4$ ,  $\text{PbAl}_{12}\text{O}_{19}$  and  $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$  (chemical shift referenced relative to  $\text{Pb}(\text{CH}_3)_4$ , the uncertainties are 7 ppm).

compound	$\delta_{\text{iso}}$ (ppm)	$\Omega$ (ppm)	K	$\delta_{11}$ (ppm)	$\delta_{22}$ (ppm)	$\delta_{33}$ (ppm)
$\text{PbAl}_{12}\text{O}_{19}$	-2790.6	356.5	-0.87	-2560.6	-2894.1	-2917.1
$\text{PbAl}_2\text{O}_4$	-432.7	3000	0.75	692.3	317.3	-2307.7
$\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$	816.2	3671.3	1	2040	2040	-1631.3

In these compounds,  $\text{Pb}^{2+}$  exhibits two very different local environments. The lead hexaaluminate possess a magnetoplumbite type structure, like  $\text{CaAl}_{12}\text{O}_{19}$  or  $\text{SrAl}_{12}\text{O}_{19}$ , and Pb occupies a twelve-fold coordinated site with bond lengths varying between 0.2772 and 0.2790 nm. In this compound, the lead coordination and the Pb-O bond lengths are characteristic of an ionic Pb bonding state. On the contrary, in  $\text{PbAl}_2\text{O}_4$  and  $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$ , Pb is three-fold coordinated in a pyramidal geometry (Pb at the apex) and the Pb-O bond length ( $\leq 0.24$  nm) are shorter than the sum of ionic radii indicating covalent Pb-O bonds. For these covalent compounds, the span of the CSA tensor exceeds 3000 ppm, resulting from the asymmetric pyramidal coordination. For  $\text{PbAl}_2\text{O}_4$ , the measured asymmetry parameter is related to the distortions of the  $\text{PbO}_3$  pyramidal unit ( $K=0.75$ ) whereas for  $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$ , the asymmetry parameter is in agreement with the location of the Pb site on a  $C_3$  symmetry axis ( $K=1$ ).

In order to use NMR chemical shifts as structural probe, it is necessary to establish a relationship between them and different local environments in different structures. For a heavy nucleus like Pb, it is very difficult to evaluate chemical shift by formal computation and it is thus more convenient to use a simplified approach and to establish empirical correlation with compounds of known structure. Based on the analysis of 21 different crystallographic  $\text{Pb}^{2+}$  sites, we have established a linear correlation between  $^{207}\text{Pb}$  chemical shift and mean Pb-O bond length [5] ( $\delta_{\text{ISO}} = 20854 - 86689.5 \text{ d(Pb-O)}$ ,  $R=0.953$ ). We observed that a decrease in the mean bond length lead to more positive chemical shift (negative slope). Considering the large variation of local environment for Pb in the compounds studied, the mean Pb-O bond length appears to be a reasonable controlling parameter for  $\text{Pb}^{2+}$  chemical shift, even if the departure from linearity increases for the more covalent compounds with short mean bond length. The mean Pb-O bond lengths deduced from crystal structure are 0.278, 0.235, 0.221 nm for  $\text{PbAl}_{12}\text{O}_{19}$ ,  $\text{PbAl}_2\text{O}_4$  and  $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$  respectively. Using the previous correlation, these distances calculated from  $^{207}\text{Pb}$  isotropic shifts are 0.273,

0.245, 0.231 nm. This is acceptable considering the simplicity of the proposed correlation and the large range of lead coordination.

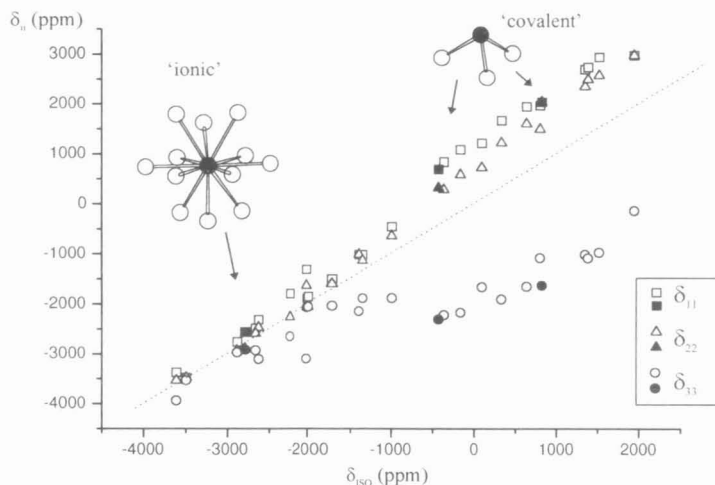


Figure 2 : Evolution of the principal components of the  $^{207}\text{Pb}$  CSA tensor vs the isotropic shift (filled symbols correspond to this study, open symbols to [5]).

Usually, empirical correlations between chemical shift anisotropy and structure are based on an average deviation of bond angles or bond lengths from that of a perfect polyhedron [8]. They yield poor result in the case of Pb. Figure 2 shows the evolution of the principal values of the CSA tensor versus the isotropic shift of  $\text{Pb}^{2+}$ . For the ionic compounds the principal values of the CSA tensor are of the same order of magnitude whereas, for the covalent Pb bonding state, a large splitting between  $\delta_{33}$  and  $\delta_{11} \approx \delta_{22}$  is observed. In the covalent compounds the lead atoms occupy the apex of a distorted pyramid and this splitting is interpreted as being due to the steric effect of the electronic lone pair of  $\text{Pb}^{2+}$  which prevent the existence of symmetric environment with short Pb-O bond lengths. This results in a close to axial symmetry shielding tensor where  $\delta_{33}$  is approximately along the lone pair ( $K \approx 1$ ).

Considering the case of covalent compounds only (lead oxides and lead silicates), the best linear empirical correlation between  $^{207}\text{Pb}$  isotropic shift and structure has been obtained by relating the bond angles to the degree of s-

hybridization of the oxygen orbital as it was previously proposed for  $^{29}\text{Si}$  chemical shift in silicates and aluminosilicates [9]. This second correlation shows the influence of both bond angles and second sphere neighboring atoms on the  $^{207}\text{Pb}$  chemical shift and should allow us to evidence the connectivity of the  $\text{PbO}_n$  pyramidal units. Such a correlation may be useful for the study of the Pb local ordering in lead silicates glasses.

Based on empirical equations between  $^{207}\text{Pb}$  chemical shift and structure, we have determined experimentally the primary influences on  $\text{Pb}^{2+}$  chemical shifts in inorganic solids. These correlations, established for simple crystalline compounds, should allow the use of  $^{207}\text{Pb}$  NMR as a structural probe for lead local environments in disordered materials of complex composition.

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