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Isotropic and anisotropic chemical shift in ^{207}Pb NMR of inorganic solids

F. Fayon[1,*], C. Bessada[1], D. Massiot[1], I. Farnan[2] and J.-P. Coutures[1]

[1] *Centre de Recherche sur la Physique des Hautes Températures, CNRS, 45071 Orléans cedex 2, France*
[2] *Department of Earth Science, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.*

* *Correspondence and reprints.*

RÉSUMÉ

Nous avons récemment développé des corrélations empiriques entre déplacement chimique de ^{207}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}Pb/déplacement chimique/corrélation

ABSTRACT

We have recently described empirical correlations between ^{207}Pb NMR chemical shift (oxidation state 2+) and structure in solids (Fayon et al.) that should allow the use of ^{207}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}Pb/chemical shift/correlation

For many spin ½ nuclei (like ^{13}C, ^{29}Si, ^{31}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}Pb (spin ½ 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}Pb NMR suffers some experimental difficulties that come from a wide ^{207}Pb chemical shift range [1-2]

(7000-8000 ppm) and strong chemical shift anisotropy [2,4,5]. In a recent work, using ^{207}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}Pb chemical shift tensors in lead aluminates and silicates. The experimental spectra of $PbAl_2O_4$, $PbAl_{12}O_{19}$ and $K_2Pb_2Si_2O_7$ 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]).

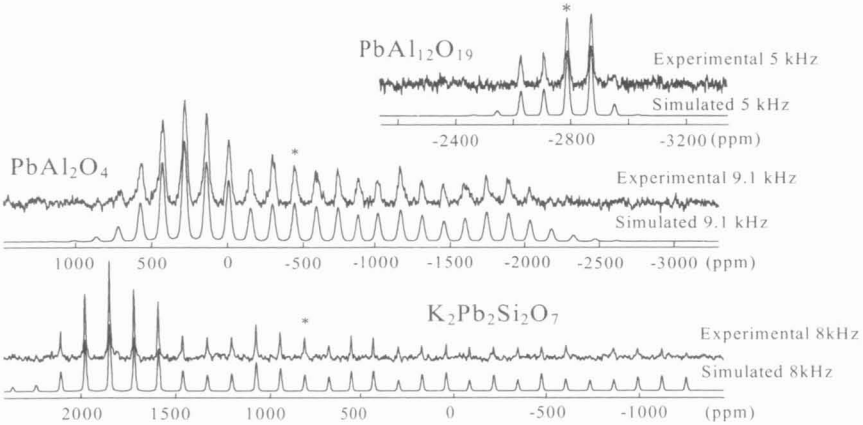

Figure 1 : Experimental MAS NMR spectra of $PbAl_{12}O_{19}$, $PbAl_2O_4$ and $K_2Pb_2Si_2O_7$, recorded on a Brucker DSX 300 spectrometer (operating at 62.6 MHz) using single pulse (π/9) acquisition (asterisk marks isotropic lines).

Table I : ^{207}Pb NMR chemical shifts for $PbAl_2O_4$, $PbAl_{12}O_{19}$ and $K_2Pb_2Si_2O_7$
(chemical shift referenced relative to $Pb(CH_3)_4$, the uncertainties are 7 ppm).

compound	δ_{ISO} (ppm)	Ω (ppm)	K	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
$PbAl_{12}O_{19}$	-2790.6	356.5	-0.87	-2560.6	-2894.1	-2917.1
$PbAl_2O_4$	-432.7	3000	0.75	692.3	317.3	-2307.7
$K_2Pb_2Si_2O_7$	816.2	3671.3	1	2040	2040	-1631.3

In these compounds, Pb^{2+} exhibits two very different local environments. The lead hexaaluminate possess a magnetoplumbite type structure, like $CaAl_{12}O_{19}$ or $SrAl_{12}O_{19}$, 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 $PbAl_2O_4$ and $K_2Pb_2Si_2O_7$, 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 $PbAl_2O_4$, the measured asymmetry parameter is related to the distortions of the PbO_3 pyramidal unit (K=0.75) whereas for $K_2Pb_2Si_2O_7$, 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 Pb^{2+} sites, we have established a linear correlation between ^{207}Pb chemical shift and mean Pb-O bond length [5] (δ_{ISO} = 20854-86689.5 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 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 $PbAl_{12}O_{19}$, $PbAl_2O_4$ and $K_2Pb_2Si_2O_7$ respectively. Using the previous correlation, these distances calculated from ^{207}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.

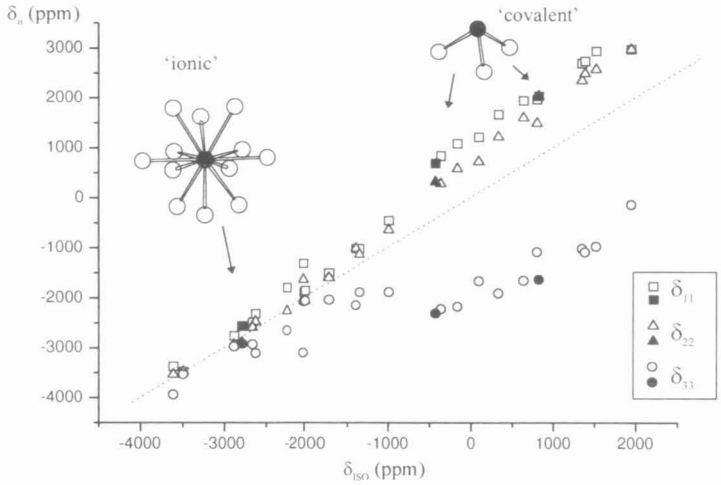

Figure 2 : Evolution of the principal components of the ^{207}Pb CSA tensor vs the isotropic shift (filled symbols correspond to this study, open symbols to [5]).

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

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