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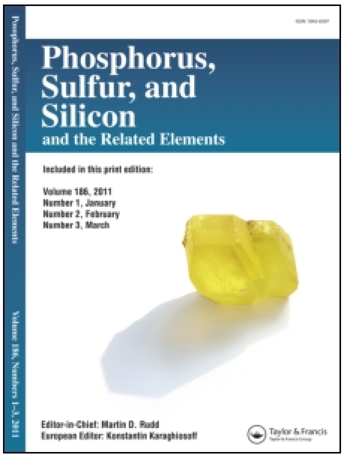

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High-Resolution Solid-State Nmr: a Versatile Tool for the Study of Al-O-P Clusters

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New Al-O-P clusters are presented. They are characterized by single-crystal X-ray diffraction (XRD) and solid-state NMR. High-resolution techniques such as magic angle spinning (MAS) and multiple quantum magic angle spinning (MQ-MAS) are used. The latest developments of high-resolution ^{1}H solid-state NMR, including very high field and very high speed MAS as well as homonuclear off-resonance Lee-Goldburg (LG) decoupling, are presented. All the experiments are described in the frame of a new pictorial representation of interactions involving quadrics and 4th degree cartesian surfaces.

Keywords: Al-O-P clusters; solid-state NMR; high-resolution; ^{1}H; multiple quantum NMR; pictorial representation

INTRODUCTION

The synthesis of new clusters which mimic SBU's of zeolites or microporous materials is now fully developed [1]. They are generally studied by XRD, vibrational spectroscopies, and NMR. The results obtained for well-defined molecular structures are then extended to the study of more complex compounds. Generally, multinuclear NMR is used as an analytical tool for solutions, after dissolution of the solid compounds (chemical shifts and J-couplings determination). Two dimensional experiments allow the precise determination of connectivity and act as an invaluable help for non ambiguous assignments. However, liquid-state NMR suffers from several drawbacks: i) dissolution of solid compounds may induce solvent effect and the solvent may also react with the clusters, leading to the deterioration of the compounds. ii) all data correspond to "averaged" data *i.e.* traces of second rank tensors. In other words, some information is "lost" when performing a simple liquid-state experiment. These drawbacks make the implementation of solid-state NMR techniques very promising.

Aluminophosphates were extensively studied by solid-state NMR experiments [2]. Recently, sophisticated techniques, including double rotation (DOR), CP, internuclear distances measurements by rotational echo double resonance (REDOR) were implemented, using $AlPO_4$ compounds as tests for the set-up of experiments [3]. To our knowledge, no solid-state NMR data related to Al-O-P clusters are available in the literature. In order to illustrate the specificity of solid-state NMR (versus liquid-sate NMR), we present a pictorial representation of anisotropy and

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of the methods used for high-resolution and multidimensional solid-state NMR.

Al-O-P CLUSTERS

We present two compounds characterized by single-crystal XRD (Figure 1). Syntheses differ in the precursor of phosphorus: H_3PO_4 (cubane shaped [4,5] cluster **1**, Fig.1a), $(C_6H_5)PO(OH)_2$ ("basket-like" cluster **2**, Fig.1b) [5]. In all cases, aluminum atoms are octahedrally coordinated to six oxygen atoms via Al-O-P oxo bonds (one Al-OH-Al hydroxo bond in **2**) and "Al-organic ligands" bonds. The octahedra deviate from perfect O_h symmetry. Phosphorus atoms are surrounded by four oxygen atoms, one of them being a hydroxyl group in **1**. Exact location of protons could not be determined by XRD.

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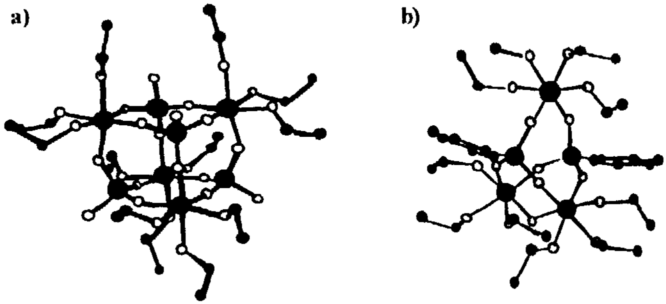

FIGURE 1: Al-O-P clusters. Red: P; blue: Al; green: O; black: C. See Color Plate I at the back of this issue.

ANISOTROPY AND HIGH-RESOLUTION SOLID-STATE NMR: A PICTORIAL APPROACH [6]

The major specificity of static solid-state NMR is related to the intrinsic anisotropy of magnetic interactions, which is not averaged by rapid molecular motion leading to broad featureless lines, and therefore not informative for chemists. Hopefully, all interactions relevant for solid-state can be described by second-rank tensors. These tensors are often used in physics, especially in the description of the physical properties of crystals. Considering a magnetic interaction T, a good representation of the anisotropy of T is given by the so-called "ellipsoid representation" (Figure 2a). Its equation in the principal axes system (PAS), centered at the nucleus, is given by:

$$T_{xx} X^2 + T_{yy} Y^2 + T_{zz} Z^2 = 1 \qquad (1)$$

In the PAS, r^{-2} is directly related to the shift of a given nucleus (the radius length r corresponds to the intersection of the ellipsoid by the B_o direction):

$$r^{-2} = (T_{xx} \cos^2\alpha_o + T_{yy} \sin^2\alpha_o) \sin^2\beta_o + T_{zz} \cos^2\beta_o \qquad (2)$$

Eq (1) is fully defined for $T_{ii} > 0$. We have shown recently [5] that every set of T_{ii} values (including $T_{ii} \leq 0$) can be represented by generalized quadrics including hyperboloids (Fig.2b) and degenerated cases.

All the first-order interactions involve the same trigonometric functions (i.e. second degree polynomials). This is very important for the understanding of macroscopic reorientation of samples (*vide infra*). When the perturbation hamiltonian H_T is comparable to the Zeeman hamiltonian H_Z, a second-order perturbation approach is required. The pictorial

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representation by generalized quadrics is not suitable as 4th degree trigonometric functions are involved. However, a general representation using 4th degree surfaces can be proposed [6] (Fig.2c).

Magic angle spinning can be easily understood by using averaged surfaces that account for the rapid macroscopic reorientation of samples. In the case of quadrics, the intersection of the averaged surfaces in the B_0 direction is *independent* on the crystallite orientation: it follows that the shift for all crystallites is unique and that high-resolution is attained. When considering averaged 4th degree surfaces, the intersection is now dependent on the crystallite orientation: the reorientation of samples around one single axis is not able to average completely second-order interactions. It was realized in the late 80's that a second degree of freedom was necessary for achieving the total suppression of second-order quadrupolar effects. These theoretical considerations led to a very elegant experiment MQ-MAS [7], involving multiple quantum transitions in a quadrupolar spin system (Fig.2d). This experiment correlates a highly-resolved dimension and a MAS dimension in a 2D map.

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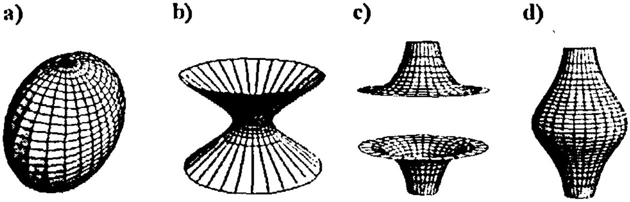

FIGURE 2: Pictorial representation of solid-state NMR.
a) ellipsoid; b) hyperboloid; c) second-order interaction;
d) MQ transition. See Color Plate II at the back of this issue.

^{1}H solid state NMR is a very difficult task, as the dominant interaction (^{1}H-^{1}H homonuclear interaction) is particularly strong (up to 50 kHz) and homogeneous in nature. MAS is effective only at very high rotation frequency (up to 35 kHz) and very high field (Figure 3). Homonuclear decoupling can also be achieved by off-resonance irradiation of protons (LG experiment). This pulse sequence is very efficient and promising for the study of H-H bonds in complex solids [8]. The LG experiment can be implemented using moderate rotation speed but remains very demanding.

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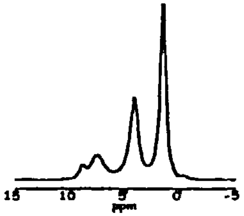

FIGURE 3: ^{1}H solid-state NMR spectrum of 1 (600 MHz and 35 kHz).

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