

SHAPE DEPENDENT INHOMOGENEOUS MAGNETIZATION OF HOMOGENEOUS SPECIMEN: CONSEQUENCES IN HR PMR IN SOLIDS

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Bulk susceptibility corrections are required to retrieve the intra molecular Shielding values both in liquid state and solid state PMR studies (single crystal specimen of organic molecules). In these considerations accounting for the contributions from within the hypothetical Lorentz sphere has not been always unambiguous. In liquids the rapid molecular motions compound the situation. But in solids, the molecules and atoms are held in fixed positions and, hence, for the evaluation of induced field contributions from within the sphere, it would be possible to devise a convenient discrete summation procedure with a point dipole model for the magnetic moment at every one of the neighboring molecules. Within the magnetized diamagnetic sample, while discussing the demagnetization effects, it is conventional to use a hypothetical Lorentz sphere, which is essentially a semi micro volume element (large compared to inter molecular distances and molecular sizes but small compared to the macroscopic size of the specimen). This has brought in a compulsion that for HR PMR in solids a spherical outer shape should be ensured. Since the macroscopic specimen and the **Inner Volume Element [IVE]** are both spheres, when the IVE is considered as a cavity, the field at the center of these concentric spheres is zero. The material within the IVE is effectively absent (a cavity) if the contributions from molecules within this IVE is calculated independently and taken into account finally. Similar argument can be applied for the case outer macroscopic ellipsoidal shape with an ellipsoidal IVE if the ellipticity factor is same for both ellipsoids and they are also confocal. Thus, if the outer macro shape and the inner shape are both ellipsoids and with same ellipticity, then the induced field within the inner element would be zero as much as for the spherically shaped sample specimen. Moreover the contribution from the neighboring molecules within the ellipsoidal IVE is the same as the spherical IVE¹. For shapes other than ellipsoidal, the magnetization would be inhomogeneous within the sample and hence calculating contributions at one point within the sample would not be enough. Thus it would be necessary to calculate the induced fields at every one of the points of interest independent of the other points. Even for shapes other than ellipsoidal, if the shape is describable as regular, then a Lorentz IVE can be carved out with the same shape and proportionate shape factors. Since the bulk susceptibility contribution is only shape dependent, it is simple enough to visualize around a given point (anywhere in the sample) an IVE which is carved out with similar shape. Even though concentric and confocal cases are mentioned above, the IVE can be around any of the points and the induced field at the center of the IVE would be zero for ellipsoidal shapes. The bulk susceptibility contribution is dependent only on shape of the volume element and not the size. Thus at a given point anywhere in the sample it is simple enough to carve out IVE of similar shape. For shapes other than ellipsoidal, the point of interest must be placed simultaneously to be within the IVE in such a way that the relative position coordinate of the point is the same; with respect to macroscopic specimen reference coordinate system, as well as coordinate system in IVE². This simple construction may not be much appreciable by describing it in such limited number of words. Hence it seems necessary to elaborate this point in the context of trying to reduce the stringent requirement of spherically shaped specimen for HR PMR in solids.

1. http://www.geocities.com/saravamudhan1944/eenc_ampere_lille.html
2. <http://nehuacin.tripod.com/id3.html>

Structural analysis on amorphous AIPO4 with high resolution heteronuclear correlation solid state NMR

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Extensive researches on aluminophosphate (AIPO₄) have been performed because of its industrial needs. While crystalline AIPO₄-based molecular sieves such as zeolites were investigated by many kinds of measurements, there are few structural analyses of amorphous AIPO₄ (*a*-AIPO₄). Solid-state NMR is capable of characterizing the structure of amorphous materials that is difficult by using diffraction methods. Previously, ²⁷Al MQMAS study indicated useful information of aluminum sites and distributions of *a*-AIPO₄[1]. Double resonance method gives clear information of heteronuclear correlation for materials. For example, ³¹P{²⁷Al}HETCOR spectrum of crystalline AIPO₄-14 easy to detect correlations between P-Al[2].

However, single nuclear analysis indicates only local structure, and one of heteronuclear correlation gives limited information on amorphous material. In the case of the structural analysis of amorphous material should be need the information on multi-nuclear and all of heteronuclear correlations.

In this research, we aim to structure analysis on *a*-AIPO₄. We prepared ¹⁷O-enriched *a*-AIPO₄ and carried out multi-nuclear and each heteronuclear correlations analysis by solid state NMR. As a result, all local structure and each correlation elucidate the 3D networks on *a*-AIPO₄ as indicated below.

1. ³¹P MAS, ¹⁷O MQMAS and ²⁷Al MQMAS; All spectra indicated multi-sites and distributions.
2. Mutual (³¹P ↔ ¹⁷O) CP MAS NMR; ¹⁷O{³¹P}CP MAS spectrum clearly showed that three different phosphorus environments correspond to Q₂, Q₃ and Q₄
3. ³¹P{²⁷Al} MAS-J-HMQC, and ³¹P{²⁷Al} 3QMAS/HETCOR: MAS-J-HMQC spectrum indicated *a*-AIPO₄ has all types of the ^{[4],[5],[6]}Al-O-P bonds. And 3QMAS/HETCOR indicated four P local environments exist.
4. ¹⁷O{²⁷Al}MQMAS/HETCOR;Detail discussion will be in poster session.

Various measurements of solid state NMR could realize multi-nuclear and all of heteronuclear correlation analysis on amorphous material.

- [1] H. Kraus Journal Physical Chemistry 100 (1996) 16336
[2] J.W. Wiench Solid State NMR 26(2004) 51