Massiot, Dominique : Materials by NMR of Quadrupoles from room to high temperature

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I came to Solid State Nuclear Magnetic Resonance incidentally in the late 80s, attracted by the increasing capacity of this spectroscopy to characterize the local structure in materials lacking from long range order. As a materials science chemist, trained in geology or geochemistry, my main concerns were silicate glasses and melts. This was the time of the mile stone work by G. Engelhardt[1], E. Lippmaa, A. Samoson[2], A. Grimmer and coworkers in Eastern Europe or of J.F. Stebbins in Berkeley and Stanford California. The former were able to evidence directly local coordination of silicon or aluminum from ^{29}Si or ^{27}Al MAS NMR in silicate and alumino-silicate glasses[3] while the later was showing that NMR spectroscopy was also able to analyze the structure and dynamics of high temperature molten materials[4]. High temperature was one of our main goals and J.P. Coutures had installed in Orleans an aerodynamic levitation device using a CO_2 laser as heating source. This device allowed to reach very high temperature (>2000°C), minimizing heterogeneous nucleation, and was also small enough to fit in a wide bore magnet NMR probe (Fig.1). With the help and guidance of F.Taulelle in Paris and D.Muller at Bruker in Germany, we were able to show that the concept of laser heating could be adapted to the acquisition of NMR spectra with a setup able to reach temperature up to ~1300°C in boron nitride crucibles and up to more than 2000°C in aerodynamic levitation conditions. The demonstration experiment[5], carried out in Paris at J.Livage's laboratory, made it possible to gather the necessary financial support and install a 300MHz MSL solid state NMR spectrometer in Orléans allowing our NMR expertise to develop.

From the first results obtained at high temperature it rapidly became clear that the motionally averaged picture of the high temperature molten state had to be complemented by an accurate description of the structure of materials at room temperature from the whole variety of observable nuclei, including quadrupolar nuclei like ^{27}Al. Aluminum spectra were easily observed at high temperature in the molten state[6,7] but much more complex for solids (static or magic angle spinning) because of the strong second order broadenings (Fig.2). Based on the work of Samoson[2] I adapted the fitting program that I developed for the analysis of Mossbauer spectra during my PhD to account for the specificity of high resolution MAS NMR : spinning sidebands, second order quadrupolar patterns… This was the beginning of the well known *dmfit* program[8] that has today a few thousand users worldwide.

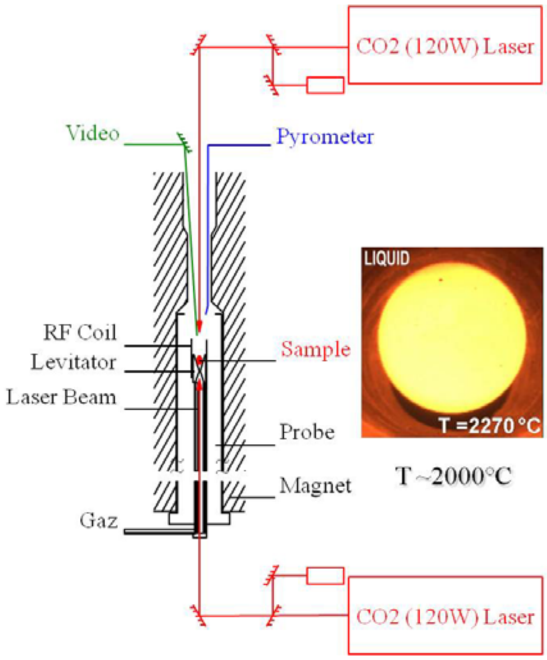

Figure 1 : High Temperature laser heating setup allowing heating up to ~2000°C under aerodynamic levitation[5,6,7].

My first contact with the NMR community took place at the X[th] ISMAR conference held in Morzine in 1989. At that time we were only acquiring 1D spectra and it was a shock to learn about multiple dimension experiments in liquids and solids involving dipolar recoupling, double orientation rotation (DOR[9]) or dynamic angle spinning (DAS[10])... Sometime later, in 1992, I had the opportunity to visit A.Pines' laboratory in Berkeley and met P.J. Grandinetti who was about to move to Ohio State University. Jointly with A. Llor we made plans for Phil to visit France with his DAS probe and this resulted in a long lasting and fruitful collaboration. Antoine and Phil were combining theoretical and practical skills of Berkeley and Saclay on quadrupolar nuclei and, from them, I understood how phase cycling could be used to select coherence pathways and that the central transition of the complex quadrupolar spin system could be manipulated as a fictitious I=1/2 spin… which still is the source of new developments. Thanks to this introduction we were ready when L.Frydman introduced MQMAS[11,12] in 1995 and among the first group to implement it, combining MQ excitation and central transition selective excitation[13]. I still have a very clear memory of the active discussions at the poster session of the Boston ENC in 1995 where L.Frydman first presented his experiment and the time spent to understand and explain triple quantum filtering.

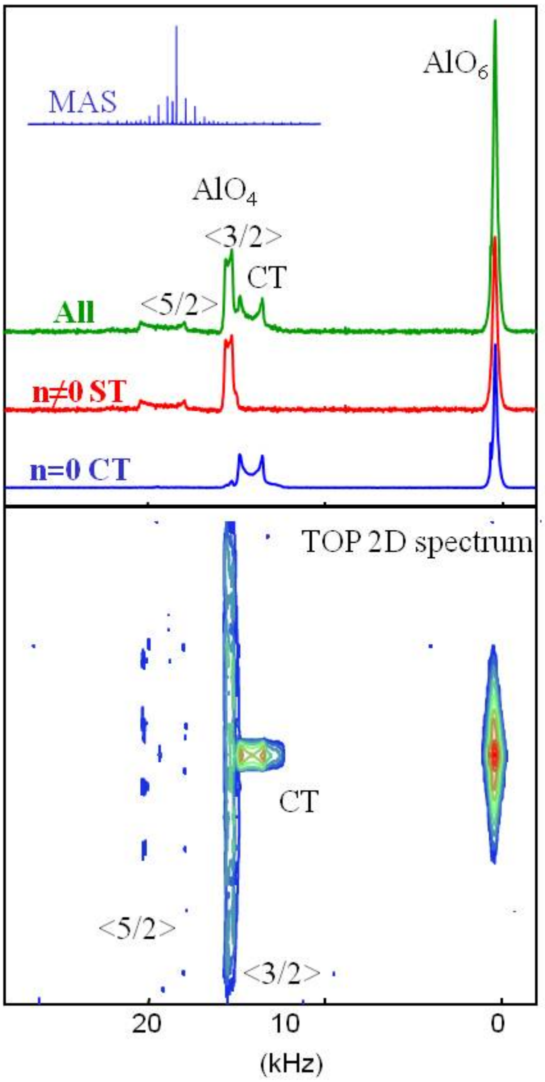

Figure 2 : 2D TOP processing[14] of the 750MHz 1D ^{27}Al MAS NMR spectrum of YAG ($Y_3Al_5O_{12}$) showing the complexity and the richness of quadrupolar MAS NMR spectroscopy (CT central transition, ST Satellite Transitions).

From these premises our activities developed around the description of new methods for application to quadrupolar nuclei and the study of inorganic or hybrid materials with numerous collaborations in France, Europe and worldwide. I would like specifically to acknowledge here the members of the Orleans group : C. Bessada, P. Florian, F. Fayon, B. Alonso, V. Montouillout, N. Pellerin, M. Deschamps, S. Cadars, A. Rakhmatullin, A.L. Rollet, the postdocs and the PhD students that made the group become what it is today with the constant support of J.P.Coutures, director of CRPHT and CRMHT. This was made possible with numerous collaborations involving F. Taulelle (Versailles France), F. Babonneau, C. Gervais, C. Sanchez and C. Bonhomme (Paris France), B. Bujoli & J.M. Bouler (Nantes France), J. Virlet & T. Charpentier (CEA Saclay France), D. Neuville & L. Cormier (Paris France), J.P. Amoureux (Lille France), T. Bastow (CSIRO, Australia), I. Farnan (Cambridge UK), R.K. Harris[15] (Durham UK), L. Emsley (Lyon France), Z. Gan (NHMFL Tallahassee Fl USA), T. Vosegaard (Aarhus Denmark)…

Among the various subject it is worth mentioning : the extension of PASS to the description of QPASS for quadrupolar nuclei[16], the access to very high field (40T!) with Z. Gan and A. Samoson[17], the development of J-coupling based approach for crystalline (with R.K. Harris[18]), or for non-crystalline (with L.Emsley[19]) phosphates, the study of alumino-silicate glasses of geological & industrial interest with D.Neuville & L.Cormier[20], the study of biocompatible materials with application to the treatment of Osteoporosis with B.Bujoli & J.M.Bouler[21], the study of sol/gel and hybrid materials with F.Babonneau, C.Sanchez, C.Gervais or C.Bonhomme at LCMCP Paris France[22,23,24,25]…

We are now at a time where Solid State NMR is a well established tool for the characterization of materials but still in the situation were new developments and applications rapidly emerge opening new avenues in terms of observation scale, characterization of through bond and through space connectivity[26], increased sensitivity, measurement on paramagnetic samples... This includes studying order and disorder in complex materials like glasses, energy related materials for battery or hydrogen storage, bioactive or biocompatible materials, zeolites and catalysts with number of pages still to be written and certainly more on subjects that we hardly imagine today.

Biographical Sketch

Dominique Massiot. *b* 1957. Ecole Normale Supérieure Paris 1977-84, Thèse de 3[ème] Cycle in Geochemistry 1983 (supervisor Pr. Michel Treuil) ; Chargé de Recherche CNRS CRPHT Orléans1984, Directeur de Recherche CRMHT Orléans 1996, Director of CEMHTI UPR3079 CNRS 2008- ; Director of TGIR RMN THC FR3050 2007- ; Silver Medal CNRS 2003 ; Approx. 215 publications, author of the *dmfit* program for the analysis of solid state NMR spectra. Current research specialty: multinuclear solid state NMR and application to inorganic and hybrid materials.

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