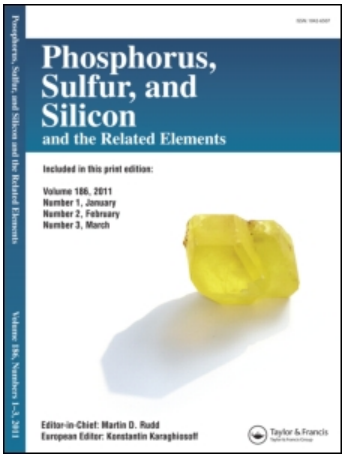

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SELENIUM AND TELLURIUM SOLID STATE NMR

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General aspects of solid state NMR applied to selenium and tellurium are discussed.

Keywords: NMR; solid; selenium; tellurium; MAS

INTRODUCTION

NMR parameters: δ, J, D are of a tensorial nature, which means that their values depend on the orientation of the molecule in the magnetic field[1, 2]. Each parameters are characterised by three principal values P_{xx}, P_{yy}, P_{zz} in three directions defined in the molecule.
More commonly, the following three parameters are used:
$P_{iso} = 1/3\ (P_{xx} + P_{yy} + P_{zz})$ (isotropy),
$\Delta P = P_{zz} - P_{iso}$ (anisotropy) and
$\eta = (P_{yy} - P_{xx})/\Delta P$ (asymmetry)

with the ordering $|P_{zz} - P_{iso}| \geq |P_{xx} - P_{iso}| \geq |P_{yy} - P_{iso}|$. New notations are proposed: P_{iso} as above, $\Omega = P_{zz} - P_{yy}$ (span) and $\kappa = 3(P_{xx} - P_{iso})/\Omega$ (skew) with $P_{zz} \geq P_{xx} \geq P_{yy}$.

DIFFERENT EXPERIMENTS IN THE SOLID STATE

Single crystals

In these cases the values of the principal components and the absolute orientation of the principal axis in the crystal are obtained, but this experiment requires large single crystals (several mm)[3].

Splittings arise from the sum of the direct D and indirect J coupling constants. D gives directly the precise distances between the two nuclei.

Powders

Most of solids are observed as powders. The observed broad spectrum is the superposition of all the spectra corresponding to all possible orientations of the microcrystals. From the spectral analysis of isolated diluted nuclei (low natural abundance such as ^{77}Se and ^{125}Te) we are able to obtain the three principal components of the shielding tensor but not its orientation - Figure 1a -

In highly symmetrical environment (octahedral, cubic, tetrahedral), narrow lines are observed[4]. This situation allows the determination of the splitting arising from the coupling constants D and J[4], or the study of the structure of alloys as in $TeCd_{1-x}Zn_x$ semiconductors[5].

In globular solids, the molecules rotate rapidly on themselves giving rise to narrow lines equivalent to the liquid state as for $Te(OMe)_6$[6].

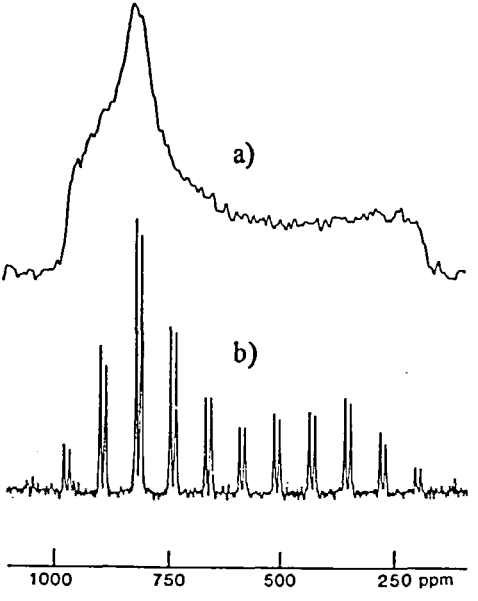

FIGURE 1 ^{77}Se NMR spectra of $(CH_3)_4C_6Se_4$, a) static, b) CPMAS (with permission of ref. 7).

Magic Angle Spinning: MAS

The effect of the chemical shift anisotropies or of the dipolar coupling constants D can be totally or partially suppressed when the powder is rotated at high speed (5 to 15 kHz) around an axis which is oriented at 54°44' with the magnetic field. Narrow lines are obtained and the result is similar to the liquid state but the tensorial nature of the parameters is lost.

If the spinning speed is smaller than the width of the interaction, spinning sidebands are observed (see Figure 1b) the analysis of which give the same informations as in static powders[7].

Cross Polarisation, CPMAS

As selenium and tellurium have a low receptivity, it is possible to increase the observed intensities using cross-polarisation experiments where the high magnetisation of essentially proton is transferred to

the observed nucleus. This interesting technique is not very efficient with Se and Te since there are very few compounds of these elements having protons directly bonded to them and the proton distances are so large that the transfer is very poor. Nevertheless decoupling can be applied to suppress the dispersion of the lines arising from D and J.

CONCLUSION

- Solid state NMR of Se and Te is an important source of informations very sensitive to small chemical or physical differences.
- This is a good complement to X ray. It is very usefull for disordered solids as glasses, polymers, amorphous materials.
- In solids, molecular motions are often frozen.
- CPMAS is the best technique
- The only problems are: long relaxation times and poor receptivities.

References

[1.] C. A. Fyfe, Solid state NMR for chemists, CFC Press: Guelph, Ontario, Canada, 1983.
[2.] E.U. Stejskal and J. D. Memory, High resolution NMR in the solid state (Oxford University Press, 1994).
[3.] A. Koma, Phys. Stat. Sol., **56b**, 665 (1973).
[4.] R. Balz, M. Haller, W. E. Hertler, O. Lutz, A. Nolle and R. Schafitel, J. Magn. Res., 40, 9 (1980).
[5.] K. Beshad, D. Zamir, P. Becla, P. A. Wolff and R. G. Griffin, Phys. Rev. B, **36**, 6420 (1987).
[6.] P. Granger and P. Laur, unpublished.
[7.] M. J. Collins, C. I. Ratcliffe and J. A. Ripmeester, J. Magn. Res., **68**, 172 (1986).