[15] J. Krause, A. E. F. Wächtler, B. S. Scheuble, G. Weber, *DE Pat.* 3734322.
[16] H. Adams, N. A. Bailey, D. W. Bruce, D. A. Dunmur, E. Lalinde, M. Marcos, C. Ridgeway, A. J. Smith, P. Styring, P. M. Maitlis, *Liq. Cryst. 2* (1987) 381, and lit. cited.
[17] R. Eidenschink, G. Haas, M. Römer, B. S. Scheuble, *Angew. Chem. Int. Ed. Engl. 23* (1984) 147; *Angew. Chem. 96* (1984) 151.
[18] W. Weißflog, D. Demus, *Cryst. Res. Technol. 19* (1984) 55.
[19] J. Malthete, L. Liébert, A. M. Levelut, Y. Galerne, *C.R. Acad. Sc. Paris, Ser. II 303* (1986) 1073.
[20] M. A. Cotter, Philos, *Trans. R. Soc. London A 309* (1983) 217, and lit. cited.
[21] E. Kleinpeter, H. Köhler, C. Tschierske, H. Zaschke, *J. Prakt. Chem. 330* (1988) 484.
[22] R. Eidenschink, *Kontakte 1* (1987) 15.
[23] B. Kohne, K. Praefcke, *Chimia 41* (1987) 196.
[24] G. Heppke, H. Kitzerow, F. Oestreicher, S. Quentel, A. Ranft, *Mol. Cryst. Liq. Cryst. Lett. 6* (1988) 71.
[25] C. Vaucher, A. Zann, P. LeBarny, J. C. Dubois, J. Billard, *Mol. Cryst. Liq. Cryst. 66* (1981) 103.
[26] K. Praefcke, B. Kohne, K. Gutbier, N. Johnen, D. Singer, *Liq. Cryst. 4* (1989) in print.
[27] N. A. Clark, S. T. Lagerwall, *Appl. Phys. Lett. 36* (1980) 899.
[28] J. W. Goodby, T. M. Leslie, *Mol. Cryst. Liq. Cryst. 110* (1984) 175.
[29] H. Zaschke, *J. Prakt. Chem. 317* (1975) 617.
[30] J. Bömelburg, G. Heppke, A. Ranft, *Z. Naturforsch. B*, in press.
[31] C. Escher, T. Geelhaar, E. Böhm, *Liq. Cryst. 3* (1988) 469.
[32] V. Reiffenrath, J. Krause, H. J. Plach, G. Weber, *Liq. Cryst. 5* (1989) 159.
[33] E. P. Janulis, J. C. Novack, G. A. Papapolymerou, M. Tristani-Kendra, W. A. Huffmann, *Ferroelectrics 85* (1988) 375.
[34] J. Bhatt, B. M. Fung, K. M. Nicholas, C. D. Poon, *J. Chem. Soc. Chem. Commun. 1988*, 1439.
[35] D. Demus, H. Zaschke: *Flüssigkristalle in Tabellen*, VEB Deutscher Verlag für die Grundstoffindustrie, Leipzig 1974, p. 34.
[36] R. Eidenschink, L. Pohl, *DE Pat.* 2918775.
[37] B. Kohne, K. Praefcke, T. Derz, H. Hoffmann, B. Schwandner, *Chimia 40* (1986) 171.
[38] Y. Matsunaga, M. Terada, *Mol. Cryst. Liq. Cryst. 141* (1986) 321.
[39] Y. Matsunaga, Y. Nakaysu, S. Sakai, M. Yanenaga, *Mol. Cryst. Liq. Cryst. 141* (1986) 327.
[40] E. Fischer, B. Helferich, *Liebigs Ann. Chem. 383* (1911) 68; C. R. Noller, W. C. Rockwell, *J. Am. Chem. Soc. 60* (1938) 2076.
[41] G. A. Jeffrey, *Acc. Chem. Res. 19* (1986) 168.
[42] A. Eckert, B. Kohne, K. Praefcke, *Z. Naturforsch. 43b* (1988) 878.
[43] K. Praefcke, A. M. Levelut, B. Kohne, A. Eckert, *Liq. Cryst.* in print.
[44] K. Praefcke, B. Kohne, P. Marquardt, P. Psaras, W. Stephan, A. Eckert, A. M. Levelut, *18. Freiburger Arbeitstagung Flüssigkristalle 1989*, paper 22, IAF, Freiburg.
[45] S. Diele, S. Geißler, H.-M . Vorbrodt, H. Zaschke, *Mol. Cryst. Liq. Cryst. Lett. 102* (1984) 181.
[46] C. Tschierske, H. Zaschke, *Tetrahedron Lett. 29* (1988) 5359.
[47] T. Shimasaki, S. Mizushima, S. Minezaki, K. Yano, M. Hijikigana, *Proc. Jpn. Disp.*, Tokyo, Sept. 1988, p. 78.
[48] J. L. Fergason, *WO Pat.* 83/01016.
[49] J. L. West, *Mol. Cryst. Liq. Cryst. 157* (1988) 427.
[50] I. C. Khoo, Y. R. Shen, *Opt. Eng. 24* (1985) 579.
[51] H. J. Eichler, R. Macdonald, unpublished.
[52] D. J. Williams in D. S. Chemla, J. Zyss (Eds.): *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1, Academic Press, New York (1987).
[53] G. G. Roberts, *Adv. Phys. 34* (1985) 475.
[54] H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem. Int. Ed. Engl. 27* (1988) 113; *Angew. Chem. 100* (1988) 117.
[55] R. G. Weiss, *Tetrahedron 44* (1988) 3413.
[56] V. Ramesh, M. M. Labes, *J. Am. Chem. Soc. 110* (1988) 738.
[57] R. Eidenschink, *Angew. Chem. Int. Ed. Engl. Adv. Mater. 27* (1988) 1579; *Angew. Chem. Adv. Mater. 100* (1988) 1639.
[58] A. G. Milaev, I. G. Gumenchuk, *Khim. Tekhnol. Topl. Masel* (1988) 18, *Chem. Abstr.* 110:117 926n.

Research News

High Resolution Solid State NMR of Quadrupolar Nuclei

By Bernhard Blümich*

Nuclear magnetic resonance spectroscopy is a standard technique used for the structural analysis of liquid and dissolved samples. The information about the molecular structure is contained in narrow resonance lines at various isotropic chemical shift values, which can be assigned to different segments of a molecule. In solids, however, the chemical shift information is hidden under overlapping wide lineshapes. As a result of the reduced molecular mobility in the solid state, a number of orientation dependent spin interactions such as the quadrupolar and the dipolar couplings and the anisotropy of the chemical shielding (chemical shift) dominate the resonance. For spin 1/2 nuclei, for instance ^{13}C, ^{29}Si and ^{31}P, there is no quadrupolar interaction, but even under dipolar decoupling from the protons, the NMR spectrum typically shows many overlapping chemical shielding powder patterns, each of which can be a few kilohertz wide. The standard approach to high resolution solid state spectra for spin 1/2 nuclei then is magic angle spinning (MAS). The sample is packed into a gas-driven turbine which is spun at a rotation frequency of 3 to 10 kHz with the rotation axis inclined against the magnetic field by the magic angle of $\Phi_m = 54.7°$. In this case liquid-like high resolution spectra are obtained, which at slow spinning rates exhibit side bands at integer multiples of the rotation frequency away from the isotropic chemical shifts.[1]

[*] Priv. Doz. Dr. B. Blümich
Max-Planck-Institut für Polymerforschung
P.O. Box 3148, D-6500 Mainz (FRG)

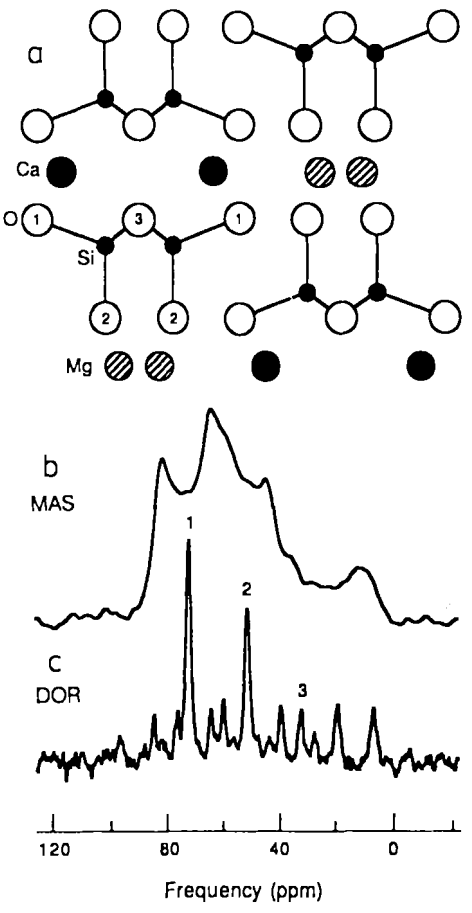

Fig. 1. a) Structure of diopside, $CaMgSi_2O_6$. Oxygen is represented by open circles with the three distinct sites labeled. b) MAS spectrum of ^{17}O in a sample of diopside. c) DOR spectrum with the outer rotor spinning at 680 Hz. (Adapted from ref. 4)

However, MAS is unable to fully remove the broadening of the central transition $(1/2 \leftrightarrow -1/2)$ of half-integer quadrupolar spins like ^{11}B, ^{17}O, ^{23}Na and ^{27}Al, because the linewidth is limited by second order quadrupolar broadening. Instead of just the second order Legendre polynomial, which determines the magic angle, the fourth order term also has to be eliminated.[2] This requires sample spinning around two axes, one at $\Phi_1 = 37.38°$ and the other at $\Phi_2 = 79.19°$. At first sight this seems impossible, but it can be done either in a 2D experiment with successive rotation around both axes involving flipping of the spinning axis (dynamic angle spinning: DAS) or by simultaneous rotation around both axes (double rotation: DOR).[3-5] Both experiments have recently been realized. A DAS probe is already available commercially with a flipping time of less than 40 ms.[6] However, the T_1 relaxation time must be longer than the flipping time for the experiment to work. The DOR experiment works with an ingeneously constructed rotor assembly, where a small rotor is embedded in a large rotor, each of the rotors spinning at one of the two angles Φ_1 and Φ_2.[3]

Figure 1 gives an example with the ^{17}O resonance of a powder of crystalline diopside.[4] The sample contains three distinct oxygen sites (a), which give rise to overlapping MAS powder patterns (b). With the DOR technique the wide line spectrum is broken down into narrow sideband resonances (c), where the isotropic centerband peaks can be assigned to the numbered oxygen sites. The linewidths are of the order of 100 Hz. This technique opens up a whole new area of NMR spectroscopy, where *high resolution spectra* can now be obtained for many nuclei of interest in ceramics, catalysis, geophysics and high temperature superconductivity.

[1] C. S. Yannoni, *Acc. Chem. Res. 15* (1982) 201.
[2] A. Llor, J. Virlet, *Chem. Phys. Lett. 152* (1988) 248.
[3] A. Samoson, E. Lippmaa, A. Pines, *Mol. Phys. 65* (1988) 1013.
[4] B. F. Chmelka, K. T. Mueller, A. Pines, J. Stebbins, Y. Wu, J. W. Zwanziger, *Nature 339* (1989) 42.
[5] K. T. Mueller, B. Q. Sun, G. C. Chingas, J. W. Zwanziger, T. Terao, A. Pines. *J. Magn. Reson.* (1989) in press.
[6] Doty Scientific, Inc., 600 Clemson Road, Columbia, S. C. 29223, USA.