³¹P MAS-NMR STUDY OF THE LAYERED FERRIELECTRIC CuInP₂S₆

X. BOURDON ¹, A.-R. GRIMMER ² and V. B. CAJIPE ³

¹ 2. Physikalisches Institut, Universität Stuttgart
Pfaffenwaldring 57
D-70569 Stuttgart, Germany

² Humboldt-Universität zu Berlin
Rudower Chaussee 5, Haus 3.51
D-12489 Berlin, Germany

³ Institut des Matériaux Jean Rouxel,
2, rue de la Houssinière
B.P. 32229, 44322 Nantes Cedex 3, France

Abstract The order-disorder ferrielectric-paraelectric transition in lamellar CuInP₂S₆ is studied using ³¹P solid-state MAS-NMR spectroscopy in the temperature range 255<T<355K. Two center bands are observed at the lowest measured temperature while only one is detected at the highest temperature. The former two represent the inequivalent positions for the P atoms in the ferrielectric phase. The latter corresponds to the appearance of a twofold axis through the P-P bond as the Cu^I ions undergo double-well hopping motions in the paraelectric phase. At intermediate temperatures both ferrielectric and paraelectric type resonances contribute to the spectrum at ratios which are T-dependent, indicating a transition temperature T_c= 312±1K (310±1K) for a warming (cooling) cycle. The temperature range for the coexistence is unusually wide (>70K). The presence of the ferrielectric type resonance in the paraelectric regime may be ascribed to the nucleation of polar order, while the persistence of the paraelectric signal below T_c implies residual hopping motions.

INTRODUCTION

The defining characteristic of a ferroelectric system is the existence of a reversible spontaneous electric polarization. This property is determined by the crystal symmetry and is macroscopic. Apart from bulk level changes that occur during a ferroelectric-paraelectric transition, modifications in the local environment of constituent atoms may be monitored to characterize the loss of polarity. Diffraction measurements yield such information but may be insufficient in detecting very small displacements and distinguishing between static and dynamic positional disorder. Resonance techniques provide the required sensitivity to internal field changes as well as a different time scale. A case in point is the order-disorder transition which occurs below 315(5)K in lamellar CuInP₂S₆ ¹⁻⁵. Solid-state NMR spectroscopy is a particularly suitable method

for studying the structural subtleties and dynamics of this phase transformation because of the presence of the nuclei ^{31}P , $^{63,65}\text{Cu}$ and ^{113}In in this material.

Electric dipole ordering in CuInP_2S_6 has been shown to be *ferrielectric*, i.e., the spontaneous polarization $P_s \approx 3 \mu\text{C}\cdot\text{cm}^{-2}$ which appears along the normal to the layer is generated mainly by polar Cu^{I} and In^{III} sublattices shifted in antiparallel directions relative to the midplane ². Fig. 1 displays a representation of the CuInP_2S_6 ferrielectric structure (monoclinic space group Cc): the metal cations and P-P pairs occupy octahedral cages defined by framework formed by the S atoms. The cation off-centering, 1.6 Å upward for Cu^{I} and 0.2 Å downward for In^{III} , is attributable to a second-order Jahn-Teller instability associated with the d^{10} electronic configuration ⁶. The antiparallel cation displacements are presumably imposed by energy minimization conditions consistent with long-range electric dipole ordering in a lamellar matrix. A weak downward shift for the P-P pair (of the order of 0.01 Å) has also been observed below 315K as the ethane-like P_2S_6 groups deform to accommodate the Cu^{I} and In^{III} off-centering. According to single-crystal x-ray diffraction results ², the copper sublattice becomes completely polar only well below the transition. Indeed, evidence has been found at $240 < T < 315\text{K}$ for copper occupation of a lower off-center site, or diffuse electronic densities thereabout, as well as residual densities around the central region. Fig. 2 reproduces a picture from ref. 2 which summarizes the thermal variation of the copper site occupancies and the corresponding probability density contours in the 153-353K range. In the paraelectric phase (space group $C2/c$), the crystallographic model requires the use of three types of partially filled copper sites with large thermal factors: an off-center and quasi-trigonal Cu1, an almost central or octahedral Cu2, and a third nearly tetrahedral Cu3 in the interlayer space. The Cu^{I} probability density then assumes a shape that is twofold symmetric about the center of the octahedral CuS_6 group, and extends along the layer normal and into the interlamellar space. Simultaneously, the In^{III} position and midpoint of the P-P bond move into the layer midplane. The contour plots for the copper probability density exhibit maxima only around Cu1 and Cu3 type sites. This is consistent with a dynamic interpretation of the disorder which has been corroborated by Raman spectroscopy ³, inelastic neutron scattering ⁴ and dielectric measurement ⁵ data. In other words, at $T > 315\text{K}$, the Cu^{I} ions hop between the minima of a double-well potential (Cu1), and between one such minimum and an interlayer site (Cu3). Ordering thus occurs via a cooperative freezing of inter-site motions which breaks the twofold symmetry and locks in a net polarization. This phase transition has

been shown to be first order^{1-3,5}. At $T \gg T_C$, ion migration through the lattice has also been detected^{5,7}.

FIGURE 1. Top left: A sulfur octahedral cage showing the various types of copper sites: the off-center Cu1, the almost central Cu2 and the Cu3 in the interlayer space. Two off-center sites become inequivalent when unequally occupied. Top right: The ethane-like P_2S_6 group. Bottom: Perspective view of two layers of $CuInP_2S_6$ shown in the ferrielectric phase (space group Cc , $T < 315K$). The framework is formed by the S atoms. The up (down) shifted Cu^I (In^{III}) ions are represented by the larger black (white) circles in the octahedra; the smaller white circles are the P. A projection onto the plane of a layer would reveal triangular arrays of Cu^I , In^{III} and $(P_2S_6)^{4-}$ ions (not shown; see ref. 2). The monoclinic cell parameters at room temperature are $a = 6.0956(4)\text{\AA}$, $b = 10.5645\text{\AA}$, $c = 13.6230(9)\text{\AA}$ and $\beta = 107.101(3)^\circ$.

FIGURE 2. Thermal evolution of the different copper site occupancies and the corresponding probability density contours in $CuInP_2S_6$ (see ref. 2). Sites Cu1, Cu2, Cu3 are disposed along the layer normal. The crosses mark the refined positions, and the dashed lines indicate the upper and lower sulfur planes of a single layer. Occupancies not adding up to 100% indicate the presence of diffuse electronic densities between the off-center sites and/or in the interlayer space. The contours are given in $\text{\AA}^3$, the values for the lowest and highest displayed temperatures being: 153K, 25-75 (50), 75-775 (100) and 775-2775 (1000); and 353K, 40-100 (30), 100-800 (100) and 800-5800 (1000), where the intervals are inscribed in parentheses.

In this paper, we present a ^{31}P solid-state MAS NMR spectroscopy study of CuInP_2S_6 . While the ^{31}P nuclei do not play a key role in the phase transition, they are good indicators of the symmetry-breaking process because the twofold axis of the paraelectric structure runs through the midpoints of the P-P pairs. Specifically, a pronounced inequivalence of the upper and lower nucleus of a pair is expected as a consequence of antiparallel distortions caused by opposite Cu^{I} and In^{III} displacements. Our approach here is to follow the thermal evolution of the relative contributions, chemical shifts and linewidths of the resonances in the phosphorus NMR spectrum. To guarantee correct temperature readings, the probe was pre-calibrated for sample heating or cooling due to magic angle spinning⁸. A qualitative discussion of the dynamics in this system is also given based on the spectral features.

EXPERIMENTAL SECTION

CuInP_2S_6 was synthesized by high temperature reaction of the elements in an evacuated tube as previously described^{1,2}. The product was ground to prepare the powder samples; grain sizes were in the $\leq 50\text{ }\mu\text{m}$ range. ^{31}P MAS NMR spectra were recorded on a MSL 400 spectrometer operating at $\nu_0=161.9\text{ MHz}$ and using a standard Bruker MAS probe with a double-bearing rotation system. The spinning rate was stabilized to $\pm 3\text{ Hz}$ using a Bruker pneumatic unit. Samples were loaded into zirconia rotors 4mm in diameter and with KelF caps. Preliminary ^{31}P MAS NMR measurements on CuInP_2S_6 at room temperature revealed a significant and reversible dependence of the spectral features on the spinning rate: two resonances at 3-5kHz, one at 15kHz and a combination of all three at intermediate rates. This observation was attributed to frictional sample heating. To quantify this effect, an empirical expression for the sample temperature T_s was determined in a separate set of experiments using $\text{Sm}_2\text{Sn}_2\text{O}_7$ as a chemical shift thermometer:

$$T_s = 0.12\nu_r^2 + (3.47 - 0.013T_b)\nu_r + 0.80T_b + 58.6, \quad (1)$$

where $T_b(\text{K})$ is the bearing gas temperature and $\nu_r\text{ (kHz)}$ is the spinning rate⁸. For example, spinning to 16kHz raises nominal room temperature to 321K. Spectra were subsequently recorded upon warming between $T_b=223$ and 353K ($T_s=254.7$ and 341.8K) at a MAS rate of 10kHz to obtain maximal resolution and eliminate magnetic dipolar and chemical shift anisotropy effects. Measurements were also made in a cooling cycle with $298 < T_b < 353\text{K}$. Difficulties associated with maintaining a high spinning rate while cooling precluded extending the measurements to lower

temperatures. The limited cooling range however covers the temperatures of interest. As in the temperature calibration experiments, the bearing gas was cooled or heated while the driving gas was maintained at ambient temperature. The bearing gas pressure was adjusted to 3 bars and the temperature controlled by the Bruker VT unit using the probe head thermocouple. ^{31}P chemical shifts were referenced to the signal for H_3PO_4 and measured to a precision of $\pm 0.06\text{ppm}$. The room temperature was stabilized to $\pm 0.2\text{K}$ to suppress measurable fluctuations in the chemical shift. After each temperature change, the sample was allowed to equilibrate for 10min before starting the next measurement. Other typical parameters used in the single pulse experiments were: a 90° pulse length of $2\mu\text{s}$, a 60s relaxation delay, a number of scans equal to 8 and a spectrum width of 32.5 kHz. Data analysis was carried out using the commercial programs WINNMR and WINFIT. Deconvolution employed lineshapes of mixed Lorentzian-Gaussian character.

RESULTS AND DISCUSSION

An overview of our variable temperature ^{31}P NMR results is given by the center bands shown in Fig. 3, recorded during a warming cycle. These central features contain the essential information since less than 5% of the integrated intensity of each complete spectrum is accounted for by the side bands; also, the chemical shift anisotropy and magnetic dipole coupling were noted to be identical for the various resonances observed. The temperature indicated for each spectrum in Fig. 3 was evaluated from the bearing gas temperature using equation (1) with a spinning rate $\nu_r=10\text{kHz}$. The thermal evolution of the resonances found here agrees with the observation of spectral changes induced by frictional heating. At temperatures far below the transition, the spectrum exhibits two center bands with an approximate 1:1 intensity ratio; well above T_c , only one band appears. Identification of these peaks is straightforward. The two lines observed at $T_b=223\text{K}$ ($T_s=254.7\text{K}$) correspond to the two inequivalent positions for phosphorus in the ferroelectric phase; the lower and higher frequency signals shall here be referred to as the A and B resonances, respectively. The one line at $T_b=353\text{K}$ ($T_s=341.8\text{K}$), designated C, corresponds to the single crystallographic P site of the paraelectric phase. Within a fairly wide thermal range enclosing T_c , both the low and high-temperature type resonances contribute to the spectrum at ratios that are T-dependent. Very similar thermal variations were found in the data recorded in a cooling cycle.

FIGURE 3. ^{31}P MAS-NMR spectra recorded from CuInP_2S_6 at bearing temperature $T_b = 223, 273, 298, 304, 308, 310, 316$ and 353K . The corresponding sample temperatures T_s are also indicated.

The observation of only one line at the highest temperature is consistent with a dynamic character for the copper disorder in the paraelectric phase. Given that the Cu^{I} ions occupy sites that are off the layer midplane at all temperatures, the single line implies that the P nuclei within a P_2S_6 group become indistinguishable because the neighbouring copper ions undergo rapid motions within a twofold-symmetric potential. These copper motions may be said to result in an effective exchange process between the paired ^{31}P nuclei which occurs at a rate determined by the separation in Hz of the two signals A and B, here estimated to be about 3846 Hz at $T_s = 254.7\text{K}$ for the observing frequency ν_0 ^{9a,10}. The chemical shift of the line at high temperature (92.37 ppm at $T_s = 341.8\text{K}$) does not coincide with the mean position of the two signals observed at low temperature (91.08 ppm at $T_s = 254.7\text{K}$). This signifies that the phosphorus environment in the paraelectric phase is not a simple motional average of that for $T < T_c$. Such is consistent with the off-centering of the P-P centroid in the ferroelectric phase². The superposition of signals characteristic of the ferri- and

paraelectric phases at intermediate temperatures agrees with the transition being first-order, i.e., the occurrence of phase coexistence.

A more quantitative description of the above findings may be obtained by performing an iterative deconvolution analysis into Lorentzian-Gaussian peaks of the complete data set. These deconvolutions were complicated by the temperature dependence of the chemical shifts as well as the asymmetry of the resonances characteristic of the ferroelectric phase. The intensity distribution of the low-T spectrum exhibits the "roof effect" typical of a second-order spectrum, specifically that of an AB spin system^{9b} rarely observed in solid-state materials¹¹. Application of resolution enhancement techniques reveals a clear splitting of the two signals into A₁-A₂ and B₁-B₂ doublets. Careful adjustment of the spectral lineshape parameters yielded a P-P coupling constant J= 130Hz for T_s= 254.7K. The value of J was assumed to be constant within the investigated temperature region; the known weak T-dependence of the P-P bond length² and the quality of the fits thus obtained prove this is a reasonable assumption. For a given T, the same linewidth for the components of a doublet was used. On the other hand, the widths of the two doublets were found to be very different. Equal intensity contributions were assumed for resonances A and B. The relative intensities within a doublet were constrained as normally expected for an AB system such that

$$I_{A1}/I_{A2} = I_{B1}/I_{B2} = (1 + \sin 2\theta) / (1 - \sin 2\theta),$$

where $\sin 2\theta = J[(\nu_0 \cdot \delta)^2 + J^2]^{1/2}$, and $\delta = |(\delta_{A1} + \delta_{A2})/2| - |(\delta_{B1} + \delta_{B2})/2|$, the subscripted δ 's being the chemical shifts determined for each peak. As T_c is approached from below, the doublets are no longer resolved. In the paraelectric regime, the single band C is representative of an A2 type system.

Based on the intensities calculated in the deconvolution, the percentage contributions of the A+B and C resonances to the total spectrum may be plotted versus temperature as displayed in Fig. 4. The derivative of the percentage C contribution with respect to T attains a maximum at 312±1K (310±1K) for the warming (cooling) curve. This agrees well with the T_c and thermal hysteresis determined by dielectric measurements and calorimetry¹. The shape of the more complete A+B curve of the warming cycle also closely matches that of the spontaneous polarization P_s(T) calculated from crystallographic results². Importantly, Fig. 4 shows that the C resonance is detectable down to T_s= 261.4K and the A+B bands up to 328.4K. This is a remarkably wide temperature range for "phase coexistence" which merits further discussion (see below).

FIGURE 4. Percentage contributions of the A+B and C resonances to the total spectrum calculated from the respective integrated intensities as a function of temperature for the warming (top) and cooling cycles (bottom). The insets show the derivative of the percentage C contribution and indicate the T_c deduced from the maximum.

More detailed information is uncovered by plotting the chemical shifts of the various resonances as a function of temperature (Fig. 5, warming cycle only). The asymmetric disposition of the A and B resonances with respect to C is made very clear here. All three curves exhibit an inflection point around 312K (310K) for the warming (cooling) cycle, as confirmed by evaluating the derivatives. An appreciable T -dependence is observed for the chemical shift of A even below T_c , while that for B appears to be constant at $254.7 < T_s < 288.2$ K. A reasonable interpretation of these results may be given by assigning resonance A (B) to the lower (upper) phosphorus of the pair. P_B would be in the vicinity of the upshifted Cu^{I} (upper CuI site), while P_A would be close to the downshifted In^{III} and the lower CuI site which may have a non-zero

occupancy below T_c . According to the known ferroelectric structure, the P_B -S bonds are longer than the P_A -S. This is consistent with the assumed assignment since the shielding for P_A may then be said to be stronger than for P_B , so that the P_A resonance frequency is lower. Crystallographic results have also shown that the In^{III} displacement increases while the occupation of the lower Cu1 site decreases with cooling below T_c . Fig. 5 implies that thermal modifications in the surroundings of P_A accompanying such changes are more pronounced than those generated around P_B as the upper Cu1 site occupancy approaches 100%. While geometric differences between the upper and lower PS_3 pyramids are clearly evidenced by x-ray diffraction, the temperature behaviour of the bond lengths and angles of the P_2S_6 group is rather subtle and barely detected using this technique^{2,3}. The curves of Fig. 5 thus illustrate the greater sensitivity of NMR to such fine, local changes (lengths $<0.001\text{\AA}$; angles $<0.5^\circ$)¹².

FIGURE 5. Thermal evolution of the chemical shifts for the various resonances (warming cycle). The positions of the A and B doublet components are given when resolved ($T < T_c$); the mean position of A and B as a function of T is indicated by the dashed curve.

As mentioned earlier, the A and B resonances also differ in their linewidths. The A_1 - A_2 is narrower than the B_1 - B_2 doublet at the lowest measured temperature (194 versus 227 Hz at 255K). Both broaden as T increases, the former at faster rate so that it is wider than the latter at T_c (356 versus 291 Hz). This is visible in the temperature dependence of the relative peak amplitudes (Fig. 3), following the conservation of the 1:1 intensity ratio for A and B. The difference in width may be due to distinct coupling effects between each type of P nucleus and a neighboring quadrupolar nuclear moment.

Coupling between phosphorus and spin 3/2 copper nuclei is likely given the natural abundances of ^{63}Cu (69.1%) and ^{65}Cu (30.9%) and their relative receptivities (6.45×10^{-2} and 3.55×10^{-2} , respectively¹³). ^{113}In is much less abundant (4.3%) and has a 1.50×10^{-2} relative receptivity. However, ^{31}P NMR broadening due to coupling with this spin 9/2 nucleus has been observed in static spectra of $\text{In}_{4/3}\text{P}_2\text{S}_6$ ¹⁴ and is conceivably present in CuInP_2S_6 as well. The peak broadening occurs as the A and B chemical shifts approach that of C, thus leading to the non-resolution of the doublets at higher temperatures. These effects may be related with the growing percentage of signal C measured between 290K and T_c (Fig. 4).

The simultaneous presence of A+B and C resonances within a wide temperature range is also made plain by Fig. 5. Given the inflection in all of the curves around 312K, it may be said that the environment for each type of resonating nucleus in the paraelectric regime is distinct from that in the ferroelectric regime. The T-dependence of the chemical shifts for A and B is much weaker and more similar for the two branches above T_c than below. The difference between the T-behaviour of the chemical shift for C in the two regimes is less clear. On the other hand, the linewidth of resonance C which was satisfactorily modeled by a large, constant value (615 Hz) for $T < T_c$ is observed to decrease when warming above T_c . The Lorentzian-to-Gaussian character ratio of the lineshape also decreases at $T > T_c$ (e.g. 0.3 at 261K and 0.0 at 324K). This line-narrowing may be attributed to thermally enhanced motions. It suggests that the attainment of full narrowing requires heating above 342K, which would be consistent with the known occurrence of ionic conductivity at such temperatures^{5,7}. The copper hopping frequency may be said to determine the C resonance width: interpreted within a cooling cycle, its T-dependence in the paraelectric regime may be related to the slowing down of these motions which triggers the first-order transition. Indeed, the derivative of the linewidth with respect to temperature drops within a 10K interval around T_c , the uncertainty being due to less accurate modeling of the width at $T < T_c$. Copper motions that remain active below T_c thus conceivably occur at frequencies lower than in the paraelectric phase.

The 70K wide temperature range for the coexistence of the A+B and C resonances lies mostly within the ferroelectric regime. The presence of A+B in the paraelectric regime may be ascribed to nucleation, i.e., the appearance of small polar regions within a crystallite as the copper hopping motions slow down and become correlated. This implies the existence of some kind of short-range order at $T > T_c$ that has yet to be detected using diffraction methods. The persistence of C at 260K implies that copper hopping motions occur down to that temperature. Long-range polar order in

CuInP₂S₆ may then be envisioned as nucleating in the central areas of the innermost layers and extending to the crystallite surfaces with cooling. Upon reaching T_c, twofold symmetry is broken in the bulk but residual motions remain in the peripheral regions. The minority occupation of the lower Cu^I site within the ferrielectric regime evidenced by diffraction (Fig. 2) was previously interpreted in terms of occasional motions of the up-shifted copper ion into a shallower, down-shifted potential minimum, or of reversely polar domains in the crystal². The present NMR data indicate that this observation may be accounted for by residual copper hopping in the superficial, non-polar regions of a crystal. Such an effect may be expected to become less visible with increasing grain size, i.e., the contribution of resonance C to the spectral intensity at T < T_c would be smaller for a large single crystal than for a fine powder sample.

SUMMARY

The order-disorder ferrielectric-paraelectric transition in lamellar CuInP₂S₆ was studied using ³¹P solid-state MAS-NMR spectroscopy. Spectra from a powder sample were recorded at various temperatures between 255 and 355K with a probe pre-calibrated for heating or cooling due to magic angle spinning. Two center bands are observed at the lowest measured temperature while only one is detected at the highest temperature. The former two represent the inequivalent positions for the P atoms of the P₂S₆ group which reflect the antiparallel displacements of the polar Cu^I and In^{III} sublattices in the ferrielectric phase. The latter corresponds to the appearance of a twofold axis through the P-P bond as the Cu^I ions undergo double-well hopping motions and the In^{III} occupy on-center sites in the paraelectric phase. At intermediate temperatures both ferrielectric and paraelectric type resonances contribute to the spectrum at ratios which are T-dependent, indicating a transition temperature T_c = 312 ± 1K (310 ± 1K) for a warming (cooling) cycle. The chemical shifts of the center bands characteristic of the ferrielectric phase are asymmetrically disposed with respect to that of the paraelectric type signal and exhibit distinct thermal variations; the linewidths likewise evolve differently with temperature. Line-narrowing attributable to thermally enhanced motions is observed for the paraelectric type resonance upon warming across the transition. The temperature range for the coexistence of the center bands representative of the two phases is unusually wide (>70K), lying mostly below T_c. The presence of the ferrielectric type resonance in the paraelectric regime may be ascribed to the nucleation of polar order, while the persistence of the paraelectric signal well below T_c implies residual hopping motions occurring in the ferrielectric regime.

ACKNOWLEDGMENTS

We are grateful to A. Kretschmer for technical assistance. V.B.C. and X.B. acknowledge helpful discussions with C. Payen and partial support from the European Commission via contract no. IC15-CT97-0712.

REFERENCES

1. a) A. Simon, J. Ravez, V. Maisonneuve, C. Payen and V. B. Cajipe, Chem. Mater., **6**, 1575 (1994). b) V. Maisonneuve, M. Evain, C. Payen, V. B. Cajipe and P. Molinié, J. Alloys and Compounds, **218**, 157 (1995).
2. V. Maisonneuve, V. B. Cajipe, A. Simon, R. von der Muhll, J. Ravez, Phys. Rev. B, **56**, 10860 (1997).
3. Yu. M. Vysochanskii, V. A. Stephanovich, A. A. Molnar, V. B. Cajipe and X. Bourdon, Phys. Rev. B, **58**, 9119 (1998).
4. V. B. Cajipe, C. Payen, X. Bourdon, H. Mutka, H. Schober, B. Frick, ILL Exper. Report 4-02-295 (1996).
5. Yu. M. Vysochanskii, A. A. Molnar, V. A. Stephanovich, V. B. Cajipe and X. Bourdon, In press, Ferroelectrics (1998).
6. a) J. K. Burdett, *Chemical Bonding in Solids*, Oxford University Press: Oxford, 1995; p. 24 and p. 246. b) J. K. Burdett, O. Eisenstein, Inorg. Chem., **31**, 1758 (1992). c) S. H. Wei, S. B. Zhang, A. Zunger, Phys. Rev. Lett., **70**, 1639 (1993).
7. V. Maisonneuve, J. M. Réau, M. Dong, V. B. Cajipe, C. Payen, J. Ravez, Ferroelectrics, **196**, 257 (1997).
8. A. R. Grimmer, A. Kretschmer, V. B. Cajipe, Magn. Reson. Chem., **35**, 86 (1997).
9. H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, VCH Publishers: New York, 1991, a) p. 269, where the rate constant is given by $2.22 \Delta\nu$; b) p. 102.
10. A. Abragam, *Principles of Nuclear Magnetism*, Oxford University Press: Oxford, 1961; p.425.
11. K. Eichelle, G. Wu, R. E. Wasylshen, J. F. Britten, Journal of Physical Chemistry, **99**, 1030 (1995).
12. A. R. Grimmer, Mol. Phys., **60**, 151 (1987).
13. R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, John Wiley and Sons: New York, 1986, p. 238.
14. X. Bourdon, A. R. Grimmer, V. B. Cajipe, unpublished results.