Molecular Motion in Solid Tetrabutylammonium Tetrafluoroborate

B. Szafrańska, Z. Pająk, and A. Kozak
Institute of Physics, A. Mickiewicz University, Poznań, Poland

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Proton and fluorine NMR second moments and spin-lattice relaxation times for polycrystalline tetrabutylammonium tetrafluoroborate have been measured over a wide range of temperatures at several Larmor frequencies. An analysis of cross-relaxation effects results in a determination of activation parameters for anion and cation reorientations. Three solid phases characterized by different ion dynamics are evidenced.

Key words: NMR, Cross-relaxation, Molecular motions, Phase transitions.

Introduction

A number of symmetrical tetraalkylammonium salts have been studied using nuclear magnetic resonance techniques. However, papers concerning molecular motions observed in crystal lattices have been devoted mainly to the behaviour of the simplest tetramethylammonium cation [1–6]. Data concerning molecular dynamics of larger cations are scarce [7–11]. Moreover, the lack of crystal structure determinations restricts a full analysis of the experimental data. Nevertheless, information about internal and overall reorientations can be obtained even for ions so spacious as tetrabutylammonium cation under resonable assumptions concerning its molecular structure [11]. Such information is of great value from the point of view of the often observed relations between the onset of various types of molecular reorientations and the revealed phase transitions in numerous solids.

In our recent study of molecular dynamics of guanidinium salts [12–15] we have exploited advantages of making ^1H and ^{19}F NMR experiments at the same time in order to explore reorientations of both ions in the same phase of the ionic crystal lattice. Ion motions can be characterized by Arrhenius behaviour of their correlation times. We have chosen tetra-n-butylammonium tetrafluoroborate $(C_4H_9)_4NBF_4$ as a convenient and interesting object for simultaneous examination of cation and anion reorientations via ^1H and ^{19}F NMR investigation.

Experimental

The polycrystalline sample of tetrabutylammonium tetrafluoroborate (puriss Fluka A.G.) was recrystallized from anhydrous ethanol, evacuated for several hours and sealed under vacuum in a glass tube. Proton and fluorine broad-line measurements were carried out, using a home-made spectrometer operating at Larmor frequencies of 28.0 MHz and 26.3 MHz for protons or fluorine nuclei, respectively. The second moments were calculated by numerical integration from the first derivative of the absorption lines with an accuracy of about 10%. The relaxation times T_1 of the ^1H and ^{19}F resonances were measured at 18.5, 25 and 60 MHz as functions of temperature using our home-made pulse spectrometers. The temperature of the sample was stabilized to within 1 K by a gas-flow cryostat. All measurements were taken on heating the sample. Differential thermal analysis was made with a Derivatograph DuPont 1090 in the temperature region: 273–473 K.

Results

a) Second Moment

The temperature dependences of the second moment of the proton and fluorine magnetic resonance lines are shown in Figure 1. The proton second moment decreases from 19.0 G^2 at 103 K to 11.0 G^2 at 333 K. Above this temperature the second moment decreases abruptly to 1.0 G^2, and this value remains constant up to 363 K (m.p. 437 K). The fluorine second moment of 2.0 G^2 between 113 and 270 K changes to 1.5 G^2 and

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Reprint requests to Prof. Z. Pająk, Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland.

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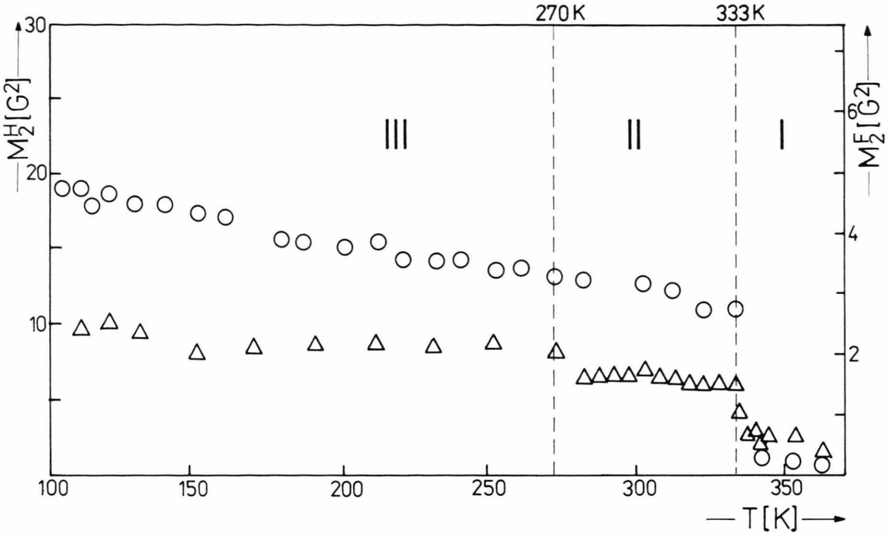

Fig. 1. Temperature dependences of proton (○) and fluorine (△) second moments.

Table 1. Experimental values of T_1^H minima.

Frequency (MHz)	$T_{1\,\mathrm{min}}$ (s)	$1000/T$ (K^{-1})	T (K)
a) 18.5	0.038	8.65	116
25.0	0.049	8.00	125
60.0	0.115	7.00	143
b) 18.5	0.113	5.60	178
25.0	0.155	5.10	196
60.0	0.255	5.00	200

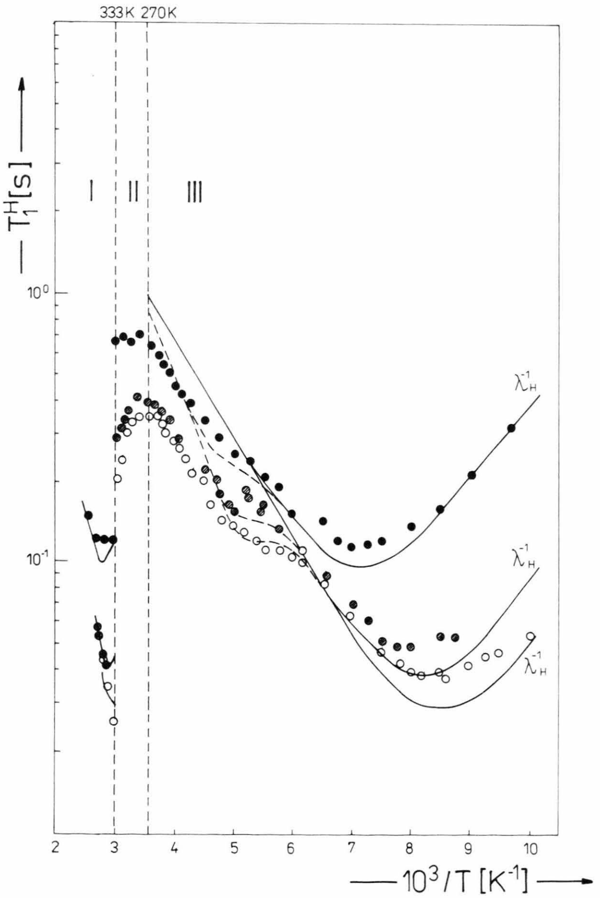

Fig. 2. Temperature dependences of proton spin-lattice relaxation times T_1^H at 18.5 (○), 25 (▨) and 60 MHz (●).

next at 333 K to 0.5 G². DSC studies show anomalies at 260*, 334 and 435 K.

b) Relaxation Times

The temperature dependences of the proton spin-lattice relaxation times T_1^H at 18.5, 25 and 60 MHz were investigated. At low temperatures the ^{1}H magnetisation decay is two-exponential. The long component of T_1^H presented in Fig. 2, corresponds to a magnetisation amplitude of about 80%.

For each frequency a broad minimum is observed at low temperatures, and another one is slightly marked at higher temperatures. The exact values of both T_1 minima with corresponding temperatures are presented in Table 1. Above 270 K for all frequencies the relaxation times start to decrease. At 333 K a sud-

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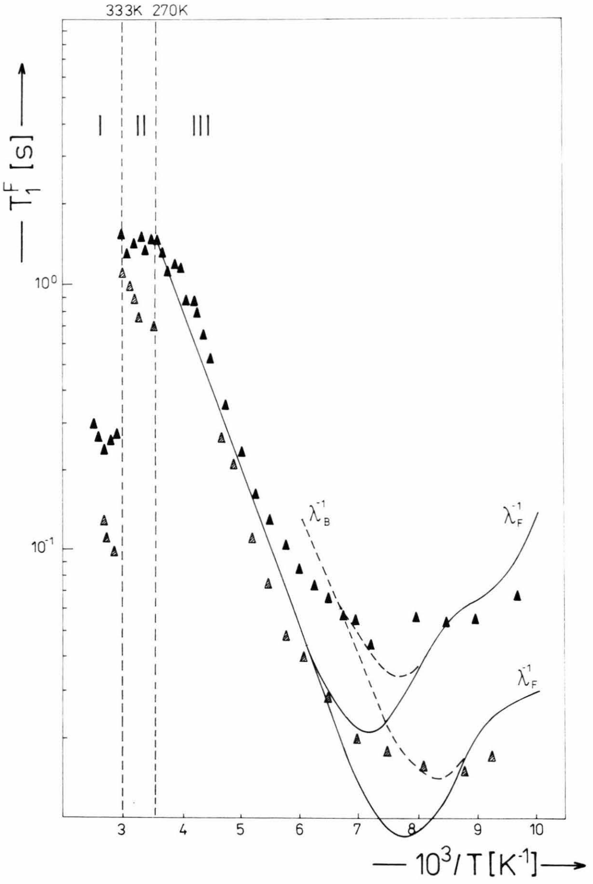

Fig. 3. Temperature dependences of fluorine spin-lattice relaxation times T_1^F at 25 (△) and 60 MHz (▲).

den jump to lower values is observed, and then the relaxation times start to increase again.

Fluorine relaxation times T_1^F were measured at 25 and 60 MHz vs. temperature. At low temperatures a non-exponential fluorine magnetisation decay is observed. A short component of T_1^F shown in Fig. 3 represents the contribution (above 50%) connected mainly with ^{19}F homonuclear interactions. Above 100 K a broad minimum is observed: 15 ms for 25 MHz and ~50 ms for 60 MHz. Above 270 K the fluorine magnetisation decay is exponential. At 270 and 333 K discontinuities of T_1^F are observed.

The discontinuities in the temperature dependences of the second moments and spin-lattice relaxation times as well as our DSC data indicate the existence of two solid-solid phase transitions. At about 270 K the determined enthalpy of the transition III→II amounts to only 5 J/g, and at 333 K (II→I) to 26 J/g. At 437 K we determined the solid-liquid phase transition enthalpy to be 32 J/g.

Discussion

a) Second Moment

The theoretical rigid lattice second moments were found using the Van Vleck formula

$$M_2 = \frac{3\gamma_I^2 \hbar^2 I(I+1)}{5N} \sum_{j,k} r_{jk}^{-6} + \sum_S \frac{4\gamma_S^2 \hbar^2 S(S+1)}{15N} \sum_{j,m} r_{jm}^{-6} \tag{1}$$

for a polycrystalline sample. All symbols have their usual meaning [16].

When molecular reorientation occurs, the second moment is reduced by a factor

$$\varrho = \tfrac{1}{4}(1-3\cos^2\theta)^2, \tag{2}$$

where θ is the angle between the respective internuclear vector and the axis of reorientation. In the absence of crystal structure data it is convenient to divide the second moment into intra- and inter-molecular parts.

For the cation investigated the intra-ionic part of M_2 can be calculated as [11]

$$M_{2\,\mathrm{intra}} = (2\cdot 4/36)\,[M_2^{\mathrm{I}}(\mathrm{CH}_2) + M_2^{\mathrm{II}}(\mathrm{CH}_2) + M_2^{\mathrm{III}}(\mathrm{CH}_2)] + (3\cdot 4/36)\,M_2(\mathrm{CH}_3)\,. \tag{3}$$

Since no structural data of the compound are known, $M_{2\,\mathrm{intra}}$ was calculated on the assumption given in [11]. This part was found to be 26.3 G^2, neglecting the small heteronuclear contribution from nitrogen atom (~0.03 G^2). The inter-cationic part of the second moment was estimated to be 1.0 G^2 only, like that for tetraethylammonium and tetrapropylammonium salts [9]. It is not possible to calculate exactly the inter-ionic contribution from H–F interaction. We evaluated the total M_2(H–F) to be 0.6 G^2 by comparison with literature data [12], taking into account the number of protons in the cation. Thus the proton total rigid-lattice second moment should be about 28 G^2 (Table 2).

The intra-ionic part of the second moment for the anion investigated was calculated assuming its structure as determined for lithium tetrafluoroborate [13]. This value amounts to 14.4 G^2. The inter-ionic contribution M_2(F–H) equals $10.12 \times M_2$(H–F) = 6.1 G^2 [12]. The inter-anion contribution M_2(F–F) can be ignored because the neighbouring anions are separated by the large tetrabutylammonium cations. Thus the fluorine total rigid-lattice second moment should be about 20.5 G^2 (Table 3).

At low temperatures the experimental values of the ^1H and ^{19}F second moments are much lower than the rigid-lattice values calculated. This means that the anion and cation undergo simultaneously reorientations which significantly reduce their second moments.

There are several motions which can be discussed for butyl chains of the cation. One can see on the Dreiding model that the freedom to reorient declines essentially due to increasing strong steric hindrances going from CH_3 groups to CH_2 groups closer and closer to the central nitrogen atom. Therefore one can expect that the end methyl groups have the highest mobility about their symmetry C_3 axes while the mobility of more internal methylene groups are strongly limited.

Table 2. The calculated proton second moment (G^2).

Type of motion	$M_{2\,\mathrm{intra}}(\mathrm{H-H})$	$M_{2\,\mathrm{inter}}(\mathrm{H-H})$	$M_{2\,\mathrm{inter}}(\mathrm{H-F})$	$M_{2\,\mathrm{total}}$
Rigid structure	26.3	1.0	0.6	27.9
C_3 methyl reor.	20.5	0.8	0.3	21.6

The experimental M_2^{H} at 103 K is smaller than 21.6 G^2 calculated for the model assuming methyl group reorientations (Table 2). This means that not only all methyl groups reorient with a frequency greater than 10^5 Hz, but that an additional motion must reduce the second moment. This motion, manifested also in a further diminishing of M_2^{H} up to 11 G^2, can be connected with the onset of reorientation of the end ethyl groups and/or reorientations of longer segments (e.g. propyl groups) of the butyl chains. The narrowing of ^1H NMR line, observed in the phase transition II → I, can be interpreted as due to the whole cation reorientation around its centre of gravity. The reduced value of the second moment for such an overall motion determined only by interionic cation-cation interaction would be about 1.0 G^2 [17], which is experimentally observed.

Table 3. The calculated fluorine second moment (G^2).

Type of motion	$M_{2\,\mathrm{intra}}(\mathrm{F-F})$	$M_{2\,\mathrm{intra}}(\mathrm{F-B})$	$M_{2\,\mathrm{inter}}(\mathrm{F-H})$	$M_{2\,\mathrm{total}}$
Rigid structure	6.2	8.2	6.1	20.5
Isotrop. reor.	0	0	2.0	2.0

The experimental value of M_2^{F} in the phase III can be interpreted as due to the isotropic reorientation of the anion around its center of gravity. This M_2^{F} value of the order 2 G^2 is in good agreement with our calculations (Table 3). The experimental values of 1.5 G^2 in phase II and 0.5 G^2 in phase I may reflect an additional diminishing of F–H anion-cation interaction averaged due to the appearing cation motions.

b) Relaxation Time

To describe theoretically the temperature dependence of spin-lattice relaxation times one has to consider homonuclear as well as heteronuclear dipolar interactions between ^1H, ^{19}F, ^{14}N, ^{11}B and ^{10}B spins. These interactions are especially important in the temperature ranges in which $\omega_{\mathrm{H}} \pm \omega_{\mathrm{F}} \approx 1/\tau$, $\omega_{\mathrm{F}} \pm \omega_{\mathrm{B}} \approx 1/\tau$, $\omega_{\mathrm{H}} \pm \omega_{\mathrm{B}} \approx 1/\tau$ and $\omega_{\mathrm{N}} \pm \omega_{\mathrm{H}} \approx 1/\tau$, where τ is a correlation time for the anion or cation reorientation. If at least one of the above conditions is fulfilled, the nonexponential magnetisation decay is expected. In our experiments we clearly observed nonexponential relaxation at low temperatures (phase III). For dipolar interactions between unlike spins the time variation of the nuclear magnetisations caused by relaxation is governed by a set of coupled differential equations which can be presented in a matrix form:

$$[\dot{M}] = [R]\,[M - M_0]\,, \tag{4}$$

where $[M]$ and $[M_0]$ are the matrices of the magnetisations for the respective nuclear spins at time t and in the equilibrium state [12].

Let us assume a simple model of ion reorientations for which the relaxation matrix $[R]$ would be the sum of matrices corresponding to the reorientation of four methyl groups $[R_{\mathrm{H}}]$ and isotropic reorientation of BF_4 anion $[R_{\mathrm{F}}]$:

$$[R] = [R_{\mathrm{H}}] + [R_{\mathrm{F}}]\,. \tag{5}$$

The relaxation matrices were calculated as functions of temperature writing diagonal elements as

$$R_{II} = \tfrac{2}{3}\gamma_I^2\,\Delta M_2^{II}\,g_1(\omega_I,\tau) + \tfrac{1}{2}\sum_S \gamma_I^2\,\Delta M_2^{IS}\,g_2(\omega_I,\omega_S,\tau) \tag{6}$$

and off-diagonal elements as

$$R_{IS} = \tfrac{1}{2}\gamma_S^2\,\Delta M_2^{SI}\,g_3(\omega_I,\omega_S,\tau)\,\frac{N_S}{N_I}\,, \tag{7}$$

where

$$\begin{aligned} g_1(\omega_I,\tau) &= \tau/(1+\omega_I^2\tau^2) + 4\tau/(1+4\omega_I^2\tau^2),\\ g_2(\omega_I,\omega_S,\tau) &= \tau/[1+(\omega_I-\omega_S)^2\tau^2] + 3\tau/(1+\omega_I^2\tau^2)\\ &\quad + 6\tau/[1+(\omega_I+\omega_S)^2\tau^2]\,,\\ g_3(\omega_I,\omega_S,\tau) &\\ &= -\tau/[1+(\omega_I-\omega_S)^2\tau^2] + 6\tau/[1+(\omega_I+\omega_S)^2\tau^2]. \end{aligned} \tag{8}$$

Table 4. Calculated contributions ΔM_2 to the second moment reduction values (G^2).

Interaction	Reorientation	
	C_3 methyl groups	Isotropic BF_4
H–H	6.0	
H–F	0.3	
F–H	3.0	4.1
F–F		6.2
F–B		8.2

The calculated reduction ΔM_2 of the second moments for the considered molecular motions are shown in Table 4. A comparison of the calculated eigenvalues $\lambda_{\mathrm{H}}^{-1}$, $\lambda_{\mathrm{F}}^{-1}$ of the total relaxation matrix $[R]$ with the experimental minima of T_1^{H} and T_1^{F} has shown that the ion motions considered above explain reasonably the relaxation behaviour in phase III. To obtain the activation parameters for the reorientations considered we fitted the temperature dependences of $\lambda_{\mathrm{H}}^{-1}$ and $\lambda_{\mathrm{F}}^{-1}$ to the experimental points for each measuring frequency. For motions treated as thermally activated we described Arrhenius correlation times as: τ_{H} for the four CH_3-groups reorientation (with $\tau_{0\mathrm{H}}$ and E_{H}) and τ_{F} for the BF_4 ion isotropic reorientation (with $\tau_{0\mathrm{F}}$ and E_{F}). The best fitted activation parameters shown in Table 5 lie in the limits of the values characteristic for ion motions considered [11, 12, 18].

Table 5. Activation parameters for the motions in phase III.

Type of motion	E (kJ/mol)	τ_0 (s)
C_3 reorientation of CH_3 groups	7.3	$3.2 \cdot 10^{-12}$
Additional motion in butyl chains	21.6	$8.5 \cdot 10^{-15}$
Isotropic reorientation of BF_4 ion	11.9	$7.6 \cdot 10^{-14}$

The calculated temperature dependences of $\lambda_{\mathrm{H}}^{-1}$ and $\lambda_{\mathrm{F}}^{-1}$ are compared with the experimental data in Figs. 2 and 3. One can see in Fig. 2 that beside the C_3 reorientations of the methyl groups another motion influences the T_1^{H} behaviour in phase III. Treating this influence as leading to a weak minimum in the vicinity of 200 K and adding to the considered relaxation matrix (5) the term $R' = C'_{\mathrm{H-H}}\, g'_1(\omega_I, \tau')$, where $C'_{\mathrm{H-H}} = 4.3 \times 10^8\ \mathrm{s}^{-2}$, one can characterise the activation parameters for this motion as $E' = 21.6$ kJ/mol and $\tau'_0 = 8.5 \times 10^{-15}$ s (the broken lines in Fig. 2 show $\lambda_{\mathrm{H}}^{-1}$ values obtained taking into account this additional motion).

One can see in Fig. 3 that the calculated $\lambda_{\mathrm{F}}^{-1}$ values at higher temperatures in phase III are in good agreement with the experimental data. The poor agreement observed at lower temperatures seems to arise from the fact that in our experiment it is difficult to extract the boron contributions ($\lambda_{\mathrm{B}}^{-1}$) to the fluorine relaxation.

It is difficult to interpret the temperature dependences of T_1^{F} and T_1^{H} in phase II. They reflect probably the onset of a motion in/of the cation which is hard to define.

In phase I, where the proton relaxation is exponential and one observes a merely marked minimum $T_1 \approx 110$ ms (60 MHz) it is possible to describe the experimental data as

$$\frac{1}{T_1} = \tfrac{2}{3}\, \Delta M_2^{\mathrm{H}}\, g_1(\omega_I, \tau) \qquad (9)$$

with $\Delta M_2^{\mathrm{H}} = 5.7\ \mathrm{G}^2$. The best fitted activation parameters are $E = 43.2$ kJ/mol and $\tau_0 = 1.1 \times 10^{-15}$ s. The ΔM_2^{H} value can not be confirmed by the experiment since the phase transition II → I takes place. The solid lines plotted in the Fig. 2 for phase I correspond to the best fitted Arrhenius parameters which describe the reorientation of the cation around its center of gravity (M_2^{H} equals 1 G^2). It seems that the T_1^{F} minimum of 240 ms observed at 60 MHz due to fulfilling of the $(\omega_{\mathrm{F}} + \omega_{\mathrm{H}}) \approx 1/\tau$ condition reflects the minimum of T_1^{H}. The corresponding interaction calculated from (6), $\Delta M_2^{\mathrm{FH}} = 1.39\ \mathrm{G}^2$, is comparable with the experimental value $\Delta M_2^{\mathrm{F}} = 1.0\ \mathrm{G}^2$.

Conclusions

1. Three solid phases of tetrabutylammonium tetrafluoroborate are evidenced between 100 K and the melting point (437 K).
2. The phase transitions at 270 K (III → II) and at 333 K (II → I) are confirmed by DSC. The corresponding transition enthalpies are 5 J/g and 26 J/g.
3. Isotropic reorientation of the anion and C_3 reorientations of the methyl groups simultaneous with a motion in the butyl chains of the cation characterise the ion dynamics in the three solid phases. Additional isotropic reorientation of the whole cation around its center of gravity is observed in phases II and I.

Acknowledgements

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[1] D. J. Blears, S. S. Danyluk, and E. Bock, J. Phys. Chem. **72,** 2269 (1968).

[2] J. Dufourcq and B. Lemanceau, J. Chem. Phys. **67,** 9 (1970).

[3] E. R. Andrew and R. C. Canepa, J. Magn. Res. **7,** 429 (1972).

[4] S. Albert, H. S. Gutowsky, and A. J. Ripmeester, J. Chem. Phys. **56,** 3672 (1972).

[5] M. Polak and M. Sheinblatt, J. Magn. Res. **12,** 261 (1973).

[6] S. Jurga, Phys. Stat. Sol. (a) **81,** 77 (1984).

[7] R. Goc, Z. Pająk, and B. Szafrańska, Proc. 18th Colloque Ampere, Nottingham 405 (1974).

[8] F. Koksal, Z. Naturforsch. **34a,** 1296 (1979).

[9] B. Szafrańska and Z. Pająk, J. Molec. Struct. **99,** 147 (1983).

[10] F. Koksal, J. Phys. Chem. Solids **45,** 263 (1984).

[11] B. Szafrańska and Z. Pająk, Z. Naturforsch. **42a,** 253 (1987).

[12] Z. Pająk, A. Kozak, and M. Grottel, Proc. 23rd Congress Ampere, Roma 419 (1986).

[13] A. Kozak, M. Grottel, A. E. Kozioł, and Z. Pająk, J. Phys. C: Solid State Phys. **20,** 5433 (1987).

[14] Z. Pająk, A. Kozak, and M. Grottel, Sol. State Communications **65,** 671 (1988).

[15] M. Grottel, A. Kozak, A. E. Kozioł, and Z. Pająk, J. Phys.: Condens. Matter **1,** 7069 (1989).

[16] A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press 1961.

[17] G. W. Smith, J. Chem. Phys. **36,** 3081 (1962).

[18] E. R. Andrew, K. Jurga, and E. Szcześniak, Mol. Phys. **65,** 1421 (1988).