Complex methyl groups dynamics in $[(CH_3)_4P]_3Sb_2Br_9$ (PBA) from low to high temperatures by proton spin-lattice relaxation and narrowing of proton NMR spectrum.

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Streszczenie

Molecular dynamics of a polycrystalline sample of $[(CH_3)_4P]_3Sb_2Br_9$ (PBA) has been studied on the basis of the T_1 (24.7 MHz) relaxation time measurement, the proton second moment of NMR and the earlier published T_1 (90 MHz) relaxation times. The study was performed in a wide range of temperatures (30–337 K). The tunnel splitting ω_T of the methyl groups was estimated as of low frequency (from kHz to few MHz). The proton spin pairs of the methyl group are known to perform a complex internal motion being a resultant of four components. Three of them involve mass transportation over and through the potential barrier and are characterized by the correlation times and of the jumps over the barrier and tunnel jumps in the threefold potential of the methyl group and the correlation time of isotropic rotation of the whole TMP cation. For and the Arrhenius temperature dependence was assumed, while for —the Schrödinger one. The fourth motion causes fluctuations of the tunnel splitting frequency, ω_T, and it is related to the lifetime of the methyl spin at the energy level. The correlation function for this fourth motion (correlation time) has been proposed by Müller-Warmuth et al. [15]. In this paper a formula for the correlation function and spectral density of the complex motion made of the above-mentioned four components was derived and used in interpretation of the T_1 relaxation time. The second moment of proton NMR line at temperatures below 50 K is four times lower than its value for the rigid structure. The three components of the internal motion characterized by, , and were proved to reduce the second moment of the NMR line. The tunnel jumps of the methyl group reduce M_2 at almost 0 K, the classical jumps over the barrier reduce M_2 in the vicinity of 50 K, while the isotropic motion near 150 K. Results of the study on the dynamics of CH_3 groups of TMP cation based on the second moment measurements were correlated with those based on T_1 time measurements.

Słowa kluczowe

Proton spin–lattice relaxation time, Proton second moment of the NMR line, Complex motion of methyl group, Low temperatures dynamics, Tunnelling of methyl groups

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