Manifestation of electron-nuclear motions in the ^{123}Sb NQR spectra of pentafluoroantimonites

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A dependence between the quadrupole coupling constants (e^2Qq_{zz}) and the asymmetry parameters of the electric field gradient (η) for the antimony atoms in the complex $[SbF_5]^{2-}$ anions of M_2SbF_5 pentafluoroantimonites (M = Na, K, Rb, Cs, NH_4, Tl, and Et_2NH_2) was revealed from the ^{123}Sb NQR spectra at 77 K.

Key words: ^{123}Sb NQR spectra, antimony(III), pentafluoroantimonites, electron-nuclear motions.

Previuosly,[1–4] it has been shown that if tunneling electron transitions between possible configurations of the electron distributions occur in a polyconfigurational molecular or complex system, then in the case of a sufficiently large number of configurations a situation characteristic of the stochastic dynamics of nonlinear vibrational systems can arise,[5] when the spectral density curve of possible fluctuations has a shape close to a rectangle. If the inversion (tunnel) splittings of the electron terms (δE) are of the same order of magnitude as kT, then the dependence between the electric field gradient (EFG) q_{zz} observed in the NQR and appearing in the expression for the quadrupole coupling constant (QCC) e^2Qq_{zz} and the EFG asymmetry parameter h, which characterizes the deviation of the electron distribution symmetry for a bond from axial symmetry (by definition, $\eta = (q_{xx} - q_{yy})/q_{zz}$),[1] can be written as follows:[2]

$$e^2Qq_{zz} = e^2Qq_{zz0} + (\delta B/2\Delta\eta)\ln|[\eta - (\eta_0 + \Delta\eta)]/[\eta - (\eta_0 - \Delta\eta)]| \quad (1)$$

Here e^2Qq_{zz0} and η_0 are the origin, $\Delta\eta$ is the depth of the fluctuation modulations, B is the coefficient of proportionality for the given type of molecular systems, and $\delta = \pm 1$. The detailed derivation of formula (1) has been reported.[1,2]

In this work an attempt was made to consider the possibility of using relationship (1) for describing the dynamics of configurational distortions in the series of complex M_2SbF_5 pentafluoroantimonites (M = Na, K, Rb, Cs, NH_4, Tl, and Et_2NH_2) whose NQR spectra have been studied previously.[6–9] The ^{123}Sb NQR spectral parameters of these compounds are listed in Table 1.

Table 1. ^{123}Sb NQR spectral parameters of M_2SbF_5 compounds at 77 K

M	e^2Qq_{zz}/MHz	η (%)	$\tau \cdot 10^{-14}$/s	Ref.
Na	529.6	17.5	12.0	6
K	589.4	8.8	41.7	6, 7
Rb	606.9	6.8		6
Cs	593.9	6.5		6
NH_4	616.2	8.4	54.7	6
Tl	565.0	3.8		8
Et_2NH_2	647.5	7.3		9

Using the data in Table 1, we obtained the following values of the parameters of Eq. (1): e^2Qq_{zz0} = 499.38 MHz, B = 537.82 MHz %, η_0 = 14.082%, and $\Delta\eta$ = 7.081%. The accuracy of determination of the QCC values from Eq. (1) is 2.0 MHz while the correlation coefficient between the experimental and calculated QCC values is 0.996 (n = 7).

The dependence between ^{123}Sb QCC and η at 77 K is shown in Fig. 1 and it can be seen that the experimental points (n = 1, 2, and 5) fall into the ($\eta_0 \pm \Delta\eta$) interval. This makes it possible to estimate (though roughly) the correlation times of complete tunnel elec-

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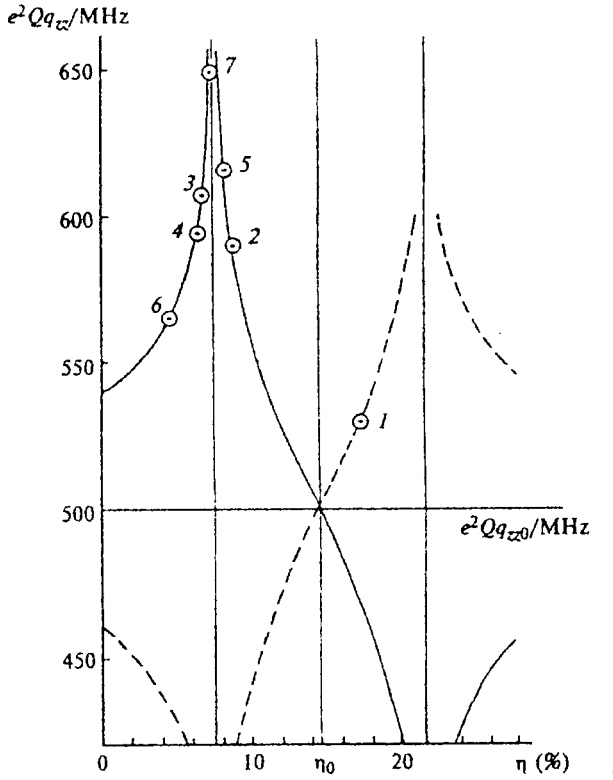

Fig. 1. Dependence between ^{123}Sb e^2Qq_{zz} and η for M_2SbF_5 compounds at 77 K; M = Na (*1*), K (*2*), Rb (*3*), Cs (*4*), NH_4 (*5*), Tl (*6*), and Et_2NH_2 (*7*). Solid lines and dashed lines correspond to $\delta = +1$ and $\delta = -1$, respectively.

tron transfer for the interconfigurational transitions from the following approximate relationship:[2]

$$(\eta - \eta_0)/\Delta\eta = x^{-1}\text{th}x, \qquad (2)$$

here $x = \delta E/kT$, δE is the tunnel (inversion) splitting of the electron term, k is the Boltzmann constant, and T is absolute temperature (in our case $T = 77$ K).

Having determined x, we can calculate the time of complete tunnel electron transfer:[3]

$$\tau = \pi\hbar/\delta E. \qquad (3)$$

The τ values found from Eqs. (2) and (3) are listed in Table 1 and lie in the interval $(12—54) \cdot 10^{-14}$ s. These times are of the same order of magnitude as the characteristic times of nuclear motions, which is the physical basis of the observed dependence (1) (see Fig. 1).

Thus, we may consider it established that the interionic coordination interactions in the series of compounds considered include such a component as simultaneous "slow" electron-nuclear motions. We believe that the compounds corresponding to the points inside and near the boundaries of the dispersion region $(\eta_0 \pm \Delta\eta)$ must exhibit nonlinear acoustooptical characteristics. This conclusion is in agreement with the reported data of studying the properties of complex M_2SbF_5 compounds (M = Na, K, Rb, Cs, NH_4, and Tl) by different methods in the temperature range 77—330 K.[10—16] It has been shown that all pentafluoroantimonites undergo specific phase transitions depending on the cation nature. Optical anisotropy was found in the $(NH_4)_2SbF_5$ crystals (they exhibit birefringence).[10,11] The most pronounced temperature anomalies of such parameters as dielectric permittivity, conductivity,[12] low-temperature heat capacity, and those of NQR spectra[13,14] were found for compounds with potassium and ammonia cations.

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