Nuclear spin exchange in the ionic clusters \([\text{Tl}_4\text{Cl}]^{3+}\), situated in the cavities of cation-substituted chlorosodalite, was investigated by the \(^{203}\text{TI}\) and \(^{205}\text{TI}\) NMR method. It was shown that nuclear spin exchange in the ionic crystals is realized by analogy with the Kramers mechanism of indirect exchange of electron spins using the electron shells of the bridging atoms.

INTRODUCTION

In [1] direct exchange interaction was detected between the thallium nuclei in the quasiunidimensional chain in the \(\text{TlHF}_2\) crystal with a record exchange constant of \(J \approx 50\) kHz, which is almost an order of magnitude greater than the values usually observed in ionic crystals [2]. However, it had been shown earlier [3,4] that the \(J\) constants in ionic crystals are proportional to the squares of the overlap integrals of the electronic wave functions of the ions. As a result, the interactions of the nuclei in them are more short-acting than in metals and semiconductors, in which the interactions are realized through the conduction electrons and their attenuation during the removal of the nuclei fluctuates [5,6]. In the ionic crystal of \(\text{TlHF}_2\), the interacting nuclei are at a distance of \(~7.3\) Å, which excludes direct overlap of the shells of the ions. It remained unclear as to whether the obtained result indicated the existence of other more effective mechanisms of indirect exchange or whether it was due to special geometric features of the specific system and its unidimensionality.

In the present work we present new experimental results indicating that nuclear spin exchange in the ionic crystals is realized by means of the electron shells of the bridging atoms, and this is analogous with the Kramers mechanism [7] of indirect exchange of electron spins. In order to investigate this question we studied the interactions of \(^{203}\text{TI}\) and \(^{205}\text{TI}\) nuclei in specially selected systems, where direct overlap of the shells of the \(\text{Tl}^+\) ions is known to be small. An example of such systems is the isolated ionic clusters in crystalline ion exchangers of the zeolite or feldspathite type. As model system in the present work we studied the thallium form of cation-substituted sodalite.

STRUCTURAL CHARACTERISTICS OF THE IONIC CLUSTER AND THE CRYSTAL MATRIX

We used one of the simplest systems in the form of the ionic cluster \([\text{Tl}_4\text{Cl}]^{3+}\) situated in the cavity of the mineral sodalite, which has a rigid aluminum–silicon–oxygen framework structure with precisely shaped internal cavities (voids). In the natural mineral \(\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}\) the cavities are filled with tetrahedral ionic clusters \([\text{Na}_4\text{Cl}]^{3+}\). The structurally similar clusters \([\text{Ag}_4\text{Cl}]^{3+}\), \([\text{Ag}_4\text{Br}]^{3+}\), \([\text{Ag}_4\text{I}]^{3+}\), \([\text{Zn}_2\text{S}]^{3+}\), \([\text{Cd}_2\text{S}]^{3+}\), etc.) in the sodalite framework were studied in detail in [8] in connection with the nonlinear optical characteristics of "quantum-confined" systems.

The individual cavity in the sodalite structure [9] is formed by 24 \([\text{AlO}_4]\) and \([\text{SiO}_4]\) tetrahedra linked by common vertices and lying on the faces of the cubic unit cell (P43n, \(Z = 2\)) (Fig. 1). The cavities are linked to each other by sixfold windows, the "planes" of which are perpendicular to the solid diagonals of the cube. The monovalent ions \(\text{M}^+\) also lie on these diagonals around the chloride ions, which occupy the vertices and the center of the unit cell. The mutual arrangement of \(\text{M}^+\)
Fig. 1. A fragment of the structure of the thallium form of chlorosodalite.

(Fig. 1) is characterized by the existence of three $M^+$ neighbors for each of them in the same cavity (at distance $R$) and six neighbors in different cavities (at distance $r$). During ionic substitution of $Tl^+$ by $Na^+$ the structure of the unit cell remains practically unchanged, but the lattice constant increases from 8.88 to 9.10 Å [8] on account of slight rotation of the $[(Al, Si)O_4]$ tetrahedra about the common oxygen atoms with increase in the $(Al, Si)-O-Si$ angles [8].

In the investigated system it is clearly possible to introduce two sets of constants \{\(J_1(R)\)\} and \{\(J_2(r)\)\}, describing the intra- and intertetrahedral exchange and pseudodipole interactions respectively of the nuclear spins. The $R$ (4.47 Å) and $r$ (4.80 Å) values are only known for the natural sodium form of the crystal. The interatomic separations $R$ (5.07 Å) and $r$ (4.75 Å) for the thallium form were estimated from the lattice parameter of 8.89 Å and the ionic radii of $Tl^+$ (1.36 Å) and $Cl^-$ (1.75 Å) [10]. On the basis of these values and of published data [2] it can be expected that the relationship $J_1 < J_2 \approx 1$ kHz must hold for the coupling constants in the investigated system on account of the direct electronic overlap of the $Tl^+$ shells.

**EXPERIMENTAL**

A polycrystalline sample of the thallium form of chlorosodalite was obtained from the natural Na form (Khibina, RF) by substitution of the sodium ions in an ionic melt of $TlNO_3$. The degree of substitution (s) was about 70% [8]. The $^{203}Tl$ and $^{205}Tl$ NMR spectra were recorded by the stationary method at 13.1 MHz at 290-460 K.

The spectra obtained at 290 K are given in Fig. 2. The corresponding values of the second moments ($M_2$) were 127 ± 5 and 320 ± 10 kHz\(^2\) for isotopes 205 and 203 and were more than three orders of magnitude greater than the theoretical values of $M_2$ obtained with allowance for only the dipole interactions of the nuclear spins. The $M_2(203-Tl)/M_2(205-Tl)$ ratio was close to the reverse ratio of the natural abundances of the nuclei (29.5 and 70.5%), from which it follows [11] that the exchange interactions of the $^{203}Tl$ and $^{205}Tl$ nuclei make a determining contribution in the spin–spin couplings. The $M_2$ values do not change over the whole investigated temperature range.

If it is assumed that with partial substitution the $J_1$ and $J_2$ constants depend little on the presence of the $Na^+$ ions in the closest environment, the contribution from the scalar interactions between the $^{203}Tl$ and $^{205}Tl$ nuclei to the second moment of the given isotope can be represented in the following form [11]:

$$M_2 = \frac{1}{\gamma^2} \cdot \left(3J_1^2 + 6J_2^2\right) p \varepsilon,$$

where $p$ is the natural abundance of the nuclei of the "foreign" isotope.

From Eq. (1) and the experimental $M_2$ values it is possible to estimate the coupling constants for the three characteristic cases: 1) $J_1 \approx J_2 \approx 17$ kHz, if all the spin interactions in the system are approximately equivalent; 2) $J_2 \approx 21$ kHz ($J_1 = 0$), if the shorter distances $r$ assure predominance of the interactions between the nuclei belonging to different $Tl_4Cl$ tetrahedra; 3) $J_1 \approx 29$ kHz ($J_2 = 0$), if the principal interactions are the intratetrahedral interactions of the spins.

The last of these cases can be realized if electronic nuclear interaction of the $Tl^+$ nuclei appears through the electronic shells of the central $Cl^-$ ion, whereas the first two must correspond to significant direct overlap of the wave functions of $Tl^+$,