19F NMR STUDY OF THE INFLUENCE OF THE NATURE OF OUTER-SPHERIC CATIONS ON THE DYNAMICS OF THE ANION SUBLATTICE IN COMPOUNDS MM'AF₆

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Dynamics of octahedral ions in crystal compounds MM'AF₆ (M, M' = Li, Na, K, Rb, Cs; A = Ge, Ti) has been studied in the temperature range 115-500 K. Types of inner motions of complex ions have been established, and their activation energies have been estimated. First-order transition has been found in compound LiRbTiF₆.

In hexafluorocomplexes of Group IV elements with mixed cations, the dynamic behavior of octahedral ions during thermal treatment was shown [1-3] to be the same as in complexes with homogeneous cation sublattices [4, 5]. Nevertheless, the data obtained in [1-3] indicate that variations in the composition of the second coordination sphere can alter the motion of complex anions during their phase transitions and sometimes lead to polymorphic transformations, not observed in similar complexes with homoatomic cations.

This communication is a continuation of our series of papers devoted to new hexafluorocomplexes with mixed alkali metal cations. It summarizes the results of studies on the effect of the nature of outer-spheric cations on the dynamic properties of the fluorine sublattice in compounds MM'AF₆ (M, M' = Li, Na, K, Rb, Cs; A = Ge, Ti).

EXPERIMENTAL

19F NMR spectra of the compounds were measured on a Bruker SWL3-100 broad-band spectrometer (84.66 and 28.8 MHz) in the temperature range 115-500 K. The measurement errors were ±0.2 G for resonance line half-widths (δB) (Fig. 1) and up to 15% for the second moments (S₂). The theoretical values of S₂ and the activation energies Eₐ were estimated by van Vleck's formula and Waugh-Fedin's equation, respectively [6]. CF₂Cl₂ was used as a reference in 19F NMR chemical shift measurements. Synthetic procedures and tentative NMR data for the compounds are given in [7, 8].

RESULTS AND DISCUSSION

According to the character of changes in the 19F NMR spectra, the hexafluorogermanates under study may be conventionally divided into two groups: NaRbGeF₆, NaCsGeF₆ (I) and NaKGeF₆, KCsGeF₆ (II). For compounds of the first group, the shape of NMR spectra and the character of their changes during temperature variations (Fig. 1) are generally similar to those described earlier for NaMSnF₆ (M = K, Rb, Cs) [1]. The constant widths and second moments in the 19F NMR spectra of hexafluorogermanates (I) below 250 K (Fig. 2) indicate the absence of nuclear motions in the fluorine subsystem at frequencies exceeding resonance linewidths [6, 9]. At 250-350 K, the spectra change in form: the resonance signal becomes symmetric and narrows to its constant width (Figs. 1 and 2), which is

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determined mainly by the nature of outer-spheric cations. The observed transformations of NMR spectra correspond to a dynamically homogeneous system.

In the NMR spectra of solids, changes in the widths and second moments with temperature variations are caused by changes in the dynamic states of resonant nuclei, for example, as a result of reorientational or diffusion motions of ions or their groups. Since \( S_2 = 0 \) for diffusion, this type of motion may be excluded from consideration based on the data obtained (Figs. 1 and 2). For octahedral ions, possible models of motion are anisotropic reorientations around \( C_2, C_3, \) or \( C_4 \) symmetry axes and isotropic rotations. We assume that the structural motifs of \( M_2 \) complexes [10] do not change significantly on passing to \( M M' \) complexes; this is indirectly confirmed by the similarity between the values of \( S_2 \) and \( \langle \delta \rangle \) of these complexes (Fig. 2, Table 1). Then it may be readily shown that the observed one-step decrease in \( S_2 \) (Fig. 2) is associated with a transition of octahedral ions from the “rigid lattice” to isotropic rotation. Indeed, the theoretical values of \( S_2 \) exceed the experimental values for any anisotropic reorientation of hexafluoroanions (Fig. 2) but correlate well (as also shown in [11], Table 2) with the latter for isotropic rotation of \([\text{GeF}_6]^2^-\) ions. Slight