

PHYSICAL METHODS  
OF INVESTIGATION

## Thermal Properties and Ion Mobility in Complex Antimony(III) Fluorides with $\alpha$ -Amino Acids

V. Ya. Kavun<sup>a</sup>, N. A. Didenko<sup>a</sup>, N. V. Makarenko<sup>a</sup>, A. B. Slobodyuk<sup>a</sup>,  
E. B. Merkulov<sup>a</sup>, N. F. Uvarov<sup>b</sup>, and L. A. Zemnukhova<sup>a</sup>

<sup>a</sup> Institute of Chemistry, Far-East Branch, Russian Academy of Sciences,  
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia

<sup>b</sup> Institute of Solid-State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences,  
ul. Kutateladze 18, Novosibirsk, 630128 Russia

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**Abstract**—Differential thermal analysis (DTA) and (<sup>19</sup>F, <sup>1</sup>H) NMR spectroscopy were used to study thermal properties and ion mobility in complex antimony(III) fluorides with amino acids of composition [(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>2</sub>)CH(NH<sub>3</sub>)COOH]SbF<sub>4</sub> (LeuHSbF<sub>4</sub>), SbF<sub>3</sub>[(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>2</sub>)CH(<sup>+</sup>NH<sub>3</sub>)COO<sup>-</sup>] (SbF<sub>3</sub> · Leu), and SbF<sub>3</sub>[(CH<sub>3</sub>)<sub>2</sub>CHCH(<sup>+</sup>NH<sub>3</sub>)COO<sup>-</sup>] (SbF<sub>3</sub> · Val). Ionic conductivity in L-leucinium tetrafluoroantimonate(III) was studied using impedance spectroscopy. LeuHSbF<sub>4</sub> was found to undergo a diffusion phase transition to a relatively highly conductive state in the range 385–415 K with an attendant loss of thermal stability (softening) of the high-temperature phase.

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Antimony trifluoride, a good fluoride ion acceptor, forms numerous complexes with SbF<sub>3</sub> : MF stoichiometries ranging between 4 : 1 and 1 : 3 [1]. The greatest attention was paid to compounds where anions were such as [Sb<sub>2</sub>F<sub>7</sub>]<sup>-</sup>, [SbF<sub>4</sub>]<sup>-</sup>, [SbF<sub>5</sub>]<sup>2-</sup>, [Sb<sub>4</sub>F<sub>15</sub>]<sup>3-</sup>, and others, for the reason that there are many compounds among them with unusual electrophysical, optical, and other properties, which certainly stipulated comprehensive studies using various physicochemical methods [2]. In the extensive family of antimony fluorides, of interest are complex tetrafluoroantimonates(III) with alkali metal and ammonium cations for the reason that in this group some compounds undergo phase transitions, in particular, superionic transitions (KSbF<sub>4</sub>, NH<sub>4</sub>SbF<sub>4</sub>, and TlSbF<sub>4</sub> [3–5]), some are piezoelectrics (MSbF<sub>4</sub>, where M = Li, Na, and Cs [1]), some compounds have biologically active properties (sodium, potassium, rubidium, and cesium tetrafluoroantimonates(III) were found to have biological activity with respect to marine bacteriocenosis [6]), and some tetrafluoroantimonates(III) were shown to be useful in hydrometallurgy [7]. A search over this class of trivalent antimony fluorides for compounds having high ion mobilities (conductivities) is just one task of this study.

In many complex fluorides of trivalent antimony with alkali cations, conductivity is known to reach values of 10<sup>-2</sup> to 10<sup>-4</sup> S/cm at *T* > 400 K due to the translational diffusion of fluoride ions [2]. The presence of proton-containing cations, for example, ammonium ions, in the cationic sublattice can initiate an increase in ionic conductivity in fluoroantimonates(III), given

diffusion in the proton subsystem occurs [8]. Inasmuch as our research is directed to finding fluorine-containing compounds with high ion-conductive properties, of certain interest in this context are studies of ion mobility in complex antimony(III) fluorides with organic cations (in particular, with amino acid cations), for the lack of such studies in the related literature. Therefore, one task of this study consisted of carrying out a comparative analysis of dynamic characteristics of the anion and proton subsystems in antimony fluorides with  $\alpha$ -amino acids, on one hand, and in ammonium tetrafluoroantimonate(III) which had been studied earlier [5, 8], on the other. One more goal of this study was to gain data on the thermal properties of fluoroantimonates(III) with some  $\alpha$ -amino acids, for the reason that studies of this class of compounds are of applied and theoretical significance because of the occurrence of these organic ligands in biological systems.

### EXPERIMENTAL

Antimony trifluoride was reacted with  $\alpha$ -amino acids (L-leucine or DL-valine) in aqueous solution of hydrofluoric acid to prepare L-leucinium tetrafluoroantimonate(III) [(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>2</sub>)CH(NH<sub>3</sub>)COOH]SbF<sub>4</sub> (LeuHSbF<sub>4</sub>) and two molecular complexes of antimony(III): with L-leucine SbF<sub>3</sub>[(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>2</sub>)CH(<sup>+</sup>NH<sub>3</sub>)COO<sup>-</sup>] (SbF<sub>3</sub> · Leu) and with DL-valine SbF<sub>3</sub>[(CH<sub>3</sub>)<sub>2</sub>CHCH(<sup>+</sup>NH<sub>3</sub>)COO<sup>-</sup>] (SbF<sub>3</sub> · Val) [9–11]. Transparent colorless single crystals of LeuHSbF<sub>4</sub> shaped as long thin needles were grown by slow crystallization at room temperature

(component ratio: 1 : 1 (mol/mol); pH: 1).  $\text{SbF}_3 \cdot \text{Leu}$  was prepared as colorless plates with the initial component ratio of 0.5 : 1 and solution pH of  $\approx 3$ . The molecular complex  $\text{SbF}_3 \cdot \text{Val}$  was prepared as colorless platy crystals from solution with pH of 2–3 and a component ratio of 1 : 1.

Powder X-ray diffraction was measured on a Bruker D 8 ADVANCE diffractometer ( $\text{CuK}\alpha$  radiation). Thermoanalytical studies involving thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a Q-1500 derivatograph. The phase transition in  $\text{LeuHSbF}_4$  was studied by differential scanning calorimetry (DSC) on a NETZSCH STA 449 C Jupiter thermal analyzer. The heating rate was 5 K/min. The reference was calcined  $\text{Al}_2\text{O}_3$ .

( $^{19}\text{F}$  and  $^1\text{H}$ ) NMR spectra were recorded on a Bruker AV-300 multinuclear digital spectrometer at Larmor frequencies ( $\nu_L = 282.404$  MHz for  $^{19}\text{F}$  and  $\nu_L = 300.13$  MHz for  $^1\text{H}$  in the range 150–420 K. The precision of temperature adjustment was  $\pm 2$  K. The mean-squared widths (or second moments) of NMR spectra ( $S_2$  in  $\text{G}^2$ ) were calculated by an original program using formulas found in [12]. Line widths at half height  $\Delta H$  (in kHz), chemical shifts  $\delta$  (in ppm), and integrated component intensities of  $^{19}\text{F}$  NMR spectra were measured with an error of no more than 3%. The chemical shifts of  $^{19}\text{F}$  NMR signals were measured relative to a  $\text{C}_6\text{F}_6$  reference (for  $\text{C}_6\text{F}_6$ , the chemical shift is  $-589$  ppm relative to gaseous  $\text{F}_2$ , for which  $\delta = 0$  ppm).

The conductivity of  $\text{LeuHSbF}_4$  was studied on tablets compacted under 400 MPa together with pressed-in silver electrodes. Electrical conductivities were measured on an alternating current in a two-probe scheme in air in the range 300–410 K using a NOVOCONTROL Beta dielectric analyzer in the frequency range from 3  $\mu\text{Hz}$  to 1 MHz. Conductivity values were calculated from frequency-dependent conductivities using the complex impedance method.

## RESULTS AND DISCUSSION

### Thermoanalytical Data

Thermogravimetric data imply the thermal stability of L-leucinium tetrafluoroantimonate(III) in the temperature range 20–95°C (Fig. 1). In the range 110–140°C, the DTA curve features an endotherm with a peak at 130°C, which corresponds to an irreversible phase transition. The attendant weight loss ( $\Delta m$ ) is about 1.5%, which is likely to arise from the elimination of “free” (sorbate) water molecules that can occur in pores of the material because it was prepared from aqueous solution. An argument in favor of this assumption is provided by  $^1\text{H}$  NMR spectra (see below). The heat of the phase transition measured by DSC is 31.8 J/g. Noteworthy, not only the phase transition occurs in the temperature range 110–140°C,

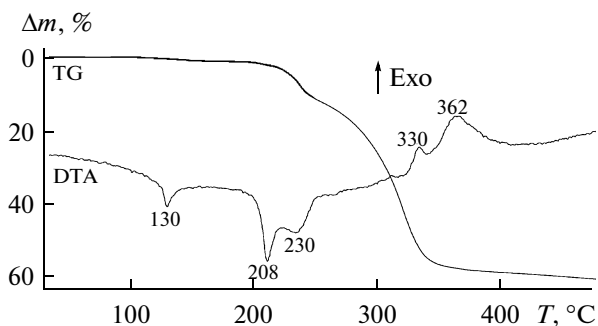
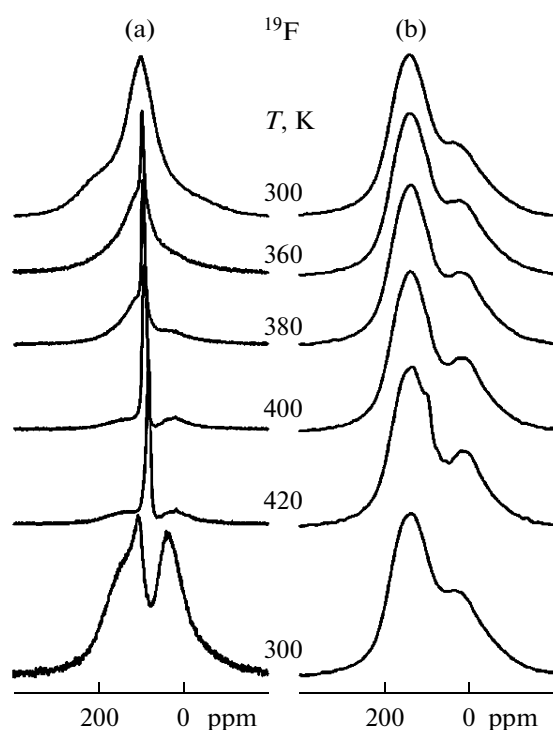


Fig. 1. TG and DTA curves for  $\text{LeuHSbF}_4$  as a function of temperature.

but also the newly formed phase loses heat tolerance : it starts to soften. As temperature rises further, the viscosity of the sample decreases, and above 201°C the DTA curve features two overlapping endotherms with peaks at 208 and 230°C. The first endotherm corresponds to melting of the sample and occurs without considerable weight loss. The second corresponds to the thermal decomposition of the sample ( $\Delta m = 9.85\%$ ). Above 243°C, strong weight loss occurs because of the evolution of volatiles with a peak decomposition rate at 317°C. The DTA curve does not feature any well-defined attendant features. This is for the reason that two processes occur at the same time in the aforementioned temperature range, namely, the thermal-oxidative destruction and thermal decomposition of the products that were formed after heating to 243°C (that is, there is a superposition of exo- and endotherms). Exotherms at 330 and 362°C are likely to arise from the post-oxidation of newly formed organic products and the burning-out of the carbonized residue from the organic component of the compound. The weight loss at 475°C is  $\approx 64\%$ . The final product of  $\text{LeuHSbF}_4$  decomposition identified by powder X-ray diffraction is metallic antimony ( $\Delta m_{\text{calc}} = 63.03\%$ ).

For the molecular antimony(III) fluoride complex with L-leucine ( $\text{SbF}_3 \cdot \text{Leu}$ ), the DTA curve in the range 180–240°C features two overlapping endotherms with peaks at 205 and 220°C. To the first endotherm, there corresponds an insignificant weight loss, and to the second, a weight loss of  $\sim 10\%$ . The observed endotherms are associated with melting of  $\text{SbF}_3 \cdot \text{Leu}$  and its subsequent decomposition. Above 240°C, the TG curve features strong weight loss associated with the elimination of volatile products. The rate of the process is maximal at 310°C with a low-intensity exotherm, which likely results from the superposition of the exotherm of the thermal-oxidative destruction of the organic component and the endotherm of the thermal decomposition (pyrohydrolysis) of the inorganic product. Exotherms at 360 and 560°C are due to burning-out of the carbonized residue of the organic material. The narrow exotherm at 630°C is likely to



**Fig. 2.** Transformation of  $^{19}\text{F}$  NMR spectra of (a) L-leucinium tetrafluoroantimonate(III) and (b) the molecular complex  $\text{SbF}_3 \cdot \text{Val}$ .

arise from the crystallization of the decomposition product (which was not studied) of the initial compound. The weight loss at  $650^\circ\text{C}$  is  $\sim 69\%$ .

The molecular complex  $\text{SbF}_3 \cdot \text{Val}$  is stable up to  $150^\circ\text{C}$ . At  $210^\circ\text{C}$ , the DTA curve features an endotherm associated with melting of the compound, without any attendant feature on the TG curve; the weight loss ( $\approx 15\%$ ) observed in the range  $220\text{--}260^\circ\text{C}$  is associated with the decomposition of the compound. In the range  $260\text{--}330^\circ\text{C}$ , a weak endotherm is noticed with an attendant strong weight loss (up to  $55\%$ ), which is due to the decomposition (pyrohydrolysis) of the inorganic product and the thermal-oxidative destruction of the organic component. Further heating gives rise to exotherms at  $430$  and  $560^\circ\text{C}$ ; the weight of the sample is reduced smoothly in association. The decomposition of  $\text{SbF}_3 \cdot \text{Val}$  ends at  $650^\circ\text{C}$ ; the overall weight loss is  $\approx 64\%$ . The final product as identified by X-ray powder diffraction is a mixture of antimony(III) and antimony(V) oxides: valentinite ( $\text{Sb}_2\text{O}_3$ ) and cervantite ( $\text{Sb}_2\text{O}_4$ ).

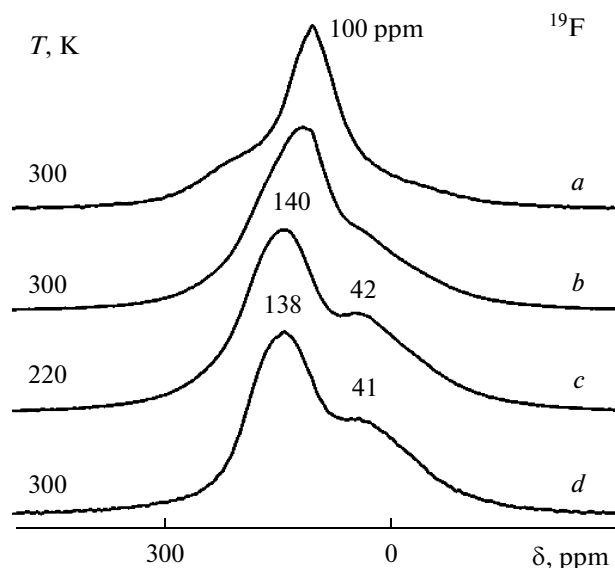
### NMR Data

Quantitative examination of  $^{19}\text{F}$  NMR spectra (Fig. 2, spectrum *b*) shows that the fluoride sublattice of the molecular complex  $\text{SbF}_3[(\text{CH}_3)_2\text{CHCH}^+(\text{NH}_3)\text{COO}^-]$  remains “rigid” (in NMR terms [12]) over the entire range of temperatures studied, and therefore, we may

infer that ion transport does not occur in this complex in the range  $300\text{--}420$  K. The same inference may be done for the proton subsystem of the complex, because from the examination of  $^1\text{H}$  NMR spectra, it follows that the line shapes and the values of the second moment remain virtually unchanged while temperature rises. In particular, a  $^1\text{H}$  NMR spectrum of  $\text{SbF}_3 \cdot \text{Val}$  represents a structureless line, which can be fitted by a Gaussian with the width  $\Delta H \approx 41\text{--}39.5$  kHz in the temperature range  $300\text{--}400$  K, and the second moment of  $^1\text{H}$  NMR spectra is almost temperature independent and has a value of  $18 \pm 1$  G<sup>2</sup>. Noteworthy, the  $^1\text{H}$  NMR spectrum of the molecular complex  $\text{SbF}_3 \cdot \text{Leu}$ , which is represented by a single symmetric line fitted by the superposition of a Lorentzian ( $\approx 40\%$ ) and a Gaussian, insignificantly narrows in the temperature range  $300\text{--}420$  K ( $\approx 33 \rightarrow 29$  kHz), which also indicates the absence of noticeable transport in the proton subsystem of this compound.

In the  $^{19}\text{F}$  NMR spectra of L-leucinium tetrafluoroantimonate(III), in contrast, a narrow component with a width less than  $3$  kHz appears as early as above  $320$  K and grows in intensity as temperature rises (Fig. 2, spectrum *a*), indicating the appearance of high-mobility fluoride ions (with movement frequencies higher than  $10^4$  Hz) in the fluoride sublattice of  $\text{LeuHSbF}_4$ . In view of the fact that, in the  $[(\text{CH}_3)_2\text{CH}(\text{CH}_2)\text{CH}(\text{NH}_3)\text{COOH}]\text{SbF}_4$  crystal structure,  $[\text{SbF}_4]_n^{2n-}$  complex anions are polymer chains of composition  $[\text{Sb}_2\text{F}_8]_n^{2n-}$  which are built of  $\text{Sb}_2\text{F}_8$  dimers formed of  $\text{SbF}_3$  and  $\text{SbF}_5$  groups and linked to one another by a bridging fluorine atom [10], we may suggest that fluorine-containing groups start rapidly reorienting as temperature rises, which can result in the rupture of fluorine bridges with a release a free fluoride ion and its travel along the chain [2].

After the sample is cooled ( $413 \rightarrow 300$  K), the pattern of its  $^{19}\text{F}$  NMR spectrum does not correspond to the NMR spectrum recorded from the intact (unheated) sample (Fig. 3; spectra *a, b*); this can arise from at least two reasons. One reason lies in a possible decomposition of the compound upon reaching a temperature of  $413$  K. According to TGA and DTA, however, this actually does not occur. Another likely reason for the discrepancy between the  $^{19}\text{F}$  NMR spectra at  $300$  K of the as-synthesized  $\text{LeuHSbF}_4$  and the cooled sample ( $413 \rightarrow 300$  K) is the occurrence of the phase transition, which goes in line with thermoanalytical data. The phase transition observed in this compound is likely associated both with orientation disorder in the anionic (cationic) sublattice (which is intrinsic to compounds that are built of complex anions, cations, or molecular groups [13]) and with structural alterations in the fluoride sublattice. The resulting  $\text{LeuHSbF}_4$  phase is unstable and transforms, over time, to the molecular complex  $\text{SbF}_3 \cdot \text{Leu}$ , as proved by  $^{19}\text{F}$  NMR data (Fig. 3; spectra *c, d*), X-ray

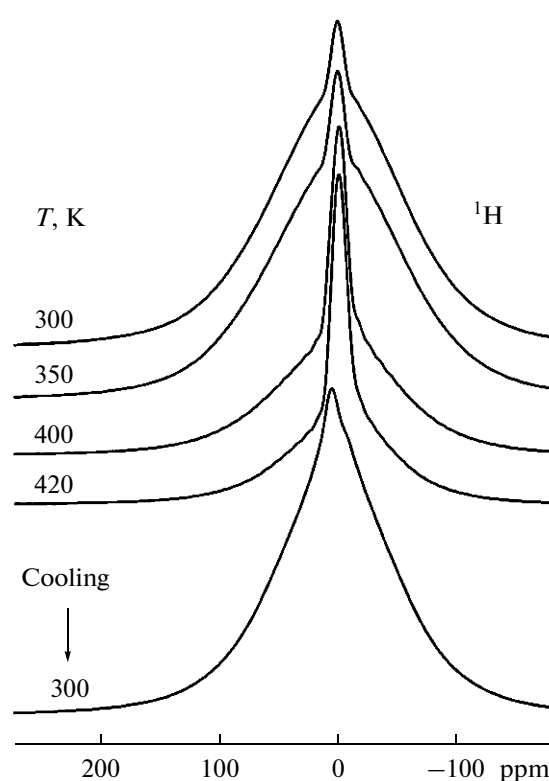


**Fig. 3.**  $^{19}\text{F}$  NMR spectra of antimony(III) complexes with amino acids at selected temperatures: (a) the precursor complex  $\text{LeuHSbF}_4$ , (b, c)  $\text{LeuHSbF}_4$  after heating to 410 K and cooling, and (d) molecular complex  $\text{SbF}_3 \cdot \text{Leu}$ .

powder diffraction, and chemical analysis. As in the molecular complex  $\text{SbF}_3 \cdot \text{Val}$ , temperature variations within the range 300–420 K virtually do not affect the character of  $^{19}\text{F}$  NMR spectra of  $\text{SbF}_3 \cdot \text{Leu}$ , which correspond to the “rigid” lattice ( $\Delta H \approx 54$  kHz).

According to chemical analysis, the antimony percentage in a  $\text{LeuHSbF}_4$  sample after it was heated to 413 K and then cooled to 300 K is 39.2%, which agrees with the result of calculations for the molecular complex  $\text{SbF}_3 \cdot \text{Leu}$  (39.31% Sb). The orthorhombic unit cell parameters measured in the sample that was heated to 413 K and then cooled to 300 K ( $a = 29.384$  Å,  $b = 6.2285$  Å,  $c = 5.8087$  Å,  $V = 1063.1$  Å<sup>3</sup>) only insignificantly differ from the parameters of the molecular complex  $\text{SbF}_3 \cdot \text{Leu}$  (an orthorhombic cell,  $a = 5.7948$  Å,  $b = 6.2433$  Å,  $c = 28.594$  Å,  $V = 1034.5$  Å<sup>3</sup>).

The room-temperature  $^1\text{H}$  NMR spectrum of L-leucinium tetrafluoroantimonate(III) consists of a broad ( $\approx 40$ -kHz) structureless band and a relatively narrow ( $\Delta H \approx 3.2$  kHz) and low-intensity signal (Fig. 4); judging from the spectral pattern in the range 420–300 K, the latter can belong to “free” (sorbate) water molecules, because this component virtually disappears from the spectrum when the sample is cooled from 420 to 300 K. Nonetheless, the  $^1\text{H}$  NMR spectrum of  $\text{LeuHSbF}_4$  in the range 300–400 K features a narrow component ( $3.6 \pm 0.2$  kHz), which grows in intensity as temperature rises (Fig. 4). The occurrence of this component implies the appearance, in the proton subsystem, of mobile proton-containing groups (protons), which account for more than 25% of the total amount of  $^1\text{H}$  atoms in the proton subsystem at 400 K. In the range 400–420 K, the integrated



**Fig. 4.**  $^1\text{H}$  NMR spectra for L-leucinium tetrafluoroantimonate(III) with temperature variations.

intensities of the broad and narrow components undergo a further redistribution in favor of the latter.

When  $\text{LeuHSbF}_4$  is cooled to 300 K, the  $^1\text{H}$  NMR spectrum (as the  $^{19}\text{F}$  NMR spectrum) slightly differs from the initial spectrum, above all, by the width of the major component ( $\Delta H \approx 28$  kHz), apparently, due to the formation of an unstable phase of L-leucinium tetrafluoroantimonate(III), which transforms over time into the molecular complex  $\text{SbF}_3 \cdot \text{Leu}$ .

#### Electrophysical Data

Temperature-dependent conductivity ( $\sigma$ ) for L-leucinium tetrafluoroantimonate(III) is plotted in Fig. 5. The temperature-dependent conductivity for this compound is well linearized in the space of the Arrhenius–Frenkel equation  $\sigma T = A \times \exp(-\Delta E_a/kT)$ , where  $A$  is the frequency factor in the form dictated by the conductivity model selected [14] and  $\Delta E_a$  is the activation energy. From electrophysical measurements, it follows that the rise in temperature from 300 to 385 K leads to a more than four-order-of-magnitude increase in conductivity of  $\text{LeuHSbF}_4$ , which agrees with the results of NMR studies: high-mobility ions, which can serve as charge carriers, appear in both (anionic and cationic) subsystems precisely in this temperature range.

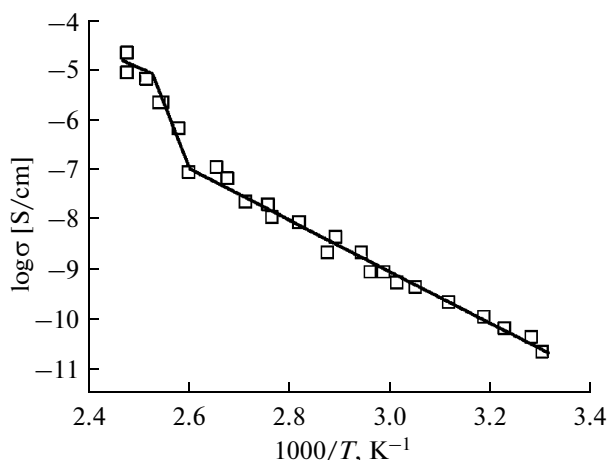


Fig. 5. Conductivity versus temperature for L-leucinium tetrafluoroantimonate(III).

According to impedance spectroscopy, a phase transition to a relatively high-conductivity state occurs at  $T > 383$  K. This qualitatively agrees with the results of thermogravimetric experiments considered above. The phase transition in  $\text{LeuHSbF}_4$  has a diffusion character; that is, the rise in conductivity occurs gradually over a temperature range of 383–403 K, rather than by a jump. The high-temperature phase is likely ductile, as proven by a smooth decrease in tablet thickness under weak clamping observed at temperatures above 383 K. Once the phase transition occurs,  $\sigma$  increases by two more orders of magnitude to reach  $\approx 2.15 \times 10^{-5}$  S/cm at 403 K. Conductivity measurements were not carried out because of the high-temperature phase being ductile above this temperature, and the true value of the conduction activation energy is difficult to determine. Estimates of this parameter give values of 1.04 eV. For this reason, it is difficult to come to a unique conclusion as regards the practical utility of this compound in engineering devices.

Thus, according to the results of our thermoanalytical studies of antimony(III) complexes with  $\alpha$ -amino acids, the phase transition to a high-conductivity state is intrinsic only to an ionic complex ( $\text{LeuHSbF}_4$ ). For molecular complexes  $\text{SbF}_3 \cdot \text{Val}$  and  $\text{SbF}_3 \cdot \text{Leu}$ , such an effect is not observed. Both for ionic compounds and neutral complexes, the loss of heat tolerance (softening) occurs at lower temperatures than the loss of thermal stability associated with intense weight loss.

The analysis of the ion mobility dynamics in the antimony(III) fluorides with  $\alpha$ -amino acids shows that, unlike in  $\text{NH}_4\text{SbF}_4$  for which the “orientational disorder” of fluoride groups  $\text{Sb}(1)\text{EF}_5$  and  $\text{Sb}(2)\text{EF}_5$  in the range 250–410 K provides for the appearance of fluoride ion diffusion in the phase-transition region

(395–415 K) [5, 8], the presence of organic cations (neutral molecules) in fluoroantimonates(III) differently affects the dynamic characteristics of the fluoride (proton) sublattice. In molecular complexes  $\text{SbF}_3 \cdot \text{Val}$  and  $\text{SbF}_3 \cdot \text{Leu}$ , a high ion mobility is not observed either in the fluoride or in the proton sublattice. In L-leucinium tetrafluoroantimonate(III), however, high-mobility ions appear in the anionic and cationic sublattices as temperature changes from 300 to 410 K. The structure of the compound is likely to be a key factor for the possibility of fluoride(proton)-containing groups to go from the rigid lattice to local motions with frequencies above  $10^4$  Hz (for the appearance of high-mobility ion groups).

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