

Fluorine Diffusion and Phase Transition in Superionic Conductor KSn_2F_5 as Studied by ^{19}F NMR, Electrical Conductivity and DSC

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The diffusion of fluorine in KSn_2F_5 has been studied by T_1 and T_2 relaxation time measurements of ^{19}F NMR (200–500 K) and pulsed magnetic field gradient techniques (390–480 K). Near 423 K a sharp transition into the superionic state has been found, the fluorine diffusion increasing by a factor of 4 within a range of 3 K. Conductivity measurements only show a change in the activation energy.

In a research for new fluorine superionic conductors based on tin(II) fluorine the investigation of the electrical and diffusion properties of RbSn_2F_5 had shown this compound to be a good fluorine conductor even at moderately elevated temperatures [1]. Therefore, we started to study the fluorine transport properties of the compounds $M_1\text{Sn}_2\text{F}_5$, where $M_1 = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Tl}^+$ and NH_4^+ . Here we report the results for KSn_2F_5 powder samples.

Preparation, sample characterization by X-ray diffraction and Mössbauer spectroscopy, electrical conductivity measurements and determination of the fluorine self-diffusion by ^{19}F NMR at 57 MHz and pulsed magnetic field gradient techniques (PMFG) were the same as described for RbSn_2F_5 in [1]. Additionally the longitudinal (T_1) and transverse (T_2) relaxation times of ^{19}F NMR have been measured by standard pulse techniques.

At all temperatures (200–500 K) ^{19}F NMR gave a single uniform signal, i.e. all fluorine ions of KSn_2F_5 are equally mobile and no immobile fraction does exist as observed in PbSnF_4 [2]. The Arrhenius plot of the temperature dependence of T_1 and T_2 of ^{19}F NMR is shown in Figure 1. All values were perfectly reversible and showed no change after repeated thermal cycling.

Below 260 K the rigid lattice $T_2^0 \approx 25 \mu\text{s}$, i.e. a second moment $M_2^0 \approx 3.5 \cdot 10^9 \text{ rad/s}^2$ was found. Above 260 K motional narrowing was observed with an activation energy of $42 \text{ kJ/mol} = 0.44 \text{ eV}$. The same activation energy was found from the temperature dependence of T_1 between 320 and 400 K. This coincidence can only be by chance and 0.44 eV is only a lower limit for the true activation energy of the fluorine diffusion, as there is additional relaxation by traces of paramagnetic impurities: The observed T_1 -relaxation is too fast, a T_1 -minimum of at least 110 ms is calculated from the dipolar rigid lattice second moment M_2^0 .

At temperatures above 400 K instead of increasing, nearly temperature independent T_1 and T_2 values were observed with $T_1/T_2 \approx 4$. Moreover, the transverse relaxation showed slight, but definite deviations from a single exponential. It is unclear whether this anomalous behaviour is caused by correlated low-frequency modes of motion of the molten fluorine sub-lattice [3] or by paramagnetic centers existing only at higher temperatures.

In contrast to T_1 and T_2 , the coefficient of fluorine self-diffusion determined by the PMFG technique clearly showed the transition into the superionic state near 423 K = 150 K (Figure 2). Within a range of 3 K the fluorine diffusion is increasing by a factor of 4. As both temperature stability and difference over the sample were about

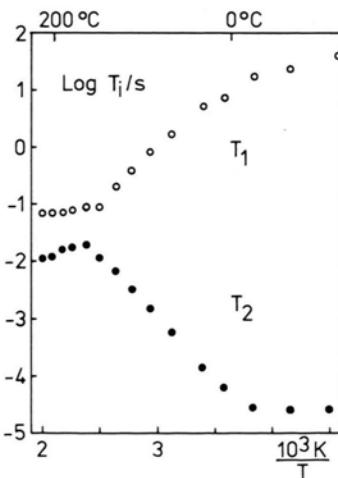


Fig. 1. Arrhenius plot of the longitudinal (T_1 , \circ) and transverse (T_2 , \bullet) relaxation times of ^{19}F NMR at 57 MHz of KSn_2F_5 .

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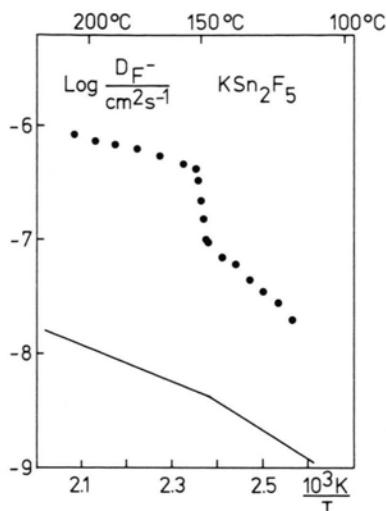


Fig. 2. Arrhenius plot of the fluorine self-diffusion in KSn_2F_5 . Points: D_{F^-} as determined by ^{19}F NMR PMFG technique. Solid line: D_{F^-} as calculated from conductivity using the Einstein relation.

0.5 K, this is probably not a first-order transition. First calorimetric studies (DSC, heating rate 1 K/min) showed an endotherm peak with half-width of 2.4 K and 7.9 J/g heat of transition. A similar discontinuity of the fluorine diffusion had been found in PbF_2 , but near 700 K [4].

Fitting to an Arrhenius equation $D = D_0 \cdot \exp(-E_A/RT)$ the fluorine self-diffusion can be described below the transition by $E_A = 69 \text{ kJ/mol} = 72 \text{ eV}$, $D_0 = 25 \text{ cm}^2/\text{s}$ and above the transition by

$E_A = 21 \text{ kJ/mol} = 0.22 \text{ eV}$, $D_0 = 1.5 \cdot 10^{-4} \text{ cm}^2/\text{s}$. These activation energies agree nearly perfectly with those reported for PbF_2 (0.73 resp. 0.20 eV) [4], but the transition temperature is decreased by nearly 300 K.

The Arrhenius plot of the specific conductivity consists of two linear parts with $E_A = 0.50 \text{ eV}$ below and 0.31 eV above the transition, but no discontinuity has been found at the transition. This is very surprising. It cannot be excluded that polarization effects or the electrode resistance affected the measurements of conductivity when the sample is highly in the superionic state, especially when using powder samples: The fluorine diffusion calculated from the measured conductivity by the Einstein relation with a correlation factor $f = 1$, is nearly two orders of magnitude lower than D (PMFG) between 400 and 500 K. This discrepancy disappears at lower temperatures, and there is good agreement between the values calculated from conductivity, extrapolated from PMFG-data and estimated from the beginning of motional narrowing, all giving $D \approx 10^{-11} \text{ cm}^2/\text{s}$ near 280 K.

Our measurements have shown that KSn_2F_5 is a good and stable fluorine conductor with a sharp transition into the superionic state at a temperature (150°C) low enough for easily studying the exact nature of the order-disorder transition in anion superionics.

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