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# Probing the Mechanism of Fluoride-Ion Conduction in $LaF_3$ and Strontium-Doped $LaF_3$ with High-Resolution $^{19}F$ MAS NMR

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The superionic conductor lanthanum fluoride has been extensively studied as a result of its favorable ionic conductivity ($10^{-5}$−$10^{-6}$ $W^{-1}$ $cm^{-1}$ at room temperature),[1−9] but the mechanism of conduction still remains under debate. $LaF_3$ adopts the tysonite structure, in which there are three crystallographically inequivalent sites for fluorine (F1, F2, and F3) with multiplicities of 12:4:2.[10] Early $^{19}F$ wide-line NMR and relaxation studies showed that the motion begins on the F1 sublattice[1−3] and that exchange between the F1, F2, and F3 sublattices occurs only at higher temperatures.[3] The F2 and F3 fluoride-ion sites could not be resolved, and consequently, differences in their mobilities were not detected. Hence, only two types of dynamic fluoride sites were proposed to exist (F1 and F2,3).[1−3,7−8] Vacancies on the F1 sublattice were observed in a neutron diffraction study of $La_{1-x}Ba_xF_{3-x}$,[11] in agreement with the increase in F1 mobility on $BaF_2$ doping. In contrast, more recent conductivity and NMR measurements on single crystals of $LaF_3$ were interpreted as being consistent with rapid motion on the F2 and F3 sublattices at low temperatures, exchange with the F1 lattice, and F1 motion, commencing only at higher temperatures.[6] Most recently, however, $^{19}F$ wide-line NMR has again shown that the motion begins on the F1 sublattice (at $\approx$17 °C), and that above approximately 247 °C, exchange between the F1 and F2,3 fluorine sublattices takes place.[7] Strontium doping lowered the temperature at which the onset of ionic mobility occurred.[8]

We recently reported a $^{19}F$ MAS NMR study of the moderate fluoride-ion conductor $\alpha$-$PbF_2$, in which we demonstrated that very fast sample spinning of up to 24 kHz provides, even in strongly dipolar-coupled systems, sufficient resolution to resolve the individual crystallographic sites for fluorine and to study the fluoride-ion motion.[12] In the present study, we extend this approach to investigate $LaF_3$ and its anion-deficient solid solution $La_{0.99}Sr_{0.01}F_{2.99}$. Individual crystallographic sites are resolved, which allows us to demonstrate, for the first time, that all three fluorine sublattices in $LaF_3$ are dynamically inequivalent.

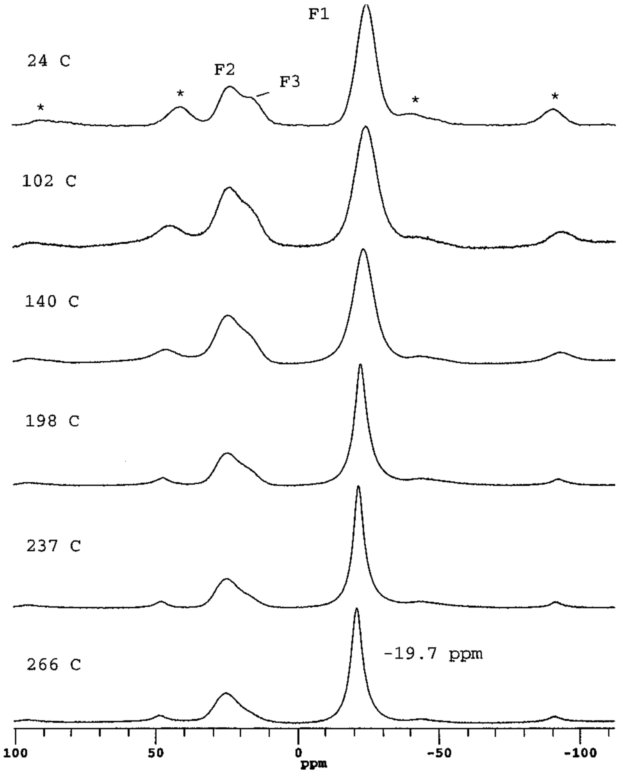

**Figure 1.** $^{19}F$ variable-temperature MAS NMR spectra of $LaF_3$, collected with a spinning speed of 23 kHz. * = spinning sideband. $Pb(NO_3)_2$ was used to calibrate the temperature.[14] Spectra were acquired on a Chemagnetics 360 MHz NMR spectrometer, at an operating frequency for $^{19}F$ of 338.75 MHz. $^{19}F$ spectra were referenced to $CCl_3F$ at 0 ppm.

The variable-temperature $^{19}F$ MAS NMR spectra of polycrystalline $LaF_3$ are shown in Figure 1. Three resonances with integrated intensities of 6:1:2 are observed at room temperature at −23.5, 17.1, and 24.9 ppm, which are assigned to the three crystallographically distinct fluorine sites F1, F3, and F2, respectively. Above 73 °C, the resonance at −23.5 ppm (F1) begins to shift gradually to higher frequencies; this is accompanied by a small decrease in the intensity of the F3 resonance. The lower frequency resonance continues to shift to higher frequencies with increasing temperature, and by 266 °C, it has shifted by 4.2 ppm to −19.7 ppm. At this temperature, the F3 resonance is visible only as a smaller shoulder on the F2 resonance. These observations are consistent with fluorine-ion exchange between F1 and F3 sites: rapid exchange between two sites at a frequency greater than the separation of the two resonances (i.e., 13.8 kHz) will result in a single resonance whose chemical shift is intermediate between the two resonances.[13] The exact position of the resonance depends on the fraction of the spins that are

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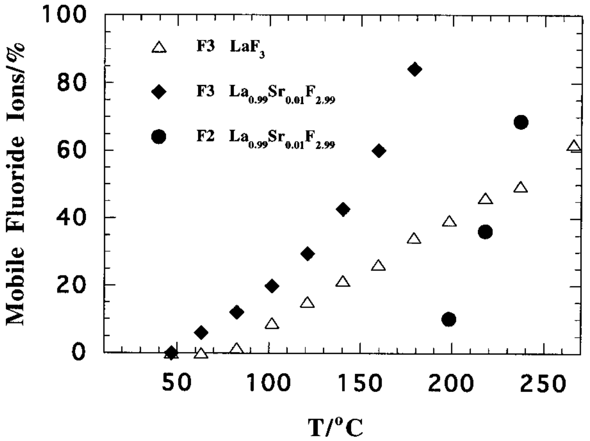

**Figure 2.** Change with temperature in the fraction of F3 and F2 ions undergoing F1 to F3 jumps (with $\tau_c < 3.3 \times 10^{-5}$ s) and F1−3 to F2 jumps ($\tau_c < 7.0 \times 10^{-5}$ s), respectively, for $LaF_3$ and $La_{0.99}Sr_{0.01}F_{2.99}$.

involved in the chemical-exchange processes. If the fluoride-ion jumps were occurring between all the F3 and F1 sites, a single resonance at −17.3 ppm would be predicted. Furthermore, if these jump processes were occurring with a narrow distribution of correlation times, variable-temperature spectra characteristic of two-site exchange processes would be observed, i.e., a broadening of the F1 and F3 resonances, as the temperature is increased, followed by a coalescence into a single resonance at −17.3 ppm. This is not observed experimentally, and instead the spectra are consistent with a gradual increase, with temperature, in the number of F3 sites that are exchanging with the F1 sublattice. The percentage of F3 ions that contribute to the "F1" resonance can be calculated from the chemical shift of the "F1" resonance (Figure 2) and the contribution from the F3 ions increases smoothly above 82 °C, until at 266 °C, 62% of the F3 ions are in exchange with F1 ions. F1/F3 coalescence occurs for a correlation time $\tau_c$ of $3.3 \times 10^{-5}$ s or less. Thus, the subset of F3 ions that contribute to the "F1" resonances are making F1−3 jumps with $\tau_c \leq 3.3 \times 10^{-5}$ s. The F1−1 jumps occur considerably faster, since a single "F1" resonance is observed throughout the whole temperature range studied. This observation indicates that above 82 °C, where the F1 resonance starts to shift, the F1 ions in the lattice are undergoing F1−1 jumps with correlation times of at least an order of magnitude less than $3.3 \times 10^{-5}$ s: during the correlation time of one F1−3 exchange, the fluoride ion that jumps from the F3 site must also undergo exchange with numerous other F1 sites, so that the F1 sites are rendered equivalent. Spectral simulations performed with DNMR-SIM,[15] demonstrate the effect of fast F1−F1 motion on the spectra, are consistent with the above model for fluoride ion motion (Figure 3). The line width and intensity of the F2 resonance remain constant with temperature, indicating that the F2 ions are rigid in the temperature range studied. Note that any F2−3 jumps that occur with $\tau_c$'s of less than $1.7 \times 10^{-4}$ s would lead to coalescence of the F2 and F3 resonances and slow F2−3 jump processes can be excluded.

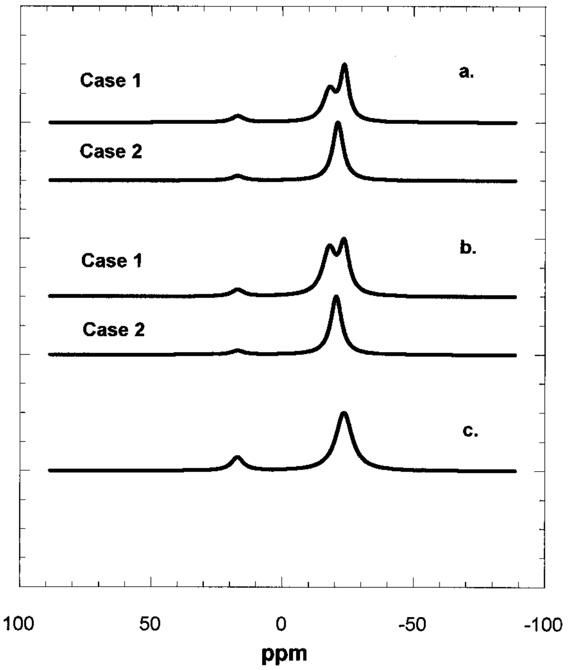

**Figure 3.** Simulations of $^{19}F$ MAS NMR spectra for F1−F3 exchange under conditions of no and rapid F1−F1 motion are shown for (a) 198 and (b) 237 °C. Case 1 shows the spectrum under conditions of no F1−F1 exchange. Case 2 shows the spectrum under conditions of fast F1−F1 motion. The spectrum of the rigid F1 and F3 sublattices is shown in (c) for comparison (i.e., no F1−F3 or F1−F1 exchange). The fraction of mobile F3 ions, which undergo exchange with nearby F1 ions with $\tau_c < 3.3 \times 10^{-5}$ s, were extracted from Figure 2. Line broadenings equal to those of the "F1" and rigid F3 resonance (Figure 1) were used in the simulations.

The variable-temperature $^{19}F$ MAS NMR spectra of the polycrystalline anion-deficient solid solution $La_{0.99}Sr_{0.01}F_{2.99}$ are similar to those of $LaF_3$ at low temperatures (Figure 4). The onset of F1−3 motion, however, occurs at more than 19 °C below the onset temperature for F1−3 motion in the pure material, and at 198 °C, the F3 resonance can no longer be observed. The fraction of mobile F3 ions (in the NMR time scale), calculated from the "F1" chemical shift, is consistently higher at all temperatures than in the pure material (Figure 2). As the temperature is raised above 198 °C, the "F1" resonance continues to shift to higher frequency, and now the intensity of the F2 fluorine sites starts to decrease in intensity, indicating an onset of exchange between the F2 and F1−3 sublattices. By 266 °C, the F2 resonance is no longer visible, and all the F2 ions are mobile. Again, the percentage of F2 ions that are exchanging with the F1 and F3 sites can be calculated from the chemical shift of the "F1" resonance (Figure 2). A minimum value of $\tau_c$ for the F2−(F1−3) exchange can be calculated from the difference in chemical shifts between the F2 resonance and the F1/F3 averaged resonance (−17.3 ppm), giving $7.0 \times 10^{-5}$ s.

The high-resolution NMR allows the rigid and mobile fluoride ions to be probed simultaneously. Fluoride ion conduction in $LaF_3$ occurs via vacancies on the fluoride-ion lattice,[2] and the correlation times for motion are a function of both the concentrations of the anion vacancies and the activation energy of the jump processes. Thus the F3−1 jump rate will depend not only on the F3−1 activation energy but also on the probability of there being a vacancy on an adjacent F1 site. It is

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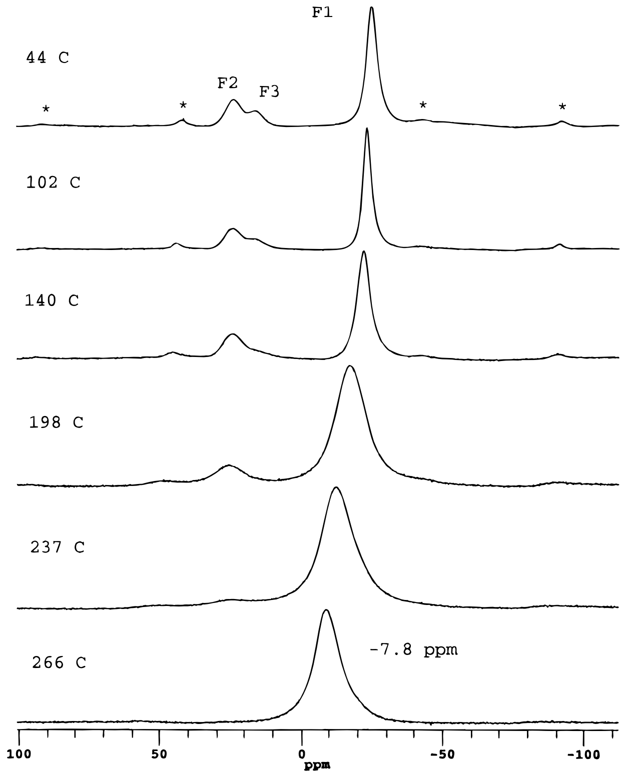

**Figure 4.** $^{19}$F variable-temperature MAS NMR spectra of $La_{0.99}Sr_{0.01}F_{2.99}$, collected with a spinning speed of 23 kHz. * = spinning sideband.

difficult to rationalize the $^{19}$F NMR spectra observed at temperatures close to room temperature, unless there is a distribution in the concentration of vacancies across the F1 sublattice. Distributions in vacancy concentrations are most likely a consequence of anion vacancy/cation vacancy or anion vacancy/defect (e.g., $Sr^{2+}$) associations, resulting from Coulombic interactions between oppositely charged species. These associations have been shown to exist in a variety of stoichiometric and doped ionic solids and result in a partial localization of the anion vacancy.[16] A distribution in vacancy concentrations (or in the probability of an adjacent vacancy) will lead to a distribution in F1−3 correlation times: the subset of mobile F3 ions that are observed by NMR are those that are sufficiently close to fluoride-ion vacancies that they undergo rapid exchange between the two sublattices, within the correlation time probed by the 1-D NMR method (e.g., $3.3 \times 10^{-5}$ s for the F1−3 exchange). The anion vacancies are not, however, completely localized and F1−1 motion occurs throughout the sublattice. Note that, in the absence of F1 motion, a distribution of F1−3 correlation times would lead to the appearance of a fourth resonance (in addition to the F1, F2, and F3 resonances) intermediate in chemical shift between the F1 and F3 resonances (see Figure 3, case 2). This behavior is similar to that observed in the $^{19}$F MAS spectra of potassium-doped $\alpha$-$PbF_2$.[12,17] As the temperature is raised, the number and mobility of the intrinsic vacancies increases, and thus the distribution in the vacancy concentrations across the F1 lattice diminishes. Under these conditions, the distribution in F1−3 correlation times also decreases, and spectra consistent with a narrower range of correlation times are observed. For example, the onset of F2−1 exchange, which occurs at more elevated temperatures, is accompanied by an initial broadening of the “F1” and F2 resonances before coalescence, as the F2−(F1−3) exchange rate enters the intermediate regime.

In conclusion, the $^{19}$F MAS NMR spectra of $LaF_3$ and $La_{1.99}Sr_{0.01}F_{2.99}$ demonstrate that the three crystallographically distinct fluoride-ion sites have very different mobilities, and the activation energies, for the different fluoride-ion jump pathways, increase in the order F1−1 < F1−3 < F1−2. High-resolution $^{19}$F MAS NMR provides an extremely effective and unique method for probing the mechanism of fluoride-ion conduction at a local level, which allows the properties of each of the different fluoride-ion sublattices to be observed directly. In addition, the $^{19}$F NMR spectra are sensitive to distributions in the rates of motion throughout the sample. Two-dimensional NMR methods will permit a greater range of correlation times to be accessed, and the application of both 1- and 2-D NMR techniques to the study of fluoride-ion conduction in a wide range of materials is currently underway.

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