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Dynamic processes in the superionic conductor LaF_3 at high temperatures as studied by spin–lattice relaxation dispersion

A F Privalov¹, O Lips and F Fujara

Institut für Festkörperphysik, Technische Universität Darmstadt, 64289 Darmstadt, Germany

E-mail: Alexei.Privalov@physik.tu-darmstadt.de

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Abstract

By nuclear magnetic resonance spin–lattice relaxation dispersion in LaF_3 , measured in the frequency range from 60 kHz to 284 MHz, dynamic processes with correlation times in the range from 10^{-5} to 10^{-10} s are studied. This allows us to trace fluorine dynamics in the temperature range from 303 to 1400 K. Two motional modes, a fast one and a slow one, are identified. Both motional processes are found not to be of Bloembergen–Purcell–Pound type but obey a log-Gaussian distribution of correlation times, thus reflecting the potential energy landscape in the superionic state. Below 1000 K, the activation energy of fluorine diffusion is 0.36 eV for the fast ions, and 0.57 eV for the slow ones. At higher temperatures, the activation energies change drastically. Above 20 MHz, where most relaxation studies have been performed so far, an additional contribution to relaxation, which is probably induced by paramagnetic centres, is found to be dominant.

1. Introduction

Superionic conductivity in ionic solids is known to be related to dynamical disorder in at least one of the ionic sublattices [1]. Nevertheless, often analyses of ionic dynamics in superionic conductors (SICs) are based on the assumption of a thermally activated Arrhenius-like process with a single activation energy and a single motional correlation time [2]. Such a concept neglects motional heterogeneities in the superionic state. Therefore, most importantly for a better understanding of the superionic state, microscopic information is still lacking.

Experimental studies of motional disorder in SICs are rare because only a few methods are sensitive to the motional heterogeneity. Here, one has to list nuclear magnetic resonance (NMR) T_1 spin–lattice relaxometry [2–9], NMR line shape analysis [10] and the measurement of frequency-dependent conductivity [4, 5, 11, 12]. These methods provide data which are usually

¹ Author to whom any correspondence should be addressed.

interpreted by models describing the hopping by a distribution of correlation times or by non-exponential correlation functions. Several models explaining the jump diffusion and the observed relaxation behaviour with non-exponential decay times have been developed [11–16]. A model employing ionic jumps over an energy potential surface with a distribution of barriers is used in [4–10, 17]. Any new experimental information is of great interest for comparing the various approaches.

Also Raman spectroscopy and quasi-elastic neutron scattering are informative on dynamic disorder. The characteristic times of some of these methods, although much shorter and lying in the vicinity of phonon modes, partly overlap with those of NMR relaxometry.

The spin–lattice relaxation time T_1 yields the spectral density of local field fluctuations at the Larmor frequency and is thus related to motional processes on the atomic scale. If only one type of relaxation process exists, for example dipole–dipole relaxation, a $T_1(\omega, T)$ -analysis is well applicable to study motional heterogeneities in SICs. In the past such analyses have been performed mostly by varying only the temperature T and keeping the NMR frequency ω constant. From the temperature dependence of T_1 it is known that in SICs, particularly in superionic glasses, spin–lattice relaxation cannot be described by the standard Bloembergen–Purcell–Pound (BPP) model with a single monoexponential motional correlation function related to an Arrhenius process [2–8]. This is evident from the following features:

- (a) the $\ln T_1$ versus $1/T$ plot is not symmetrical with respect to the temperature at which the T_1 minimum occurs;
- (b) for the low-temperature branch the proportionality $T_1 \propto \omega^2$ is violated [3, 6, 7].

Therefore, a more detailed analysis becomes necessary. In an earlier approach the motional processes were modelled by a distribution of activation energies in order to describe the highly asymmetric $\ln T_1$ versus $1/T$ dependence, observed in ^{23}Na in β -alumina [8]. Likewise in the glassy SIC $(\text{Li}_2\text{S})_{0.35}(\text{GeS}_2)_{0.65}$ the deviation from BPP behaviour as well as the anomalous conductivity $\sigma(\omega)$ was explained satisfactorily by a model employing a Gaussian distribution of activation energies for the lithium motion [4]. The same approach has been used to explain spin–lattice relaxation in germanate glasses [5], phosphate glasses [6] and the perovskite structure of lithium lanthanum titanate [7]. A model with a simultaneous barrier- and site-energy distribution was proposed for nuclear spin relaxation in disordered systems to analyse the relaxation rates as a function of temperature [18].

When measuring only the temperature dependence of T_1 one faces the following problems.

- (1) According to the BPP relation the ionic motion leads to a minimum of the spin–lattice relaxation time at $\omega\tau \approx 1$, with τ being the correlation time. However, for many substances the minimum cannot be reached since the motion is not fast enough compared with the NMR frequency in the applicable temperature range (see for example [6]).
- (2) Relaxation by paramagnetic impurities can have a distinct effect on the temperature dependence of T_1 , which can make it difficult to gain information about the ionic motion or can even lead to severe misinterpretations [19].
- (3) The use of a given motional process may not be valid over the whole temperature range. New motional modes, phase transitions etc can occur with varying temperature.

The analysis of the frequency dependence of NMR spin–lattice relaxation times $T_1(\omega)$ does not bear the problems mentioned above. This kind of relaxometry has become increasingly popular in investigations of various systems with complex dynamics [20, 21]. Only in a very few cases this technique has been applied to ionic conductors [6, 22–24] due to the limited availability of commercial equipment. Since the sensitivity of standard NMR drops rapidly with decreasing Larmor frequency, most $T_1(\omega)$ -data have been measured either at frequencies higher than

10 MHz, using several NMR spectrometers at fixed frequencies, or one spectrometer operating at a variable magnetic field.

At frequencies below 100 kHz spin–lattice relaxation in the rotating frame, the so-called $T_{1\rho}$, has been studied. Besides experimental difficulties with maintaining high amplitudes of the radiofrequency field B_1 , the $T_{1\rho}$ technique has its limitation when γB_1 becomes comparable to, or smaller than, the NMR spectral width. In this case cross relaxation between spectral components locked to the B_1 field and unlocked off resonance components disturbs the $T_{1\rho}$ analysis. Moreover, the data from T_1 and $T_{1\rho}$ methods are not directly comparable. Altogether, results in the range from 100 kHz to 5 MHz are lacking.

An alternative approach of measuring the frequency dependence of spin–lattice relaxation times is the so-called field-cycling (FC) NMR. By fast switching the magnetic field between a fixed level for observation and a variable field for relaxation one can combine high detection sensitivity and a wide frequency range for relaxation as long as T_1 does not become much shorter than the switching times. This method has been developed in the last two decades and successfully applied to dynamic processes in many complex systems such as liquid crystals, polymers, biological systems etc [20, 21, 24–26]. An advantage of analysing the $T_1(\omega)$ dispersion is that it is done at a fixed temperature and thus leaves the dynamic processes unchanged. By measuring relaxation times in a frequency range of several decades it is possible to analyse the spectral density of the dynamical process. In particular, motional heterogeneities and the eventual occurrence of several motional processes can be analysed.

However, there are still some limitations of relaxometric investigations: cross-relaxation among different spin species tends to average the characteristic rates and thus causes a loss of information. Also, the extraction of motional correlation times from the relaxation dispersion is mathematically ill posed [27] and sensitive to unavoidable noise. For this reason the combination of temperature and frequency variation is of great importance for a reliable T_1 analysis. FC NMR just fulfills these requirements of measuring $T_1(T, \omega)$.

In SICs until now most T_1 -studies of motional disorder have been performed on glassy systems, where the motional disorder is caused by structural disorder. In crystalline SICs, where the sublattices retain an ordered structure, a much less pronounced motional heterogeneity is expected. Recently, motional disorder has been studied in crystalline LaF₃ with tysonite structure using NMR line shape analysis [10, 17]. The first use of relaxation spectroscopy has evidenced the sensitivity of the spin–lattice relaxation dispersion to motional disorder in the crystalline SIC La_{1-x}Sr_xF_{3-x} [24]. The purpose of the present article is to confirm these studies by applying T_1 dispersion relaxometry in a wide temperature range and to extend the dynamic time window down to correlation times of $\tau \approx 10^{-10}$ s in comparison with $\tau \approx 2 \times 10^{-6}$ s as characteristic for NMR line shape analysis [17].

In the tysonite structure the La³⁺ cations remain immobile up to the melting point of about 1770 K. The fluorine anions are responsible for the high ionic conductivity. They are located in three non-equivalent sublattices, F₁, F₂ and F₃, with a population of 12:4:2 per unit cell [28–30]. They are not only structurally but also dynamically non-equivalent. For the temperature range between 240 and 400 K the motion is restricted mainly to ions in the F₁ sublattice, while the F⁻ ions in the F₂ and in the F₃ sublattices are slow, with correlation times $\tau > 10^{-3}$ s [31]. Hence, the spectral density of local field fluctuations in the frequency range above 50 kHz is determined by the motion of the F₁ ions only. Above 500 K additional exchange between the F₁ and F_{2,3} sublattices becomes fast enough to be observable in ¹⁹F NMR line shapes. The line shape analysis also shows that the ionic exchange among the F₁ positions in LaF₃ is strongly heterogeneous [10]. The motional disorder can be well described by a broad log-Gaussian distribution of correlation times $g(\tau)$ [17]. Such a distribution has the following physical interpretation: it is known that the ionic mobility in LaF₃ is initiated

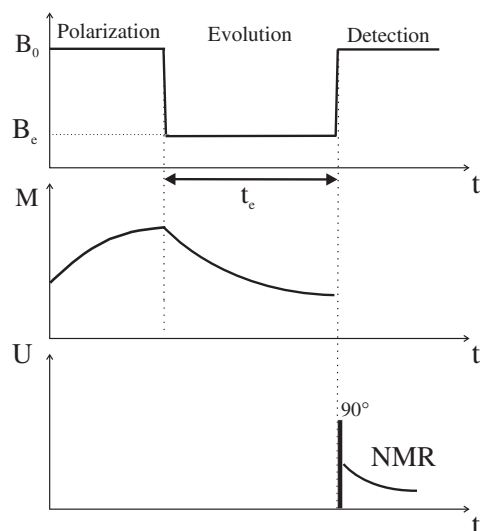


Figure 1. Timing diagram of the FC method with polarization and detection field B_0 , evolution field B_e , longitudinal magnetization M and NMR signal U .

by the formation of F^- vacancies [32]. The distribution of vacancies in the tysonite lattice causes a distribution of potential barriers and under the assumption of a thermally activated process thus leads to a distribution of correlation times [17]. In pure LaF_3 at around 310 K the exchange within the F_1 sublattice enters the fast motional limit, hence a heterogeneity cannot be seen any longer by line shape analysis. At temperatures higher than 1100 K substantial disorder is found from Brillouin scattering studies [33, 34].

In this work we apply NMR relaxometry in the frequency range from 6×10^4 to 2.8×10^8 Hz and the temperature range from 300 to 1400 K to study the motional heterogeneities in single crystals of pure LaF_3 .

2. Experiments

The idea of a typical FC experiment is represented in figure 1. The spin system is initially polarized in a strong magnetic field B_0 (polarization period). Then, after switching to a preselected field level B_e ($0 < B_e \leq B_0$) the spin system relaxes during the time t_e (evolution period) in this field with a time constant $T_1(B_e)$. To monitor the polarization decay, a high magnetic field, for example B_0 , is applied again and the nuclear polarization is detected by a standard NMR technique (detection period). By stepwise increments of t_e the relaxation decay curve is traced. The field dependence, $T_1(B_e)$, is obtained by repeating the experiment at different B_e levels.

The measurements are carried out using a home-built fast FC relaxometer. The magnetic field is produced in the low-inductance coil, allowing short switching times [35]. A detection and polarization field of $B_0 \approx 1$ T, corresponding to a ^{19}F NMR frequency of 40 MHz, is used. The evolution field can be varied from $10 \mu\text{T}$ up to 1 T. The switching rate was 0.2 T/ms in the experiments presented in this work. We attempt to increase the rate up to 5 T/ms using an active switching circuit. The magnetic field inhomogeneity over a sphere of 1 cm diameter is better than 30 ppm. The accessible temperature range is 200–1400 K. In this FC spectrometer we span a frequency range from 400 Hz to 40 MHz (for ^{19}F). Supplemented by standard NMR

we currently cover frequencies up to 300 MHz. Results of the FC technique and standard NMR are fully consistent.

Typically, the number of accumulations has been chosen to meet a relative error in T_1 of about or below 5%. At frequencies below 100 kHz, where T_1 in LaF₃ becomes shorter than 1 ms, the relative error increases up to 30%. The shortest measurable T_1 time is around 0.5 ms. Note that this value is significantly below the currently achievable switching time (see p 140 of [21]). To monitor the magnetization the free induction decay signal after a 90° pulse is measured. The length of a 90° radio frequency excitation pulse was 1 μ s, the dead time 10 μ s.

In all experiments the magnetization decay is found to be monoexponential over at least two decades in the entire temperature range. The temperature was set with a nominal accuracy of 1 K and stabilized to ± 0.5 K. At the highest achieved temperatures systematic errors (temperature gradients) up to about 20 K cannot be excluded.

In the present study we have used a new, nominally pure LaF₃ sample. The reason is that in our current work (to be published) we find diffusion coefficients in annealed LaF₃ samples [10, 17, 24] of one order of magnitude above those in a virgin sample. Not knowing the thermal prehistory of LaF₃ samples other than ours, we hesitate to include literature T_1 - and $T_{1\rho}$ -data [36, 37] in our analysis. The single LaF₃ crystal of the present study has a size of $4 \times 4 \times 8$ mm³. Its quality and orientation was checked optically and by Laue x-ray diffraction.

3. Experimental results and data analysis

The frequency dispersion in LaF₃ is observed over four decades and shows a complex behaviour involving several contributions to T_1 . Thereby, a model-free analysis of the relaxation dispersion [38] is not appropriate. Nevertheless, with increasing temperatures some characteristic changes in the relaxation dispersion occur. Figure 2 represents an overview of the experimental data.

- From 300 to 600 K the relaxation rate decreases with increasing frequency up to 20 MHz without showing a constant level at low frequency, as expected for the slow motional limit $\tau\omega > 1$. The motional correlation times are above 10^{-6} s. The drop in T_1^{-1} shifts to higher frequencies as the temperature increases, thus reflecting a thermally activated process which can be related to motion. At frequencies above 20 MHz, a faster relaxation process contributes, as is seen from another change in slope. This feature does not change with temperature up to 1000 K. Thus, we can conclude that this process is not thermally activated. Moreover, since such a process is not observed by the spectral line shape analysis [17], it is not caused by ionic hopping. We assign this process to paramagnetic centres, in agreement with earlier temperature-dependent T_1 in different LaF₃ samples [36]. Since this high-frequency contribution is not related to ionic motion, it was parametrized with the BPP model and subtracted in the further analysis.
- At temperatures below 500 K and above 1000 K there is an additional substructure in the T_1 -dispersion at around 1–10 MHz due to level crossing with the quadrupolar levels of ¹³⁹La. This structure is perfectly reproducible (see the inset in figure 2 for better-resolved data) and contains valuable information about the La local environment. The detailed analysis of the quadrupolar La spectra is not the goal of this study. In an intermediate-temperature regime this contribution cannot be seen because of the dominating relaxation rates due to motion. At higher temperatures cross-relaxation reappears but with reduced intensity due to partial averaging of the electric field gradients, as also found in [39].
- Above 600 K a low-frequency plateau appears, signalling that more processes enter the dynamic range, but the motions are still restricted within the F₁ sublattice. At 700 K an

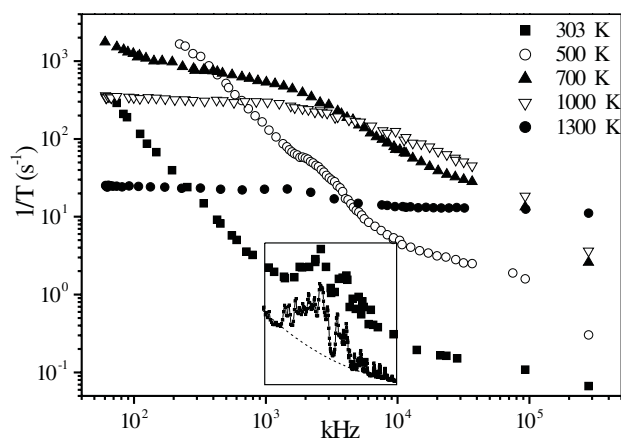


Figure 2. Frequency dispersion of ^{19}F spin-lattice relaxation rates T_1^{-1} in LaF_3 at various temperatures as indicated in the figure.

additional slow process appears. With increasing temperature this process shifts to higher frequencies, which indicates that it is a thermally activated motional mode.

- Above 1000 K a clear plateau at low frequencies can be seen, reflecting that the correlation times for all processes are shorter than 10^{-6} s. With the temperature increasing toward 1400 K all motions are in the fast limit $\tau\omega \ll 1$.

For the analysis of the motionally induced relaxation we apply a model which was gained from previous NMR line shape studies of LaF_3 [17]. It suggests two dynamic modes for the fluorine ions: a fast one within the F_1 sublattice and a slow one in-between the F_1 and the common $\text{F}_{2,3}$ sublattices. Both motional processes are found to be not of Debye type but obey a log-Gaussian distribution of correlation times. Due to the wider time window of our $T_1(\omega)$ analysis, as compared with that of line shape studies, we can test this model over a larger temperature range. Obviously, in the overlap temperature range a consistency of the data gained by both methods is required. Thereby, our previous line shape results represent a valuable countercheck for the validity of our present approach.

Being aware that the motion in pure LaF_3 irreversibly changes after a heating cycle up to above 1000 K, we measured the ^{19}F spectra as well as the relaxation on new samples, cut from the same LaF_3 single-crystal ingot to avoid ageing effects. The NMR line shapes have been reanalysed for such a new ‘virgin’ sample and show lower mobility as compared with that found in a previously heated crystal [17]. It turns out that to reach a dynamics comparable to that reported in [17, 24] a virgin sample needs to be heated up to 200 K higher. A detailed analysis of the annealing phenomena in LaF_3 will be reported elsewhere.

At temperatures below 600 K the spectral density function in the frequency range above 60 kHz is essentially determined by the hopping of the F_1 ions [17]. This process leads to motionally averaged dipole–dipole interactions and thus causes the spin–lattice relaxation. No reliable fit parameters can be deduced from the experiments since the low-frequency plateau is not seen in the $T_1(\omega)$ dependence. In this limiting case we describe our relaxation data using the parameters from the line shape analysis. Indeed, below 600 K this parametrization turns out to be reasonable and thus supports our previous finding of a non-BPP-type relaxation, characteristic for heterogeneous processes [2–9]. To characterize quantitatively the deviation from the BPP-type behaviour, we apply a phenomenological model with a log-Gaussian distribution of correlation times, usually used for the analysis of motional heterogeneity [40],

and found to be well suited for modeling the NMR line shape of LaF₃ [17]. In accordance with this description the moving ions are located on a potential surface where the barrier heights are distributed as described by the Gaussian function

$$G(E) = \frac{1}{\sqrt{2\pi}\Delta} \exp\left(-\frac{(E - E_c)^2}{2\Delta^2}\right) \quad (1)$$

where E_c is the centre of the distribution and Δ is the width parameter.

If one assumes the exchange processes to be thermally activated, a Gaussian distribution of potentials (1) can be rescaled to a log-Gaussian distribution of correlation times $g(\ln \tau)$ [17,40]

$$g(\ln \tau) = \frac{1}{\sqrt{2\pi}\delta} \exp\left(-\frac{\ln^2 \tau/\tau_c}{2\delta^2}\right) \quad (2)$$

where τ_c is the centre of the distribution and δ the width parameter.

Since for the mobile F₁ ions in LaF₃, especially in low fields, fluctuations of dipole–dipole interactions are considered to be the main relaxation mechanism, the BPP relation for T_1^{-1} can be generalized taking into account a distribution of correlation times [40]:

$$T_1^{-1} = C \left[\int_0^\infty \frac{g(\tau)\tau}{1 + \omega^2\tau^2} d\tau + 4 \int_0^\infty \frac{g(\tau)\tau}{1 + 4\omega^2\tau^2} d\tau \right], \quad (3)$$

where C represents the dipole coupling strength. Substitution of equation (2) into (3) gives

$$T_1^{-1} = \frac{C\tau_c}{\sqrt{2\pi}\delta} \int_{-\infty}^\infty \left[\frac{\exp(z - z^2/2\delta^2)}{1 + \omega^2\tau_c^2 e^{2z}} + \frac{4 \exp(z - z^2/2\delta^2)}{1 + 4\omega^2\tau_c^2 e^{2z}} \right] dz \quad (4)$$

with $z = \ln \tau/\tau_c$. Equation (4) contains only two fit parameters, τ_c and δ . Using (4) we modelled the experimental data for the fast motional process.

At temperatures above 700 K an additional slow motional process appears (see the low-frequency dispersion in figure 2). Following line shape analysis [41] one can relate this contribution to ionic exchange among the F₁ and the F_{2,3} sublattices. This process is about one order of magnitude slower than the exchange within the F₁ sublattice, and thereby it can be traced up to about 800 K. This process cannot be modelled by a single correlation time, and again a model with a log-Gaussian distribution of correlation times (2) is used [41].

We describe the whole relaxation dispersion by a superposition of the two motional processes as discussed above, the exchange within the F₁ sublattice, $T_1^{-1}(\omega)_{F_1}$, that among the F₁–F_{2,3} sublattices, $T_1^{-1}(\omega)_{F_1-F_{2,3}}$, and a non-motional (paramagnetic) contribution $T_1^{-1}(\omega)_{param}$:

$$T_1^{-1}(\omega) = T_1^{-1}(\omega)_{F_1} + T_1^{-1}(\omega)_{F_1-F_{2,3}} + T_1^{-1}(\omega)_{param}. \quad (5)$$

Both motional contributions are described by a model using a log-Gaussian distribution of correlation times (4) and are individually illustrated in figure 3 by the dotted curves. The high-frequency paramagnetic contribution (dashed curve) is parametrized by the BBP model. The figure also shows that the superposition of all processes according to (5) gives excellent fits to the experimental data (solid curves).

We used in our analysis only homonuclear dipolar ¹⁹F–¹⁹F interactions; however, taking into account ¹⁹F–¹³⁹La heteronuclear interactions may cause a slight change in τ , estimated as 10% [19].

The fitted centre parameters τ_c of both motional components are presented in figure 4. The consistency between line shape and relaxation data is obvious. At around 1000 K a change in the diffusion mechanism occurs, as can be seen in figure 4 as a change of the activation energy for the intra-F₁-motion from 0.36 to above 1.2 eV and for the F₁–F_{2,3} exchange motion

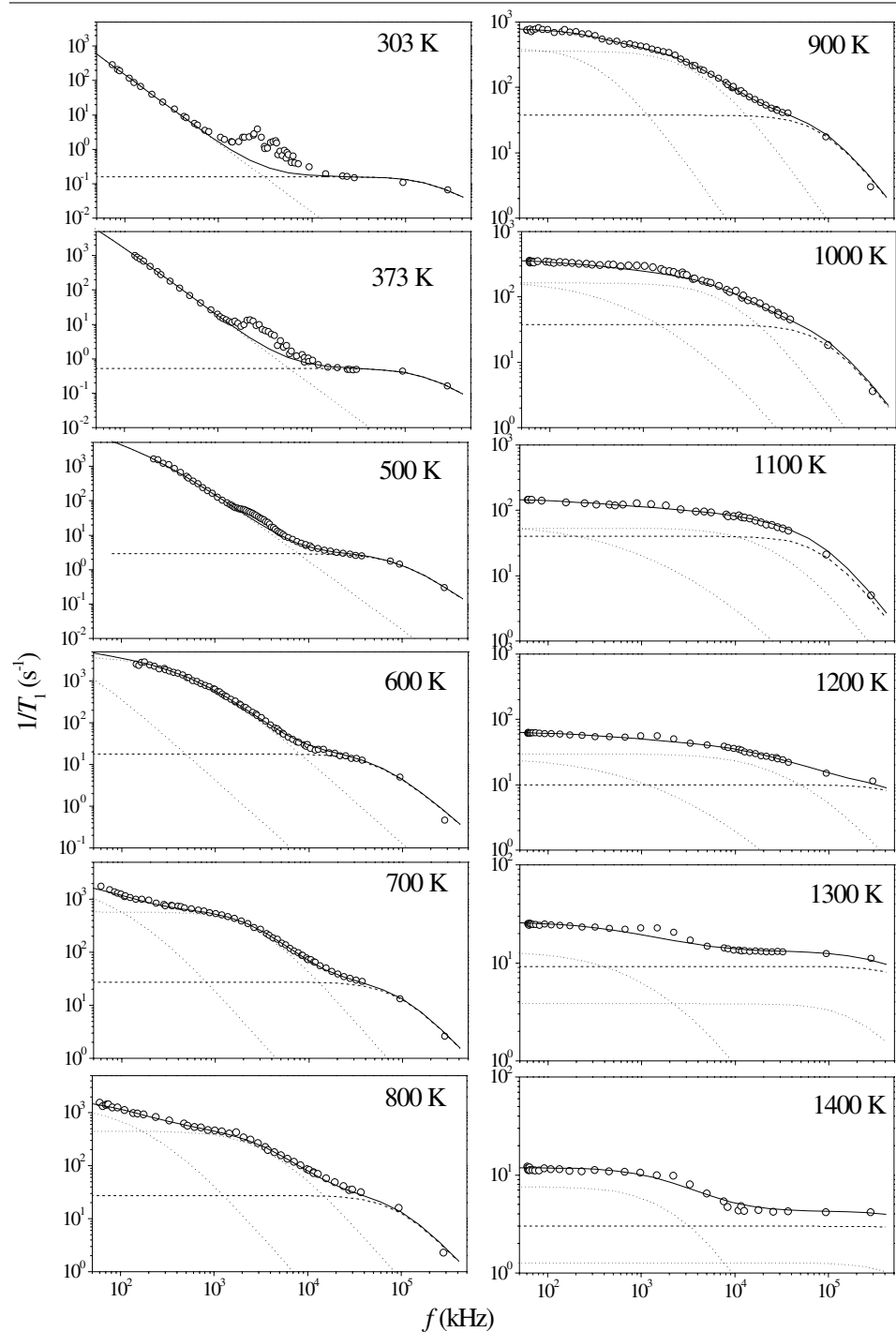


Figure 3. Experimental frequency-dependent T_1^{-1} data and their fits. The contributions of the two individual motional processes are represented by the dotted curves and that of a high-frequency paramagnetic contribution by the dashed curves. Full curves are the superpositions of all contributions. An additional contribution from level-crossing with ^{139}La in the frequency range from 10^3 to 10^4 kHz dominates the relaxation at 303–500 K and 1000–1400 K. This contribution is not considered in the fits. Note the varying ordinate scales.

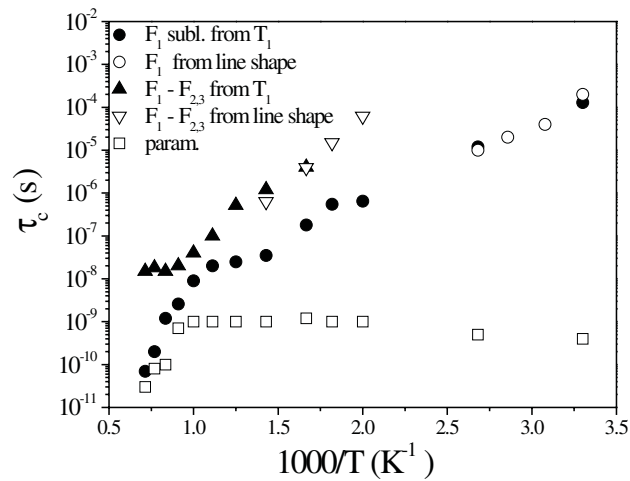


Figure 4. Temperature dependence of the centre, τ_c , of the correlation time distribution from both T_1 and line shape analyses.

from 0.57 to about 0.05 eV. Note that precise high-temperature values for the activation energies cannot be given since the accuracy of the fits becomes increasingly worse.

Without assuming wide distributions of correlation times it is clearly not possible to fit the data. However, the width parameters δ can only roughly be estimated but do not change significantly with temperature. Within about 50% (on a logarithmic scale) δ corresponds to a correlation time distribution width of about one decade, for both processes. When trying to qualitatively understand the T -independence of the width parameters of both motional processes, we have to consider at least two competing factors. The first one is due to the fact that with increasing thermal energy the ionic motion becomes less sensitive to variations of potential barrier heights. This factor leads to a narrowing of the distribution with increasing temperature. The second one is due to additional distortions in the potential landscape since more vacancies are generated with more moving ions at higher temperature and leads to a broadening of the distribution.

Additional information can be gained from the temperature dependence of the coupling constants of the three processes under consideration, C_{F_1} , $C_{F_1-F_{2,3}}$ and C_{param} , respectively (figure 5). Whereas this parameter turns out to be constant for the F_1 motion (fast process), it is approximately constant for the $F_1-F_{2,3}$ exchange (slow motion) only below 1000 K. At higher temperatures it drops dramatically. This fact is hard to explain on the base of the existing set of experimental results. We envisage performing high-temperature diffraction experiments to look for eventual structural changes which might influence the geometry of the elementary jump process. The amplitude of the contribution C_{param} increases with temperature. So far, the origin of this component and its temperature behaviour is not clear. A more detailed study of this phenomenon is in progress.

Let us finally comment on the inconsistency of our present results with previous literature data [36, 37]. As will be pointed out in a forthcoming paper, there is a dramatic irreversible change in the ionic dynamics in LaF₃ after thermal treatment. While in the present work only a virgin sample has been used, we obtain relaxation rates comparable (similar) to the above-cited literature data when using annealed samples.

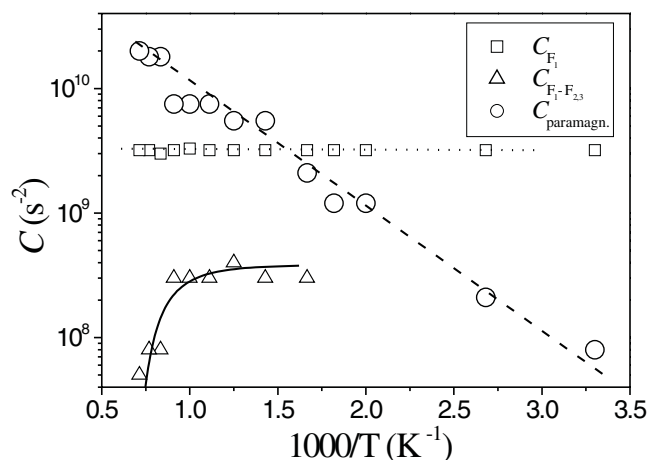


Figure 5. Temperature dependence of the coupling constants of the three processes contributing to relaxation dispersion.

4. Conclusions

We can conclude that frequency-dependent spin–lattice relaxation times T_1 contain valuable information on the nature of dynamic processes in SICs in a wide frequency range. Using the FC method in combination with standard NMR techniques allows us to cover a time window from 10^{-5} to 10^{-10} s. Even slower motions become accessible for systems with longer T_1 values and/or by using an FC set-up with shorter switching time (work in progress). In the present case of crystalline LaF_3 , our $T_1(\omega)$ -experiments turn out to be sensitive to heterogeneities in the ionic motion, avoiding ambiguities of earlier $T_1(T)$ -studies. One and the same simple empirical model using a log-Gaussian distribution of correlation times is well applicable in both the line shape and the $T_1(\omega)$ -analysis. We see two dynamic processes in LaF_3 , a fast one being attributed to ionic motion within the F_1 sublattice and a slow one to ionic exchange among the F_1 and the $F_{2,3}$ sublattices. A third high-frequency contribution to T_1 does not correspond to a motional process. It may be attributed to relaxation caused by paramagnetic centres. Around 1000 K, the two motion-induced processes approach each other. Phenomenologically, the data do not even exclude a crossing. At present, this kind of merging cannot be explained but it may be related to the observed change in the diffusion mechanism (change in the apparent activation energy and in the coupling constant of the slow process).

Outlook: in the near future we shall attempt to combine this microscopic information with mesoscopic data such as long-range diffusion and conductivity coefficients.

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