

Non-Arrhenius conductivity in the fast ionic conductor $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$: Reconciling spin-lattice and electrical-conductivity relaxations

C. León and J. Santamaría

Departamento de Física Aplicada III, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Avda, Complutense s/n, 28040 Madrid, Spain

M. A. París and J. Sanz

Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain

J. Ibarra and L. M. Torres

División de Estudios Superiores (CIDEMAC), Universidad Autónoma de Nuevo León, Guerrero y Progreso s/n. Monterrey, Nuevo León, México

(Received 30 December 1996)

Nuclear magnetic resonance and electrical conductivity measurements are conducted to study the dynamics of the ionic diffusion process in the crystalline ionic conductor $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$. dc conductivity shows a non-Arrhenius temperature dependence, similar to the one recently reported for some ionic conducting glasses. Spin-lattice and conductivity relaxations are analyzed in the same frequency and temperature range in terms of the non-Arrhenius dependence of the correlation time. Both relaxations are then described using a single correlation function of the form $f(t) = \exp(-(t/\tau)^\beta)$, with $\beta=0.4$ over the whole temperature range. [S0163-1829(97)04933-3]

Fast ionic conductors have been a subject of considerable interest in recent years mainly due to their potential applications in solid-state devices. The optimization of materials and electrical properties for practical applications has given rise to many fundamental questions, regarding the dynamics of the conduction process. Ion-ion interactions play a crucial role in ion diffusion, and a great effort has been focused in understanding its influence on the ion conduction process, particularly in glassy ionic conductors. In this context, NMR spin-lattice relaxation (SLR) and electrical conductivity relaxation (ECR) measurements have been often proposed to be useful tools to study the effect of correlations in the ionic conduction process.^{1,2} The correlation functions describing either SLR or ECR in fast ionic conductors show frequently significant deviations from the simple exponential behavior characteristic of ideal Bloembergen-Purcell-Pound or Debye-like relaxations, and follow usually stretched exponentials of the Kohlrausch-Williams-Watts (KWW) form,³ $f(t) = \exp(-(t/\tau)^\beta)$. Several models, such as the coupling model,^{4,5} diffusion-controlled model,^{6,7} or the jump relaxation model,⁸ have been proposed to explain the “nonexponentiality” observed in both relaxations. Nevertheless, it is still not clear whether the parameters defining the relaxation functions (relaxation times τ , the exponent β , and the activation energies for the ionic motion), obtained from ECR and from SLR, should be the same or not. In fact, different authors have reported discrepancies in the parameters obtained from the two kinds of relaxations in glassy systems.^{1,2,9} Discrepancies have been also predicted from Monte Carlo simulations of ionic motion in a disordered media.¹⁰

Recently, an interesting feature has been reported to appear in ionic conducting glasses: the dc electrical conductivity shows a non-Arrhenius temperature dependence in glasses with chemistry and composition specially optimized

to obtain high conductivity values. Kincs and Martin¹¹ have described this behavior as a general feature of these materials, and Ngai and Rizo¹² have proposed an explanation which points to ion-ion correlation effects as the ultimate reason for this non-Arrhenius dependence.

In this paper we present a study of ECR and SLR in a crystalline ion conductor, $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$, reported as one of the best lithium conducting crystalline materials.¹³⁻¹⁵ Interestingly, the temperature dependence of the conductivity shows a non-Arrhenius behavior similar to that found in glassy systems,¹¹ suggesting that this feature could be more general and not only restricted to ionic conducting glasses. We propose that this non-Arrhenius temperature dependence can be responsible for discrepancies in the correlation functions determined for SLR and ECR if measurements are not carried out over the same frequency and temperature ranges.^{1,2,9,16}

Polycrystalline samples were prepared by heating a stoichiometric mixture of high purity Li_2CO_3 , La_2O_3 , and TiO_2 reagents at 1200 °C. The reacted powder was pelleted and fired at 1350 °C in air for several hours (5–11 h) and then quenched to room temperature. The metal molar ratio was determined by inductively coupled plasma spectroscopy using a JY-70 PLUS spectrometer. The tetragonal perovskite structure, space group $P4mm$, as reported previously,¹⁷ was verified by x-ray and electron diffraction. The ^7Li NMR spin-lattice relaxation times (T_1) were measured with a SXP 4/100 Bruker spectrometer. Determination of T_1 values at each temperature was done by using the classical $\pi - \tau - \pi/2$ sequence.¹⁸ The frequencies used were 31, 20, and 10.6 MHz and the experiments were carried out between 100 and 500 K. Admittance spectroscopy was measured in the frequency range 20 Hz–30 MHz using automatically con-

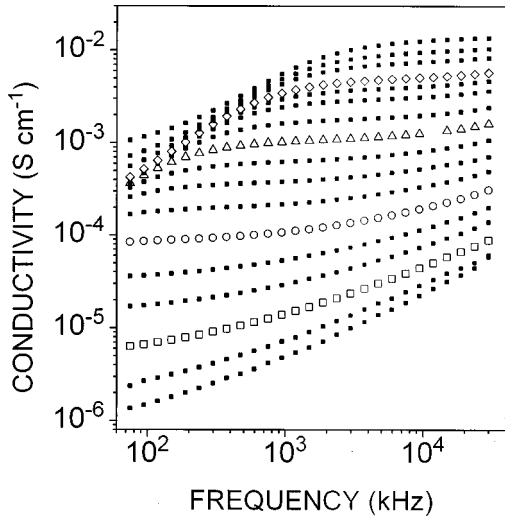


FIG. 1. Real part of the conductivity vs frequency at several temperatures (200–500 K). Open symbols are data at 225 K (\square), 271 K (\circ), 338 K (\triangle), and 407 K (\diamond).

trolled HP 4284A and HP 4285A precision LCR meters, at temperatures comprised between 150 and 500 K. The samples were cylindrical pellets 5 mm in diameter and 0.7 mm thick on whose faces gold electrodes were deposited by evaporation. Measurements were conducted under a N_2 flow to ensure an inert atmosphere.

Figure 1 shows conductivity data in the frequency range 75 kHz–30 MHz in a double logarithmic scale, and at temperatures ranging between 200 and 500 K. Conductivity measurements conducted at lower frequencies have been published previously.¹⁶ The frequency dependence of the real part of the conductivity shows a low-frequency plateau and a crossover to a power-law dependence at high frequencies. This well-known behavior, characteristic of ion hopping, can be described according to a complex conductivity $\sigma^*(\omega)$ of the form

$$\sigma^*(\omega) = \sigma_{dc} [1 + (i\omega/\omega_p)^n], \quad (1)$$

where σ_{dc} is the dc conductivity, ω_p is a crossover frequency, and the exponent $n \cong 0.6$ is related to the degree of correlation among moving ions. The crossover frequency ω_p turns out to be temperature activated like σ_{dc} , and in fact, the relation $\omega_p = \sigma_{dc}/\epsilon_\infty$ holds,¹⁹ where ϵ_∞ is the high-frequency permittivity. ϵ_∞ has been obtained from the high-frequency value of the capacitance, and shows a slight linear temperature dependence according to $\epsilon_\infty = 1.75 \times 10^{-12} + 3.15 \times 10^{-12} T$ F/m.

This dispersive behavior of the conductivity in the frequency domain can be alternatively interpreted in terms of a KWW correlation function $\phi(t)$ in the time domain, which takes the form of a stretched exponential:

$$\phi(t) = \exp(-(t/\tau_\sigma)^{\beta_\sigma}), \quad (2)$$

with τ_σ as the temperature-dependent relaxation time, inversely proportional to the dc conductivity, and $\beta_\sigma = 1 - n$. Although expressions (1) and (2) cannot be obtained analytically one from each other, either one can be used to get an empirical description of the relaxation process.²⁰ The electric

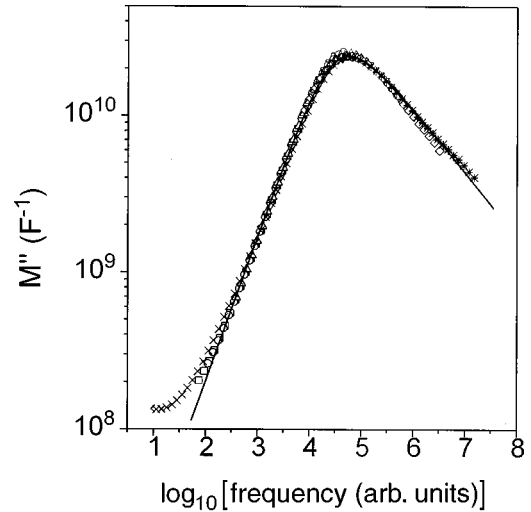


FIG. 2. Imaginary part of the electric modulus vs frequency at several temperatures from 225 K ($*$) to 375 K (\times). Curves have been displaced laterally to gather all data points on a single master curve. Solid line represents a fit according to a KWW correlation function with $\beta_\sigma = 0.4$.

modulus can be expressed as a function of the time derivative of the ECR correlation function, providing a connection between both representations:

$$M^*(\omega) = \frac{1}{\epsilon_\infty} \left[1 - \int_0^\infty \left(-\frac{d\phi}{dt} \right) e^{-i\omega t} dt \right], \quad (3)$$

which allows determining the correlation function in the time domain from experimental data measured in the frequency domain. Nearly temperature-dependent β_σ values close to 0.4 have been obtained,¹⁶ confirming the relationship $\beta_\sigma = 1 - n$. This is remarked by the master curve of the imaginary part of the electric modulus shown in Fig. 2.

The temperature dependence of the dc conductivity σ_{dc} is presented in Fig. 3. dc conductivity data have been obtained from conductivity vs frequency plots fitting to expression (1), and from the parameters obtained for the KWW function through the equation $\sigma_{dc} = \epsilon_\infty \beta_\sigma / \Gamma(1/\beta_\sigma) \tau_\sigma$.⁵ The temperature dependence of the conductivity over the whole temperature range is clearly non-Arrhenius, but Arrhenius local fits of the form $\sigma_{dc} = \sigma_\infty \exp(-E_\sigma/kT)$ yield activation energies E_σ of 0.4 eV at low temperatures and 0.26 eV in the high-temperature range.

On the other hand, the results obtained for the temperature dependence of the spin-lattice relaxation rate, $1/T_1$, at Larmor frequencies of 10, 20, and 31 MHz, are displayed in Fig. 4. The rate $1/T_1$ is related to the SLR correlation function through the equation

$$\frac{1}{T_1(\omega_L, T)} = C [J'(\omega_L, T) + 4J'(2\omega_L, T)], \quad (4)$$

where the spectral density function, $J(\omega)$, is the Fourier transform of the SLR correlation function, C is a constant, and ω_L is the Larmor frequency.

The asymmetry of $1/T_1$ peaks results from a nonexponential correlation function of the KWW form, $C(t) = \exp(-(t/\tau_s)^{\beta_s})$. According to Ngai's coupling model, ac-

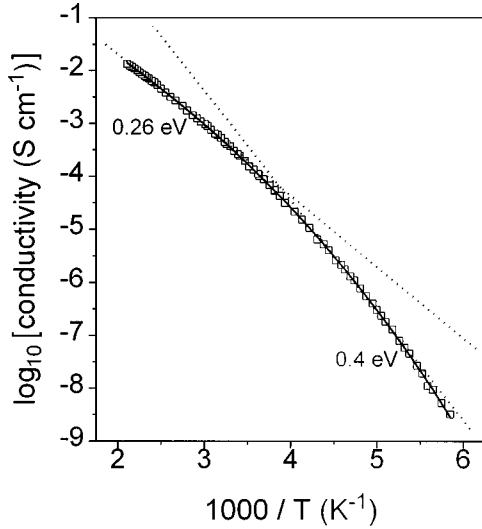


FIG. 3. dc conductivity vs $1000/T$ showing a strongly non-Arrhenius behavior. Dashed lines are Arrhenius local fits in the temperature ranges where activation energies are calculated in $1/T_1$ plots. Activation energies of 0.4 and 0.26 eV are obtained. Solid line is a fitting to a Vogel-Fulcher-Tamman function ($\sigma_{dc} = \sigma_{\infty} \exp[-A/(T-T_K)]$) with $A = 1990$ K and $T_K = 73.3$ K.

tivation energies E_s and E_a are defined such that E_s is an activation energy for long-range motion and E_a is a microscopic activation energy free of the effect of cooperativity. On the base of a thermally activated relaxation mechanism, E_s and E_a are directly obtained from the slopes of the high- and low-temperature sides of the $1/T_1$ plot, respectively, and both energies are related through the β exponent according to $E_a = \beta_s E_s$. However, in the case of a non-Arrhenius relaxation process, activation energies for ionic motion depend on temperature and the relation $E_a = \beta_s E_s$ holds only if both energies are calculated in the same temperature range. Experimental $1/T_1$ curves obtained for $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ show an

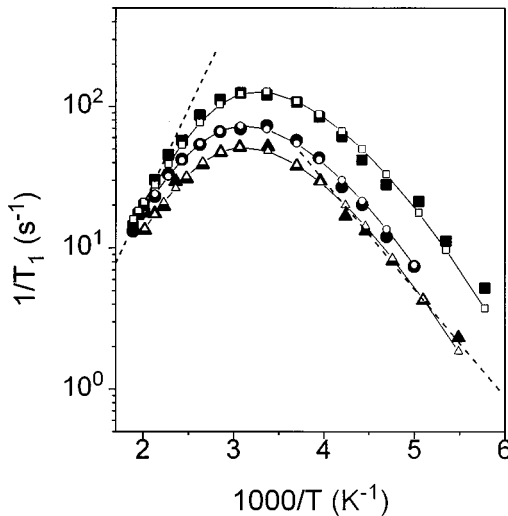


FIG. 4. Temperature dependence of $1/T_1$ at 10.6 MHz (■), 20 MHz (●), and 31 MHz (▲). Dashed lines have slopes of 0.26 eV at high temperatures and 0.15 eV at low temperatures. Open symbols are theoretical values for $1/T_1$ obtained from experimental conductivity data at the same frequencies. Lines connecting these symbols are guides for the eye.

activation energy $E_a = 0.15$ eV at low temperatures. The activation energy for the high-temperature side of the peak cannot be estimated unambiguously except for data measured at 10 MHz, where a value of $E_s = 0.26$ eV is obtained. An activation energy of 0.26 eV has been also obtained from conductivity measurements in the same temperature range, suggesting that long-range activation energies might be the same if they are measured at the same temperature. If we tentatively assume that at low temperatures E_s equals the low-temperature activation energy of the dc conductivity (0.4 eV), since the activation energy from the low-temperature branches of $1/T_1$ curves is $E_a = 0.15$ eV, the value deduced for β_s is 0.38, which is close to the value of 0.4 found for β_{σ} . In fact the frequency dependence of $1/T_1$ at a fixed temperature at the low-temperature side of $1/T_1$ plots yields the same 0.4 value for β_s .

The above reasoning suggests that correlation functions governing SLR and ECR might be actually the same, and in that case $1/T_1$ plots should be reproduced from conductivity measurements.²¹ The electric modulus is related to the Fourier transform of the time derivative of the ECR correlation function ($\hat{\Phi}(\omega)$) as quoted by expression (3), which can be rewritten as $M^*(\omega) = (1 + \hat{\Phi}(\omega))/\epsilon_{\infty}$. Since $M^*(\omega) = j\omega/(\sigma^*(\omega) + j\omega\epsilon_{\infty})$ and $\hat{\Phi}(\omega) = j\omega\hat{\Phi}(\omega) - 1$, the Fourier transform of the correlation function can be written as

$$\hat{\Phi}(\omega) = \frac{1}{\sigma^*(\omega)/\epsilon_{\infty} + j\omega} = \frac{1}{(\sigma^*(\omega)/\sigma_{dc})\omega_p + j\omega}. \quad (5)$$

In an ideal Debye case $\sigma^*(\omega) = \sigma_{dc}$ and the ECR rate is $\sigma_{dc}/\epsilon_{\infty}$. But in the general case of a frequency dispersive conductivity there is a ‘‘frequency dependence’’ for the effective relaxation rate of the form $\sigma^*(\omega)/\epsilon_{\infty}$. The SLR rate is the mean jump rate of the mobile ions γ , which is connected to the ECR rate through the expression $\sigma_{dc}/\epsilon_{\infty} = (nq^2x_0^2/6k_bT\epsilon_{\infty})\gamma$,²¹ where n is the mobile ions concentration, q is their charge, x_0 is their hopping distance, and k_b is the Boltzmann’s constant. Introducing a parameter T_0 , defined as $T_0 = nq^2x_0^2/6k_b\epsilon_{\infty}$, the above expression can be rewritten as $\sigma_{dc}/\epsilon_{\infty} = (T_0/T)\gamma$. The parameter T_0 only depends on material properties and its calculated value for this compound is 135 K.

Therefore the $1/T_1$ rates can be calculated using experimental conductivity data according to expression (4) and

$$J(\omega) = \frac{1}{(\sigma^*(\omega)/\epsilon_{\infty})(T/T_0) + j\omega} = \frac{1}{(\sigma^*(\omega)/\sigma_{dc})\gamma + j\omega}, \quad (6)$$

assuming that the spectral density function $J(\omega)$ has the same form as $\hat{\Phi}(\omega)$ [see Eq. (5)] but with a different relaxation rate.

Theoretical $1/T_1$ curves obtained from electrical conductivity results are compared with experimental $1/T_1$ data in Fig. 4. $1/T_1$ plots of 20 and 31 MHz have been calculated using extrapolated conductivity values at 40 and 62 MHz according to expression (1). The good agreement found with experimental $1/T_1$ data supports that both SLR and ECR processes are governed by the same mechanism, and character-

ized by a single correlation function. However, if NMR and electrical measurements are not conducted in the same frequency and temperature ranges, unnoticed non-Arrhenius temperature dependence of the dc conductivity can lead to ‘‘apparent’’ discrepancies and to the conclusion that correlation functions for SLR and ECR are different.

Finally, we would like to remark that there is an interesting similarity between data obtained for a crystalline system and those obtained for glassy materials (KWW decay functions for the relaxation process and the non-Arrhenius temperature dependence of the conductivity and consequently of the relaxation time). The temperature dependence of the dc conductivity can be fitted to an empirical Vogel-Fulcher-Tamman (VFT) function of the form $\sigma_{dc} = \sigma_{\infty} \exp[-A/(T - T_K)]$ which is usually found in glasses (continuous line in Fig. 3 corresponds to this fitting with $A = 1990$ K and $T_K = 73.3$ K). Moreover, dynamical measurements (permittivity,

specific heat, viscosity) on many glass-forming supercooled liquids and polymers show also clear non-Debye dependence of the susceptibility on frequency (and the KWW has been often proposed to fit the data), and relaxation times growing with decreasing temperatures faster than in a thermally activated process usually following VFT functions.^{22–24} Glass-like properties in crystalline ion conducting solids could be related to positional disorder in the mobile ions sublattice, i.e., a disordered configuration of Li ions in which all Li sites cannot be regarded as equivalent. However, additional work should be done to establish this point.

In summary, we have analyzed ECR and SLR in $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ in the same frequency and temperature range, showing that, on the basis of the non-Arrhenius temperature dependence of the relaxation time, both relaxations can be described by a single stretched-exponential correlation function.

-
- ¹F. Borsa, D. R. Torgeson, S. W. Martin, and H. K. Patel, *Phys. Rev. B* **46**, 795 (1992).
- ²K. L. Ngai, *Phys. Rev. B* **48**, 13 481 (1993).
- ³R. Kohlrausch, *Ann. Phys. (Leipzig)* **72**, 393 (1847).
- ⁴K. L. Ngai, *Comments Solid State Phys.* **9**, 121 (1979); **9**, 141 (1980); for a recent review, see, K. L. Ngai, in *Effects of Disorder on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994), p. 89.
- ⁵K. L. Ngai, R. W. Rendell, and H. Jain, *Phys. Rev. B* **30**, 2133 (1984).
- ⁶S. R. Elliott and A. P. Owens, *Philos. Mag. B* **60**, 777 (1989).
- ⁷S. R. Elliott and A. P. Owens, *Phys. Rev. B* **44**, 47 (1991).
- ⁸K. Funke, *Prog. Solid State Chem.* **22**, 111 (1993).
- ⁹M. Tatsumisago, C. A. Angell, and S. W. Martin, *J. Chem. Phys.* **97**, 6968 (1992).
- ¹⁰M. Meyer, P. Maass, and A. Bunde, *Phys. Rev. Lett.* **71**, 573 (1993).
- ¹¹J. Kincs and S. W. Martin, *Phys. Rev. Lett.* **76**, 70 (1996).
- ¹²K. L. Ngai and A. K. Rizos, *Phys. Rev. Lett.* **76**, 1296 (1996).
- ¹³Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, T. Uchida, M. Ikuta, and M. Wakihara, *Solid State Commun.* **86**, 689 (1993).
- ¹⁴Y. Inaguma, L. Chen, M. Itoh, and T. Nakamura, *Solid State Ion.* **70/71**, 196 (1994).
- ¹⁵M. Itoh, Y. Inaguma, W. Jung, L. Chen, and T. Nakamura, *Solid State Ion.* **70/71**, 203 (1994).
- ¹⁶C. León, M. L. Lucía, J. Santamaría, M. A. Paris, J. Sanz, and A. Várez, *Phys. Rev. B* **54**, 183 (1996).
- ¹⁷A. Várez, F. García-Alvarado, E. Morán, and M. A. Alario-Franco, *J. Solid State Chem.* **118**, 78 (1995).
- ¹⁸E. Fukushima and S. Roeder, *Experimental Pulse NMR: A Nuts and Bolts Approach* (Addison-Wesley, New York, 1981).
- ¹⁹C. León, M. L. Lucía, and J. Santamaría, *Phys. Rev. B* **55**, 882 (1997).
- ²⁰C. León, M. L. Lucía, and J. Santamaría, *Philos. Mag. B* **75**, 629 (1997).
- ²¹K. Funke and D. Wilmer, *Europhys. Lett.* **12**, 363 (1990).
- ²²N. Menon, S. R. Nagel, and D. C. Venerus, *Phys. Rev. Lett.* **73**, 963 (1994).
- ²³P. K. Dixon and S. R. Nagel, *Phys. Rev. Lett.* **61**, 341 (1988).
- ²⁴R. D. Deegan and S. R. Nagel, *Phys. Rev. B* **52**, 5653 (1995).