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NONSTOICHIOMETRIC COMPOUNDS

Ionic transport and localized ionic motion in Na-β''-alumina, $Na_{1.70}Li_{0.32}Al_{10.66}O_{17}$

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Abstract Frequency-dependent conductivities of the two-dimensional sodium-ion conductor Na-β''-alumina, of composition $Na_{1.70}Li_{0.32}Al_{10.66}O_{17}$, have been taken between 100 MHz and several THz, at different temperatures. In their low-frequency sections, the spectra are affected by the polycrystallinity of the sample, i.e. by inter-grain polarization, while the vibrational component prevails in the far infrared. In a first step, these two contributions are identified and removed from the spectra. In a second step, the remaining frequency-dependent conductivities are explained in terms of the displacive movements performed by the sodium ions within the crystal volume. Here, two kinds of motion are distinguished. One is translational via vacant local residence regimes, establishing macroscopic transport. The other is localized within a residence regime. The experimental conductivities are well reproduced by model spectra. The values of the parameters used agree with the available structural information.

Introduction

The motion of mobile ions in materials with disordered structures is a complicated many-particle process. Information on the essential features of the vibrational, relaxational and translational ion dynamics is obtained by taking complete spectra of the (complex) ionic conductivity. Such spectra extend up to the infrared regime, spanning more than 17 decades on the frequency scale [1].

The vibrational component can often be removed from the total conductivity spectrum. This is possible due to its characteristic frequency-squared low-frequency behavior. The remaining ''non-vibrational'' conductivity is caused by ionic displacements [2].

Two kinds of ionic displacements may be distinguished, resulting in entirely different contributions to the ''non-vibrational'' conductivity spectrum. If the motion considered remains localized within a small area or volume, which consists at most of a few neighboring atomic sites, then the corresponding conductivity will decay to zero in the limit of low frequencies. At sufficiently low temperatures, it will display the famous nearly constant loss (NCL) behavior [3]. If, on the other hand, the ions move on an extended network of interconnected sites and passageways, then this will result in macroscopic transport, i.e., in a non-zero DC conductivity. Both kinds of motion have been studied in crystalline [4], glassy [5] and polymeric ion-conducting materials [6]. It is the purpose of this contribution to show that their unique identification is also possible in the non-stoichiometric compound Na-β''-alumina, of composition $Na_{1.70}Li_{0.32}Al_{10.66}O_{17}$.

Considering experimental conductivity spectra of quite different ion-conducting disordered materials and removing from them not only the vibrational but also the strictly localized components, a most remarkable result emerges. The resulting conductivity spectra are found to display very similar characteristics of their

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dependence on both frequency and temperature. This characteristic behavior is sketched in Fig. 1.

In the last few years, we have been able to reproduce these experimental findings by formulating simple rules for the dynamics of the ions. These rules have been expressed in terms of coupled rate equations, and model spectra have been derived from them. The model is called the MIGRATION concept [7]. The acronym stands for MIsmatch Generated Relaxation for the Accommodation and Transport of IONs. In the physical picture conveyed by the acronym, we emphasize the *mismatch* introduced by any hop of an ion, the resulting *relaxation* (rearrangement) of the neighborhood and, as a consequence of the relaxation, the *accommodation* (stabilization) of the ion at its new position. Once accommodation at the new site is achieved, an elementary step of macroscopic *transport* is completed by the *ion*.

In Fig. 1, the activation energy for an elementary hop, Δ_{hop}, is seen to determine the temperature dependence of the conductivity at high frequencies, σ_{HF}. At sufficiently high temperatures, the rearrangement of the neighborhood is so fast that an ensuing backward hop is not preferred energetically. In this case, the DC conductivity, σ_{DC}, and σ_{HF} are identical and the temperature dependence of σ_{DC} is also determined by Δ_{hop}. With decreasing temperature, however, correlated backward hops become quite frequent. Now only a fraction, σ_{DC}/σ_{HF}, of the elementary hops may be considered "successful" in the sense that a random sequence of them will constitute macroscopic transport. The activation energy for σ_{DC} is now Δ_{DC}, and the difference, $\Delta_{DC} - \Delta_{hop}$, is regarded as the energy required for the rearrangement of the (ionic) neighborhood.

Figure 2 is a log–log plot of the frequency-dependent ionic conductivity of Na-β''-alumina, $Na_{1.70}Li_{0.32}Al_{10.66}O_{17}$, at a temperature of 473 K. In the Terahertz regime, the conductivity is largely determined by its vibrational component, $\sigma_{vib}(\nu)$. At lower frequencies, i.e., in the millimeter-wave and microwave regimes, the observed frequency dependence is well described in terms of the MIGRATION concept. The solid line included in the figure is a model spectrum.

The agreement between the experimental data points and the model curve seems to signify that Na-β''-alumina is a good example for a MIGRATION-type dispersion of the conductivity. This has, indeed, been our interpretation over the last few years [4]. More recently, however, we have detected inconsistencies. These have been found to arise as soon as the data of Fig. 2 are considered in a wider context, see next section. Therefore, in our present work, the dynamics of the mobile ions in Na-β''-alumina are revisited and reinterpreted.

Structure and DC conductivity

There are three different pieces of experimental information that need to be combined in order to explain the ion dynamics in Na-β''-alumina consistently. One of them concerns the structure, the other the temperature-dependent DC conductivity, and the third the frequency dependence of the conductivity at

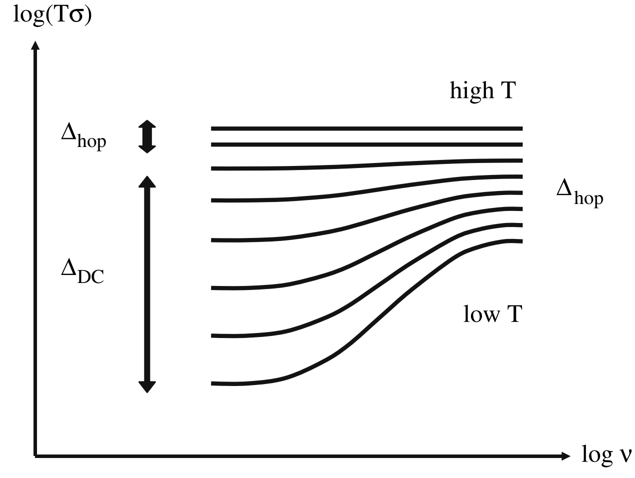

Fig. 1 Conductivity isotherms according to the MIGRATION concept, schematic. For details, see main text

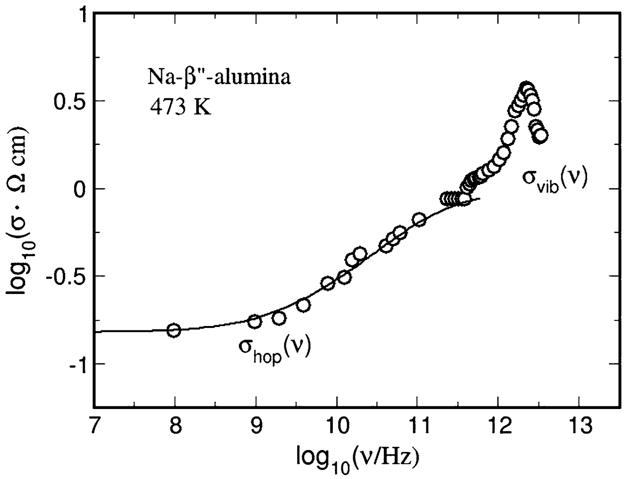

Fig. 2 Conductivity spectrum of Na-β''-alumina at 473 K. The solid line is a model spectrum derived from the MIGRATION concept

fixed temperature. In this section, we focus on structure and DC conductivity.

Figure 3 is a sketch of part of the conduction plane, according to the single-crystal structural refinement done by Dunn et al. [8]. The oxygen ions form a regular hexagonal structure, leaving approximately triangular areas between them for the sodium ions. In Fig. 3, the shape of these areas roughly follows the contour lines given in Ref. [8] for the sodium-ion probability density. Comparing the numbers of oxygen and sodium ions in $Na_{1.70}Li_{0.32}Al_{10.66}O_{17}$, we find that on an average about one out of six of these areas should be unoccupied.

We may, therefore, envisage a hopping motion of the sodium ions via a ‘‘vacancy mechanism’’, with the number density of the ‘‘vacancies’’ being well defined and unusually high. The distance between neighboring ‘‘vacancies’’ is about 224 pm.

Second, we may also consider the movement of each sodium ion within its own approximately triangular local area of residence. Dunn et al. [8] have indicated three maxima of the probability density within each area, situated at a distance of about 90 pm from each other, forming a regular triangle. The particular kind of motion performed by the sodium ions within their little areas is probably highly attenuated and irregular, suggesting that in a first approximation it should be treated as a localized diffusion rather than a vibration.

In Fig. 4 we reproduce the Arrhenius plot of the ionic conductivity in Na-β''-alumina of composition $Na_{1.68}Mg_{0.67}Al_{10.4}O_{17.1}$ as published by Farrington and Briant [9]. Note that the sodium-ion number density agrees very well with the one of $Na_{1.70}Li_{0.32}Al_{10.66}O_{17}$, the difference being only about 1%. Note also that the conductivities of Fig. 4 were measured along the conduction planes of a single crystal, while the frequency-dependent conductivity data of Fig. 2 were obtained from a crunched powder of irregularly oriented crystallites. Therefore, we should expect the DC values of our conductivities to be two thirds of those of Farrington and Briant.

A remarkable property of the Arrhenius plot of Fig. 4 is the change of slope observed at about 465 K. This feature is well in line with our expectations according to Fig. 1. The slope at 1,000 K/T < 1,000 K/465 K should, therefore, directly reflect the activation energy for an elementary hop, Δ_{hop}. Moreover, again according to Fig. 1, it should be possible to use Fig. 4 for estimating values of the high-frequency conductivity at different temperatures, $\sigma_{\text{HF}}(T)$, by simply extrapolating the high-temperature data to lower

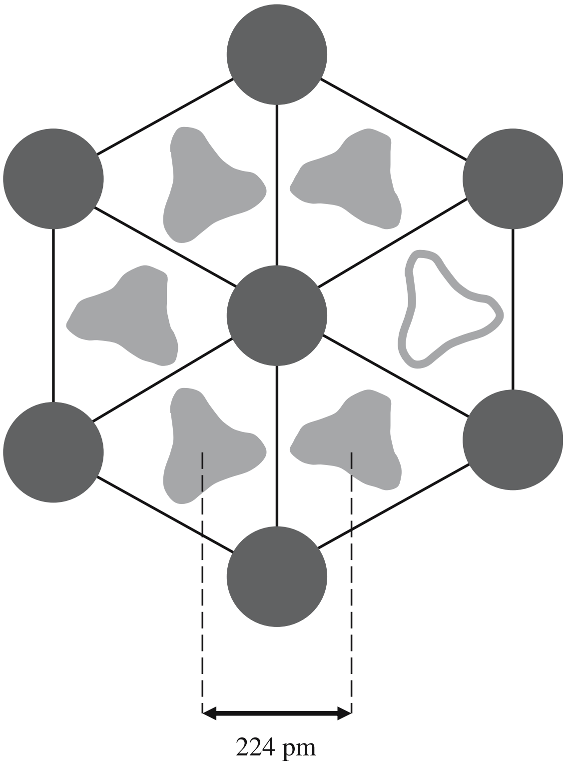

Fig. 3 Section of the conduction plane in Na-β''-alumina. The hexagonal arrangement of the oxygen ions provides regimes of residence for the sodium ions, one out of six remaining unoccupied [8]

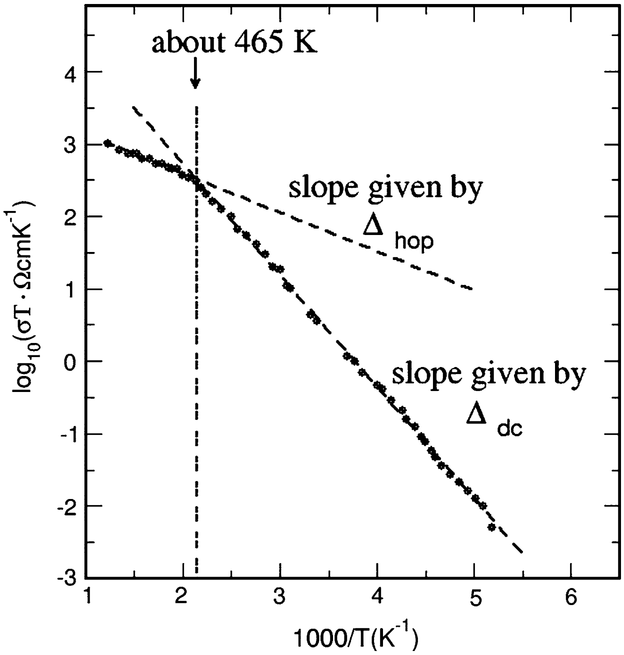

Fig. 4 Arrhenius plot of the DC conductivity of single-crystalline Na-β''-alumina of composition $Na_{1.68}Mg_{0.67}Al_{10.4}O_{17.1}$ along the conduction plane, after Ref. [9]. For the change of slope, see main text

temperatures. This procedure will be applied in the next section.

Conductivity spectra and ion dynamics

Figures 5 and 6 are log–log representations of experimental frequency-dependent conductivities of Na-β''-alumina, $Na_{1.70}Li_{0.32}Al_{10.66}O_{17}$, measured in our laboratory [10], with the vibrational component already removed. The data have been obtained at 293 and 473 K, respectively, at frequencies ranging from 100 MHz to about 1 THz. The material studied was a highly compressed powder of irregularly oriented small crystallites. For more information on the techniques employed, see Ref. [1].

In the figures, we have explicitly marked those limiting values of the conductivity at low and high frequency, σ_{DC} and σ_{HF}, which are to be expected on the basis of the data of Fig. 4, cf. the preceding section.

From the spectrum taken at 293 K, see Fig. 5, two facts are immediately evident.

(i) Although, with decreasing frequency, the DC conductivity appears to be attained at about 1 GHz, an additional feature is identified at still lower frequencies. The further reduction of the conductivity at frequencies below 400 MHz is characteristic of polarization effects as they occur at grain boundaries where charges pile up. In the material studied here, the effect is easily explained as a consequence of lacking contact between the conduction planes of neighboring grains.

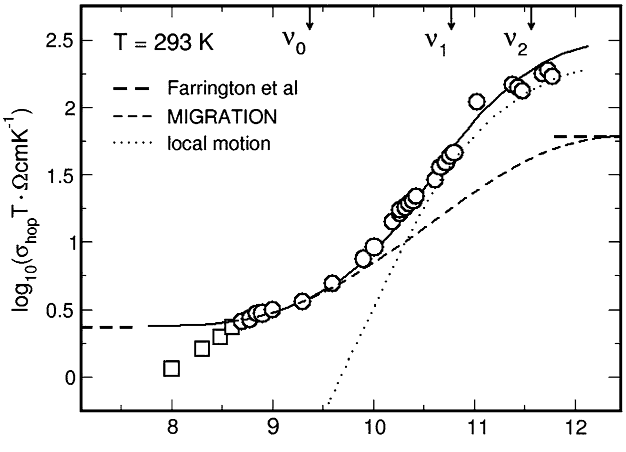

Fig. 5 Conductivity spectrum of Na-β''-alumina, $Na_{1.70}Li_{0.32}Al_{10.66}O_{17}$, at 293 K, after removal of the vibrational component. The solid line is a model curve obtained by superposition of the localized and MIGRATION-type contributions. Below 400 MHz, the data represented by boxes are affected by surface polarization

(ii) Even disregarding the low-frequency grain boundary effects, we are still unable to reproduce the experimental data in terms of the MIGRATION concept. In a log–log plot such as Fig. 5, MIGRATION-type model spectra cannot attain a slope close to unity at frequencies just one or two decades above the onset of the dispersion. Rather, a possible model spectrum is as indicated by the dashed line included in the figure. Here, the parameters are so chosen, that the high-frequency conductivity, σ_{HF}, coincides with the value for σ_{HF} expected from the data of Fig. 4.

Quite similar deviations between the shapes of experimental and MIGRATION-type model spectra have been encountered earlier, in crystalline, glassy and polymeric fast ion conductors [11]. In all of these cases, as mentioned earlier, it has been possible to explain them in terms of displacive ionic movements that remain localized. In the low-temperature phase γ-$RbAg_4I_5$, for example, a localized motion of silver ions was thus detected on the basis of the frequency-dependent conductivity, even before structural information became available, providing a unique identification of this motion within the crystal structure [12].

We are thus led to assume that a localized kind of motion is responsible for the particular shape of the frequency-dependent conductivity of Na-β''-alumina as well. Of course, the motion of the sodium ions within their extended local regimes of residence, cf. Fig. 3, is an excellent candidate for this kind of motion. Indeed, the dotted line included in Fig. 5 has been derived from a model treatment which is consistent with the structural information of Fig. 3 (see below). Forming the sum of the dashed and dotted lines in Fig. 5, we obtain the solid line, which reproduces the experimental data quite well.

According to Fig. 4, the values of σ_{DC} and σ_{HF} should be almost identical at 473 K, so hardly any frequency dependence of the ionic conductivity should be detectable in Fig. 6. We have, therefore, included a straight horizontal line in the figure, in accordance with the respective lines at the highest temperatures in Fig. 1. It thus becomes immediately clear that our former interpretation of the experimental data in terms of MIGRATION-type dispersion, cf. Fig. 2, is incorrect. In view of our discussion of Figs. 4, 5, a different interpretation is seen to emerge.

(i) On the one hand, the data of Fig. 6 are strongly affected by the low-frequency polarization already discussed at 293 K. At 473 K, $\sigma_{DC}(T)$ is larger

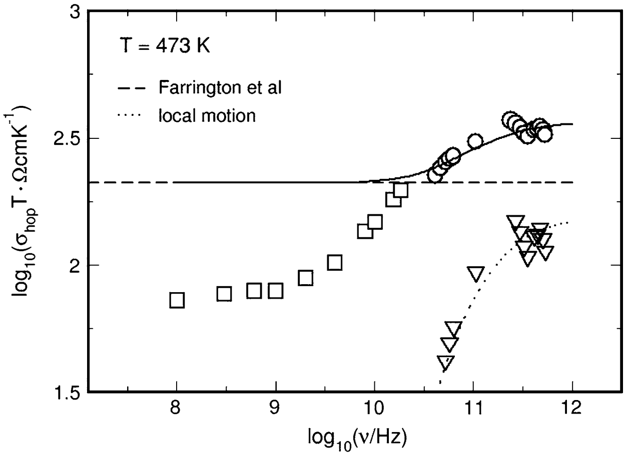

Fig. 6 Conductivity spectrum of Na-β''-alumina, $\mathrm{Na_{1.70}Li_{0.32}Al_{10.66}O_{17}}$, at 473 K, after removal of the vibrational component. The solid line is a model curve obtained by superposition of the localized and (constant) MIGRATION-type contributions. Below 30 GHz, the data represented by boxes are affected by surface polarization. Above 40 GHz, the difference between the experimental data and the constant MIGRATION-type contribution is marked by triangles. The dotted line is a model spectrum for the localized motion

than at 293 K by some 1.9 orders of magnitude. Correspondingly, we expect the range of visibility of the polarization effect to extend further towards higher frequencies by about 1.9 decades. This is a consequence of the so-called time-temperature superposition principle. The "partial blocking" effect at the contacts between grains should, therefore, result in values of the measured conductivity that lie below σ_{DC} at frequencies lower than 30 GHz. Indeed, inspecting Fig. 6, we find that the low-frequency data points meet the horizontal line at about 30 GHz. Moreover, the inter-grain polarization effect is now visible over two decades in frequency, and it does, indeed, display the shape characteristic of a relaxation process.

(ii) On the other hand, the data of Fig. 6 are seen to deviate from the horizontal line also at frequencies above 30 GHz. In the figure, the differences between the conductivities measured above 30 GHz and those expected from the MIGRATION concept (horizontal line) have been marked by triangles. In spite of considerable experimental uncertainties at 473 K, the differences clearly resemble the contribution to the 293 K spectrum that has been attributed to the motion of the sodium ions within their local regimes of residence. Of course, such a contribution should be present at 473 K as well.

We thus arrive at the unexpected conclusion that a spectrum which seems to display the dispersion that is characteristic of the MIGRATION concept does, in fact, owe its shape to quite different physical processes. At an intermediate temperature, 373 K, the frequency-dependent conductivity is again well reproduced by the procedure employed at 293 K, the MIGRATION-type component showing less dispersion but more relative weight than at 293 K, and the component due to local motion being similar to those found at lower and higher temperature in both shape and weight.

Denoting the frequency-dependent conductivity of Na-β''-alumina, $\mathrm{Na_{1.70}Li_{0.32}Al_{10.66}O_{17}}$, that does not contain a vibrational component and is not influenced by inter-grain polarization processes by $\sigma_{\mathrm{NON\text{-}VIB}}(\nu)$, we now write

$$\sigma_{\mathrm{NON-VIB}}(\nu) = \sigma_{\mathrm{MIG}}(\nu) + \sigma_{\mathrm{LOC}}(\nu). \tag{1}$$

For the construction of $\sigma_{\mathrm{MIG}}(\nu)$ from the MIGRATION concept, see Ref. [7]. One of the parameters of the model is the rate, $\omega_0 = 2\pi\nu_0$, of successful hops that contribute to macroscopic transport, say diffusion or conduction. This rate marks the position on the frequency scale (see Fig. 5), where the dispersion of the conductivity begins. Here, with defects, i.e. "vacancies", playing the role of mobile charge carriers, $2\pi\nu_0$ is the average rate of uncorrelated hops of an individual mobile defect. If d is the mutual distance of centers of neighboring sodium residence areas, then the coefficient of self-diffusion of "vacancies" is given by $2\pi\nu_0 d^2/4$, where the factor of four indicates that in this system transport is confined to two dimensions. Denoting the DC conductivity of a polycrystalline material without surface polarization by $\sigma_{\mathrm{DC}}(\mathrm{poly})$, this quantity must be two-thirds the value σ_{DC} of a single crystal in the conduction plane. The Nernst–Einstein relation then yields

$$n_{\mathrm{VAC}} \cdot d^2 = \frac{6k_{\mathrm{B}}T \cdot \sigma_{\mathrm{DC}}(\mathrm{poly})}{2\pi\nu_0 \cdot e^2}. \tag{2}$$

Here, n_{VAC} is the number density of "vacancies", i.e. of vacant local regimes of residence (see Fig. 3), and k_{B} and e are Boltzmann's constant and the elementary charge, respectively.

From the composition and the structural refinements [8] we know that n_{VAC} and d^2 are close to $3.3 \cdot 10^{20}\ \mathrm{cm}^{-3}$ and $5.0 \cdot 10^{-16}\ \mathrm{cm}^2$, respectively, yielding the temperature-independent value of $1.65 \cdot 10^5\ \mathrm{cm}^{-1}$ for their product. Using the parameter $2\pi\nu_0$ of the model spectra obtained from the MIGRATION concept, we find exactly the same temperature-independent value for the right-hand side of Eq. 2. This then implies that the measured frequency-dependent conductivities are in good agreement with a vacancy-type model for the self-diffusion of the mobile sodium ions.

To create model spectra for the conductivity component due to the motion of the sodium ions within their local regimes of residence, we have considered the mean square displacement, $\langle r^2(t)\rangle$, pertaining to this kind of motion and, in particular, its normalized time derivative, $W_{\mathrm{LOC}}(t)$. According to linear response theory [13], the frequency-dependent conductivity caused by the localized motion, $\sigma_{\mathrm{LOC}}(\nu)$, is then proportional to the Fourier transform of the time derivative of $W_{\mathrm{LOC}}(\mathrm{t})$.

Note that the local confinement of each moving charge carrier is expressed by the decay of $W_{\mathrm{LOC}}(t)$ from one to zero, the integral of the function and, therefore, $\langle r^2(\infty)\rangle$ being finite. Note also that the shape of $W_{\mathrm{LOC}}(\mathrm{t})$ determines the shape of the resulting frequency-dependent conductivity.

The function, $W_{\mathrm{LOC}}(t)$, which has been used here is

$$W_{\mathrm{LOC}}(t) = \frac{1}{(\nu_2/\nu_1 + 1)\exp(2\pi\nu_1 t) - \nu_2/\nu_1}. \qquad (3)$$

This particular function was derived earlier [5] on the basis of a suitably modified version of the MIGRATION concept. This version differs from the original one, which we use to derive $\sigma_{\mathrm{MIG}}(\nu)$, by considering a spatial confinement for each charge carrier while retaining interactions.

Frequency-dependent conductivities resulting from the above function, $W_{\mathrm{LOC}}(\mathrm{t})$, display the famous nearly constant loss (NCL) behavior at low temperatures, when ν_1 becomes much smaller than ν_2. Indeed, the conductivity is then found to be a linear function of frequency in a very broad range extending from ν_1 to ν_2.

In Fig. 5, the component $\sigma_{\mathrm{LOC}}(\nu)$ of $\mathrm{Na}_{1.70}\mathrm{Li}_{0.32}\mathrm{Al}_{10.66}\mathrm{O}_{17}$ at 293 K, as derived from our model, is plotted as a dotted curve, and the frequencies ν_1 and ν_2 are marked by arrows. Evidently, the experimental spectrum is well reproduced when this component and the MIGRATION-type component are superimposed. To check the procedure for self-consistency, the following relation may be used:

$$\langle r^2(\infty)\rangle = 4D_{\mathrm{LOC}} \cdot \int_0^\infty W_{\mathrm{LOC}}(t)\mathrm{d}t. \qquad (4)$$

Here, D_{LOC} is meant to be a coefficient of localized self-diffusion within a residence regime. The factor of four signifies that the treatment is in two dimensions only. The integral over the function $W_{\mathrm{LOC}}(t)$, used to construct the model spectrum of Fig. 5, is $1.2\cdot10^{-12}$ s. From Ref. [8], cf. Fig. 3, we may roughly estimate that $\langle r^2(\infty)\rangle$ will be some $0.5\cdot10^{-16}$ cm^2. Inserting these values into Eq. 4, we obtain a liquid-like value for D_{LOC}, viz., some 10^{-5} cm^2 s^{-1}, which is not unexpected.

In conclusion we state that in Na-β''-alumina, $\mathrm{Na}_{1.70}\mathrm{Li}_{0.32}\mathrm{Al}_{10.66}\mathrm{O}_{17}$, a careful modeling of the frequency dependence of the ionic conductivity shows that

(i) the sodium ions move translationally via vacant residence regimes, thus establishing macroscopic transport, and that, additionally,
(ii) each sodium ion performs a localized motion within the confinement of its residence regime.

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