Mixed Alkali Effect in Crystals of β- and β''-Alumina Structure

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We develop a microscopic model for the mixed alkali effect in crystals of the β- and β''-alumina type, which is based on the formation of certain mobile defects and the fact that different types of mobile ions have a different preference to become part of these defects. Our computer simulations for the ionic conductivity are in excellent agreement with experimental data. Our model predicts a common shape of the rescaled conductivity isotherms independent of temperature and the specific type of probe, which is also in agreement with the available experimental results.

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When in certain ion conducting crystals two different types of mobile ions are mixed, one finds that the ionic conductivity does not linearly decompose into the two conductivities of the corresponding pure systems. Rather, the conductivity of the mixture can be several orders of magnitude smaller. This spectacular phenomenon was originally found by mixing different types of alkali ions and is therefore known as the mixed alkali effect (MAE). The MAE occurs also in ion conducting glasses and presents a fundamental problem in the physics of solid electrolytes (for reviews, see [1,2]).

In this Letter we focus on the microscopic understanding of the MAE in crystals of the β- and β''-alumina structure with composition $[(1-x)A_2\text{O}-xB_2\text{O}]_{(1+c_e)}$-$11M_2\text{O}_3$, where A and B are two different alkalis or other monovalent metals (e.g., Ag), M a threevalent metal (Al, Ga, or Fe), and c_e the excess of mobile ions compared to the stoichiometric composition (typically $c_e \approx 0.22$ in the β and $c_e \approx 0.7$ in the β'' modification) [3–7]. The change of the conductivity $\sigma(x)$ upon varying the mole fraction x of B ions is different in the β and β'' modifications. In the β systems, the conductivity isotherms display a pronounced minimum at $x \approx 0.7$ (or $1-x \approx 0.7$), while in the β'' systems the conductivity is almost constant for $x \lesssim 0.8$ (or $1-x \lesssim 0.8$) and then increases strongly for $x \gtrsim 0.8$.

The different shape of the conductivity isotherms is related to a different structural environment of the mobile ions. In both the β and β'' systems, the ionic diffusion is confined to conduction planes that are located between two $M_{11}\text{O}_{16}$ spinel blocks (for a detailed description of the crystal structure, see [8–11]). In the β'' modification, the possible sites for the mobile ions form a honeycomb lattice. The number of mobile ions per lattice site is $p_s = (1+c_e)/2$. Hence, typically 85% of the lattice sites are occupied and the rest of them are vacancies. In the β modification, the sites of the honeycomb lattice are not equivalent, because of different relationships to the spinel blocks, but belong to two different triangular sublattices of Beevers-Ross (BR) and anti–Beevers-Ross (aBR) sites. The BR sites are preferentially occupied, but since the number of mobile ions per BR site is $p_{\text{BR}} = 1 + c_e > 1$, not all of the ions can occupy a favorable BR site. As was shown in x-ray diffraction experiments [12–14], each of the excess ions displaces an ion from a BR site with which it forms a so-called midoxygen (mO) pair [15]. The ions in the mO pairs occupy mO sites that are located halfway along the bonds connecting the BR and aBR sites [see Fig. 1(a)].

The x-ray diffraction experiments have provided even more detailed knowledge about the site occupation numbers of different types of mobile ions [16]. The basic result of these measurements is that in the mixed β systems one type of mobile ion prefers to be on a mO site, while the other prefers to be on a BR site. For example, in Na/K-β-alumina with small K content, all K^+ ions are found to occupy the BR sites. Only when the number of K^+ ions exceeds the number of accessible BR sites, are mO pairs with K^+ ions formed.

The preference of one type of ion to become part of a defect is the key ingredient of our model, which we will develop in the following. In both the β and β'' modifications the conductivity is caused by the mobility of certain defects. In the β system these are the mO pairs. In the β'' system, we consider a vacancy as a "triple defect," since it attracts the three nearest neighboring ions, thereby causing them to be slightly displaced towards the vacancy [10] [see ions 1–3 in Fig. 1(c)]. An ion is called a defect ion when it is part of a defect and a BR ion otherwise. We require that an ion cannot be part of more than one defect, which implies that two defects do not come very close to each other, i.e., they experience a "hard-core repulsion" (see the shaded areas in Fig. 1).

We assume that the defects diffuse by performing thermally activated jumps between neighboring lattice sites. During each defect jump, the actual movements of the ions can be considered as in Fig. 1. In the β system, similar to a proposal by Wang, Gaffari, and Choi [17], ion 1 of a jumping mO pair passes an aBR site [Fig. 1(a)] and moves

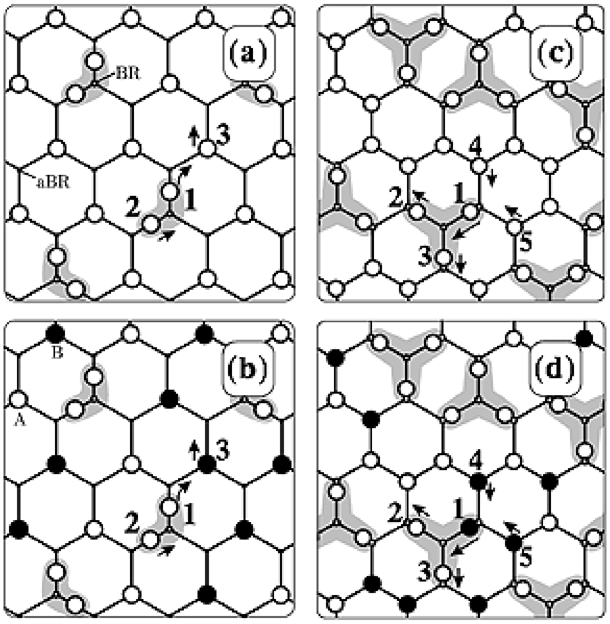

FIG. 1. Sketch of the collective ion movements during two jumps of an *m*O pair in the β system (a), (b) and two jumps of a vacancy triple defect in the β'' system (c), (d). The open circles mark the *A* ions and the filled circles the *B* ions. In the pure *A* systems [upper figures (a), (c)] the jump rates assigned to the jumps shown are $w_d = \nu_A \exp(-U_A/k_BT)$ in (a) and $w_d = \nu_A'' \exp(-U_A''/k_BT)$ in (b), while in the mixed systems [lower figures (b), (d)] the rates are $w_d = \nu_A \exp[-(U_A + \Delta_1)/k_BT]$ in (b) and $w_d = \nu_B'' \exp[-(U_B'' + \Delta_2'' + \Delta_3'')/k_BT]$ in (d).

to a new *m*O site. During this process, it pushes ion 3 from a BR site to an *m*O site, while ion 2 of the original *m*O pair relaxes onto a BR site. It has been shown [17] that this collective jump process requires a particularly low activation energy. In the β'' system [Fig. 1(c)], ion 1 of the triple defect moves towards the original vacancy, passing an unfavorable *m*O site. Thereby it creates a new triple defect together with ions 4 and 5. Ions 2 and 3 of the original triple defect relax onto the next BR site.

To account for the preference of certain types of ions to become defect ions, we assign different energies to the various possible defect configurations. Indeed, such defect energies have been estimated by *ab initio* calculations for β-alumina [18]. In the β system we denote by E_A and E_B the energy of an *A* and *B* ion on a BR site and by E_0, E_1, and E_2 the energy of an *m*O pair with 0, 1, and 2 *B* ions, respectively. Equivalently, the BR ions in the β'' system have energies E_A'' and E_B'' and the defects the energies E_i'' ($i = 0, \ldots, 3$), where E_i'' is the energy of a triple defect with i *B* ions. To simplify the notation, we suppress the double-prime superscript in the following, keeping in mind, however, that the energies in the β and β'' system are considered to be different. In the β (β'') system there exist 8 (18) possible jump processes for the defects, which differ from each other by the types of ions which are involved (four examples are shown in Fig. 1). The energy changes ΔE associated with these jump processes can all be expressed by the 2 (3) energy differences

$$\Delta_i \equiv (E_i - E_{i-1}) + (E_A - E_B). \tag{1}$$

These energy differences have a simple meaning: Δ_i is the energy needed to create a defect with i *B* ions by substituting an *A* defect ion by a *B* BR ion in a defect with $i - 1$ *B* ions. Without loss of generality, we assume that the *A* ions prefer to become defect ions and thus require $\Delta_i > 0$.

The total activation energy E_a for a defect jump with energy change ΔE is given by

$$E_a = \begin{cases} U + \Delta E & \text{for } \Delta E > 0, \\ U & \text{for } \Delta E < 0, \end{cases} \tag{2}$$

where U is an energy barrier. For simplicity we assume that U depends only on the type of the "moving" ion (ion 1 in Fig. 1), $U = U_A$ for *A* ions and $U = U_B$ for *B* ions. Both U_A and U_B determine the activation energies for $x = 0$ and $x = 1$ and can be directly taken from the experiments. With the specification of E_a, the jump rates w_d of the defects are given by $w_d = \nu \exp(-E_a/k_BT)$, where we assume that the prefactor ν depends only on the type of the moving ion, i.e., $\nu = \nu_A$ or $\nu = \nu_B$.

To explore the consequences of this model, we have performed extensive computer simulations. Since the defects can be considered as effective charge carriers and interactions among them have been neglected (except for their hard-core repulsion), the conductivity can be calculated in a good approximation from the diffusion coefficient with the help of the Nernst-Einstein relation. The diffusion coefficient was determined from the time dependent mean square displacement of the defects by using the standard Monte Carlo algorithm [19].

Figure 2 shows our results (solid line) for the conductivity $\sigma(x)$ for the β and β'' systems. The results are compared with the experimental curves (dotted lines) for Na/K-β-alumina [5] and Na/K-β''-alumina [6], each for two temperatures. The parameters we used are summarized in Table I. The barrier energies U_A and U_B as well as prefactors ν_A and ν_B were taken from experiment [5,6].

For estimating the values of the energy differences in the β'' system, we note that $\sigma(x)$ varies only slowly for $x \lesssim 0.8$. Hence the variation of the activation energy E_a [see Eq. (2)] should be comparable to k_BT even for the low temperature curve at $T = 200$ K; i.e., Δ_1'' and Δ_2'' should not be significantly larger than 17 meV. We have chosen $\Delta_1'' = \Delta_2'' = 20$ meV, but also smaller values give close fits to the experimental curves. More important is the choice of Δ_3. In order to obtain the steep increase of $\sigma(x)$ for $x > 0.8$ we have to require (see the discussion below) $\Delta_3'' > \Delta_{1,2}''$. We found $\Delta_3'' = 90$ meV to be a good value.

For estimating the values of the energy differences in the β system, we note that $\sigma(x)$ varies strongly for small x, which implies that Δ_1 is of the order of U_A. Accordingly, we have chosen $\Delta_1 = 140\,\text{meV}$. Requiring $\Delta_2 > \Delta_1$ (see the discussion below) we found that $\Delta_2 = 2\Delta_1 = 280$ meV gave a close fit to the experimental curves.

The c_e values of the experimental probes used in [5,6] are not known very precisely. They were reported as $c_e \approx 0.22$ in the β system and $c_e \approx 0.67$ in the β''

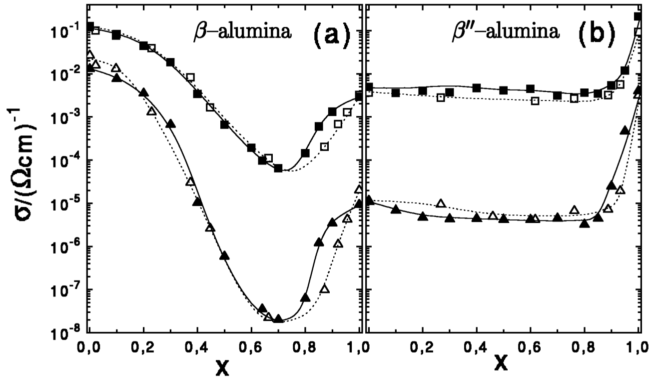

FIG. 2. Comparison between the conductivity found for the model (filled symbols) and in the experiments (open symbols) for (a) Na/K-β-alumina at $T = 273$ K (▲,△) and $T = 423$ K (■,□), and (b) Na/K- β''-alumina at $T = 200$ K (▲,△) and $T = 271$ K (■,□). (The experimental data were redrawn from [5] and [6].) The solid lines (model) and dotted lines (experiment) are guides for the eye.

system. In the simulations we have used $c_e = 0.22$ (β system) and $c_e = 0.7$ (β'' system). Despite the simplicity of our approach, the agreement between the results of the models and the experimental data is very good. Small deviations between model and experiment occur mainly on the K-rich side ($x \longrightarrow 1$) [20].

The agreement between the model predictions and the experimental data enables us to give a coherent microscopic explanation of the MAE in crystals. In the β system for small x, the conductivity is dominated by the motion of *m*O pairs consisting of two *A* ions (*AA* pairs). Since $\Delta_1 > 0$, *B* ions replacing *A* ions occupy the BR sites (at low temperatures) and thereby block diffusion paths of the *AA* pairs. This blocking process continues until long range diffusion paths for the *AA* pairs cease to exist, i.e., until the concentration of *B* ions relative to the number of BR sites becomes $1 - p_c$, where $p_c = 0.5$ is the percolation threshold [21] in the triangular sublattice of BR sites. The corresponding mole fraction is $x_c \equiv p_c/(1 + c_e) = 0.41$. Accordingly, when x_c is approached from below, $\sigma(x)$ decreases very strongly [see the steep decrease of $\sigma(x)$ in Fig. 2(a)]. Different from ordinary percolation, $\sigma(x)$ does not vanish at $x = x_c$, since *AA* pairs can overcome blocked sites by thermally activated formation of mixed *AB* pairs. At low temperatures, however, we expect a strong percolation effect to occur with a power law behavior $\sigma(x) \sim (x_c - x)^\mu$ for x approaching x_c from below with $\mu \simeq 1.3$ [21]. We note that the occurrence of a percolation effect in β structures was suggested also in [22,23].

For $x > x_c$, $\sigma(x)$ continues to decrease, because *B* ions block further (short-range) diffusion paths for the *AA* pairs beyond the critical threshold. The decrease of the conductivity becomes increasingly weaker until at $x_{\min} \equiv (1 - c_e)/(1 + c_e) = 0.64$ all accessible BR sites are occupied by *B* ions. This is the value at which $\sigma(x)$ has its minimum at low temperatures [16] [see the low temperature curve in Fig. 2(a)]. At high temperatures the *B* ions tend to occupy *m*O sites and more of them are needed to block all BR sites. Thus the minimum is slightly shifted to the right. For $x > x_{\min}$, only *m*O sites are left for the occupation of *B* ions. The *B* ions might either form *AB* pairs by replacing one *A* ion of a *m*O pair or form *BB* pairs, by replacing both *A* ions of an *m*O pair. Because of $\Delta_2 > \Delta_1$ the *B* ions prefer to form mixed *AB* pairs at low temperatures. The now highly mobile *BB* pairs are not formed until x becomes larger than $x_1 \equiv 1/(1 + c_e) = 0.82$. Consequently, the conductivity increases only slowly for $x_{\min} < x < x_1$ and then strongly for $x > x_1$ [see Fig. 2(a)].

In the β'' system the barrier energy $U_B = 370$ meV is much larger than the barrier energy $U_A = 280$ meV, which causes the conductivity isotherm to display a strong asymmetry. Analogous to the β system, the conductivity of the β'' system for small x is dominated by the mobility of triple defects with 3 *A* ions (*A*3 triples). *B* ions preferentially replace *A* ions that are not part of a defect. However, since the energies $\Delta_1'' = \Delta_2''$ are comparable to $k_B T$ at $T = 200$ K, there is no strong blocking effect, and thus a strong decrease of $\sigma(x)$ is not observed. In fact, for a fairly good *qualitative* agreement with the experimental results, one could even set $\Delta_1'' = \Delta_2'' = 0$. Our choice $\Delta_1'' = \Delta_2'' > 0$, however, improves the *quantitative* agreement significantly. Only the *B*3 triples have a much larger defect energy $\Delta_3 \gg k_B T$. Accordingly, these defects practically do not exist until the concentration of *B* ions is finally so large that they must form. This is the case for $x > x_1''$, where $x_1'' \equiv 2c_e/(1 + c_e) = 0.82$. In this regime the conductivity increases very strongly with increasing x due to the formation of the highly mobile *B*3 triples [see Fig. 2(b)], analogous to the increase of $\sigma(x)$ in the β system for $x > x_1$ due to the formation of *BB* pairs.

Our results suggest that in both the β and β'' systems some kind of universal behavior can be expected: The values values x_c, $x_{\min}$, x_1, and x_1'' characterizing the shape of the conductivity isotherms depend only (at low temperatures) on c_e, but neither on temperature, nor on the types of ions that are mixed, nor on the particular type

TABLE I. Numerical values of the parameters [5,6].

	U_A (meV)	U_B (meV)	ν_A (s^{-1})	ν_B (s^{-1})	Δ_1 (meV)	Δ_2 (meV)	Δ_3 (meV)
β-alumina	135	370	10^{11}	1.7×10^{12}	140	280	···
β''-alumina	370	280	5×10^{13}	5×10^{13}	20	20	90

of crystal (Al2O3, Ga2O3, Fe2O3). These parameters should only affect the conductivities of the pure systems and the depth of the conductivity minimum. To test this prediction, we show in Fig. 3 the (logarithmic) relative conductivity $\Sigma(x) \equiv \log_{10}[\sigma(x)/\sigma_0(x)]$ vs x for various β systems, where $\sigma_0(x) \equiv (1-x)\sigma_A + x\sigma_B$ is the conductivity expected for a simple additive mixing behavior. $\Sigma(x)$ is a measure for the strength of the "nonlinearity" in the MAE. In order to normalize the minimum, we have divided $\Sigma(x)$ by $|\Sigma(x_{\min})|$ in Fig. 3. As can be seen from the figure, all data follow indeed one master curve as suggested by the model. We expect an analogous behavior for the β'' systems, but were not able to test this prediction seriously because a sufficient number of probes with comparable c_e values have not been investigated so far. New experiments would be very helpful in this respect.

In summary, we have developed a coherent picture for the MAE in crystalline probes of the β- and β''-alumina type. Our model describes the distinct shapes of the conductivity isotherms quantitatively, and predicts a universal conductivity behavior, which is confirmed by the available experimental data.

A problem that has been debated for a long time is the question if or to what extent the MAE in crystals has the same origin as the MAE in glasses. From a general point of view, there exist indeed intrinsic similarities to the dynamic structure model that has been suggested recently to account for the ion transport anomalies in glassy electrolytes [24]. Also in the dynamic structure model the preference of different types of ions to occupy certain types of sites (equivalent to B ions preferring to be on BR sites) plays a key role. But different from the crystalline systems, the "sites" in the glassy network are not predetermined by the quenched periodic structure but are formed by the interaction of the mobile ions with their local environment during the process of cooling.

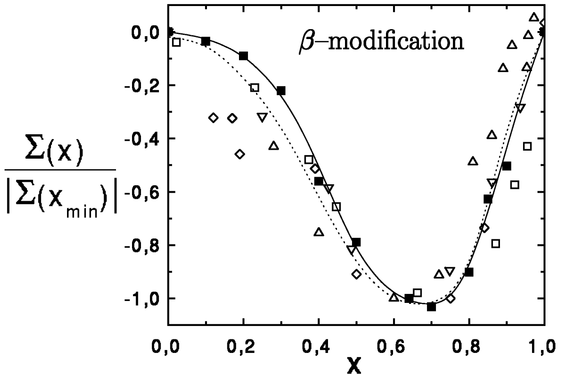

FIG. 3. Scaling plot of the conductivity isotherms for several probes of the β modification: Na/K-β-alumina at $T = 273$ K (□) [5], Ag/Na-β-alumina at $T = 273$ K (△) [5], Na/Li-β-alumina at $T = 298$ K (◇) [5], and Na/K-β-gallate at $T = 422$ K (▽) [3]. For comparison the simulation result for 273 K is also shown (■). The solid lines (model) and dotted lines (experiment) are guides for the eye.

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