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Activation entropy and Gibbs free energy for conduction in yttria–stabilized-zirconia single crystals

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The temperature dependence of the activation Gibbs free energy $[\Delta G(T)]$ and entropy $[\Delta S(T)]$ associated with electric conduction in 12 mol% yttria–stabilized-zirconia single crystals was analyzed. In order to determine the $\Delta G(T)$ and $\Delta S(T)$ functions exactly, it was necessary to impose temperature-behavior conditions on the activation Gibbs free energy to give $\Delta S(T \to \infty) = 0$. The temperature dependence of the entropy was similar to that of the activation enthalpy. Both reach stable values at low temperatures (extrinsic associated range). In this temperature range, $\Delta G(T)$ shows a linear behavior. At higher temperatures, $\Delta G(T)$ decreases asymptotically to a value approximately equal to the migration enthalpy of the oxygen vacancies. A value of 5.6×10^{-7} eV/K was calculated for the variation of entropy associated with the migration of the vacancies. Assuming the cation-vacancy-cation association to be a first-neighbor structure, a value of 4.85×10^{-4} eV/K was found for the association entropy of the vacancies. These results are in very good agreement with those obtained by applying the method used in alkaline halide studies.

I. INTRODUCTION

The yttria–stabilized-zirconia systems are among the most important solid electrolytes due to their excellent electrical properties. Nevertheless, the nonlinear Arrhenius behavior shown by the ionic conductivity in ZrO_2-Y_2O_3 single-crystal systems[1–3] is not yet understood. A fit to this nonlinearity was achieved for 12 mol% Y-FSZ single crystals using the Arrhenius local fit procedure (LF) (Ref. 4) and assuming an empirical temperature-dependent activation enthalpy. Subsequently, assuming equally probable jumps for the oxygen vacancy, a theoretical equally-probable-jumps model (EPJ) was developed,[5] which proposed an activation enthalpy temperature-dependent function [Eq. (26) in Ref. 5] similar to the fit function [Eq. (5) in Ref. 5] from the earlier work. Comparison between the fit and the theoretical expressions yielded us the values 0.57 eV and 0.73 eV for the enthalpies of association (ΔH_a) and migration (ΔH_m) of the vacancies, respectively. Thus, considering the vacancies as either free or associated, the gradual change from one situation to the other could explain the nonlinear behavior of the ionic conductivity observed in these samples. However, the fitting function uses four parameters and the theoretical function only three, which causes a slight lack of accuracy in the parameter determinations. Also, if the theoretical dependence is known, it is not necessary to use an empirical function. In the present work, three points have been studied. First, in order to improve the accuracy of the parameters ΔH_a, ΔH_m, etc., we repeated the fitting procedure used previously for 12 mol% Y-FSZ samples.[4,5] However, the fit of the enthalpy values determined with the LF method was now made using the theoretical enthalpy function given by the EPJ model. This procedure will hereafter be denoted the LF-EPJ method. This avoids the inaccuracy introduced when the fit was made using four parameters instead of three. Second, the temperature dependence of the activation Gibbs free energy $\Delta G(T)$ and entropy $\Delta S(T)$ in the conduction process was analyzed in depth, determining the change of entropy for the migration (ΔS_m) and association (ΔS_a) of the vacancies. Finally, the LF-EPJ results were compared with those found by applying the fitting method used in alkaline halide materials.

II. THEORETICAL ANALYSIS

The EPJ theoretical model gives an activation enthalpy associated with the ionic conduction process of[5]

$$\Delta H(T) = \Delta H_m + \frac{\Delta H_a}{2} + \frac{\Delta H_a}{2} \tanh\left[\frac{\Delta H_a}{2kT} - \Theta\right], \quad (1)$$

where Θ is a fitting parameter related to ΔS_a and to the number of energetically equivalent configurations of a cluster or any type of cation-vacancy association Z_c (configurational degeneration) by the equation

$$\Theta = \frac{\Delta S_a}{2k} - \frac{\ln Z_c}{2}, \quad (2)$$

k being the Boltzmann constant. From Eq. (1), one can deduce $\Delta S(T)$ and $\Delta G(T)$:[5–7]

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$$\Delta S(T) = \frac{\Delta H_a}{2T} \tanh\left[\frac{\Delta H_a}{2kT} - \Theta\right] - k\ln\left[\cosh\left(\frac{\Delta H_a}{2kT} - \Theta\right)\right] + \Delta S_0, \quad (3)$$

$$\Delta G(T) = \Delta H_m + \frac{\Delta H_a}{2} + kT\ln\left[\cosh\left(\frac{\Delta H_a}{2kT} - \Theta\right)\right] - T\Delta S_0. \quad (4)$$

Here, ΔS_0 is an integration constant related to ΔS_m, and Θ by the equation[5]

$$\frac{\Delta S_0}{k} = \frac{\Delta S_m}{k} + \Theta - \ln 2. \quad (5)$$

The parameters ΔH_a, ΔH_m, and Θ can be determined by fitting Eq. (1) to the values of enthalpy calculated from the LF method. However, in order to analyze the temperature dependence of $\Delta S(T)$ and $\Delta G(T)$ and determine ΔS_m, it is necessary to find ΔS_0 (a temperature-independent constant). Also, to calculate ΔS_a, one has to know the configurational degeneration (Z_c).

To evaluate ΔS_0, we assumed that the activation Gibbs free energy of the oxygen vacancies decreases when the temperature increases:

$$\frac{d\Delta G(T)}{dT} \leq 0. \quad (6)$$

This can be reasonably justified by considering the thermal excitation of the vacancies around their anionic sites. Then, because the ionic conductivity is measured in an isobaric process, one has[6]

$$T\frac{d\Delta S(T)}{dT} = \frac{d\Delta H(T)}{dT}, \quad (7)$$

and taking into account Eq. (6), one has at any temperature

$$\Delta S(T) \geq 0. \quad (8)$$

On the other hand, since moving the oxygen vacancies requires energy, their activation free energy for a jump between two equilibrium sites cannot be negative [$\Delta G(T) \geq 0$], i.e.,

$$\Delta H(T) - T\Delta S(T) \geq 0, \quad (9)$$

and, because the activation enthalpy always takes finite non-negative values at any temperature, in the asymptotic high temperature limit, $\Delta S(T)$ will satisfy

$$\Delta S(T) \leq 0. \quad (10)$$

Therefore, consistency of Eqs. (8) and (10) requires that

$$\Delta S(T \to \infty) = 0. \quad (11)$$

By imposing this boundary condition on $\Delta S(T)$ in Eq. (3), one obtains

$$\frac{\Delta S_0}{k} = \ln[\cosh\Theta], \quad (12)$$

which gives ΔS_0 as a function of a parameter deduced directly from the fit. Now the temperature dependence of the entropy and Gibbs free energy can be analyzed. The activation entropy of the vacancies in the extrinsic associated regime (all the oxygen vacancies are associated) can be evaluated by taking $T \to 0$ in Eq. (3), giving

$$\Delta S(T \to 0) = k\Theta + \Delta S_0 + k\ln 2, \quad (13)$$

and, by taking into account Eqs. (2) and (5), one has that

$$\Delta S(T \to 0) = \Delta S_a + \Delta S_m - k\ln Z_c. \quad (14)$$

In this range, therefore, the activation entropy of the vacancy is corrected by a term related to the configurational disorder of the cation-vacancy associations. In a similar way, one can determine the Gibbs free energy variation at absolute zero as

$$\Delta G(T \to 0) = \Delta H_a + \Delta H_m, \quad (15)$$

which coincides with the activation enthalpy of the extrinsic associated state. The asymptotic behavior at the highest temperatures ($T \to \infty$) will be

$$\Delta G(T \to \infty) = \Delta H_m + \frac{\Delta H_a}{2} - \frac{\Delta H_a}{2}\tanh\Theta. \quad (16)$$

III. RESULTS AND DISCUSSION

By applying the LF procedure to the ionic conductivity-temperature values of 12 mol % Y-FSZ single crystals, an enthalpy-temperature data set was obtained. Then, least-squares fitting the theoretical activation enthalpy [Eq. (1)] to the enthalpy-temperature data (see Fig. 3 in Ref. 5) yielded the values $\Delta H_a = 0.58$ eV, $\Delta H_m = 0.71$ eV, and $\Theta = 2.516$ (the LF-EPJ procedure). These values are slightly different from those obtained by fitting with the empirical function due to the use of a different number of fitting parameters. From Θ and Eq. (12), one finds $\Delta S_0/k = 1.8299$, which is 1% larger than the result of using the empirical function. Equations (15) and (16) yield a Gibbs free energy value of 1.29 eV at absolute zero, and an asymptotic high-temperature value ($T \to \infty$) of 0.72 eV. As $\tanh(\Theta) = 0.987$, one has that $\Delta G(T \to \infty) \simeq \Delta H_m$. Therefore the activation Gibbs free energy and enthalpy are equal in the asymptotic high-temperature limit. Although this theoretical result is impossible to verify, it can be estimated to a very good approximation (error $\leq$ 3%, as is seen in Fig. 1) from the $\Delta G(T)$ behavior from 2400 K to the melting point. However $\Delta G(T)$ and $\Delta H(T)$ present very different temperature behaviors, as can be seen in Fig. 2 [$\Delta H(T)$ is a hyperbolic tangent function and $\Delta G(T)$ is the logarithm of a hyperbolic cosine]. At this point, it is important to remark that the free energy does not reach a stable value in the intrinsic associated temperature range ($T < 673$ K). From Eq. (4), one can obtain

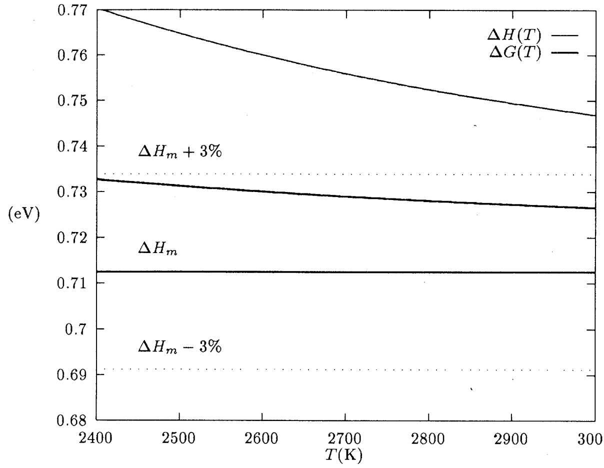

FIG. 1. Magnification of the asymptotic high-temperature behavior of $\Delta H(T)$ and $\Delta G(T)$. One sees that the differences between $\Delta G(T)$ and ΔH_m are less than 3% from 2400 K to the melting point.

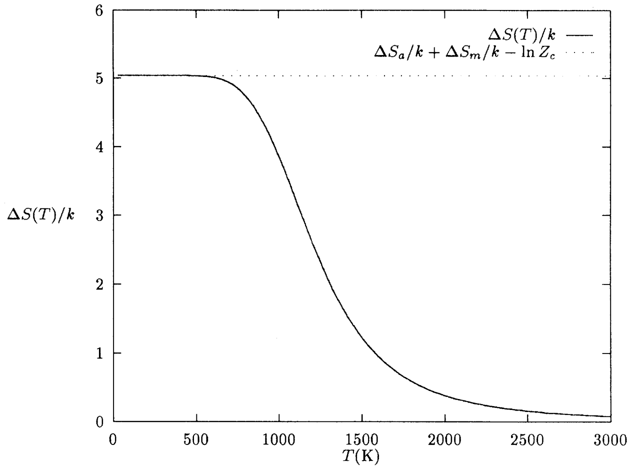

FIG. 3. Temperature behavior of the $\Delta S(T)$ function. It has a similar shape to $\Delta H(T)$, although with a sharper drop. The extrinsic associated range is marked as $(\frac{\Delta S_a}{k} + \frac{\Delta S_m}{k} - \ln Z_c)$.

$$\Delta G(T < 673\,\mathrm{K}) = \Delta H_m + \Delta H_a - T(\Delta S_m + \Delta S_a - k \ln Z_c), \qquad (17)$$

where $(\Delta S_m + \Delta S_a - k \ln Z_c)$ is the value of the activation entropy in the associated range, as shown in Fig. 3. One observes that $\Delta S(T)$ has a similar behavior to the enthalpy at low and at high temperatures (Figs. 2 and 3), although it falls faster as the temperature increases. Equations (5) and (12) yield a ΔS_m value of 5.6×10^{-7} eV/K ($\Delta S_m/k = 6.5 \times 10^{-3}$), showing that this is a negligible parameter, as is assumed in alkaline halide studies.[8,9] To find ΔS_a, it is first necessary to evaluate Z_c, and this requires knowing the vacancy-cation local structure, which is an unsolved problem. However, the microscopic structure of ZrO_2-Y_2O_3 systems has been studied and defect association models proposed in a number of studies. Thus, by means of extended x-ray-absorption fine structure (EXAFS), Catlow *et al.*[10] proposed that the anion vacancies are sited adjacent to the Zr^{4+} rather than to the Y^{3+} ions. Li *et al.*[11] found preferential locations to be nearest neighbors of Zr^{4+} constituting (Zr-V_O-Zr) associations and leaving Y^{3+} with eightfold coordination. On the other hand, Yashima *et al.*,[12] applying an ion-packing model based on defect associations, determined that the vacancies are sited near Y^{3+} cations, configuring a (Y-V_O-Y) association. Although these proposed local configurations have different chemical natures, all of them show an oxygen vacancy first neighbor (1N) of two equal cations. In this relative anion-cation situation, for both associations, there are only two energetically equivalent configurations, so that Z_c=2 in both. Then, assuming (M-V_O-M) (with M=Y^{3+} or Zr^{4+}) associations and from Eq. (2), $\Delta S_a/k$ was evaluated to be 5.63. Table I lists the $\Delta S_a/k$ values calculated assuming these types of association, but considering different relative situations between cation and anion in the lattice. It can be observed that $\Delta S_a/k$ takes an equal value in the 1N1N and 1N3N configurations. There was no influence of the relative cation-anion

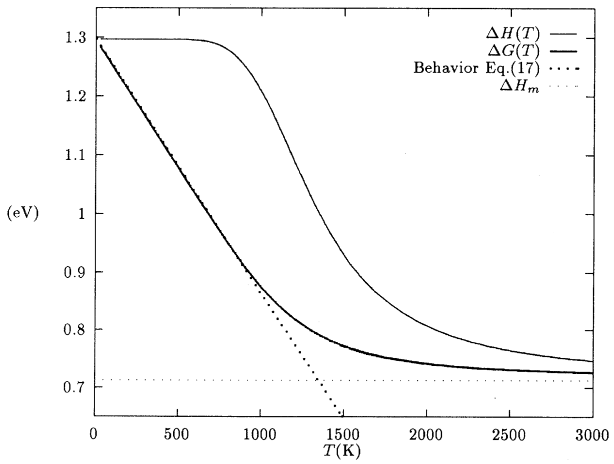

FIG. 2. Temperature behavior of the $\Delta H(T)$ and $\Delta G(T)$ functions. On the same plot are $\Delta G(T)$ in the extrinsic associated range [Eq. (17)] and the asymptotic high-temperature value, ΔH_m.

TABLE I. Variation of the association entropy ($\Delta S_a/k$) assuming associations (M-V_O-M) ($M = Y'_{Zr}$ or Zr) when the cations are sited as first (1N), second (2N), etc., neighbor in relation to the oxygen vacancy. The asterisk denotes an association type obtained by an EXAFS study (Refs. 10 and 11).

Neighbor M-M	First cation M-V_O	Second cation M-V_O	Z_c	$\Delta S_a/k$
(1N)	(1N)	(1N)	2	5.63 *
(1N)	(1N)	(2N)	4	6.32
(1N)	(1N)	(3N)	2	5.63
(1N)	(2N)	(2N)	6	6.72
(1N)	(2N)	(3N)	4	6.32

distance because the EPJ model did not take into acount the interaction between vacancies.[5]

Although the LF-EPJ procedure allowed us to determine the parameters ΔH_a, ΔH_m, ΔS_a, and ΔS_m, due to the lack of experimental results on zirconia materials, it is not possible to know the exact meaning of these values. In order to verify the validity of the results, we applied an alternative method used in alkaline halide materials, which is based on the minimization of the equation[8,9]

$$\varphi = \sum_{i=1}^{i=N} [\log_{10} (\sigma T)^i_{\rm th} - \log_{10} (\sigma T)^i_{\rm expt}]^2, \tag{18}$$

with $(\sigma T)^i_{\rm expt}$ being the experimental values and $(\sigma T)^i_{\rm th}$ a function of the parameters defined by the theoretical model used to describe the system. The sum runs over all the experimental data points. We shall call this method total fit (TF), because it fits, simultaneously, the whole of the experimental data. The LF method,[4,5] by contrast, only analyzes small temperature intervals. Then, assuming for $(\sigma T)^i_{\rm th}$ the EPJ theoretical expression[5]

$$\sigma T = A_0 e^{\Delta S_m/k} \times \frac{\exp[-(\Delta H_a + \Delta H_m)/kT + \Delta S_a/k - \ln Z_c]}{1 + \exp[-\Delta H_a/kT + \Delta S_a/k - \ln Z_c]}, \tag{19}$$

the parameters ΔH_a, ΔH_m, $\Delta S_a/k - \ln Z_c = 2\Theta$, and $A_0 e^{\Delta S_m/k}$ were determined by using the Levenberg-Marquardt nonlinear least-squares fitting procedure.[13] The parameter values found are summarized in Table II together with those obtained by the LF-EPJ method. The small discrepancy between the two methods is because the relative fitting errors are not small in relation to their corresponding experimental ones. In this situation, a logarithmic fit causes distortion, as is shown in Fig. 4. In this figure, $[(\sigma T)^i_{\rm th} - (\sigma T)^i_{\rm expt}]/(\sigma T)^i_{\rm expt}$ has been plotted versus T (K), and one observes that, for the TF procedure, a very high value was reached for many data points (even a value as high as 30%). This difficulty can be easily solved. If one assumes that the experimental errors are proportional to the measured values, one can proceed in a similar way to a complex nonlinear least squares fit,[14] minimizing the equation

$$\varphi' = \sum_{i=1}^{i=N} \frac{[(\sigma T)^i_{\rm th} - (\sigma T)^i_{\rm expt}]^2}{[(\sigma T)^i_{\rm expt}]^2}. \tag{20}$$

This procedure shall be denoted the proportional total fit (PTF), and is equivalent to the TF method when the relative differences between theoretical and experimental values are very small. In effect, let $\delta(\sigma T)_i = (\sigma T)^i_{\rm th} - (\sigma T)^i_{\rm expt}$ be the fitting error associated with the ith data point, then Eq. (20) can be written as

$$\varphi' = \sum_{i=1}^{i=N} \frac{[\delta(\sigma T)_i]^2}{[(\sigma T)^i_{\rm expt}]^2}. \tag{21}$$

If, for the whole set of data points, one has $\delta(\sigma T)_i \ll (\sigma T)^i_{\rm expt}$, then the approximation $\ln(1+x) \simeq x$ can be used for $x \simeq 0$, and Eq. (21) can be rewritten as

$$\varphi' \simeq \sum_{i=1}^{i=N} \ln \left[1 + \frac{\delta(\sigma T)_i}{(\sigma T)^i_{\rm expt}}\right]^2 = \sum_{i=1}^{i=N} \left[\ln (\sigma T)^i_{\rm th} - \ln (\sigma T)^i_{\rm expt}\right]^2. \tag{22}$$

Therefore, only when the fitting errors are very small are the PTF and TF methods equivalent. When we repeated the fit using Eq. (20), very good agreement with the LF-EPJ values was obtained (Table II). The agreement obtained between the LF-EPJ and PTF values and the EXAFS results allows us to take the value of 5.63 in k units for the variation of association entropy of the vacancies in these materials.

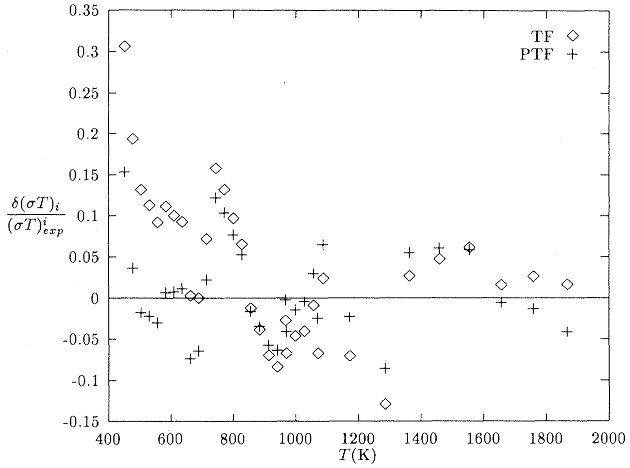

FIG. 4. Relative fitting errors found by applying the TF (◇) and PTF (+) procedures to the σT data measured in 12 mol % Y-FSZ single crystals.

TABLE II. Comparison between the LF-EPJ, TF, and PTF parameters in 12 mol % Y-FSZ single crystals.

Parameter	LF+EPJ	TF	PTF
ΔH_a (eV)	0.58	0.63	0.57
ΔH_m (eV)	0.71	0.69	0.73
2Θ	5.03	5.46	4.92
$\ln A_0 + \Delta S_m/k$	16.77	16.53	16.88
$\Delta S_a/k \quad (Z_c = 2)$	5.63	6.15	5.61
$\Delta S_m/k \ (\times 10^{-3})$	6.51	4.25	7.27

IV. CONCLUSION

The LF-EPJ method allows the thermodynamic functions $\Delta G(T)$ and $\Delta S(T)$ to be determined from conductivity-temperature experimental data for Y-FSZ single crystals. This was made possible by assuming that the Gibbs free energy variation decreases as the temperature increases. This method is thus an effective procedure for calculating the parameters associated with the dynamics of oxygen vacancies in the electric conduction process. In the present work, by applying the LF-EPJ method to 12 mol % Y-FSZ samples, we fully determined $\Delta S(T)$ and $\Delta G(T)$ from the ionic conductivity data. It was seen that, although there is coincidence in the values of $\Delta G(T)$ and $\Delta H(T)$ at absolute zero and at high temperatures, they have very different temperature behavior. While $\Delta H(T)$ reaches a stable value at low temperatures, $\Delta G(T)$ follows a linear dependence. On the other hand, the $\Delta S(T)$ curve is similar in shape to the enthalpy curve although it falls faster at high temperatures. It was also possible to determine a value of 5.6×10^{-7} eV/K for ΔS_m, showing that this is a negligible parameter, as in the case of alkaline halide. According to the EPJ model, the variation of association entropy of the vacancies depends only on the configurational degeneration Z_c. To evaluate Z_c, it is necessary to know the local structure of the cation-vacancy associations. Then, to find ΔS_a, we assumed the cation-vacancy association models proposed by EXAFS studies. The value thus calculated for $\Delta S_a/k$ was equal to 5.63 by choosing the (M-V_O-M) (with M=Y^{3+} or Zr^{4+}) association.

To check the LF-EPJ results for ZrO_2-Y_2O_3 systems, since there are no values of these parameters published, we compared the above result with those obtained by applying the procedure used for alkaline halides. When a logarithmic procedure was used, a significant difference with the LF-EPJ results was observed. The reason is that the logarithmic fit is not a very good approximation to these experimental data, because the relative fitting error is not negligible in relation to the experimental value for many of the data points being fitted. However, when we performed a fit assuming the experimental errors to be proportional to the measured value, we observed very good agreement between the parameters determined with each procedure.

In summary, the local fit of the Arrhenius law together with the equally probable jumps model allowed us to analyze the temperature behavior of the $\Delta G(T)$ and $\Delta S(T)$ functions for 12 mol % Y-FSZ single crystals, and also to determine the values of ΔH_a, ΔH_m, ΔS_a, and ΔS_m, even though the interaction between vacancies had not been taken into account.

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