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Temperature dependence of the Haven ratio in β-alumina

Hiroshi Sato and Klaus Gschwend
School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907

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A strong temperature dependence of the Haven ratio H_R, which has been found in β-alumina along with a strange discontinuity in the H_R vs T curve of Na-β-alumina at low temperature, is explained by a many-body diffusion theory utilizing the newly improved pair approximation of the path probability method of irreversible statistical mechanics based on a simple two-site model. The effect is due (1) to a strong temperature dependence of the "correlation effects" in both diffusion and conduction of ions as a result of changes with temperature in the population of conduction ions among different kinds of available lattice sites, and (2) to a difference in the statistical nature of tracer diffusion and ionic conduction. An apparent discontinuity in the H_R vs T curve observed for Na-β-alumina at low temperatures is connected to a percolation difficulty which occurs only for tracer diffusion near the stoichiometric composition because of the existence of preferred sites for conduction ions. The H_R vs T curves are very sensitive to the occupancy ratio of available sites of conduction ions (or the degree of nonstoichiometry), to the ratio of the site-occupancy energy difference w between the preferred sites and the interstitial sites, and to the mutual interactions among conduction ions ϵ. A remarkable difference in behavior between Na– and Ag-β-alumina is explained by the difference in the magnitude of w for these two compounds.

The Haven ratio H_R which is defined as the ratio of the tracer diffusion coefficient D and the charge diffusion ceofficient D_c $[=\sigma/(ne^2/kT)$: σ is the ionic conductivity, and n and e are the density and the charge of conduction ions, respectively] is generally considered to give the correlation factor f of tracer diffusion. Because of this reason, H_R is often used in ionic conductors to investigate the diffusion (conduction) mechanism.[1-3] Based on the random-walk theory of diffusion, the correlation factor has a fixed value which is characteristic of the lattice geometry and the mechanism of diffusion. In β-alumina, the value of H_R has been found to be close to 0.6,[4] and, based on this value, the mechanism of diffusion has been believed to be the interstitialcy mechanism.[5] However, according to recent direct measurements of H_R for some β-alumina-type compounds shown in Fig. 1, the value of H_R is found to be strongly temperature dependent,[6-7] and, for Na-β-alumina, even a strange discontinuity in the temperature dependence of H_R is found at low temperatures.[6] This deviation reflects the situation that in superionic conductors such as β-alumina, in which the number of available sites for conduction ions is far larger than the number of conduction ions themselves, the concept based on the random-walk theory is not applicable. It has been shown, based on a many-body diffusion theory utilizing the pair approximation of the path probability method of irreversible statistical mechanics,[8,9] that the value of H_R by itself cannot be an indicator of the diffusion mechanism. Even the distinction among diffusion mechanisms is almost meaningless when the number of defects through which the motion of ions takes place is large.[10] The previous version of this theory,[8,9] however, included some inappropriateness in the averaging processes and lacked important features necessary for explaining the behavior of H_R fully. This note, therefore, is intended to clarify the physical mechanism involved in the temperature dependence of H_R for β-alumina-type superionic conductors and in the discontinuity of the H_R vs T curve observed in Na-β-alumina utilizing the newly improved (but not yet published) pair approximation of the path probability method. The new version of the path probability method can be derived in a step-by-step fashion parallel to the previous treatment which has been published for some time.[8,9] The results are found to be the same except for a single correction factor in the present application. Therefore, theoretical explanations are kept to a minimum in presenting the physical backgrounds.

In the pair approximation of the path probability method, the many-body effect of isotope diffusion and ionic conduction for superionic conductors can be represented by three factors V, W, and f or f_I in the following fashion[8,9]:

$$D = a^2\theta e^{-\beta u} VWf\,, \tag{1a}$$

$$\sigma = \frac{ne^2}{kT} a^2\theta e^{-\beta u} VWf_I\,. \tag{1b}$$

Here, a is a numerical factor related to the jump distance and the dimensionality of the crystal lattice, $\beta=(kT)^{-1}$, and $\theta e^{-\beta u}$ gives the jump frequency of a conduction ion.[8,9] These factors are formally the same as those in the random-walk theory. V, W, and f or f_I represent the many-body effect: V is related to the vacancy (vacant available site) distribution with respect to a con-

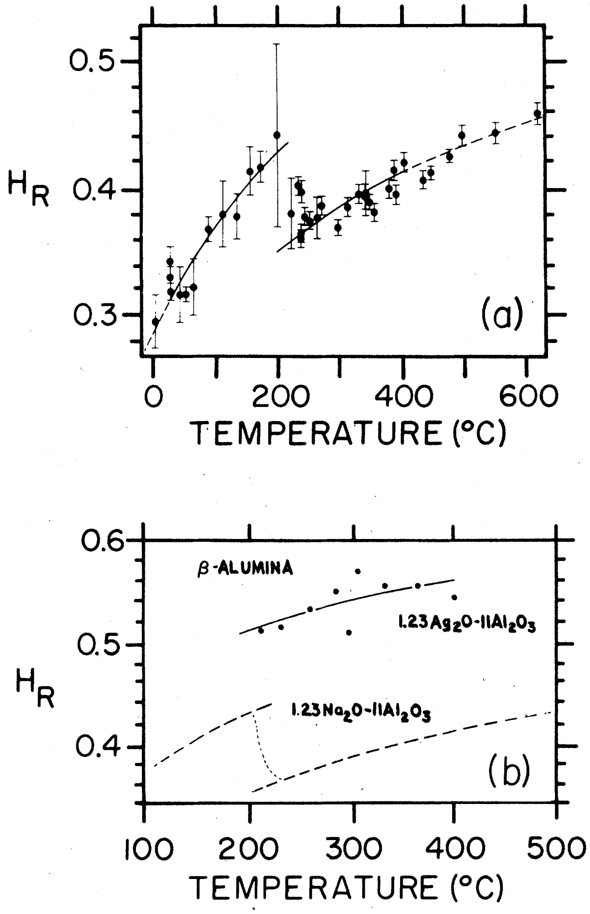

FIG. 1. Temperature dependence of the Haven ratio observed for β-alumina. (a) Na – β-alumina (K. K. Kim *et al.*, Ref. 6). (b) Ag – β-alumina (K. K. Kim *et al.*, Ref. 7).

duction ion and is called the vacancy availability factor, W is related to the effect of interaction of neighboring ions on the jump frequency of conduction ions and is called the effective jump-frequency factor, and f is the generalized correlation factor defined as the relative efficiency of motion of isotope ions towards long-range diffusion with respect to that of random-walk motion.[8,9] This indicates the degree of deviation of particle motion from the random walk in either direction and it coincides with the correlation factor for the vacancy mechanism in the limit of self-diffusion. The factor f_I in Eq. (1b) represents the correlation factor for ionic conduction which is defined in the same way as f and is unity unless there are physical causes producing correlation effects.[10] The Haven ratio H_R is then defined as

$$H_R = f/f_I\,. \tag{2}$$

It should be pointed out that the many-body factor VWf or VWf_I, which appears in Eq. (1), is strongly temperature dependent. But it can also be shown that, in most cases, this factor takes approximately the form of the Arrhenius equation and modifies both the preexponential factor θ and the activation energy u in Eq. (1).[11] Therefore, it is difficult to extract this factor experimentally by simply measuring D or σ.

The previous version of the theory was applied not only to superionic conductors, where the number of vacant available sites is large, but also to tracer diffusion in both ordered and disordered alloys.[12-14] In these calculations, however, it was noticed that values of transport properties such as f in Eq. (1a) deviate somewhat from those expected for the pair approximation while V and W, which are related to the distribution of ions in the steady state, are more satisfactory.[8,9,12-14] Especially disturbing was that the theory could not predict the existence of the percolation limit in random alloys[14,15] while the static version of the theory (the cluster variation method[16]) of the corresponding approximation predicts the percolation limit without any difficulty.[17] Computer simulation results by the Monte Carlo method on the same model[18,19] also showed a marked but systematic discrepancy in the values of f. The cause of the discrepancy has since been traced to somewhat inappropriate time and space averaging in the treatment of flow, and a new and correct formalism of the theory of diffusion and ionic conduction has been worked out in detail. (Details of the theory will be published elsewhere shortly.) The trouble was basically due to an inappropriateness of the formalism of the path probability method of nonequilibrium statistical mechanics as applied to mass transport problems which was not fully appreciated in the previous version.[8,9,12-14] This difference was found to be taken care of in the case of diffusion by introducing into the previous formalism the concept of self-consistency between the "macroscopic" flow (long-range flow) and the "microscopic" flow (short-range flow) similar to the concept of self-consistency found in the Bethe approximation.[20] The corrected version of the theory yields not only the correct values of f and the mass-diffusion coefficient such as D_c within the pair approximation, but also predicts the existence of the percolation limit in random alloys which agrees with that predicted by the pair approximation of the cluster variation method. The consistency relation can formally be divided into two parts, the "space-consistency relation" and the "time-consistency relation." The path probability method, when the change of the system in short-time interval Δt is derived, utilizes an ensemble concept similar to that utilized in the cluster variation method in the calculation of the path entropy. When the mass transport problem is involved, the change of state is created from the motion of atoms in the same lattice and not of any atom in the ensemble. In order to ensure that the change of state is created by atoms from the nearest-neighboring site, therefore, it is necessary to correct the statistical weight of atoms which creates the change from the value specified by the ensemble concept. This correction is called the space-consistency relation. On the other hand, when the "efficiency of motion" of tracer ions to derive the correlation factor is calculated, the motion of atoms must be followed for an infinite length of time under the steady-state condition rather than the averaged motion in Δt only as was done in the previous treatment. This correction is called here the time-consistency relation. While both consistency relations enter in the tracer-diffusion case, only the space-consistency relation is required for the mass-diffusion case. Inclusion of the time consistency in the new tracer-diffusion treatment ensures that the specific difference in the statistical nature of tracer and mass diffusion is properly taken into account: for tracer diffusion to be detected, tracer ions should percolate through the whole specimen while, for mass diffusion, only the averaged motion of ions is to be detected. This specific feature, which was largely missing in the previous version, turns out to be of major importance for understanding the behavior of H_R in β-alumina.

In the calculation of the Haven ratio by the improved version of the theory, an idealized two-sublattice model is used again as adopted earlier for β-alumina.[8] β-alumina is a two-dimensional superionic conductor, and the conduction layer is simulated by the two-dimensional honeycomb lattice consisting alternately of Beevers-Ross (A) sites and anti-Beevers-Rose (B) sites. The occupancy ratio or the density of conduction ions on A and B sites combined are indicated by ρ. $\rho = 0.5$, then, corresponds to the stoichiometric composition. For ordinary β-alumina, the value of ρ is approximately 0.6. The A sites are the preferred sites for conduction ions, and the site-occupancy energy difference w between A and B sites is thus imposed. In addition, a nearest-neighbor repulsive energy $-\epsilon$ ($\epsilon > 0$) among conduction ions is assumed. Based on this model, the A sites are preferentially occupied by conduction ions, but repopulation to B sites occurs at higher temperatures. The repulsive interaction $-\epsilon$ tends to promote the cooperative excitation of ions from A to B sites, especially when $\rho > 0.5$. If $w = 0$, there is no distinction between A and B sites, and this case corresponds to β''-alumina.[8] The adoption of the idealized two-sublattice model here completely neglects the importance of the mid-oxygen sites. However, the major effect presented here is based on the sensitivity of the tracer diffusion on the percolation problem. Because the percolation problem is a topological problem, the qualitative feature of the result is rather insensitive to the details of the model.

The tracer-diffusion coefficient and the ionic conductivity are thus calculated for this model. The previous result for the correlation factor f can be written as [Ref. 8, Eq. (5.21)]

$$1/f = \tfrac{1}{2}(1/f^{AB} + 1/f^{BA}), \tag{3a}$$

where

$$f^{AB} = 1 - \frac{(\Upsilon_o^A)^2}{\Upsilon_o^A + \Upsilon_o^B}, \tag{3b}$$

and

$$f^{BA} = 1 - \frac{(\Upsilon_o^B)^2}{\Upsilon_o^A + \Upsilon_o^B}, \tag{3c}$$

$$\Upsilon_o^A \equiv \frac{y_{ov}}{y_{ov} + y_{vv}} \equiv \frac{y_{ov}}{q_v} = \frac{y_{oo}\, e^{-\beta\epsilon}}{y_{oo}\, e^{-\beta\epsilon} + y_{vo}}, \tag{3d}$$

$$\Upsilon_o^B \equiv \frac{y_{vo}}{y_{vo} + y_{vv}} \equiv \frac{y_{vo}}{p_v} = \frac{y_{oo}\, e^{-\beta\epsilon}}{y_{oo}\, e^{-\beta\epsilon} + y_{ov}}. \tag{3e}$$

Here, f^{AB} and f^{BA} correspond to partial correlation factors for ions jumping from A and from B sites, respectively.[8,9] The y's in Eqs. (3d) and (3e) specify the distribution of conduction ions (including tracer ions) and vacancies by expressing their nearest-neighbor pair relations. For example, y_{ov} is the probability that a conduction ion (o) on an A site has a vacant available site (v) on a nearest-neighboring B site. The p's and q's, on the other hand, specify the density of conduction ions and vacancies on A and B sites, respectively. For example, p_v is the probability that an A site is a vacant available site. The y's, p's, and q's are calculated according to the pair approximation of the cluster variation method as given earlier[8,9] and are determined by the four simultaneous equations

$$\frac{p_o q_v}{q_o p_v} = \left(\frac{y_{ov}}{y_{vo}}\right)^{3/2} e^{-(1/2)\beta w}, \tag{4a}$$

$$\frac{y_{oo} y_{vv}}{y_{ov} y_{vo}} = e^{\beta\epsilon}, \tag{4b}$$

$$p_o + p_v = q_o + q_v = 1, \tag{4c}$$

$$\tfrac{1}{2}(p_o + q_o) = \rho. \tag{4d}$$

According to the previous treatment, f_I is given by

$$f_I = 1 - \frac{(\Upsilon_o^A - \Upsilon_o^B)^2}{(\Upsilon_o^A + \Upsilon_o^B)[2 - (\Upsilon_o^A + \Upsilon_o^B)]}. \tag{5}$$

These equations indicate that the transport properties are determined by the distribution of ions on the lattice sites in the steady state assumed for the calculation of transport properties.

In the improved version of the treatment, expressions corresponding to Eqs. (3b) and (3c) are

$$f^{AB} = 1 - \frac{(\Upsilon_o^A)^2}{\Upsilon_o^A + \Upsilon_o^B(1-t)} \tag{6a}$$

and

$$f^{BA} = 1 - \frac{(\Upsilon_o^B)^2}{\Upsilon_o^A(1-t) + \Upsilon_o^B} \tag{6b}$$

with an additional relation which determines the consistency parameter t

$$f = \frac{1-t}{1+t}. \tag{6c}$$

The new expression for f_I is exactly the same as Eq. (5). This is because only one kind of conduction ion is dealt with and the space-consistency relation does not change matters in this case. f in Eq. (6), on the other hand, includes the time-consistency parameter t in the previous expression of f in Eq. (3). This is the only difference caused by the inclusion of the consistency relations in the present case. Although simple, the time-consistency relation, nevertheless, changes the value of f for self-diffusion from the previous value of $(z-1)/(z+1)$ to $(z-2)/z$ (z is the coordination number of the crystal lattice) and makes the value of f tend to zero near the percolation limit.

In order to make the physical situation clearer, the Haven ratio calculated as a function of ρ from Eqs. (3) through (6) for both the previous and the present calculation is compared in Fig. 2. The temperature is indicated by the reduced scale $kT/|\epsilon|$, and $w/|\epsilon|$ is taken to be 5. Although both f and f_I are strongly temperature dependent, and both tend to zero as the temperature goes to zero, the physical correlation effect[10] included in both terms is eventually divided out in f/f_I.[8] Therefore, only the difference in the statistical nature between tracer and mass diffusion appears in H_R. In addition to the change of the value of H_R from $\frac{1}{2}$ to $\frac{1}{3}$ ($z=3$ for the two-dimensional honeycomb lattice) in the self-diffusion limit, a major change by the inclusion of the time consistency is observed near the stoichiometric composition. While the value of H_R is limited within the range of 1 and $\frac{1}{2}$ in the previous calculation, it decreases steeply toward zero in the new treatment. The decrease beyond the value of $\frac{1}{3}$ is created by the time consistency relation, and, hence, this decrease is connected to the percolation difficulty[21] for tracer ions as A sites are preferentially occupied by conduction ions so that the percolation paths for tracer ions are blocked. If this region is excluded, the qualitative behavior described by the previous and present calculation is almost the same. The strong temperature dependence of H_R is related to the repopulation of conduction ions among the two sites, to the tendency of creating preferred sites because of the existence of w and of repulsive interactions,[22] and to the percolation sensitivity characteristic of tracer diffusion.

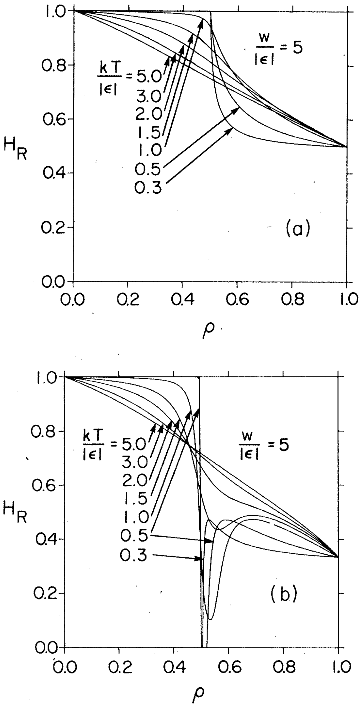

FIG. 2. Composition dependence of H_R as a function of temperature for $w/|\epsilon|=5$. (a) The previous calculation. (H. Sato and R. Kikuchi, Ref. 8.) (b) The corrected calculation.

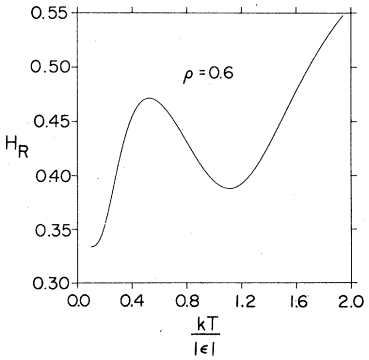

FIG. 3. Temperature dependence of H_R for the composition $\rho=0.6$ ($w/|\epsilon|=5$).

At $\rho = 0.6$, the temperature dependence of H_R is given in Fig. 3. There is a remarkable break in the value of H_R at low temperatures. This break, which was largely lacking in the previous calculation, should then have the same cause as that of the appearance of the decrease in the value of H_R beyond $\frac{1}{3}$ near the stoichiometric range in Fig. 2(b). Therefore, the major cause for this break should be ascribed to the percolation difficulty of tracer ions. This behavior of H_R in Fig. 3 should be compared to that of Na–β-alumina in Fig. 1. The qualitative agreement between theory and experiment is so striking that the interpretation of the inexplicable break in the H_R vs T curve observed in Na–β-alumina in Fig. 1 in terms of the percolation difficulty must be qualitatively correct. The calculated values of H_R also agree well with experimental values.

The dip in H_R is very sensitive to ρ because it is related to the percolation difficulty near the stoichiometric region. The dependence of the H_R vs T curve on ρ for $w/|\epsilon| = 5$ is shown in Fig. 4. The dip in H_R even reaches zero at low temperatures for $\rho = 0.52$ while for $\rho = 0.75$, such a dip becomes nonobservable and H_R increases monotonously with temperature. In view of this fact, it would be interesting to see how H_R changes with the degree of nonstoichiometry of Na–β-alumina if it can be controlled. For $w/|\epsilon| = 5$, the curve for $\rho = 0.6$ seems to explain the observed result best.

The H_R vs T curve should also be sensitive to the ratio of $w/|\epsilon|$ because the region of the percolation difficulty depends on the value of w at a fixed value of ρ. In this respect, H_R vs T curves for $\rho = 0.6$ but for values of $w/|\epsilon|$ between 5 and 0 are shown in Fig. 5. The magnitude of the dip at $\rho = 0.6$ decreases with $w/|\epsilon|$, and, for $w/|\epsilon| = 0$ (β''-alumina), H_R increases monotonously with temperature. Ag–β-alumina shows higher values of H_R with far less temperature dependence than Na–β-alumina and the low-temperature dip in H_R is missing. This difference in the behavior of Ag–β-alumina and Na–β-alumina is well explained by the curves for $w/|\epsilon| = 1$ and 5, respectively, in Fig. 5 which indicates that the site-occupancy energy difference w is expected to be far smaller for Ag–β-alumina. Indeed, a comparison of the relative occupancy by conduction ions of Beevers-Ross (BR) sites and anti-Beevers-Ross (ABR) sites in Ag–β-alumina and Na–β-alumina corroborates the above conclusion. A considerable portion of ABR sites is occupied by Ag^+ ions in Ag–β-alumina[23] while, in Na–β-alumina, no Na^+ ions are found on ABR sites. The dramatic difference in the H_R vs T curve between Na–β-alumina and Ag–β-alumina adds further support to the concept that the dip in the H_R vs T curve for Na–β-alumina is due to the percolation difficulty for tracer ions. A difference in the value of the repulsive interaction energy $|\epsilon|$ itself can also contribute to the difference between Na- and Ag–β-alumina.

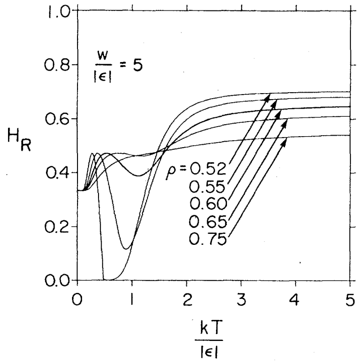

FIG. 4. Temperature dependence of H_R as a function of composition ($w/|\epsilon| = 5$).

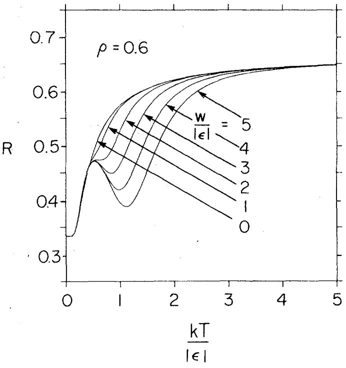

FIG. 5. Temperature dependence of H_R for $\rho = 0.6$ as a function of $w/|\epsilon|$.

So far, a strange dip in the H_R vs T curve at low temperatures in Na–β-alumina and a dramatic difference in the H_R vs T behavior between Na- and Ag–β-alumina are explained by a general theory of many-body diffusion based on a simple model with a reasonable choice of a few parameters. Of major importance in β- and β″-alumina-type compounds is the percolation sensitivity of the tracer diffusion and the preferential occupation of certain types of sites by conduction ions which blocks the percolation paths. From this point of view, the two-sublattice model proposed for β-alumina is basically sound if not exact. The decrease in H_R as temperature goes to zero is due both to a site-occupancy energy difference and to a strong mutual interaction among conduction ions which tends to create preferred sites near the stoichiometric composition ($\rho = 0.5$) for the conduction ions at low temperatures. The results also indicate the importance of correlation effects which accompany many-body diffusion problems, and, hence, the need for a general many-body diffusion theory in order to understand the mechanism of a variety of diffusion problems in general. It is especially important to point out the danger of determining the mechanism of diffusion solely from the value of H_R based on the common sense of the random-walk theory. Strong mutual interactions among conduction ions are typical of many-body diffusion problems, and a strong temperature dependence of H_R is to be expected in such cases.

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[21] Because of a finite jump frequency of conduction ions, the percolation never stops completely and there is no true percolation limit. The words "percolation difficulty" are therefore used to refer to this situation.

[22] H. Sato and R. Kikuchi, in *Fast Ion Transport in Solids*, edited by P. Vashishta, J. N. Mundy, and G. K. Shenoy (North-Holland, New York, 1979), p. 337. Although the time-consistency relation was introduced in this paper to correct the value of H_R in the self-diffusion limit from $\frac{1}{2}$ to $\frac{1}{3}$, a detailed calculation of H_R at low temperature was not made here, and the existence of the region of percolation difficulty was overlooked.

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