

Cationic conduction and diffusion and the compensation law

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It is shown that measurements of ionic conductivity or diffusion made in the region intermediate between the intrinsic and extrinsic ranges closely obey the compensation law $\log D_0 = a + b\Delta H_d$, where D_0 is the pre-exponential term in the equation for the diffusion coefficient, ΔH_d is the experimentally determined activation enthalpy, and a and b are constants. It is further shown that such measurements can allow determination of defect formation energies. A procedure for analysing results in the intermediate region is proposed and tested for ion conduction by Li^+ in LiF . Data for oxides are presented to show semi-quantitative agreement with the procedure.

1. Introduction

Ionic conduction and diffusion in ionic crystals are commonly discussed [1] in terms of ranges, e.g. intrinsic, extrinsic, association, where particular approximations for the concentrations of the compensating charged defects may be made [2-4]. Measured values of conduction and diffusion are then said to correspond to one or several of these ranges.

Little attention has been given to the properties of crystals which show mixed behaviour, i.e. which show behaviour intermediate between one range and the next, as for example between intrinsic and extrinsic. This omission can be serious, particularly in the case of the more refractory ionic compounds such as MgO , because in measurements made at high temperature, the intermediate region can cover a large temperature span (typically some 400 K). As a consequence, arguments based on determining whether such measurements represent intrinsic or extrinsic behaviour can be unrewarding [5].

The omission most probably arises because no convenient procedure for analysing data in the intermediate region has been proposed. It is the purpose of the present paper to suggest such a procedure, and to test it by analysing results of cation conduction measurements [6] made on LiF .

2. Analysis of mixtures of intrinsic and extrinsic behaviour

The compensation law [7] has the form

$$\log D_0 = a + b\Delta H_d \quad (1)$$

where D_0 is the pre-exponential factor in the expression for the diffusion coefficient, ΔH_d is the experimentally determined activation enthalpy, and a and b are constants.

Qualitative agreements with the law have been observed on a number of occasions [7, 8], though without indication of the physical basis for the agreement. In the matter of electronic conductivity, an analogous expression exists in the form of the Meyer-Neldel rule [9], and a number of derivations for a rule of this form have been proposed [10].

In another paper, the authors show that the compensation law arises wherever several mechanisms contribute to an observed process provided that the mechanisms are exponentially related to temperature [11]. The law therefore applies with some generality in diffusion processes and conduction processes where activated jumps are involved.

In the present paper, the particular example taken is that of diffusion in a crystal whose behaviour is intermediate between extrinsic and intrinsic; the contributing mechanisms are in this instance

diffusion by thermally generated defects and diffusion by impurity-generated defects. This breakdown into mechanisms is artificial and it is not implied or necessary to assume that the two types of defect can be in any way physically distinguished.

Taking LiF as example, one can write for the Schottky product [12]

$$[V'_{\text{Li}}][V_{\text{F}}] = K = [V'_{\text{Li}}]_i^2 \quad (2)$$

where $[V'_{\text{Li}}]_i$ represents the Li⁺-vacancy concentration in an intrinsic crystal, i.e. where thermally generated defects control the defect equilibria. The notation is that proposed by Kröger and Vink [13].

Considering a crystal containing MgF₂ as additive, one can write for the overall charge neutrality equation [12]

$$[V'_{\text{Li}}] = [V_{\text{F}}] + [\text{Mg}_{\text{Li}}] \quad (3)$$

Substituting (2) in (3) gives, as a quadratic equation for $[V'_{\text{Li}}]$,

$$[V'_{\text{Li}}]^2 - [\text{Mg}_{\text{Li}}][V'_{\text{Li}}] - [V'_{\text{Li}}]_i^2 = 0 \quad (4)$$

from which

$$[V'_{\text{Li}}] = \frac{1}{2}([\text{Mg}_{\text{Li}}] + \sqrt{([\text{Mg}_{\text{Li}}]^2 + 4[V'_{\text{Li}}]_i^2)}). \quad (5)$$

The diffusion coefficient for Li⁺ transport may be written

$$D_{\text{Li}} = \frac{1}{z} \nu_0 \lambda^2 \exp\left(\frac{\Delta S_m}{R}\right) \exp\left(\frac{-\Delta H_m}{RT}\right) [V'_{\text{Li}}] \quad (6)$$

where the symbols have their conventional meanings [14]. An expression for the experimental activation enthalpy, ΔH_d , may then be found at a particular temperature T^* by substituting Equation 5 in 6 and differentiating with respect to $1/RT$. Hence

$$\Delta H_d = -\left(\frac{d \ln(D_{\text{Li}})}{d\left(\frac{1}{RT}\right)}\right)_{T^*} = -\Delta H_m - \frac{\Delta H_s}{2} \times \left[\frac{4[V'_{\text{Li}}]_i^2}{([\text{Mg}_{\text{Li}}] + \sqrt{([\text{Mg}_{\text{Li}}]^2 + 4[V'_{\text{Li}}]_i^2)})} \right]_{T^*} \quad (7)$$

where ΔH_m and ΔH_s are the enthalpies for cation vacancy migration and for Schottky pair formation respectively. The consistency of Equation 7 with

enthalpies in the intrinsic and extrinsic regions may be seen by using the appropriate simplifying approximations. Thus for the intrinsic side of the intermediate region, one may put $[V'_{\text{Li}}]_i > [\text{Mg}_{\text{Li}}]_i$ whence from Equation 7

$$\Delta H_d = \Delta H_m + \frac{\Delta H_s}{2} \left(1 - \frac{[\text{Mg}_{\text{Li}}]}{2[V'_{\text{Li}}]_i}\right)_{T^*} \quad (8)$$

which approaches the expected intrinsic value as $[\text{Mg}_{\text{Li}}]_i$ goes to zero. Similarly for the extrinsic side, $[V'_{\text{Li}}]_i < [\text{Mg}_{\text{Li}}]_i$,

$$\text{and } \Delta H_d = \Delta H_m + \frac{\Delta H_s}{2} \left(\frac{2[V'_{\text{Li}}]_i^2}{[\text{Mg}_{\text{Li}}]^2}\right)_{T^*} \quad (9)$$

which again gives the expected value as the extrinsic defect concentration becomes large.

The form of the compensation law may be obtained by noting, from the plot of $\ln D_{\text{Li}}$ against $\frac{1}{RT}$, Fig. 1, that

$$\ln(D_{\text{Li}})_{T^*} = \ln(D_{\text{Li}})_0 + \left(\frac{d \ln D_{\text{Li}}}{d\left(\frac{1}{RT}\right)}\right)_{T^*} \left[\left(\frac{1}{RT}\right)_{T^*} - \left(\frac{1}{RT}\right)_0\right], \quad (10)$$

where the zero subscript indicates $\frac{1}{T} = 0$, and where $\ln(D_{\text{Li}})_0$ is evaluated from data measured at the temperature T^* .

Hence

$$\ln(D_{\text{Li}})_0 = \ln(D_{\text{Li}})_{T^*} + \frac{\Delta H_d}{RT^*}. \quad (11)$$

On substituting Equation 5 in Equation 6 and evaluating the differential of $\ln(D_{\text{Li}})_{T^*}$ with respect to ΔH_d , it is then found that

$$\frac{d \ln(D_{\text{Li}})_{T^*}}{d \Delta H_d} = -\frac{2}{\Delta H_s} \left(1 + \frac{[\text{Mg}_{\text{Li}}]^2}{4[V'_{\text{Li}}]_i^2}\right)_{T^*}, \quad (12)$$

from which the following expression may be obtained

$$\frac{d \ln(D_{\text{Li}})_0}{d \Delta H_d} = \frac{1}{RT^*} - \frac{2}{\Delta H_s} \left(1 + \frac{[\text{Mg}_{\text{Li}}]^2}{4[V'_{\text{Li}}]_i^2}\right)_{T^*}. \quad (13)$$

As a consequence of Equation 13, diffusion data will, when plotted as $\ln(D_{\text{Li}})_0$ versus ΔH_d , give a

straight line, i.e. obey the compensation law, either:

(i) for crystals which show mixed extrinsic/intrinsic behaviour, but in which the intrinsic term predominates in the mixture (a 10% deviation in the second term occurs when $[Mg_{Li}^{\cdot}]$ reaches 60% of the $[V_{Li}^{\cdot}]_i$ value or when ΔH_d has a value approximately halfway between the intrinsic and extrinsic values), or

(ii) in crystals for which the first term in Equation 13 dominates. For LiF, measurements are typically in the 400 to 800° C span so that $\frac{1}{RT^*}$ takes the value $\approx 1.4 \times 10^{-4} \text{ J}^{-1} \text{ mol}$; this may be compared with $\frac{2}{\Delta H_s} \approx 10^{-5} \text{ J}^{-1} \text{ mol}$ [6]. The first term therefore dominates, and it is expected that approximate linearity will extend over a wide range of the mixed region, the point of 10% deviation now occurring at $[Mg_{Li}^{\cdot}] = 2[V_{Li}^{\cdot}]_i$ where ΔH_d has a value $\Delta H_m + \frac{\Delta H_s}{2}$ (0.1). For oxides a similar picture is expected since higher ΔH_s values will compensate for the higher values of RT^* .

3. Representation

In the light of these considerations, data are first presented in the form of an Arrhenius plot and then analysed by determining, at any temperature T^* , the values of $\log D_0$ and ΔH_d (Fig. 1). By taking the results for $\log D_0$ and ΔH_d for a variety of samples each with a different dopant level

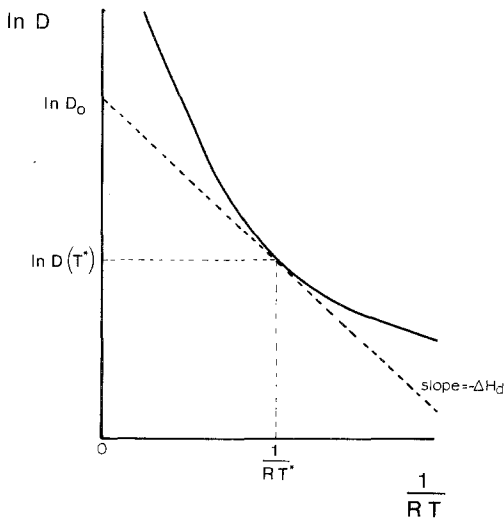


Figure 1 The determination of D_0 and ΔH_d at a particular temperature T^* from the Arrhenius plot.

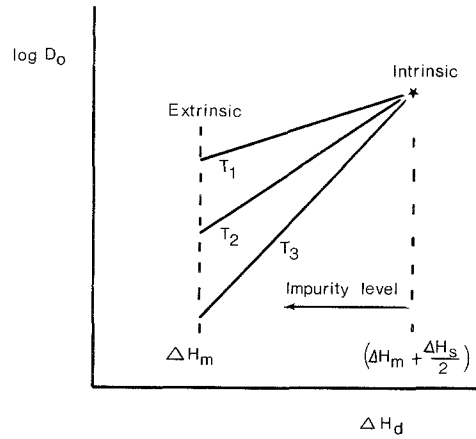


Figure 2 Presentation of diffusion data in the mixed extrinsic/intrinsic range, $T_1 > T_2 > T_3$.

(intentional or otherwise), plots of $\log D_0$ versus ΔH_d may be prepared. These plots will take the form of Fig. 2.

For cases where the donor dopant concentration ($[Mg_{Li}^{\cdot}]$ in the above example) is less than 60% of the intrinsic defect concentration, Equation 13 becomes

$$\frac{d \ln D_0}{d \Delta H_d} \approx \frac{1}{RT^*} - \frac{2}{\Delta H_s} \quad (14)$$

and data plot out as a set of lines, intersecting at the point corresponding to an intrinsic crystal, and increasing in slope as the temperature of measurement falls. At the intrinsic end of the plot, Equation 8 applies, and hence the impurity level should be observed to increase in a linear manner as the ΔH_d value falls from the intrinsic value $\Delta H_m + \frac{\Delta H_s}{2}$.

From the approximations made in the preceding section, departures from linearity should become apparent when the donor concentration approaches twice the intrinsic defect concentration; by substituting in Equation 7, it is seen that this occurs at a point some 90% of the way towards the extrinsic side on the activation enthalpy scale.

In heavily doped crystals, the donor concentration dominates in Equation 3 and the graph becomes a vertical line at the value $\Delta H_d = \Delta H_m$ as may be seen from Equation 7. This corresponds to experience, in that extrinsic crystals are expected to show [14] a variety of D_0 values at the activation enthalpy ΔH_m , each D_0 value corresponding to a different dopant level.

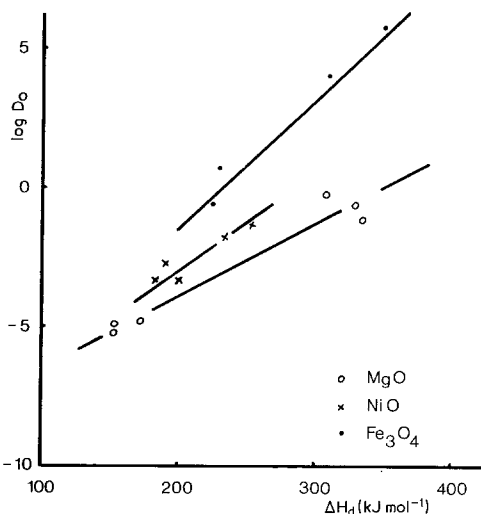


Figure 3 Cation diffusion coefficient data for MgO, NiO and Fe_3O_4 . D_0 has units $\text{m}^2 \text{sec}^{-1}$.

The use of this representation and the applicability of the most approximate form of Equation 13, namely

$$\frac{d \ln D_0}{d \Delta H_d} = \frac{1}{RT^*} \quad (15)$$

are shown in Fig. 3 for values of cation diffusion coefficients in three oxides as taken from the literature [15]. The points are the quoted data, each one being the result of a set of diffusion measurements; the lines have slope $1/RT^*$ where the temperature T^* is taken as the mid-point temperature for the set of measurements. Thus Mg^{++} diffusion in MgO is measured at predominantly high temperatures and the slope of the line is correspondingly shallow.

In the refractory oxides, the errors in diffusion measurements can be substantial [5] and there is consequently little hope of measuring, for a given sample, small variations in ΔH_d as the temperature is changed. As a result it is probably not sensible to pick out different lines (as in Fig. 2) corresponding to measurements made on several crystals at different temperatures; rather, the approximate obedience to Equation 15 may be noted and with it the indication that, in these samples, diffusion is neither intrinsic nor extrinsic but mixed, the particular mixture depending on the purity of the sample.

4. Lithium fluoride

For the alkali halides, more exact measurements of diffusion (or ionic conductivity) are possible [16],

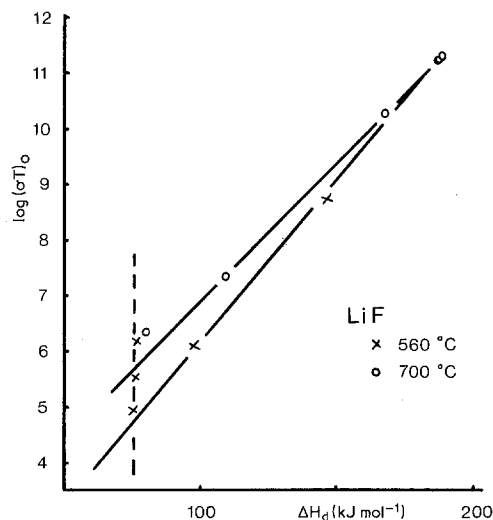


Figure 4 Cation conduction data for LiF plotted according to the format of Fig. 2. $(\sigma T)_0$ has units $\text{sec m}^{-1} \text{K}$.

and the use of the above procedures to estimate defect formation energies can be illustrated by considering data for lithium fluoride [6]. Though measured in a way that is not optimally suited to these procedures, the data can give some indication of the possible approach.

Using the data of Stoebe and Pratt [6] for five differently doped crystals, the values of ΔH_d and $\log(\sigma T)_0$ are calculated at two temperatures for each of the crystals, and the results are then plotted as in Fig. 4. The similarity to the form of Fig. 2 is apparent, the extrinsic line, the two mixed behaviour lines meeting at the intrinsic point, and the steeper slope for the lower temperature mixed line all being indicated by the data.

The solid lines are drawn in their theoretically predicted form on the basis of best values of ΔH_s and ΔH_m [6], namely, with slope

$$\frac{1}{2.303} \left(\frac{1}{RT^*} - \frac{2}{\Delta H_s} \right)$$

and with intersection at

$$\Delta H_m + \frac{\Delta H_s}{2};$$

the validity of the analysis is therefore tested by the extent to which the measured points in the mixed region fall on the solid lines.

5. Defect formation energies

An interesting objective, and one that is especially pertinent for oxides showing predominantly mixed

behaviour (Fig. 3), is the use of the procedure to determine defect formation energies. For this objective, the form of plot shown in Fig. 2 is not the most suitable because of the dominating effect of the $1/RT^*$ term. Although $\Delta H_m + \Delta H_s/2$ should in principle be detectable from measurements of D_0 and ΔH_d at two different temperatures in the mixed region, the construction of the intersection of the two $1/RT^*$ lines, and the consequent iteration are rather inaccurate. Similarly, isothermal measurements of differently doped crystals should in principle give ΔH_s directly from the slope of Equation 14, but the dominating effect of the $1/RT^*$ term in the slope again ensures a low degree of accuracy.

A more tractable form of diagram can be prepared by eliminating the $1/RT^*$ term from the analysis. This can be achieved by plotting in D_{T^*} against ΔH_d ; then as seen from Equations 11 and 13, the slope is given by

$$\begin{aligned} \frac{d \ln D_{T^*}}{d \Delta H_d} &= \frac{d \ln D_0}{d \Delta H_d} - \frac{1}{RT^*} \\ &= \frac{1}{RT^*} - \frac{2}{\Delta H_s} \left(1 + \frac{[Mg_{Li}]^2}{4[V'_{Li}]_i^2} \right) - \frac{1}{RT^*} \\ &= -\frac{2}{\Delta H_s} \left(1 + \frac{[Mg_{Li}]^2}{4[V'_{Li}]_i^2} \right) \end{aligned} \quad (16)$$

giving the defect formation energy directly.

Data abstracted from [6] are plotted in Fig. 5 according to this procedure, namely as $\log(\sigma T)_{T^*}$ against ΔH_d ; lines with the theoretical slope are

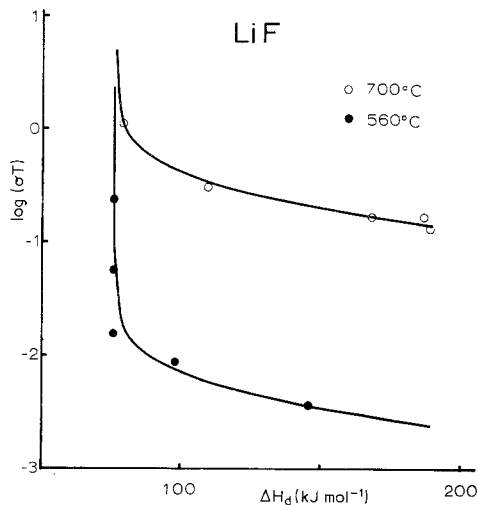


Figure 5 Cation conduction data for LiF plotted in the format of Equation 16.

shown in the figure for comparison. The graph is most readily constructed by plotting Equation 7 against the logarithm of Equation 6 (in its conductivity form) for different values of $[Mg_{Li}]/2[V'_{Li}]_i$.

Alternatively, use may be made of the vertical separation between the lines for measurements at different temperatures, which is given by

$$\begin{aligned} \ln D_{T_2^*} - \ln D_{T_1^*} &= \Delta \ln D_{T^*} \\ &= \left(\Delta H_m + \frac{\Delta H_s}{2} \right) \left(\frac{1}{RT_1^*} - \frac{1}{RT_2^*} \right) \end{aligned} \quad (17)$$

at any ΔH_d value $> \Delta H_m$.

The use of this second method can be illustrated using the example of lithium fluoride. From the data of Fig. 5,

$$\begin{aligned} \left(\Delta H_m + \frac{\Delta H_s}{2} \right) &\approx 2.303 \Delta \log(\sigma T)_{T^*} \cdot 8.31 \\ \left[\frac{1}{833} - \frac{1}{973} \right]^{-1} &= 190\,000 \text{ J mol}^{-1} \end{aligned}$$

which is to be compared with the value of 180 kJ mol^{-1} measured directly on intrinsic crystals [6]. In assessing this comparison, it should be emphasized that better agreement would be expected in measurements made in the form most appropriate for the proposed analysis (accurate ΔH_d determinations at particular temperature values); errors are also introduced into Fig. 5 by inaccuracies in abstracting ΔH_d values from the published data. In view of these factors, it is believed that the result is in satisfactory agreement with the measured value.

The suggested procedure may be summarized as follows. Data are taken in the form of measurements of D or σT at particular temperatures together with assessments of the experimental activation energy at those temperatures. A plot of the form shown in Fig. 5 is then prepared and an estimation of ΔH_s made either from the slope (Equation 16) or from the separation between the lines for different temperatures (Equation 17). The latter procedure requires in addition an estimation of the position of the vertical extrinsic line, ΔH_m , for the calculation of the defect formation energy.

6. Conclusions

Observation of the compensation law is expected for crystals whose ion conduction or diffusion behaviour is intermediate between the intrinsic and extrinsic conditions. When results are plotted as $\ln D_0$ or $\ln (\sigma T)_0$ against ΔH_d , a line of slope approximately equal to $1/RT^*$ is predicted.

Data for cation diffusion in several oxides are shown to fit the suggested expressions, indicating that the measurements are drawn from samples exhibiting mixed behaviour.

When measurements of the appropriate form are available, the suggested analysis allows determination of defect formation energies. This is an attractive possibility for oxide systems where a clear definition of the extrinsic and intrinsic regimes has been difficult to achieve and where, as a consequence, the conventional procedure for determining these energies has not been possible.

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