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Enhanced ionic motion in some fluorite-structured solid solutions

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Abstract. — Bulk ionic conductivity, Ionic Thermal Current (I.T.C.), and Thermally Stimulated Polarization Current (T.S.P.C.) studies are reported for the system \( \text{Ba}_{1-x}\text{La}_x\text{F}_{2+x} \) \((0.12 \times 10^{-2} < x < 0.45)\). The obtained results are illustrative for the compositional dependence of the ionic conductivity of anion-excess solid solutions. For small solute content simple associates as well as free mobile fluoride interstitials are present. For \( x > 0.01 \) defect clusters form. The ionic conductivity in this concentration range is characterized by Enhanced Ionic Motion.

1. Introduction. — For ionic solids with very small solute content \((< 0.1 \text{ mole } \% \text{ (m/o)})\), simple relations between dopant concentration and observed ionic conductivity hold. Lidiard [1] has applied the Debye-Hückel approach on ionic solids, and showed this approach to provide a good description of conductivity results up to about 1 m/o of defects. Systems with much higher defect concentrations have attracted considerable attention in recent years. Of these alkaline earth fluorides and cubic lead fluoride doped with tri- and tetra-valent cations have been studied in some detail.

In this concentration range a new region is observed in the ionic conductivity of the fluorite-structured solid solutions. The conductivity now increases exponentially with dopant content, while simultaneously the conductivity activation enthalpy \((\Delta H)\) decreases. The approach presented here to account for these observations differs from the Debye-Hückel-Lidiard theory, which is valid for moderate defect concentrations. The main influence of the surrounding defects on the jumping defects for moderate concentration is a decrease of their activities resulting in higher defect concentrations, while in the concentrated solid-solutions an enhancement of their effective mobility results. For this reason the new region is indicated as the enhanced mobility region.

2. Experiments on \( \text{Ba}_{1-x}\text{La}_x\text{F}_{2+x} \). — Figure 1 shows Arrenius plots of the temperature dependent conductivities for several compositions. The low temperature data are derived from T.S.P.C. spectra. For the most dilute solid solution \((x = 0.12 \times 10^{-2})\) a conductivity activation enthalpy of 0.93 eV is found. It has been shown [2, 3], that at the concentration- and temperature-range involved, mobile defects are
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generated by the dissociation of simple associates. The I.T.C. and T.S.P.C. spectra of this sample contain two peaks which can be attributed to the reorientation of nearest neighbour (nn) \((T_{\text{max}} = 147 \, \text{K})\), and next nearest neighbour (nnn) \((T_{\text{max}} = 202 \, \text{K})\) associates, and another peak at a higher temperature \((T_{\text{max}} = 290 \, \text{K})\). So far the observations are in line with the data of Laredo et al. [4]. A careful analysis of the high-temperature peak reveals, however, that it behaves non-Arrhenius, and probably consists of two closely related relaxations. The high-temperature part is identified as due to ionic conductivity (see Fig. 1), while the low temperature tail is most probably related with the motion of interstitial fluoride ions in close proximity to dislocations [4].

In the 2.4 m/o sample, the situation has drastically changed. The conductivity at room temperature has increased a factor of \(10^2-10^3\), while \(\Delta H\) has decreased to 0.73 eV. These effects can be described satisfactorily with the Debye-Hückel-Liadi theory. According to this theory the association activation enthalpy \((\Delta H_a)\) is lowered by the interaction between the free defect and its surrounding charge-cloud with, for this case, an amount of about 0.3 eV. This value is larger than the values quoted for \(\Delta H_a\) in the literature [2, 3]. So hardly any association is to be expected.

However, the I.T.C. and T.S.P.C. spectra show that a fraction of the interstitial fluoride ions is still in simple associates. This indicates that the actual value of \(\Delta H_a\) in the undisturbed lattice is slightly larger than 0.3 eV. Consequently the value of the activation enthalpy for motion \(\Delta H_m\) will be slightly lower than 0.73 eV. This will be confirmed later on.

Another feature of the spectra is a weak relaxation around \(T_{\text{max}} = 120 \, \text{K}\). This relaxation can most probably be ascribed to a reorientation within a cluster.

The other compositions examined \((13 < x < 0.45)\) cannot be interpreted with the aid of classical defect chemistry. Figures 2a and 2b show \(\log \sigma T\) and \(\Delta H\), respectively, as a function of the fluoride excess. Included in figure 2b are data for the system \(\text{Ba}_{1-x-y}\text{La}_x\text{Fe}_{2+y}^+\,^-,\,^+\) [5]. The features characteristic for the enhanced mobility region, i.e. an exponential increase of the conductivity, and a simultaneous linear decrease of \(\Delta H\) with the dopant concentration are readily apparent from this figure. The preexponential factors of the Arrhenius plots of \(\log (\sigma T)\) vs. \(1/T\) are almost identical for all the compositions in this concentration regime. The relaxation spectra are completely dominated by the displacement current peak. The area under this peak, which directly correlates with the preexponential factor in the Arrhenius plots, does not vary much with concentration either, and is in fact smaller than the same area in the spectrum of the 2.4 m/o sample.

3. Discussion. — It has been concluded that the enhancement of the ionic conductivity is a mobility effect, while the concentration of the mobile defects is limited [5]. This is in line with the occurrence of defect clusters, in that at higher defect concentrations most defects are bound into stable clusters and consequently not mobile at all. The increase of the mobility is entirely accounted for by the decrease of the conductivity activation enthalpy. To understand this effect it should be realised, that the reorientation enthalpy for dipoles \((\Delta H_R)\), always has a lower value than the activation enthalpy for motion in the undisturbed lattice, nn reorientation having a lower value for \(\Delta H_R\) than nnn reorientation. The reason for this is, that lattice ions relax from their crystallographic positions in the neighbourhood of lattice disturbing defects, thus influencing the equilibrium and saddle point energies of the jumping defects. Recent lattice defect calculations by Wapenaar and Catlow on defect jumps close to lattice disturbing ions yielded \(\Delta H\) values ranging from 0.05-1.10 eV. Therefore, in the enhanced mobility region a distribution of \(\Delta H\) values exists.

It has been shown that on the basis of a simple model, accounting for Coulombic interactions between monopoles only, a Gaussian distribution function of \(\Delta H\) values results [5]. This function, together with the well-known conductivity equation, yielded for the description of the conductivity:

\[
\sigma T = \sigma_0 \exp \left\{ -\frac{1}{kT}\left(\Delta H_m - \frac{p^2}{4kT}\right) \right\}
\]

where \(p\) stands for the width of the distribution function, and \(\Delta H_m\) for the activation enthalpy for motion.
in the undisturbed lattice. The conductivity activation enthalpy then reads:

$$\Delta H = \Delta H_m - \frac{p^2}{4kT}. \quad (2)$$

This equation accounts for the decrease of $\Delta H$ with increasing dopant concentration, if the width of the distribution function increases with increasing dopant concentration.

If Coulombic interactions between monopoles and dipoles are included we obtain for the concentration dependence of the width of the distribution function:

$$p_{m-m} = p_{m-m}^0 x_m^{1/2}, \quad \text{and} \quad p_{m-d} = p_{m-d}^0 x_d^{3/4},$$

where the subscripts stand for: $m =$ monopole, and $d =$ dipole. Substitution of $p_{m-m}$, respectively $p_{m-d}$ into equation (2) yields for $\Delta H: \Delta H \sim -x_m$ and $\Delta H \sim x_d^{3/2}$. Comparing these results with the experimental observation $\Delta H \sim -x$ (Fig. 2b), and assuming linear relations between $x$ and $x_m$, respectively $x$ and $x_d$, qualitative agreement with experiment is obtained with monopole-monopole interaction as predominant effect. Figure 2b further reveals that tetravalent dopant ions ($U^{4+}$) have a stronger influence on $\Delta H$, than trivalent ($La^{3+}$) have. The same tendency has been observed for the systems $\text{Pb}_{1-x}\text{Bi}_x\text{F}_2+x$ and $\text{Pb}_{1-x}\text{Th}_x\text{F}_2+2x$ [6].

Extrapolation of the data presented in figure 2b into the low dopant concentration regime ($x_m = 0$) should yield a reliable value for $\Delta H_m$, the activation enthalpy for interstitial fluoride ion motion in the undisturbed BaF$_2$ lattice. The value 0.71 eV is obtained, in good agreement with the calculated value of 0.69 eV [7].

The values quoted in the literature, 0.76 eV [2], and 0.83 eV [3], are rather large, since they have been obtained directly from the slopes of the Arrhenius plots in the dissociation region. This region is, however, very small for $\text{Ba}_{1-x}\text{La}_x\text{F}_2+x$ and the correct value is obscured by the interference of the intrinsic- and association-region. The present value for $\Delta H_m$, together with the value for $\Delta H$ obtained for the most dilute sample (0.93 eV) also leads to a new value for $\Delta H_A$. Taking into account the Debye-Hückel-Lidiard correction for this sample, $\Delta H_A = 0.37$ eV results, which is higher than the quoted values: 0.15-0.24 eV [2, 3].

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References