Suplemento de la Revista Latinoamericana de Metalurgia y Materiales 2009; **S1** (4): 1609-1612

LATTICE DEFECTS MODEL AND FAST-ION TRANSPORT IN SOLID ELECTROLYTES

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- ✓ Este suplemento constituye las memorias del congreso "*X Iberoamericano de Metalurgia y Materiales (X IBEROMET)*" celebrado en Cartagena, Colombia, del 13 al 17 de Octubre de 2008.
- ✓ La selección y arbitraje de los trabajos que aparecen en este suplemento fue responsabilidad del Comité Organizador del *X IBEROMET*, quien nombró una comisión *ad-hoc* para este fin (véase editorial de este suplemento).
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Trabajos presentados en el X CONGRESO IBEROAMERICANO DE METALURGIA Y MATERIALES IBEROMET
Cartagena de Indias (Colombia), 13 al 17 de Octubre de 2008
Selección de trabajos a cargo de los organizadores del evento

Publicado On-Line el 29-Jul-2009
Disponible en: *www.polimeros.labb.usb.ve/RLMM/home.html*

Resumen

El esquema de defectos reticulares como excitaciones químicas en sólidos se utiliza para explicar, sobre la base de la termodinámica, la transición a la fase electrolítica sólida. Una combinación apropiada de varias contribuciones a la energía libre del desordenamiento de los iones móviles en una red, siendo aquellos que se relacionan con la interacción defecto-defecto, la formación de defectos y la entropía de fonones, predice un comportamiento térmico de la densidad de iones móviles semejante a aquellos que se encuentran en los electrolitos sólidos. En particular dos configuraciones de defectos estables se encontraron a la temperatura de transición, T_t, donde la conducción de iones desordenados cambia drásticamente cuando se encuentra en la transición superiónica del sistema AgI a 420 K.

Palabras Claves: *Conducción iónica, Energía libre, Transición superiónica.*

Abstract

The scheme of lattice defects as chemical excitations in solids is used to explain on a thermodynamics basis, the transition to a solid electrolyte phase. By properly combining the various contributions to the free energy of the disordering mobile ion sublattice, such as those related to the defect-defect interaction, defect formation and phonon entropy the predicted thermal behaviors of the mobile-ion density resemble those found in solid electrolytes. In particular two stable defect configurations are found at a transition temperature, T_t in which the conduction of disordered ions changes abruptly as is found in the superionic transition of AgI at 420 K.

Keywords*: Ionic Conduction, Free-energy, Superionic Transition*

1. INTRODUCTION

A substance that conducts electricity through the movement of ions is called electrolyte. Most electrolytes are solutions or molten salts, but some electrolytes are solids and some of those are crystalline solids. Ion conduction in crystalline solids is an issue of central interest because of its importance in technological uses, for example, batteries, electrochromism, fuel-cells, and oxygen membranes form a variety of technologies of potential application.

The superionic conductors such as the AgX- (X = I, Br), MAg_4I_5 (M = Rb, K, NH_4) families had been studied during various decades because they have a high conductivity, σ, greater than 10^{-1} S/cm at moderately high temperature, and negligible electronic conductivity [1, 2]. The order parameter has been related with the carrier density. Some theoretical models have been proposed to explain the transition in terms of the conventional hopping mechanism [3–5] leading to an Arrhenius type of behavior.

This work concerns about a model of cooperative effects in AgI-based solid ionic conductors to explain the temperature dependence of their dc-conductivity. The reported cooperative study was done using a AgI-KI prototype combination of ionic salts.

2. THEORETICAL ASPECTS

A model of cooperative effects in ionic solids to explain this phase transition can be based on a free-energy density [3]

$$F(n_i) = U_i n_i - U n_i^2 + 2k_B T[n_i \ln(n_i) + (1-n_i)\ln(1-n_i) + \frac{3}{2} n_i \ln(\Gamma)] \quad (1)$$

where n_i is the variational parameter, U_i is the activation energy for promotion an ion into an

interstitial site (i.e., for a Frenkel-pair formation) and U is the attractive pair interaction energy. The third term is the contribution from combinational entropy, and the last term is the contribution from the vibrational entropy, represented by Γ which is given by the ratio of the localized interstitial phonon frequency ω′, to that of the lattice ω or $\Gamma = (\omega'/\omega)^{1/3}$. k_B is the Boltzmann's constant and T is the absolute temperature.

To try to explain the conductivity behavior in the whole temperature region for an AgI-type solid ionic conductor, we are proposing a random Huberman model by choosing conveniently the probability distribution function $P(n_i)$ for the ionic carrier density

$$P(n_i) = p\delta(n_i - n) + (1 - p)\delta(n_i) \qquad (2)$$

where p is the probability of having an ionic carrier taking part in the conduction and $(1 - p)$ that does not. Under this condition, the trial free-energy (1) of the completely disordered ions can be rewrite as

$$F(n) = pU_i n - p^2 U n^2 + 2k_B T[pn\ln(pn) + (1 - pn)\ln(1 - pn) + \frac{3}{2}pn\ln(\Gamma)] \qquad (3)$$

Minimizing this expression with respect to n gives a self-consistent expression for the carrier density n:

$$n = \frac{1}{p\left[1+\Gamma^{\frac{3}{2}}\exp\left(\frac{\tau}{\Gamma^{\frac{3}{2}}}(2n-pn)\right)\right]} \qquad (4)$$

In this model there are four adjustable parameters, x, Γ, τ , and p. The equilibrium configurations $n = \bar{n}$ are the ones that solve Equation (4) and produce an absolute $F(\bar{n})$ minimum at a given temperature. In general, depending on the values of the four adjustable parameters, it is possible to obtain a continuous increase of the values of $\bar{n}$ as a function of temperature or an increase of $\bar{n}$ with a discontinuity at a transition temperature T_t, whose magnitude depending on the value of x, as well as being scaled with p. This transition point is due to the coexistence of two stable configurations $\bar{n} = \bar{n}_1$, $\bar{n} = \bar{n}_2$ with $\bar{n}_1 \neq \bar{n}_2$ at the same temperature T_t with equal free-energy minima $F(\bar{n}_1) = F(\bar{n}_2)$.

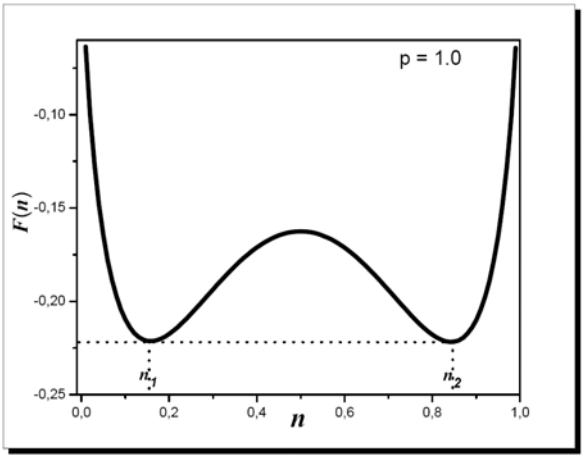
The variation of Equation (3) is driving by adimensional parameters:

$$x = \frac{U_i}{U} = 1.16, \qquad \Gamma = 0.77, \qquad (5a)$$

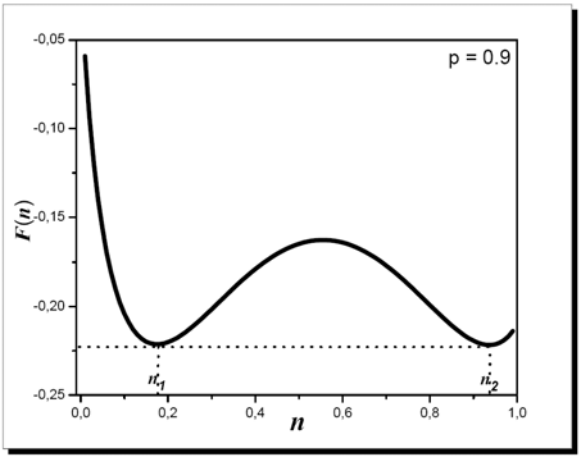
and at particular transition temperature

$$\tau = \frac{U_i}{k_B T} = 5.68 \qquad (5b)$$

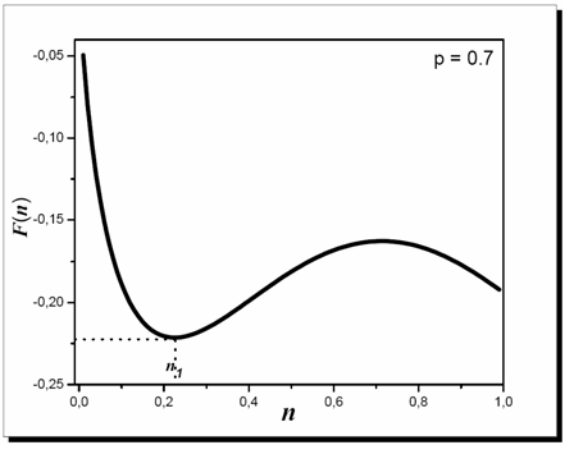
for different values of probability p (=1.0, 0.9, and 0.7), are shown in Figures 1*a*, 1*b*, and 1*c*, respectivabily.



(*a*)



(*b*)



(c)

Figure 1. Variation of the trial free-energy F minima with defect concentration n for different values of p, at transition temperature T_t.

3. EXPERIMENTAL TECHNIQUES

A representative sample of the system AgI-KI, which was used for electrical measurements, was prepared by solid-state reaction. XRD patterns showed that the sample was two-phase mixtures, β/γ-AgI and KI. Thermal analysis of KI-AgI also confirmed the γ-to-α transition of the AgI component at 420 K with no hysteresis loop on successive heating-cooling runs. The electrical characterization of the pressed powder samples was done using the two-electrode configuration Ag|sample|Ag [6]. All measurements were performed in dry nitrogen atmosphere. The measurements were done with a Hewlett-Packard 4174A LCR meter controlled by a microcomputer.

4. RESULTS AND DISCUSSION

Figure 2 shows the functionality of the dc-conductance data ($G = 1/R$) with inverse temperature dependence ($1000/T$) for the sample with composition AgI-KI during the first cooling run (similar behavior is observed but for the first heating run) between 470 K and 390 K. The conductivity data was taken on the sample after being annealed at 480 K for 2 h. The plot shows an abrupt change in conductance at about T_t = 430 K, similar to that observed in other AgI-based solid electrolytes in which AgI is a segregated phase [7, 8] and attributed to the first-order phase transition, β/γ- to α-AgI. The best fitting parameters are given by relations (5*a*)-(5*b*) and $p = 1$.

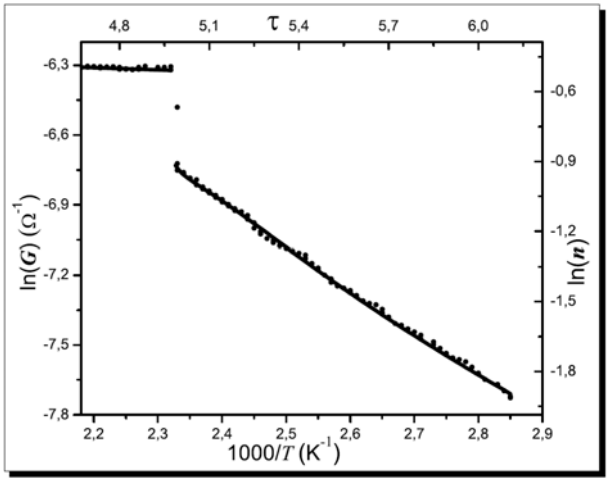


Figure 2. Temperature dependence of the conductance for AgI-KI near 430 K, plotted as ln(*G*) as a function of 1000/T (full circles), during a typical cooling run. The best fitting curve (full line) to the data points was generated by using the describe model (see text).

It was found that the observed step change in conductivity is mainly due to the carrier density n_i. The ratio between the concentration of the disordered cations after (n_g) and below (n_l) the transition, respectively, at the transition temperature (5*b*) is

$$\frac{n_g}{n_l} = 1.52 \qquad (6)$$

Below the transition, the conductance data increase in a thermally activated way, while above T_t it is almost constant.

Starting from low temperature (right hand), the curve exhibits an increase exponential behavior of $\overline{n}$ with increasing temperature followed by the sharp discontinuity, at the critical temperature T_t. At this temperature, two equal free-energy minima, $F(\overline{n})$, are found for two different roots ($\overline{n}$) of Equation (4), indicating the onset of a first-order phase transition.

However, the conductance data (full circles in Figure 2) in the whole temperature range, including the step change at T_t could only be fitted well to the model predictions if the parameter p varies with temperature. The continuous line curve in Figure 2, is the best fitting curve and was then obtained with the parameters given by (5*a*), (5*b*) and

$$0.97 < p \leq 1.$$

The experimental values to the concentration of the disordered cations after (n_g) and below (n_l), at transition temperature are:

$$G_l = 1.20 \times 10^{-3}\ \text{S}, \qquad G_g = 1.84 \times 10^{-3}\ \text{S},$$

$$\frac{G_g}{G_l} = 1.52, \qquad T_t = 430\ \text{K}.$$

Notice that

$$\frac{n_g}{n_l} = \frac{G_g}{G_l}$$

at T_t, thus explaining the step change in conductance.

5. CONCLUSIONS

We propose a phenomenological model that explains the step change observed in the dc-conductivity found in AgI-type ionic conductors near their superionic transitions and the behavior of conductance data in the whole temperature range. The model is based on a lattice defects free-energy density with an appropriated probability distribution function $P(n_i)$ given by (2) and compared with the sample AgI-KI conductivity experimental results.

This model simulates the first-order phase transition because it presents an abrupt order parameter ($\Delta \overline{n}$) discontinuity and predicts a p_l limiting value for the probability of having an ionic carrier which the trial free-energy has one root (one solution), in contrast to original model [3] and reported literature [7, 8] where the step change observed in conductivity is fitting by a trial free-energy with three solution.
In summary, this model allows for first-order phase transitions in a well defined range of variation of the model parameters representing the energy of the disordered ions (defect generation, defect-defect interaction) and the contribution from the phonon entropy.

6. ACKNOWLEDGEMENTS

This work was supported in part by Excellence Center for Novel Materials (CENM) for economical support.

7. REFERENCES

[1] S. Chandra, *Superionic Solids*, Amsterdam: North-Holland, 1981.

[2] H. Sato, *Topics in Applied Physics*, 21, Springer-Verlag (1997).

[3] B. A. Huberman, Phys. Rev. Lett. 1974; **32**: 1000.

[4] M. J. Rice, S. Strässler, and G. A. Toombs, Phys. Rev. Lett. 1974; **32**, 596.

[5] D. O. Welch and G. J. Dienes, J. Phys. Chem. Solids 1977; **38**, 311.

[6] H. Correa, *Master Thesis*, Universidad del Valle, Colombia (1996).

[7] D. Peña Lara, H. Correa, and R. A. Vargas, Solid Stat. Ionics 2004; **175**, 451.

[8] C. A. Lozano Z., H. Correa, D. Peña Lara, and R. A. Vargas, Phys. Stat. Sol. *b* 2008; /pssb.200844134