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Phase transition study in the AgI – Al_2O_3 system

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Abstract – In this paper we show that the rapid change in the dc-conductivity observed in AgI-type ionic materials near their fast-ion transitions can be explained by using a model of lattice defects. This model allows 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. The comparison of the model predictions on the equilibrium configuration of lattice defects with the dc-conductance data, G, points to the temperature variation of the carrier concentration, η(T), as the main source of the anomalous behavior observed in G(T). We have also included a temperature dependent fractional factor, *p*. that varies between 0 and 1 to take into account the variation of the ion mobility with temperature. This parameter contributed to a more precise description of the temperature dependence of the conductivity away from the transition. The model also predicts a second-order phase transition by properly adjusting the model parameters. The temperature dependence of the dc-conductivity for the AgI-Al_2O_3 composite has been well fitted to the η'(T) equilibrium configuration obtained from the trial free-energy function.

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Various theories [1] have been proposed to describe the phase transitions in materials called superionic conductors based on a trial free-energy density, $F(\eta)$, as a function of ionic carrier density η.These theories based on phenomenological models differ from each other by the manner in which defect interaction are introduced. The equilibrium defect concentration can be obtained by minimizing $F(\eta)$ with respect to η giving a transcendental equation which can be resolved by numerical methods.

Ionic conductivity due to an ionic charge *i*, σ_i, arises when an electric field, $\boldsymbol{E}$, is applied to an ionic solid, and is expressed as $\sigma_i(T) = \eta_i'(T)Ze\mu_i(T)$. We are proposing a model of cooperative effects in ionic solids to explain the phase transition to the superionic state based on a free energy of the general form

$$F(\eta) = pU_i\eta - p^2U\eta^2 + 2k_BT[p\eta\, ln(p\eta) + (1-p\eta)ln(1-p\eta)+1.5p\eta ln(\Gamma)]$$

where U_i is the activation energy for promoting a cation into an interstitial site (i.e., for a Frenkel-pair formation) and U represents the magnitude of the screening interaction between the cation at an interstitial site and the vacancy. The third term is the contribution from the vibrational entropy that depends on the ratio of the localized interstitial phonon frequency to that of the lattice (Γ), k_B is the Boltzmann's constant and T is the absolute temperature. p is the fraction of defects which are not nearest neighbors to any other that impede their disordering. Minimizing this expression with respect to η gives a self-consistent expression for the carrier density

$$\eta = \frac{1}{p\,[1+\Gamma^{3/2}\exp(\frac{\tau}{x}\{\frac{x}{2}-p\,\eta\})]}$$

where $\tau = U_i/k_BT$ and $U_i = xU$ ($x > 1$). So, in this model there is four adjustable parameters, x; Γ; τ , and p. The equilibrium configurations $\eta = \eta'$ are the ones that solve the previous equation and produce an absolute $F(\eta')$ minimum at a given temperature. The evaluation of the obtained analytical expressions based on a trial free-energy $F(\eta_i)$ was made by considering a typical Ag^+-ion conductor such as AgI in which nanoparticles of Al_2O_3 have been dispersed.This AgI-salt combination still shows a first-order phase transition close to the β-to-α transition of pure AgI at 426 K (Figs. 1,2). However, the step change in conductivity, $\sigma = \sigma_g - \sigma_l$ at T_t, as well as the temperature behavior, $\sigma(T)$, in both high-low temperature phase is very sensitive to the Al_2O_3 content.

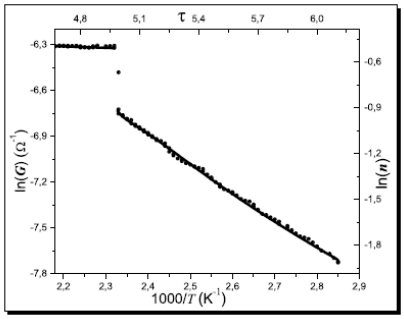

Figure 1: Typical temperature dependence of the conductance of the AgI-based composite The best fitting curve (full line) to the data points was generated by using the described model.

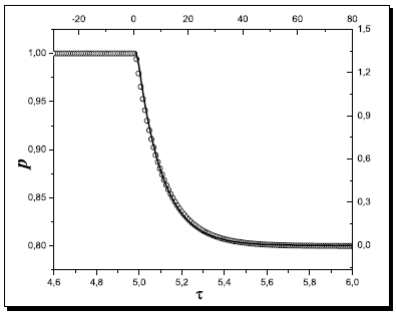

Figure 2: Temperature variation of the *p*-parameter used to obtain the best fitting curve to the conductance.

[1]. M. Aniya and S. Ichihara, J. Phys. Chem. Solids **66**:288 (2005).