

RELATIONSHIP BETWEEN MACROSCOPIC AND MICROSCOPIC ENERGIES NEAR γ -TO- β PHASE TRANSITION FOR γ -RbAg₄I₅H. Correa¹, D. Peña Lara² and Daniel Suescún-Díaz³¹Laboratorio de Optoelectrónica, Universidad del Quindío, Armenia, Colombia²Departamento de Física, Universidad del Valle, Cali, Colombia³Departamento de Ciencias Naturales, Avenida Pastrana, Universidad Surcolombiana, Neiva, Huila, ColombiaE-Mail: daniel.suescun@usco.edu.co

ABSTRACT

In this paper, we are reporting on specific heat and complex conductivity measurements in crystalline γ -RbAg₄I₅ close to the γ -to- β phase transition at 120 K. Using the electric modulus formalism for analysis of ionic conductivity relaxation in γ -RbAg₄I₅, microscopic interaction energy for a single-mobile ion whose temperature derivative is proportional to the specific heat was found. The results suggest that a common ion-ion and ion-lattice mechanism for both ionic migration and thermodynamic energy (i.e., the enthalpy) of mobile defects are present in this highly-dense system. The cooperative behavior observed in this transition region drives the phase transition at 120 K in γ -RbAg₄I₅.

Keywords: specific heat, ionic correlation, activation energy, phase transitions.

INTRODUCTION

Interest in the dynamics of mobile ions in solid state has increased over the last few years [1–4]. Silver-ion conductors have been considered as model compounds to study fast ionic conducting behavior, with RbAg₄I₅ [5, 6] being the ionic solid with the highest dc conductivity near room temperature. The high mobility of silver ions in the α -RbAg₄I₅ cubic phase is known to be responsible for the high ionic dc-conductivity value ($\sigma_0 = 0.21(6)$ S/cm) at 300 K [7]. Upon cooling, the α -RbAg₄I₅ phase transforms into the rhombohedral β -RbAg₄I₅ phase at 209 K and into the trigonal γ -RbAg₄I₅ at 120 K. The γ -RbAg₄I₅ phase shows no appreciable self-diffusion and its dc conductivity is low and highly activated as a normal salt ($\sigma_0 < 10^{-4}$ S/cm). The γ -to- β phase transition is a first-order transition which has been partially characterized [8], showing a discontinuous change of the dc-conductivity with an associated peak in the excess specific heat excess. Moreover, with decreasing temperature, the disorder in the silver sublattice decreases, so that at low-temperature γ -phase point defects serve as a vehicle for its poor ionic conduction. Previously, theoretical models based on trial free energy densities of cooperative effects in ionic solids have been proposed [9, 10], which points to the ionic carrier density as the main source of the anomalous behavior found in many solid ionic conductors, so their thermodynamic properties also follow in a straightforward way. In these models, a trial free energy function is proposed in which it is assumed that the ground state of an ionic solid is a perfectly ordered crystal with no defect present, with a given number of interstitial sites available per ion. As the temperature increases, the system exhibits disorder by forming point defects such as Frenkel pairs that contribute to the ionic conductivity as follow:

$$= e^2 N \bar{n}(T) \mu(T) \quad (1)$$

where N is the total number of ions, e their charge, \bar{n} the fractional number of cations in interstitial sites, and μ their

mobility. In these models of lattice defects, both phonon entropy and the attractive pair interaction play a central role in determining whether the transition to a disordered state takes place in a continuous or abrupt way. For the case in which the models allow for first-order phase transitions in the lattice order parameter to take place, a consequent increase in the number of ionic carriers and, therefore, in the ionic conductivity are observed, according to Eq. (1).

A detailed study of the crystal structure of γ -RbAg₄I₅ has been reported by Funke *et al.*, in which it is considered that localized displacive motion performed by individual silver ions are in “clusters” or “pockets” [11, 12]. These regions are interconnected by three dimensional passageways through which silver ions might diffuse. Previously reported ac ionic conductivity data for γ -RbAg₄I₅ at fixed temperatures, 83 K, 103 K, and 113 K [13], far below the γ -to- β phase boundary at 120 K, have shown independent of temperature dispersions due to ion-ion correlation in ion hopping, indicating that the ionic transport mechanism is preserved at those temperatures. Funke and Banhatti formulated a set of phenomenological rules that are written as rate equations in terms of correlation functions [12].

In this paper, we present results of specific heat and complex conductivity data (in the radio frequency range) in a temperature range close to and below the γ -to- β phase transition of RbAg₄I₅ at 120 K. The temperature dependence of these thermodynamics and transport data are compared to analyze the disordering of the Ag-ion sublattice as temperature is increased towards 120 K. In other words, in a larger view, the present work is aimed to establish that the ionic transport behavior is a manifestation of a common mechanism that connects the microscopic energy for ions, obtained by impedance measurements, and the thermodynamic energy (i.e. the enthalpy) of a dense system of interacting mobile defects that might drive to the first-order phase transition.



EXPERIMENTAL DETAILS

Crystals of RbAg_4I_5 were grown at 318 K using the solution technique with high-purity reagents [4], and then dried at 390 K for 6 hours. Crystals were chosen as representative specimens for crystallographic identification. XRD patterns showed quite uniform alignment and a cubic unit cell with a lattice constant of 11.24 Å, in good agreement with previous determinations [14, 15].

The specific heat data of RbAg_4I_5 single crystals were continuously obtained by using the ac-calorimetry technique [16, 17]. Crystal slices were thinned to 0.1 mm using dry abrasives. The sample was heated by light chopped at 1.5 Hz. The temperature oscillations induced in the sample, inversely proportional to the specific heat, were monitored using a 25 μm type-K thermocouple. From the amplitude of the temperature oscillations, ΔT_{ac} , the specific heat at constant pressure, $c_p(T)$, was obtained as a function of the temperature as the sample was swept slowly through the region of the phase transitions.

On the other hand, crystals were cut into wafers. An electrical measurement was made using the two-electrode configuration $\text{Ag}|\text{RbAg}_4\text{I}_5|\text{Ag}$ with silver paste as electrodes. The electrical characterization was made by admittance spectroscopy in the 20 Hz–3 MHz frequency range using a precision LCR meter HP 4284A, and at different fixed temperatures between 105 K and 121 K under a dry N_2 atmosphere. The amplitude of the applied ac signal was 10 mV. Possible nonlinear effects were absent at amplitudes up to 0.1 V over the entire frequency range for a typical cell.

RESULTS AND DISCUSSIONS

Specific heat behavior of RbAg_4I_5 as a function of temperature over the 110–130 K temperature range, verifying the existence of one phase boundary between the γ - RbAg_4I_5 and β - RbAg_4I_5 at 120 K [5, 6], is shown in Figure-1. The transition phase with approximately 1.5 K hysteresis on successive heating and cooling runs, and a large latent heat of 190.9 ± 0.8 cal/mol [5] is found being of first-order.

The angular frequency (ω) dependence of the real part of the ac conductivity $\sigma'(T, \omega)$ at several isotherms in the (117.5–119.6) K temperature region (chosen as the most representative), obtained from the conductance data, $G'(T, \omega) = A\sigma'(T, \omega)/d$, where A is the electrode sample contact surface and d the thickness of the sample, is shown in Fig. 2. The research results should be presented clearly and right to the point with accompanying figures and tables. These figures and tables should be referred to in the content. Explanation must not repeat what is already given in the content.

A typical behavior consisting of a crossover region to a power-law dependence at higher frequencies is observed. In ionically conducting materials, the frequency dependence $\sigma'(\omega)$ is usually described in the crossover region by using a power law of the form [18]:

$$\sigma'(T, \omega) = \sigma_0 \left[1 + \left(\frac{\omega}{\omega_p} \right)^n \right] \quad (2)$$

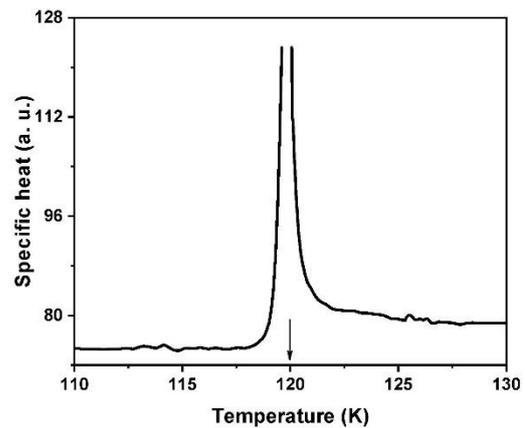


Figure-1. Specific heat behavior of RbAg_4I_5 as a function of temperature over the 110–130 K temperature range. The large latent heat of 190.9 ± 0.8 cal/mole [5] is for this first-order transition at 120 K.

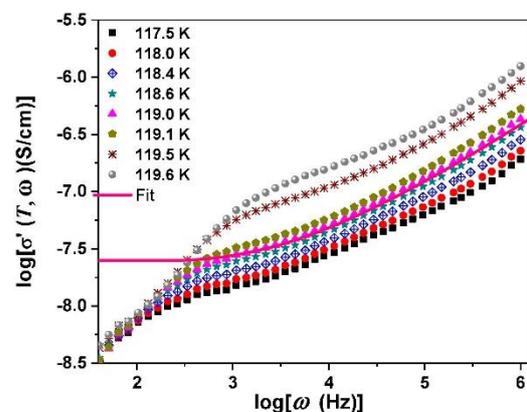


Figure-2. Frequency dependence of the real part of the ac conductivity σ' as function of frequency ω in the (117.5–119.6) K temperature range. The solid line represents the theoretical results what is expressing in Eq. (2).

where σ_0 is the dc conductivity, ω_p is a characteristic relaxation or crossover frequency, and n is the power law exponent which is related to the degree of correlation among moving ions [19]. The decrease observed for $\sigma'(\omega)$ at lower frequencies is due to the blocking of ions at grain boundaries or at electrodes, but these blocking effects do not affect the analysis on the frequency dependence of the bulk conductivity in terms of Eq. (2).

By fitting the $\sigma'(\omega)$ data at various isotherms to expression (2), we obtained the fitting parameters $\sigma_0(T)$ and $\omega_p(T)$. The Arrhenius plot of the dc-conductivity data as a function of the inverse of temperature in the 114.5–



119.8 K temperature range is shown in Figure-3. It is apparent that activation energy, $E_{act} = \partial \ln(\sigma_0) / \partial (1/T)$, is not constant or non-Arrhenius. It is quite apparent that as the temperature increases toward 120 K, E_{act} increases monotonically from 0.44 eV at 117.5 K comparable to literature reported [20]. Close to first-order phase transition at 120 K an anomalous behavior in the dc conductivity attributed to this transition is observed.

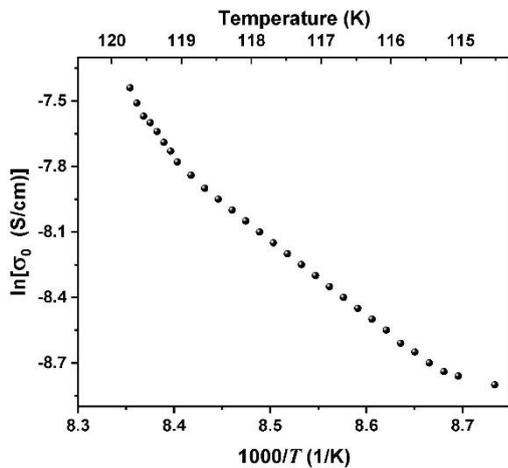


Figure-3. The Arrhenius plot of the dc-conductivity data as a function of the inverse of temperature in the 114.5–119.8 K.

The experimental information regarding electrical relaxation at a given temperature is usually obtained from the modulus formalism, $M^*(\omega) = M'(\omega) + iM''(\omega)$ where $\omega = 2\pi f$ is the angular frequency [18, 21]. To analyze the relaxation behavior, the electric modulus representation for the impedance data has commonly been used, considering that the main contribution to ionic conduction in the frequency range studied is due to silver ions [12]. This analysis starts with the argument that for the mobile ions the appropriate quantity to be considered is the decay of the electric field $E(t) = E(0)\phi(t)$ where initial electric field applied and $\phi(t)$ is the electric field relaxation function ($0 \leq \phi(t) \leq 1$). The complex electric modulus $M^*(\omega)$ in the frequency domain is related to the more familiar complex conductivity $\sigma^*(\omega)$ and $\epsilon^*(\omega)$ permittivity through

$$M^*(\omega) = \frac{1}{\epsilon^*(\omega)} = \frac{i\epsilon_0(\omega)}{\sigma^*(\omega)} \quad (3)$$

Thus $M^*(\omega)$, $\epsilon^*(\omega)$, and $\sigma^*(\omega)$ are just alternative and interchangeable representations of the same impedance data.

Frequency dependence of the imaginary part of the electric modulus [$M''(\omega)$] for some typical isotherms (chosen as the most representative), in the range between 116.0 K and 119.8 K, in crystalline γ -RbAg₄I₅ phase, close to the γ -to- β phase boundary, is shown in Fig. 4. Not all isotherms were taken into account in order to avoid data

overload. The electric field decay function $\phi(t)$ is obtained as [21, 22]:

$$M(\omega) = \frac{1}{\epsilon_\infty} \left[1 - \int_0^\infty \left(-\frac{\partial \phi}{\partial t} \right) e^{-i\omega t} dt \right] \quad (4)$$

where ϵ_∞ is the high frequency dielectric permittivity. Kohlrausch-Williams-Watts (KWW) “stretched” exponential function of the form:

$$\phi(t) = e \left(-\left(\frac{t}{\tau} \right)^\beta \right) \quad (5)$$

have been used to fit the modulus plots to expression (3) where τ is a characteristic relaxation time and $0 \leq \beta \leq 1$ is a temperature dependence function, and is referenced in literature as the correlation function between mobile ions.

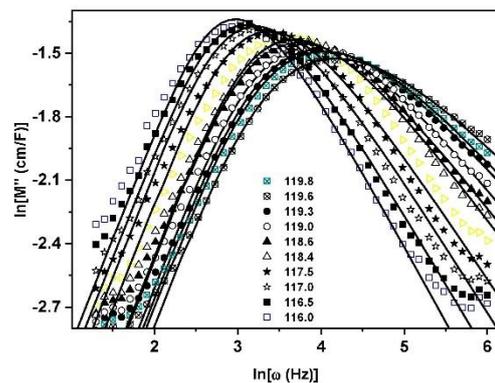


Figure-4. Frequency dependence of the imaginary part of the dielectric modulus $M''(\omega)$, for some typical isotherms close to the transition temperature. The solid lines represent the fit to expression (4).

Solid lines in Figure-4 are fit to expressions (3) and (4) where a dispersive peak is observed for each electric modulus curve at fixed T . The β -correlation function can be obtained from this fit, which is plotted in Figure-5. Decreasing values between 0.6 and 0.4 for the β -correlation function are obtained with increasing temperature in the 116.0–119.8 K temperature range. Since $\beta < 1$ indicates stronger correlation among ion hopping [21, 22], then the results indicate that ion-hopping correlations are increasing with increasing temperature. This behavior of ion-hopping correlations is quite different to what is observed in γ -RbAg₄I₅ far below the γ -to- β phase boundary where the transport mechanism is preserved as the temperature is changed [12].

The coupling parameter $n = 1 - \beta$, according to the coupling model [23, 24], increases from 0 to 1 as the interaction strength or ion-ion constraints increase. This seems not to be the case for γ -RbAg₄I₅, in which the concentration of mobile defects, serving as vehicles for the translational motion of Ag-ions, and the conductivity is dramatically increased when the temperature approaches 120 K from below, as can be evidenced by the data behavior. This indicates that the interaction among mobile



ions decreases with increasing temperature. However, since the concentration of mobile defects also increases, that may enhance instead cooperative correlations among them, leading to a decrease of β (or an increase of n , as observed in Figure-5). We have used the electric modulus representation of our ac conductivity data, which has been widely used in the analysis of correlated ion motion in ionic conductors [25, 26]. Moreover, it has been shown that the relaxation of experimental data is directly related to the microscopic dynamics of ion hopping [21–24].

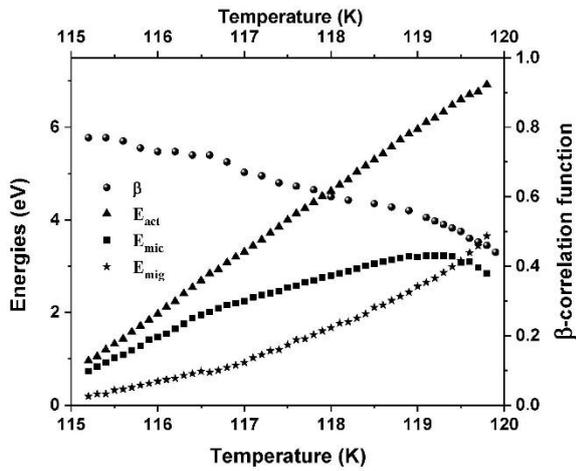


Figure-5. Temperature dependence of “stretched” β -correlation function and the energies E_{act} , E_{mic} , and E_{mig} as a function of the temperature T .

According to Ngai's coupling model [23, 24] the dc conductivity activation energy ($E_{act} = \partial \ln(\sigma_0) / \partial (1/T)$) and the exponent β can be used to obtain the single ion microscopic energy, E_{mic} ,

$$E_{mic}(T) = \beta E_{act}(T) \tag{6}$$

and

$$E_{act}(T) = E_{mic}(T) + E_{mig}(T) \tag{7}$$

being $E_{mig}(T)$ the migration energy.

Since we have simultaneously measured the specific heat and the electrical conductivity of γ -RbAg₄I₅ close to its γ -to- β phase transition at 120 K, we examined the relative behavior of the temperature derivatives of E_{act} , E_{mic} , E_{mig} , and we then compared them with the ΔC_p data in the same narrow temperature region below 120 K. It is evident from Figure-6, where the results of $d(\beta E_{act})/dT$ and ΔC_p are plotted, that these quantities exhibit similar behavior with temperature.

Since ΔC_p is related to the temperature derivative of the enthalpy h of the mobile Ag-ion subsystem, then the results show an accurate proportionality between βE_{act} or E_{mig} and h in this transition region near 120 K. No attempt has been made to subtract the temperature dependence portion of the lattice specific heat, and this undoubtedly

causes some deviations of the linear relations between the curves far below 120 K since the excess specific heat, ΔC_p due to mobile ions subsystem are very small.

On the other hand, the lattice dynamics effect on the ionic motion must include an active free energy for ionic migration E_{mig} . Thus, activation energy must include the energy “barrier” separating one minimum energy configuration from a neighboring one, i.e., the difference between a mean potential field associated with a minimum energy configuration P_1 and the saddle point P_2 :

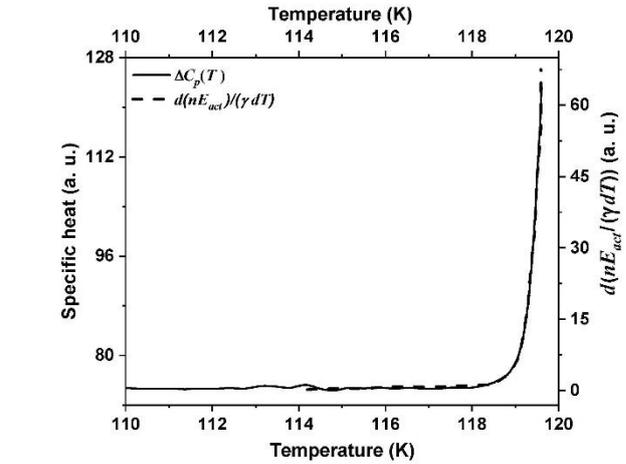


Figure-6. Temperature dependence of $d(nE_{act})/dT$ (solid line) and $\Delta C_p(T)$ (filled spheres) in the transition region below 120 K.

$$E_{mig} = \Phi(P_2) - \Phi(P_1) \tag{7}$$

$$E_{mig} = \Phi(P_2) - \Phi(P_1), \tag{8}$$

where Φ is the potential function of the ionic system. Furthermore, Φ also includes the pairwise interactions among the occupied lattices sites. Thus, an additional contribution to E_{act} resulting from the thermal average of this interaction must be considered, this being just the enthalpy of interaction per interstitial, h . Taking this additional contribution to E_{act} , proportional to h , then

$$E_{act} = E_{mic} + \gamma h \tag{9}$$

where γ is temperature-independent and by microscopic details of interaction among the mobile ion defects is determined. Assuming the current view of the coupling model [23, 24] of associating the activation energy E_{act} with single ion migration energy $E_{mig} = (1 - \beta)E_{act}$, The relationship between the activation energy and the microscopic energy for β -RbAg₄I₅ near the phase transition can be write as follow:

$$\Delta C_p \equiv \frac{dh}{dT} = \frac{1}{\gamma} \frac{d(nE_{act})}{dT} = \frac{1}{\gamma} \frac{dE_{mig}}{dT} \tag{10}$$



CONCLUSIONS

Simultaneous measurements of the ionic conductivity and the specific heat in γ -RbAg₄I₅ near the γ -to- β at 120 K, establish an accurate proportionality between the interaction enthalpy h [i.e., Eq. (10)], obtained from specific heat data and the migration activation energy E_{mig} obtained from impedance spectroscopy data. Here we have used the Ngai coupling model for ionic migration, in which a single ion activation microscopic energy is associated with that of ionic conduction [i.e., Eq. (6)]. In other words, this concordance between the ΔC_p and the E_{mig} provides evidence that the energetics of the partially occupied silver sites as described by the enthalpy and the availability of these sites for Ag-ion displacement are closely related, indicating that they obey the same mechanism. We emphasize the importance of using these different experimental techniques, such as specific heat measurements and impedance spectroscopy, in a highly correlated ionic motion, as these allowed us to find matching energy results.

REFERENCES

- [1]. Lunkenheimer P. and Loidl A. 2003. Response of Disordered Matter to Electromagnetic Fields. *Phys. Rev. Lett.* 91: 207601 (4 pp).
- [2]. Schuch M., Müller C. R., Maass P. and Martin S. W. 2009. Mixed Barrier Model for the Mixed Glass Former Effect in Ion Conducting Glasses. *Phys. Rev. Lett.* 102: 145902 (4 pp).
- [3]. Düscher M., Huber B., Passerini S. and Roling B. 2010. Hysteresis Effects in the Potential-Dependent Double Layer Capacitance of Room Temperature Ionic Liquids at a Polycrystalline Platinum Interface. *J. Phys. Chem. C* 114: 3614-3617.
- [4]. Kruempelmann J., Mariappan C. R., Schober C. and Roling B. 2010. Electrochemical double layers at the interface between glassy electrolytes and platinum: Differentiating between the anode and the cathode capacitance. *Phys. Rev. B* 82: 224203 (6 pp).
- [5]. Johnston W. V., Wiedersich H. and Lindberg G. W. 1969. Heat Capacity, Transformations, and Thermal Disorder in the Solid Electrolyte RbAg₄I₅. *J. Chem. Phys.* 51: 3739-3747.
- [6]. Owens B. B. and Argue G. R. 1967. High-Conductivity Solid Electrolytes: MAg₄I₅. *Science* 157: 308-310.
- [7]. Hull S., Keen D. A., Sivia D. S. and Berastegui P. 2002. Crystal Structures and Ionic Conductivities of Ternary Derivatives of the Silver and Copper Monohalides. *J. Sol. State Chem.* 165: 363-371.
- [8]. Lederman F. L., Salamon M. B. and Peisl H. 1976. Evidence for an order-disorder transformation in the solid electrolyte RbAg₄I₅. *Sol. Stat. Comm.* 19: 147-150.
- [9]. Huberman B. A. 1974. Cooperative Phenomena in Solid Electrolytes. *Phys. Rev. Lett.* 32: 1000-1002.
- [10]. Burbano J. C., Vargas R. A., Peña Lara D., Lozano C. A., and Correa H. 2009. Defect interaction and solid electrolyte transition in AgI-based materials. *Sol. Stat. Ionics* 108: 1553-1557.
- [11]. Funke K., Banhatti R. D., Wilmer D., Dinnebier R., Fitch A., and Marti J. 2006. Low-Temperature Phases of Rubidium Silver Iodide: Crystal Structures and Dynamics of the Mobile Silver Ions. *J. Phys. Chem. A* 110: 3010-3016.
- [12]. Funke K. and Banhatti R. D. 2006. Ionic motion in materials with disordered structures. *Sol. Stat. Ionics* 177: 1551-1557.
- [13]. Funke K., Banhatti R. D., Brückner S., Cramer C., Krieger C., Mandanici A., Martiny C. and Ross I. 2002. Ionic motion in materials with disordered structures: conductivity spectra and the concept of mismatch and relaxation. *Phys. Chem. Chem. Phys.* 4: 3115-3167.
- [14]. Geller S. 1967. Crystal Structure of the Solid Electrolyte, RbAg₄I₅. *Science* 157: 310-312.
- [15]. Geller S. 1976. Low-temperature phases of the solid electrolyte RbAg₄I₅. *Phys. Rev. B* 4: 4345-4355.
- [16]. Vargas R., Salamon M. B. and Flynn C. P. 1976. Ionic Conductivity near an Order-Disorder Transition: RbAg₄I₅. *Phys. Rev. Lett.* 37: 1550-1553.
- [17]. Jurado J. F., Ortiz E., and Vargas R. A. 1997. An AC calorimeter probe for a closed-cycle cryogenic station. *Meas. Sci. Technol.* 8: 1151-1155.
- [18]. Jonscher A. K. 1983. Dielectric Relaxation in Solids, Chelsea Dielectric Press, London.
- [19]. Jonscher A. K. 1981. Review: A new understanding of the dielectric relaxation of solids. *J. Mater. Sci.* 16: 2037-2060.



- [20]. Pinkowski A., Chierchie T. and Lorenz W. J. 1990. Low-temperature ion conductivity of RbAg_4I_5 . *J. Electroanal. Chem.* 285: 241-248.
- [21]. Ngai K. L. and León C. 1999. Relating macroscopic electrical relaxation to microscopic movements of the ions in ionically conducting materials by theory and experiment. *Phys. Rev. B* 60: 9396-9405.
- [22]. Rivera A., Santamaría J. and León C. 2001. Electrical conductivity relaxation in thin-film yttria-stabilized zirconia. *Appl. Phys. Lett.* 78: 610-612.
- [23]. Ngai K. L., Greaves G. N., and Moynihan C. T. 1998. Correlation between the Activation Energies for Ionic Conductivity for Short and Long Time Scales and the Kohlrausch Stretching Parameter β for Ionically Conducting Solids and Melts. *Phys. Rev. Lett.* 80: 1018-1021.
- [24]. Ngai K. L. 1996. A review of critical experimental facts in electrical relaxation and ionic diffusion in ionically conducting glasses and melts. *J. Non-Cryst. Solids* 203: 232-245.
- [25]. Pathmanathan K. and Stevens J. R. 1990. Improved analysis of ionic conductivity relaxation using the electric modulus with a Cole-Davidson distribution. *J. Appl. Phys.* 68: 5128-5132.
- [26]. Papathanassiou A. N., Mykhailiv O., Echevoyen L., Sakellis I. and Plonska-Brzezinska M. E. 2016. Electric properties of carbon nano-onion/polyaniline composites: a combined electric modulus and ac conductivity study. *J. Phys. D: Appl. Phys.* 49: 285305 (p. 8).