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Analysis of the Critical Exponents for Imidazolium Perchlorate Close to the Phase Transition Temperature of 373 K

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Keywords

Critical exponents, Specific heat, Polarization, Susceptibiliy, Im-ClO_4

Abstract

The critical exponents α, β and γ for the specific heat, polarization and the dielectric susceptibility, respectively, have been deduced below to the phase transition temperature of T_C = 373 K for the Imidazolium Perchlorate (Im-ClO_4) crystal. The analysis of the critical behavior of the specific heat has been carried out using the compressible Ising model, while analysis of the polarization and the dielectric susceptibility has been performed in terms of the power-law equations. Our results show that the Rushbrooke inequality is satisfied for the Im-ClO_4 crystal below the phase transition temperature of T_C = 373 K.

1. Introduction

Imidazolium perchlorate ($C_3N_2H_5ClO_4$ or Im-ClO_4) is a member of the organic-inorganic molecular ferroelectrics family. Unlike ferroelectric oxides, organic-inorganic molecular ferroelectrics have become more popular because of their advantageous characteristics including being inexpensive, mechanically flexible, and ecologically beneficial [1, 2]. The Im-ClO_4 material is unable to form bonds with metals and hydrogen, so it can interact electrostatically with biological systems [3]. It has also been reported that [4] Im-ClO_4 can be used as an efficient 3D printed metamaterial that generates rapid prototype, cutting the manufacturing time of ferroelectrics from hours to minutes. Furthermore, the Im-ClO_4 thin films exhibit better electromechanical coupling than the PZT films, as reported in [5], making them a viable lead-free alternative for a range of applications in electro-optics and sensor technologies.

Three consecutive solid-solid phase transitions have been reported in the literature [6] for Im-ClO_4 at the temperatures of 487, 373, and 247 K. As previously stated, [6], below and above the room temperature, the Im-ClO_4 crystal structure is trigonal. Cations are highly disordered at ambient temperature, whereas perchlorate ions are ordered. All the ionic sublattices, however, are disordered above the ambient temperature. Czapla et al. [7] have determined the dielectric and optical characteristics of Im-ClO_4 via the x-ray diffraction, dielectric, and birefringence measurements. Przeslawski and Czapla [8] have used an ac calorimeter to accurately measure the specific heat fluctuation of this crystal. A Differential Scanning Calorimeter (DSC) measurement have been carried out to investigate the phase transition behavior of Im-ClO_4 by Wenru *et. al.* [9]. Very recently, Li *et. al.* [10] have investigated the domain switching dynamics under a local bias through a Piezoelectric Force Microscopy (PFM) tip for Im-ClO4 thin films by employing both thermodynamic calculations and the phase-field approach in their study. Regarding the thermodynamic quantities of the order parameters S, susceptibility χ and specific heat C, near T_C, their critical behavior can be described by the power-law formulae [11,12]. In the

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case of ferroelectric Im-ClO_4 the order parameter can be considered as the polarization P with the dielectric susceptibility χ. The relation among the critical exponents of β (polarization), γ (dielectric susceptibility) and α (specific heat) known as the Rushbrook inequality ($\alpha+2\beta+\gamma \geq 2$) [11,12] can be examined for the ferroelectric Im-ClO_4. This then provides whether the scaling laws can be applied to the ferroelectric crystals, in particular, Im-ClO_4 under study.

In earlier studies [13,14] we have calculated quantities such as the relaxation time, activation energy, entropy, enthalpy, and the free energy for the Im-ClO_4 crystal in the lower phase transition temperature of T_C = 247 K. Since the Im-ClO_4 exhibits a second order solid-solid transition at T_C=373K, it is of interest to describe its critical behaviour by analyzing the temperature dependence of the polarization (P), dielectric susceptibility (χ) and specific heat (C) in the vicinity of T_C. This description can be performed by determining the critical exponents of those thermodynamic quantities, as also stated above. In this study, the anomalous behavior of the observed [5] polarization and the dielectric susceptibility of the Im-ClO_4 crystal is analyzed using the power-law formulae below the solid-solid phase transition temperature T_C = 373 K. A compressible Ising model [15] is used to investigate the critical behavior of the observed specific heat data [8] below T_C = 373 K. Below, we present our calculations and results by analyzing the observed data in section 2. Our discussion and conclusions are given in sections 3 and 4, respectively.

2. Calculations and Results

The correlation between the reduced temperature $\varepsilon = |T - T_C|/T_C$ and polarization P has been investigated below the solid-solid transition temperature of T_C = 373 K for the Im-ClO_4 crystal. According to the power-law formulae, the value of the critical exponent β can be calculated by using the average dipole [5] at the critical temperature T_C. The average polarization data [5] have been used to extract the critical exponent β according to

$$P = P_0 \varepsilon^{\beta} \tag{2.1}$$

where P_0 is the amplitude of the polarization. By taking the logarithm of both sides, we get a linear relation,

$$\ln P = lnP_0 + \beta \ln \varepsilon \tag{2.2}$$

Figure 1 gives the polarization P as a function of the reduced temperature ε in ln-ln scale. The slope of this plot gives the value of the critical exponent β while the intercept enables us to calculate the amplitude of the polarization P_0 (Equation 2.2).

Similarly, the critical behavior of the dielectric susceptibility χ can be analyzed according to a power-law formula that reads as

$$\chi = \chi_0 \varepsilon^{-\gamma} \tag{2.3}$$

where γ is the critical exponent and χ_0 is the amplitude of the dielectric susceptibiliy. The observed permittivity data [5] were used to analyze dielectric susceptibility χ which is plotted as a function of temperature in the ln-ln scale (Figure 2). The slope of this plot gives the value of the critical exponent γ and the intercept is the amplitude of the susceptibility χ_0 according to

$$\ln \chi = ln\chi_0 - \gamma \ln \varepsilon \tag{2.4}$$

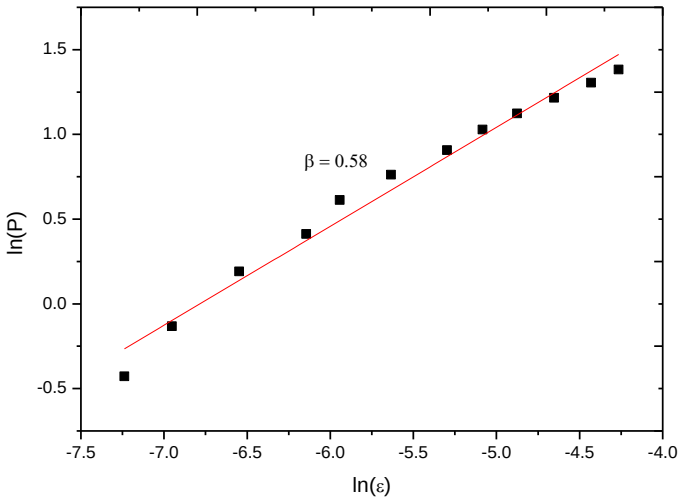

Figure 1. Polarization P as a function of the reduced temperature ε in an ln-ln scale (Equation 2.2) in the vicinity of the second-order phase transition temperature (T_C= 373K) in Im-ClO_4.

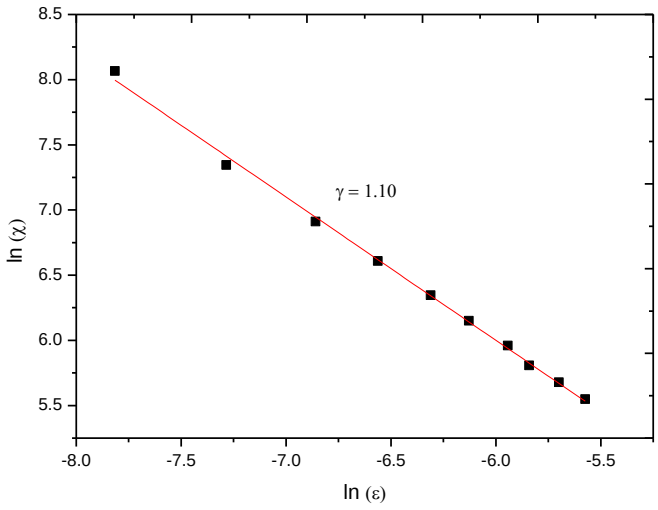

Figure 2. The susceptibility χ as a function of reduced temperature ε in an ln-ln scale (Equation 2.4) in the vicinity of the second-order transition temperatures (T_C =373 K) in Im-ClO_4.

A compressible Ising model can be used to analyze the critical behavior of the specific heat C for the Im-ClO_4 crystal below the transition temperature of T_C = 373 K. In their study Yurtseven [16], Yurtseven and Sherman [17] have reported an analytical expression to investigate the anomalous behavior of the specific heat C in terms of the critical exponent α according to

$$C = -\frac{JAT}{T_C^2}(1-\alpha)(2-\alpha)|\varepsilon|^{-\alpha} \tag{2.5}$$

where J is the interaction parameter between the nearest neighbor molecules with a constant A and JA is the parameter in the dimensions of energy. Using Equation (2.5), the observed specific heat data of the Im-ClO_4 crystal [8] have been analyzed below the phase transition temperature (T_C = 373 K). The specific heat per unit temperature (C/T) can be constructed as a function of the reduced temperature ε in the linear form by taking the logarithm of both sides in Equation (2.5) which then gives;

$$\ln\left(\frac{C}{T}\right) = \ln\left(\frac{-JA(1-\alpha)\,(2-\alpha)}{T_C^2}\right) - \alpha\ln\,(\varepsilon) \tag{2.6}$$

Our plot of C/T versus the reduced temperature ε in the ln-ln scale (Equation 2.6) is given in Figure 3.

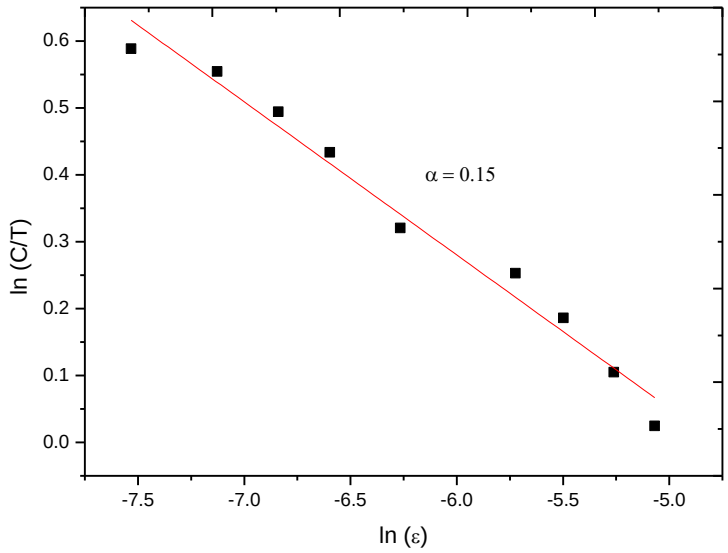

Figure 3. Specific heat C [8], as a function of the reduced temperature ε in an ln-ln scale (Equation 2.6) in the vicinity of second-order transition temperature (T_C=373 K) in Im-ClO_4.

We extracted the values of the critical exponent α and the interaction parameter JA from our plot (Figure 3) Their values were also extracted as the temperature approaches the critical temperature *Tc*, as plotted in Figures 4 and 5. We tabulate our extracted values of the critical exponents with the errors and the amplitudes in the vicinity of T_C (nearly 2K close to T_C) in Table 1;

Table 1. Values of the critical exponents and the amplitudes for the polarization P (Equation 2.1), dielectric susceptibility χ (Equation 2.2) and the specific heat C (Equation 2.3) of the Imidazolium Perchlorate in the vicinity of the transition temperature T_C.

Im-ClO_4	**β**	**P_0 (μC/cm^2)**	**γ**	**χ_0**	**α**	**-JA (J/mol)**
T_C =373K	0.58 ± 0.01	52.77±7.68	1.10 ± 0.20	0.55±0.12	0.15 ± 0.01	26.25±1.23

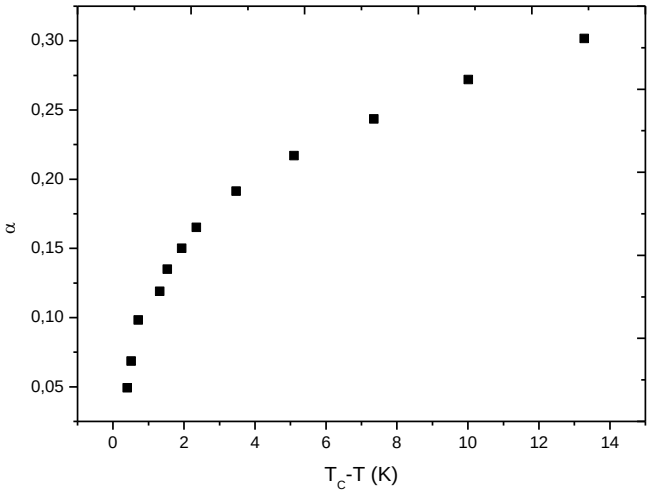

Figure 4. Variation of the critical exponent α with the temperature close to the second-order transition (T_C =373K) in Im-ClO_4.

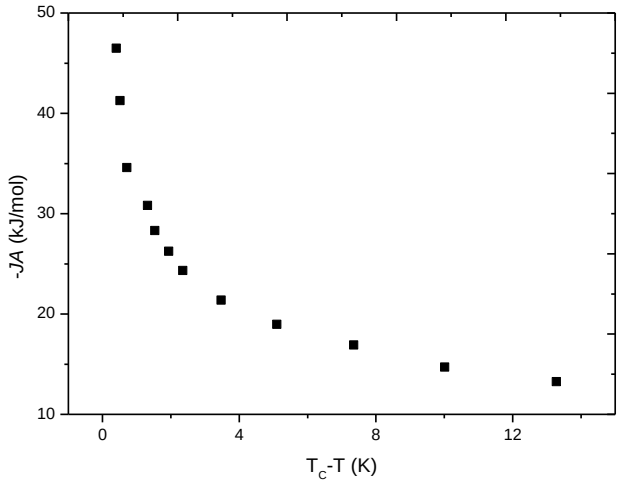

Figure 5. Variation of the interaction parameter JA with the temperature interval close to the second order transition (T_C =373K) in Im-ClO_4.

3. Discussion

Critical exponents are a useful tool for expressing how a system's thermodynamic properties vary around its phase transition temperature. Near the transition point, the order parameter, specific heat, susceptibility, and the other system properties may show some abrupt changes or leaps. These discontinuities or singularities can induce critical behaviors in the system, which can be described by the power laws. For this reason, the critical behavior of the polarization, susceptibility and the specific heat has been analyzed below the transition temperature of T_C =373 K in Im-ClO_4.

Firstly, we analyzed the observed polarization data [5] according to Equation (2.1) below T_C as plotted in Figure 1. We deduced the value of β = 0.58 (Table 1) in the vicinity of T_C (nearly within 2K temperature interval). When we approach closer (smaller than 2K) the β value increases slightly, which indicates that the β is close to the 0.5 as expected from the mean field value. This value does not agree with the value of β ≈ 5/16 due to the three-dimensional (d=3) Ising model. Then, the anomalous behavior of the observed susceptibility data [5] was

analyzed (Equation 2.3) below the transition temperature (T_C =373K) in Im-ClO_4 (Figure 2). We extracted the value of γ=1.10 in the vicinity of T_C (Table 1) which is close to the mean field value (γ=1) and also the Ising (d=3) value (~5/4). Our γ value did not change considerably as $T \rightarrow T_C$.

Lastly, a compressible Ising model (Equation 2.5) was used to analyze the critical behavior of the observed specific heat data [8] below the transition temperature T_C of Im-ClO_4 as shown in Figure 3 the ln (C/T) versus ln (ε) graph (Equation 2.6). In the vicinity of the T_C (nearly within the temperature interval 2K), we extracted the value of the critical exponent as α = 0.15 which is compatible with the 3d Ising model (~1/8). However, as we approach the critical temperature T_C closer than 2K, our α value tends to approach zero, which is the mean field value of α'=0 (discontinuity) (Figure 4). Also, the extracted values of the interaction parameter JA in the temperature interval (0< $T_C - T$ <12 K) increase rapidly as the temperature interval gets closer to the T_C (Figure 5).

Finally, our extracted values of 0.15, 0.58, and 1.10 for the α, β, and γ, respectively, for the Im-ClO_4 crystal (Table 1) were used to examine the applicability of the Rushbrooke inequality [11,12,18] according to

$$\alpha + 2\beta + \gamma \geq 2 \tag{3.1}$$

As easily can be evaluated the scaling law gives 2.39 within the temperature interval 2 K in the vicinity of T_C. Consequently, we conclude that the extracted values of critical exponents are in agreement with Rushbrooke's inequality for the solid-solid (second order) transition in Im-ClO_4.

4. Conclusions

The temperature dependences of the polarization (P), dielectric susceptibility (χ) and the specific heat (C) were analyzed by the power-law formulae in the vicinity of the solid-solid transition (T_C =373K) in the Imidazolium Perchlorate (Im-ClO_4) using the observed data from the literature. Our values of the critical exponents extracted from the analysis are close to those predicted from the Ising model and also the mean field theory. Rushbrooke's inequality was tested, and it was found that it is valid for the second-order solid-solid transition in Im-ClO_4.

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Declaration of Competing Interest

The author declares that there are no competing financial interests or personal relationships that influence the work in this paper.

Authorship Contribution Statement

Nazan Kara: Reviewing and editing, Methodology, Visualization
Ali Kiracı: Writing-Original draft preparation, Software, Visualization
Hamit Yurtseven: Writing-Original draft preparation, Software

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