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CRITICAL PHENOMENA AT PHASE TRANSITION TO SUPERIONIC STATE

Z.Vučić, Z.Ogorelec and A.Tonejc
Institute of Physics of the University, P.O.B.304,
41000 Zagreb, Yugoslavia

Abstract

The cuprous selenide was investigated in the wide range of concentrations from Cu_2Se to $Cu_{1.77}Se$. It is shown that the continuous change of concentration cause the transition from one characteristic type of behaviour of superionic conductor to another. The unusual behaviour of the most quantities is established implying the critical interactions between the anion and the cation subsystems and within the cation subsystem itself.

1. Introduction

Phase transitions to superionic state in various crystals have been intensively investigated in the last few years. A wide variety of effects found in experiments have suggested a clear classification of these transitions. The most recent one was given by Lam and Bunde$^{1)}$ (LB). According to them, the temperature dependence of the ionic conductivity of a superionic conductor may be classified into three categories: 1.- it does not show phase transitions at all, 2.- it shows one phase transition (1st or 2nd order), and 3.- it shows two phase transitions. In the cases 2. and 3. the change of structure of the anion sublattice may occur at the same temperature at which the conductivity becomes critical.

In contrast to many simple superionic conductors, cuprous selenide shows intricate properties which prevent to classify it into the LB categories without very careful examination. Its wide range of stoichiometric deviation distinquishes it from all other superionic conductors, in a sense that some microscopic parameters can be changed continuously. Thus, we feel that our detailed investigation of cuprous selenide in the concentration range between Cu_2Se and $Cu_{1.77}Se$ may contribute both to better understanding of its superionic properties and to a determination of the position of Cu-Se in the LB classification.

2. Equilibrium diagram

There are several publications$^{2-7)}$ concerning the equilibrium diagram of Cu-Se system in the vicinity of Cu_2 Se. In spite of these efforts, the phase diagram connot be considered as completely solved. The common idea, that the equilibrium diagram may be described in a simple way, resulted in substantial discrepancies$^{5,7)}$.

Our new equilibrium diagram (Fig.1) is deduced from the measurements of the electrical conductivity, the magnetic susceptibility, the lattice parameter, the thermal dilatation, the differential thermal analysis (DTA) and the nuclear magnetic resonance (NMR). There are several lines in this diagram which did not appear in any published one. First of all, there is a vertical line at the concetration $Cu_{1,954\pm0,002}Se$ which represents the line of first order phase transitions.
This line itself defines the region in the equilibrium diagram-called region I-which covers the concetration range from about Cu_2Se to $Cu_{1,954}Se$. The samples from the region I, when heated, undergo the first order phase transition to the superionic state at the range of critical temperatures T_c. At these temperatures most of X-Ray studies$^{2,3,5)}$ show the change of structure from probably tetragonal (low temperature) to fcc (superionic) phase.

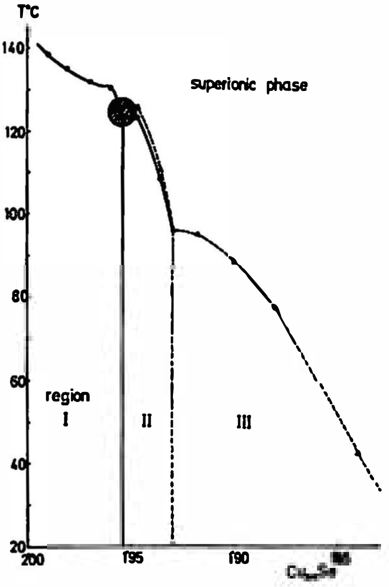

Fig.1. **Equilibrium phase diagram of cuprous** selenide. Full lines represent the first order phase transitions, while dashed lines include electronic transitions only.

According to Takahashi et al$^{7)}$ the temperature dependent ionic conductivity undergoes the second order phase transition at T_c. Therefore, in terms of LB classification, cuprous selenide in this concentration range, behaves as if it belonged to category 2.

It must be pointed out that the stoichiometric compound Cu_2Se is not included in this description because it shows substantial differences in comparison with samples from the region I. The reason for these qualitative differences is probably in the existance of another vertical line close to Cu_2Se.

The evidences which support the existance of the vertical line at the concentration $Su_{1,954\pm0,002}Se$ are shown in Figs.2. and 3.. Sorokin et al$^{8)}$ investigated the concentration dependence of density, lattice parameter and Hall constant at room temperature. These measurements are shown in Fig.2. and, as can be seen, the lattice parameter as well as the electronic carrier density suddenly increase between $Cu_{1,95}Se$ and $Cu_{1,96}Se$. Our

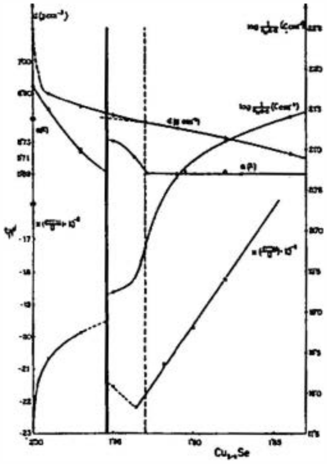

Fig.2.The density (d), the lattice parameter (a), the density of electronic carriers ($n=1/R_H.e.c$) and the magnetic susceptibility (χ) as a function of concentration at the room temperature. The vertical lines represent transitions; full line - structural transitions, dashed line - electronic transitions.

lattice parameter data confirm the existance of discontinuity of 1% arround $Cu_{1,955}$ Se. As the electronic conductivity exhibits the linear temperature dependence at temperatures well below T_c for the concentration range between Cu_2Se and $Cu_{1,930}Se$, the temperature coefficient of the conductivity and the residual conductivity are evaluated. Both, the temperature coefficient of the conductivity and the residual conductivity show the sudden decrease of about 50 percents as shown in the Fig.3..

Such the expansion of lattice parameter can not explain the increase of the electronic carrier density of the order of magnitude. Thus, the strong increase (a factor of

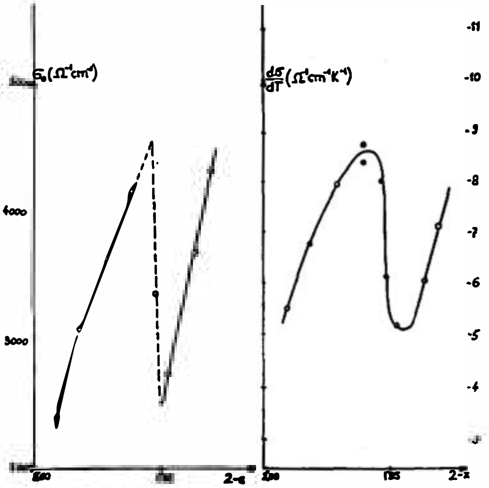

Fig.3. The temperature coefficient of the electronic conductivity ($d\sigma/dT$) and the residual conductivity (σ_0) as a function of concentration.

three) in the number of electronic carriers per cell must be emphasized. On the contrary, the residual conductivity decrease which means that the dominant change (ofthe order of magnitude) is caused by the decreasing of a relaxation time.

All these changes could be taken as being due to a structural transition. Anyhow these are the indirect evidences and for a direct proof X-ray measurements are nedeed.

In the phase diagram we found another vertical line at $Cu_{1,930}Se$. This line represents higher order phase transitions, because as seen from Fig.2., all quantities change continously at this concentration. From the electronic point of view this line could be treated as a line of transition from metal-like (right side) to semiconductor-like (left side) behaviour.

The concentration range between $Cu_{1,930}Se$ and $Cu_{1,770}Se$ called region III seems to be another homogeneous phase area. The samples from this region, in the low temperature phase, retain most features of the superionic phase. When heated, system undergoes a transition to the pure superionic phase, which seems to be of the second order in respect of electrical conductivity and magnetic susceptibility.

Lattice parameter is steeply linearly temperature dependent below Tc. At around Tc it shows a small continuous contraction while above Tc the normal linear increasing is observed. As there is no change in the ionic conductivity[5)] the continous transition is ascribed to the anion lattice contraction.

The last region (the region II) is most complicated one and seems to be the transition region between regions I and III. Upon heating the samples from this region undergo two succesive transitions. The first one is of 1st order like in the region I followed by a higher order transition like in region III. Such a behaviour is unexpected within

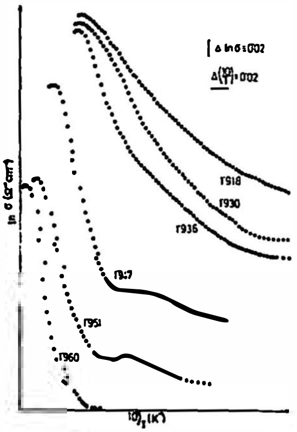

Fig.4. Logarithm of conductivity as a function of inverse temperature arround critical range of concentrations.
The relative positions of the different concentrations are arbitrary.

the LB classification. One can take the system to be a mixture of two surrounding phases with a strong mutual interaction. From Fig.4. can be clearly seen the continuous transition from one type behaviour to another. The sample $Cu_{1,960}Se$ shows the typical temperature dependence of electronic conductivity in the region I below T_c, while the sample $Cu_{1,918}Se$ is the exemplar of the region III.

It is shown that cuprous selenide is a superionic conductor with an unusual behaviour in the whole concetration range of investigation. Concerning the LB classification, cuprous selenide is a uniqe example of superionic conductor that change the category varying only its stoichiometry.

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