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Theoretical and experimental study of AC electrical conduction mechanism in the low temperature range of p-$CuIn_3Se_5$

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ABSTRACT

In the present work, an attempt has been made to study theoretically and experimentally the AC electrical conduction mechanism in disordered semiconducting materials. The key parameter considered in this analysis is the frequency exponent $s(\omega, T) = \left(\frac{\partial \ln(\sigma_{AC}(\omega,T))}{\partial \ln(\omega)}\right)_T$, where σ_{AC} is the AC electrical conductivity that depends on angular frequency ω and temperature T. In the theoretical part of this work, the effect of the barrier hopping energy, the polaron radius and the characteristic relaxation time is considered. The theoretical models of Quantum Mechanical Tunneling (QMT), Non overlapping Small Polaron Tunneling (NSPT), Overlapping Large Polaron Tunneling (OLPT) and Correlated Barrier Hopping (CBH) are considered to fit experimental data of σ_{AC} in p-$CuIn_3Se_5$ (p-CIS135) in the low temperature range up to 96 K. Some important parameters, as the polaron radius, the localization length and the barrier hopping energies, are estimated and their temperature and frequency dependence discussed.

1. Introduction

Disordered semiconducting materials have attracted much attention due to their potential industrial applications. These materials are good candidate for understanding carrier transport phenomena under an external electric field, at a given temperature. Due to the presence of intrinsic defects, impurity bands can be formed in the forbidden gap and electrical conduction by hopping mechanisms can occur at low temperatures when free carriers cannot be excited to the valence and conducting bands. The conduction of mobile charges including electron, hole and polaron hopping is of great interest. In the DC-regime (static electric field), the electrical resistivity is usually expressed as [1]

$$\rho_{DC}(T) = \rho_0(T)\exp\left(\left(\frac{T_o}{T}\right)^{\frac{1}{p}}\right) \quad (1)$$

where ρ_0 is the pre-exponential factor that can be considered constant or weakly temperature dependent. The value of the exponent p is expected to be ''1'' in the activation regime when carriers are excited from impurity to free allowed bands, and ''4'' in the case of Mott-variable range hopping (Mott-VRH) [2] for a constant and non-vanishing density of states $g(E_F)$ at the Fermi level in a three dimensional system. At very low temperatures, due to coulomb interactions, $g(E_F)$ can vanish and p will then be 2. This is the Shklovskii-Efros-VRH regime (SE-VRH) [3]. The characteristic temperature T_o is related to impurity ionization energy E_d in the activation regime at high temperatures and to the localization length ξ in the hopping regime at low temperatures.

Different methods were made to characterize the AC conductivity behaviors observed in various disordered materials including semiconductors, ionics and dielectrics. The simplest description is the power frequency dependence-law [4] given by Eq. (2).

$$\sigma_{AC}(\omega, T) = A(T)\,\omega^{s(\omega,T)} \quad (2)$$

The frequency exponent s represents the degree of interaction between mobile carriers and their surrounding lattices. Usually s is considered to be frequency independent. However, this assumption is slightly inaccurate, because this exponent can change considerably by frequency.

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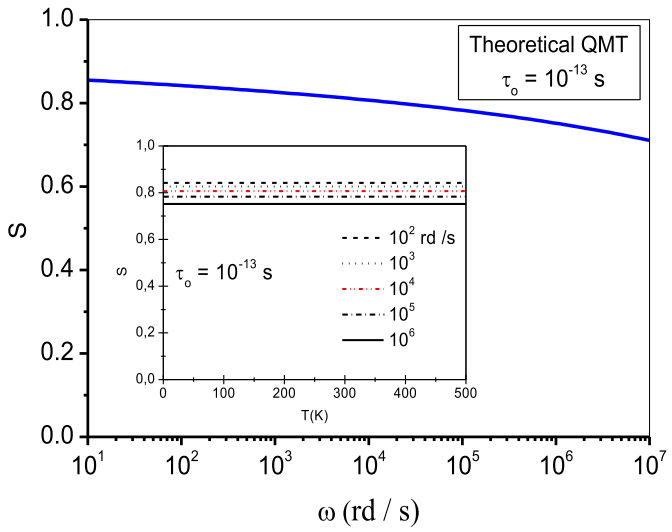

Fig. 1. Frequency and temperature dependence of the frequency exponent *s* in the QMT of electrons model.

According to Eq. (2), $s(\omega, T)$, at a given temperature T, can be expressed in terms of σ_{AC} as

$$s(\omega, T) = \left(\frac{\partial \ln(\sigma_{AC}(\omega, T))}{\partial \ln(\omega)}\right)_T \tag{3}$$

Several theoretical models have been proposed to explain the behavior of *s* on *T* and ω [5]. In particular two types of conduction mechanisms have been the subject of many theoretical and experimental works [5–9]: a) conduction due to Quantum-Mechanical Tunneling (QMT) that covers Electronic Tunneling (ET), Non-overlapping Small--Polaron Tunneling (NSPT), Overlapping Large Polaron Tunneling (OLPT) and Atomic Tunneling (AT); and b) conduction due to hopping mechanisms that covers Atomic Hopping (AH) and Correlated Barrier Hopping of electrons (holes) (CBH). To our knowledge, these models in their general form have not been reported in the literature to analyze experimental data of AC-conductivity.

Thus, the aim of this paper is, first, to present a theoretical study for each conduction mechanism namely, the QMT, the NSPT, the OLPT and the CBH models with the effect of the barrier hopping energies, the polaron radius and the characteristic relaxation time. By comparing these different behaviors of *s*(ω,T) with the experimental data of any semiconducting disordered material will help us to identify the dominant conduction mechanisms in a given ranges of temperature and frequency.

We are interested to the compound *p*-$CuIn_3Se_5$ (CIS135), an important technological material which has received considerable attention recently due to their possible use in solar cells [10]. To identify the type of conduction mechanisms that governs the electrical conductivity of CIS135 in different ranges of temperature between 96 K and 300 K and frequency between 20 Hz and 1 MHz, a detailed analysis of the data based on impedance spectroscopy measurements is considered. The variation of the frequency exponent *s* as a function of frequency and temperature is also analyzed and compared with the existing theoretical models of QMT, CBH, OLPT and NSPT.

2. Experimental details

The ternary semiconductive material $CuIn_3Se_5$ was grown by vertical Bridgman technique [10]. The chemical composition was obtained by energy dispersive X-ray diffraction analysis. This gave Cu (9.47): In (29.24): Se (61.28) in atomic percentage, very close to 1:3:5 stoichiometry, with slight excess of Se. From the analysis of the XRD pattern, it is confirmed that $CuIn_3Se_5$ crystallize in a tetragonal unit cell corresponding to a chalcopyrite related structure with space group $P\bar{4}2c$. Unit cell constants were calculated to be a = 5.7541(5) and c = 11.538(3) Å [11]. The p-type conductivity was obtained through thermal probe analysis. The electrical measurements were performed using two electrodes which are deposited at the end parts of the sample. Representative dimension of polycrystalline samples in the form of parallelepiped were approximately $5 \times 1 \times 1$ mm^3. Electrical impedances were measured for frequency ranging from 20 Hz to 1 MHz, by using impedance spectrometer HP4284A in a compatible interface with computer controller. The temperature variation in the range of [96 K—300 K] was achieved using a liquid nitrogen cryostat.

3. Theoretical models

In this section we present a detailed analysis of the temperature and frequency dependence of the exponent *s* for each theoretical model QMT, NSPT, OLPT and CBH. Some important parameters involved in these models like polaron radius, barrier energies for tunneling and hopping process are introduced. In these calculations the temperature varies between 80 and 400 K while the frequency between 100 Hz and 1 MHz. Based on this, the experimental data will be presented and discussed in section 4.

In the QMT of electrons process, where some overlap of the wave function of the localized state exists, electrons tunnel through the potential barrier that separates two localized states. Electronic relaxation is treated as the origin of the dielectric loss. In this model, the characteristic tunneling distance R_ω, the AC conductivity σ_{AC} and the exponent *s* calculated from σ_{AC} according to Eq. (3) at a given temperatures *T* are given as [5,6]

$$R_\omega(\omega, T) = \frac{1}{2\alpha}\ln\left(\frac{1}{\omega\tau_0}\right) \tag{4a}$$

$$\sigma_{AC}(\omega, T) = \frac{\pi^2}{12}\frac{e^2 k_B T}{\alpha}(g(E_F))^2\, \omega\, R_\omega^4 \tag{4b}$$

$$s(\omega, T) = 1 - \frac{4}{\ln\left(\frac{1}{\omega\tau_0}\right)} \tag{4c}$$

where α is the inverse of the localization length, $g(E_F)$ is the density of states at the Fermi level and τ_0 a constant characteristic relaxation time. A typical value of τ_0 is given by the atomic vibrational period ($\tau_0 = 10^{-13}$ s) [12].

As we can see from Eqs. (4a) and (4c), respectively, R_ω and *s* are predicted to be temperature independent but frequency dependent. In the frequency range from 20 Hz to 1 MHz, *s* is expected to be less than unity and decrease slightly with frequency. This is shown in Fig. 1 where *s* is plotted against ω and *T*.

A temperature dependent exponent *s* can be obtained within the QMT model by assuming that the charges carriers arise from NSPT process. A small polaron may be formed if the addition of a charge carrier to a site causes a large local distortion so that the total energy of the system (electron, distortion) is reduced by W_h; the polaron hopping energy. These small polarons are assumed to be highly localized and their distortion clouds do not overlap. In this model, σ_{AC} is given again by Eq. (4b) but the tunneling distance R_ω is changed to be [5,6]

$$R_\omega(\omega, T) = \frac{1}{2\alpha}\left(\ln\left(\frac{1}{\omega\tau_0}\right) - \frac{W_h}{k_B T}\right) \tag{5a}$$

with the corresponding change in *s*

$$s(\omega, T) = 1 - \frac{4}{\ln\left(\frac{1}{\omega\tau_0}\right) - \frac{W_h}{k_B T}} \tag{5b}$$