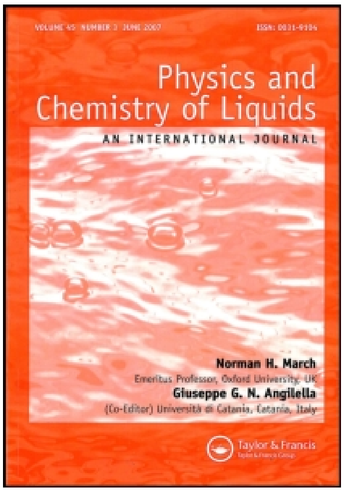

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DIELECTRIC RELAXATION AND A.C. CONDUCTION OF $CuSbSe_2$ SEMICONDUCTOR IN THE SOLID AND LIQUID STATES

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Measurements of the dielectric properties of $CuSbSe_2$ in the solid and liquid states were carried out in a wide range of frequencies and temperatures. The material displays dielectric dispersion and a loss peak was observed. Cole–Cole diagrams have been used to determine the distribution parameter (α) and the molecular relaxation time (τ). The process of dielectric relaxation (loss) and ac conduction was attributed to the correlated barrier hopping model suggested by Elliott for amorphous solids where two carriers simultaneously hop over a barrier between charge defect D^+ and D^- states.

KEY WORDS: Cole–Cole plot, relaxation time.

INTRODUCTION

A lot of theoretical and experimental efforts have been devoted to understand the electronic relaxation phenomena in amorphous and liquid semiconductors. Various models[1–4] have been proposed to explain the conductivity behaviour, and it has been demonstrated that some semiconductors retain their predominantly covalent semiconductor properties in the amorphous and liquid states, whereas other semiconductors acquire metallic properties above the melting point.

Measurements of the frequency and temperature dependence of the dielectric properties of amorphous and liquid semiconductor allow to obtain critical information concerning the electronic structure as well as the conduction and relaxation mechanisms.

The ternary semiconductor $CuSbSe_2$ possesses the chalcopyrite structure[5,6] whose unit cell apparently consists of a zineblende cell doubled in height, its melting point is 452°C.

The aim of the present work is to investigate the dielectric properties of $CuSbSe_2$ in the liquid and solid phases in a wide range of temperatures and frequencies with the object of seeing if any of the existing theories could consistently explain the dielectric data obtained and to clarify the mechanisms of dielectric relaxation.

EXPERIMENTAL

The samples were prepared by melting the proper amounts of highly pure component elements (99.999%). The material was sealed in a quartz tube at 10^{-3} Pa and heated at 1200°C for 12 hrs with frequent rocking to ensure homogenization of the melt. Then the tubes were quenched in ice to obtain the sample in amorphous state. The solid material is then heated in inert atmosphere until it melts and then transferred to the measuring cell.

A cylindrical measuring cell was used which consists of two concentric graphite cylinders. The cell contains a temperature controlled heater, a chromel-alumel thermocouple for accurate measurements of temperature and was fitted with a guard ring electrode.[7]

Measurements of the dielectric constants were carried out in an inert atmosphere at different frequencies and temperatures using a well shielded ac Schering bridge connected with a Farnell ESG2 oscillator, and a sensitive broad band oscilloscope type Trio CS-1560A was used as a null indicator.

THEORY OF MEASUREMENTS AND EXPERIMENTAL RESULTS

Figures 1 and 2 show the frequency dependence of the real part of the dielectric constant (ε') and the dielectric loss ($\tan\delta$) at different temperatures. All curves displayed a dielectric dispersion peak and the frequency at the peak maximum shifts towards higher frequencies on increasing temperature. Moreover, the height of the loss peak $(\tan\delta)_{\max}$ increases with temperature.

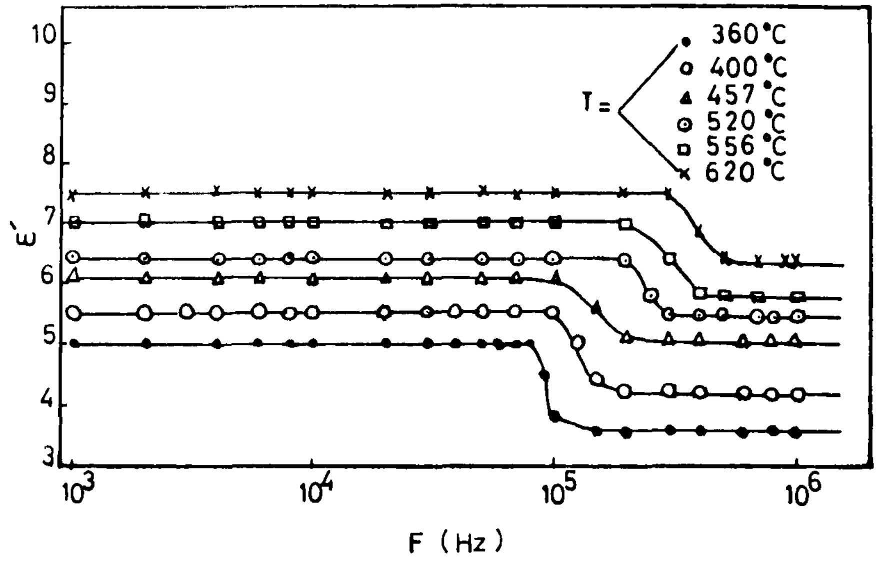

Figure 1 The frequency dependence of the real part of the dielectric constant ε' at different temperatures.

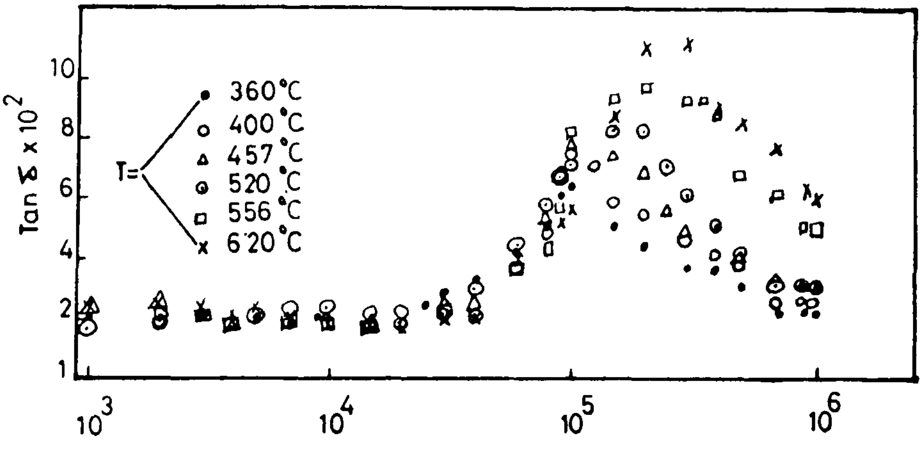

Figure 2 The frequency dependence of the loss angle δ at different temperatures.

Distribution Parameter and Relaxation Time

Cole and Cole[8] showed that if a dielectric system has a distribution of relaxation times, then the complex plane locus, obtained by plotting ε'' versus ε', is generally an arc of a circle intersecting the abscissa axis at the values ε_∞ and ε_s and having its center lying below the abscissa axis where ε_s and ε_∞ are the static and optical dielectric

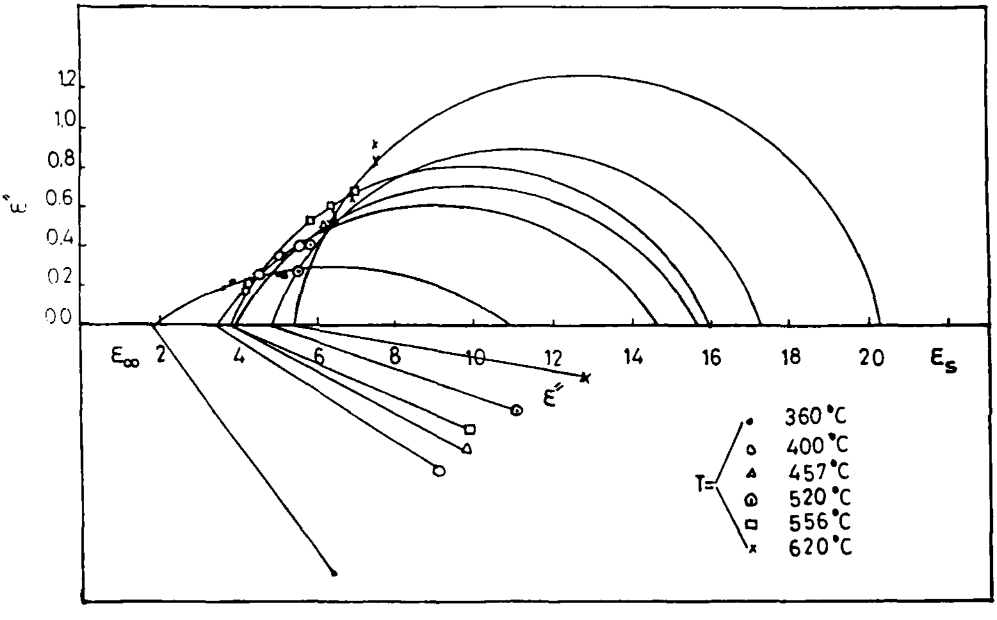

Figure 3 The Cole-Cole plots at 360, 400, 457, 556, 520 and 620°C.

Table 1

Temperature °C	ε_s	ε_∞	α	*Macroscopic relaxation time,* τ_0(s) *Eq. (1)*	*Molecular relaxation time* $\tau(s)$		*Free energy of activation (kJ/mol)* ΔF
					Cole-Cole Eq. (2)	$\tau = 1/\omega_m$	
360	10.9	1.8	0.6	1.1×10^{-5}	0.81×10^{-5}	1.6×10^{-6}	97.3
400	14.5	3.4	0.366	9.5×10^{-6}	7.1×10^{-6}	1.4×10^{-6}	103.0
457	15.6	3.8	0.322	7.4×10^{-6}	5.5×10^{-6}	1.3×10^{-6}	110.8
520	17.3	4.8	0.2226	4.4×10^{-6}	3.3×10^{-6}	9.1×10^{-7}	117.5
556	...	3.7	0.226	2.13×10^{-6}	1.5×10^{-6}	8.0×10^{-7}	117.8
620	20.1	5.4	0.1222	1.8×10^{-6}	1.33×10^{-6}	5.3×10^{-7}	126.2

constants. The diameter drawn through the centre from ε_∞ makes an angle $\alpha\pi/2$ with the ε axis, $\tan(\alpha\pi/2)$ being determined from the plots and α is calculated. Knowing α, one can determine the macroscopic relaxation time τ_0 by using the relation[8]

$$\frac{V}{U} = (\omega\tau_0)^{1-\alpha} \tag{1}$$

where V is the distance on the Cole-Cole diagram between ε_s and the experimental point, U is the distance between that point and ε_∞, and ω is the angular frequency. The parameter α is equal to zero when the dielectric has only one relaxation time and the larger α is, the larger is the extent of the distribution of the relaxation times $(0 < \alpha < 1)$. The molecular relaxation time (τ) can be estimated from (τ_0) using[9]:

$$\tau = \tau_0(2\varepsilon_s + \varepsilon_\infty)(3\varepsilon_s)^{-1} \tag{2}$$

Cole-Cole diagrams for different temperatures are shown in Figure 3 and the calculated values of ε_s, ε_∞, α, τ_0 and τ are indicated in Table 1. The data show that the molecular relaxation time decreases with temperature, while the static dielectric constant increases.

ACTIVATION ENERGY (ΔF) FOR DIPOLE RELAXATION

Eyring[10,11,12] had shown that the molecular relaxation time in the chemical rate theory is given by:

$$\tau = (h/kT)\exp(\Delta F/RT) \tag{3}$$

where ΔF is the free energy of activation for dipole relaxation, k is Boltzmann's constant, and h is Planck's constant. Therefore the free energy of activation can be calculated from:

$$\Delta F(\text{k.J/mole}) = 2.303RT\log(\tau\ \text{T.k/h}) \tag{4}$$

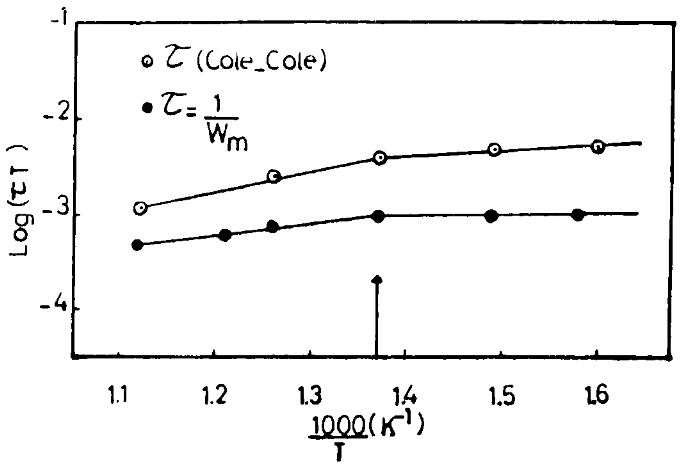

Figure 4 Temperature dependence of the molecular relaxation time for the high frequency dispersion peak.

The calculated values of ΔF at different temperatures are shown in Table 1. Since the free energy of activation (ΔF) is related to the enthalpy of activation (ΔH) and the entropy of activation (ΔS) by:

$$\Delta F = \Delta H - T\Delta S, \tag{5}$$

then from (3) and (5) one obtains:

$$2.303 \log(\tau \text{ T.k/h}) = (\Delta H/RT) - \Delta S/R \tag{6}$$

which indicates that the plot of $\log(\tau T)$ versus $1/T$ should give approximately a linear relation.

Figure 4 shows the plots of $\log(\tau T)$ vs. $1/T$ for the loss peak, the plots are linear. However in the liquid state $\log(\tau T)$ decreases with temperature faster than in the solid state and a change of slope occurs near the melting point.

DISCUSSION

Figures 1 and 2 show that ε' and $\tan \delta$ increase with temperature. The rate of increase being different at different frequencies. This behaviour can be explained by assuming that the system exists in the form of molecular dipoles. As the temperature increases the dipoles slowly get activated, since the relative influence of the molecular interaction energy decreases with respect to that of the thermal energy.

According to the Debye-theory for the intrinsic relaxation time, the curves $\tan \delta$ versus ω must be symmetrical. Figure 2 does reveal that the curves are nearly symmetrical around ω_m where the frequency ω_m corresponds to the maximum absorption:

$$\omega_m = 1/\tau \tag{7}$$

where τ represents the most probable value of a spread of relaxation times. The values of τ calculated from (7) are inserted in Table 1. From Table 1 it is clear that there is a close proximity in the values of τ determined from the Cole-Cole diagrams and those obtained by using (7) which is to be expected because both methods provide an average or most probable value of τ. Moreover, τ decreases with temperature and the rate of decrease is faster in the liquid state than in the solid state, which may be attributed to the effect of thermal energy, since it tends to weaken the forces of intermolecular interaction.

According to Eyring's (3) and Debye's concept[13] of the viscosity dependence of the relaxation time, τ decreases exponentially with increasing temperature which implies that ε' should increase exponentially with temperature.

This is confirmed by plotting log ε' versus $1/T$ which have been found to be linear for all frequencies as shown in Figure 5.

In general, dielectric relaxation follows the Cole-Cole equation[8-14]:

$$\varepsilon^* = \varepsilon_\infty + \Delta\varepsilon'/[1 + (j\omega\tau_0)^{1-\alpha}] \tag{8}$$

where $\Delta\varepsilon'$ is the magnitude of the dielectric dispersion. Moreover, the height of the loss peaks should represent the density of the corresoponding dipoles:

$$(\tan\delta)_{\max}\alpha N\mu^2/\varepsilon\varepsilon_0\, kT$$

The magnitude of the dielectric dispersion $\Delta\varepsilon'$ is proportional to the number of dipoles per unit volume. Therefore the observed increase in the height of the loss peak and the magnitude of dielectric dispersion with temperature suggests an increase in the density of the dipoles.

The measured dielectric loss data can be adequately interpreted in terms of the correlated barrier hopping model developed by Elliott[17] for ac conductivity and

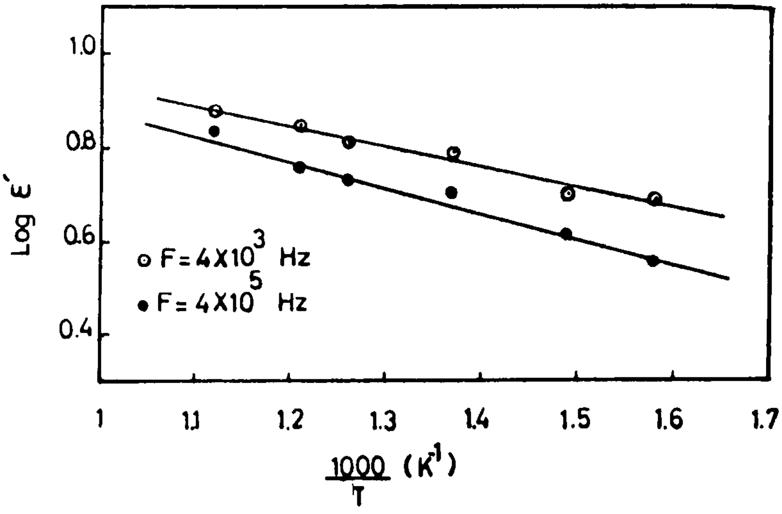

Figure 5 The temperature dependence of the log ε' at different frequencies.

dielectric loss in amorphous semiconductors. This model is based on the charged defect concept suggested by Mott *et al.*[15,16] in which dangling bonds can exist in paired states ($D^+ + D^-$) and are responsible for the density of states in the gap pinning the Fermi level. Elliott's theory[17] considers hopping of carriers between two sites over a barrier separating them, and the distribution of relaxation times for this process arises from the exponential dependence of the relaxation time on the barrier height. The hopping species were considered to be the doubly-occupied bipolaron state,[16,18] and the defect states were assumed to be sufficiently close (intimate valence alternation pairs[18]) that appreciable interaction occurs, thereby giving rise to a distribution of barrier heights separating them. Carriers ejected from a D^- site into one of the excited levels and then drop into D^+ centre, converting it to a D^- (or the opposite process). The theory predicts a dielectric loss peak when $\omega\tau_{\max} \cong 1$ and the ac conductivity is given by[17]:

$$\sigma(\omega) = \frac{\pi^2 N^2 \varepsilon'}{24}\left[\frac{8e^2}{\varepsilon' W_M}\right]^6 \frac{\omega^s}{\tau_0^\beta} \tag{9}$$

where W_M is the energy required to take two carriers from the D^- state to the continuum (the conduction band) in the absence of a nearby D^+ centre, τ_0 is the effective relaxation time, N is the concentration of the localized sites, ε' is the bulk dielectric constant, $\beta = 6kT/W_M$ and $s = 1 - \beta$.

According to the theory the ac conductivity has a slightly sublinear frequency dependence and W_M is given by:

$$W_M = B - W_1 + W_2 \tag{10}$$

where B is the band gap of the material and W_1 and W_2 are approximately the distortion energies associated with the neutral D_0 and D^+ states respectively. Following Elliott's assumption[17] that $W_1 = W_2$ as a first approximation, then $W_M = B$ ($B = 0.4$ eV for. $CuSbSe_2$ measured from the slope of the temperature dependence of the dc electrical conductivity).

Equation (9) can be used to calculate the density of defects N at different temperatures using the experimental values of ε', ω, T, τ_0 and $\sigma(\omega)$, where the ac

Table 2 Representative data for the density of defects

Temperature (°C)	*N calc (m^{-3})*
360	7.4×10^{20}
400	1.5×10^{21}
457	1.7×10^{21}
520	2.5×10^{21}
556	2.5×10^{21}
620	3.2×10^{21}

conductivity was calculated directly from the experimental data using[19]:

$$\sigma_{ac}(\omega) = \left(\frac{\omega C \tan\delta}{1 + (\tan\delta)^2}\right)\frac{L}{A}(1 - 2D_0 \tan\delta),$$

where C is the sample capacitance, L/A is the geometric factor, D_0 is a correction factor.[19]

Table 2 gives representative data for the estimated values of N calculated at different temperatures and at the loss peak $(\tan\delta)_{max}$. For Table 2 it is clear that the density of defects N increases with the temperature.

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