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CONTRIBUTION OF SINGLE POLARON HOPPING TO AC CONDUCTION IN AMORPHOUS CHALCOGENIDES

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Abstract - Although it is now fairly well established that defects in amorphous chalcogenide semiconductors are normally charged (D⁺ and D⁻), it is proposed that neutral defects D⁰ (generated by the reverse reaction of 2D⁰ + D⁺ + D⁻) can be important for a.c. conductivity. It is shown that the contribution to σ(ω,T) from correlated barrier hopping of single polarons exceeds that of bipolarons at high temperatures (T) and/or low frequencies (ω). An expression for σ(ω,T), which includes terms due to electrons hopping between D⁰ and D⁺ and holes between D⁰ and D⁻, as well as two electrons hopping between D⁻ and D⁺ (bipolarons), is able to account for all the features observed in many materials. The energy levels and densities of the defect states for Se, two Se-Te alloys, As₂Te₃ and As₂Se₃ are deduced from a comparison of the theory with experimental data.

Introduction - Correlated barrier hopping (CBH) of bipolarons (i.e. two electrons hopping between charged defects D⁺ and D⁻) has been proposed by Elliott (1) to interpret the frequency dependence of a.c. conductivity in amorphous chalcogenides (σ_ac = nω). The theory has explained many features at relatively low temperatures. However, it does not predict the strong temperature dependence of σ_ac which has been observed at higher temperatures in some materials.

It is proposed that an increasing density of neutral defects D⁰ at higher temperatures is important and that CBH of single polarons (holes hopping between D⁰ and D⁻ and electrons between D⁰ and D⁺) is then the dominant contribution to a.c. conduction in amorphous chalcogenides.

Expression for the a.c. conductivity due to CBH of bipolarons and single polarons - The expression for the real part of σ_ac derived for CBH with a random distribution of centre is written as (1)

\[ \sigma_{ac} = \frac{n^2 N_p \kappa \omega}{\beta} \cdot R_\omega^6, \]

where N is the total density of levels participating, N_p the number of carriers, \( \kappa \) the bulk dielectric constant, and \( \omega \) the angular frequency. \( R_\omega \), the distance of pairs for which \( \omega \tau = 1 \), is given by

\[ R_\omega^6 = \left\{ \frac{4n_0^2 \kappa \omega}{(\kappa \omega M_0)^{\beta}} \cdot \frac{\omega}{(\omega \tau_0)} \cdot \exp \left[ \frac{3}{2} \ln \left( \frac{1}{\omega \tau_0} \right) \right] \right\} \]

\[ \beta = \frac{6kT}{\kappa M_0}, \]

* Interestingly Elliott assumed that single polarons were present in as-deposited evaporated films giving rise to dielectric-loss peaks; however he did not take the expected temperature-dependent concentration of D⁰ defects explicitly into account when interpreting a.c. data.
where e is the electronic charge, $W_M$ the maximum barrier height, $\tau_0$ the characteristic relaxation time ($5 \times 10^{-12}$ s in the present study), and $n = 2$ for bipolarons and $n = 1$ for single polarons.

For bipolarons (process I), $N_{Np}$ in eq. (1) can be written as $N \cdot N/2 = N^2/2$ by assuming $N_- = N_+$ (we denote by $N_-$ and $N_+$ as spatial densities of $D^-$ and $D^+$ centres, respectively), and $W_M$ is defined by $B - W_1 + W_2$ as shown in Fig.1(a). For single polarons, $N_0$, the density of $D^0$, can be determined by the law of mass action (see Fig.1(b)) as

$$[D^+] + [D^-] \xrightarrow{U_{\text{eff}}} 2[D^0].$$

We thus obtain $N_0$ as

$$N_0 = 2 \frac{[D^0]}{N} = N \exp \left( -\frac{U_{\text{eff}}}{2kT} \right).$$

We assume here that half of the $D^0$s created by the reaction (eq.(3)) contribute to relaxation between $D^0$ and $D^-$ (holes: process II) and the other half to relaxation between $D^0$ and $D^+$ (electrons: process III). The situation is shown schematically in Fig.2. $NN_p$ in eq.(1) for single polarons is obtained as

$$NN_p = N_- \cdot \frac{N_0}{2} = \frac{N^2}{4} \exp(-U_{\text{eff}}/2kT), \quad \text{(process II)}$$

$$= N_+ \cdot \frac{N_0}{2} = \frac{N^2}{4} \exp(-U_{\text{eff}}/2kT), \quad \text{(process III)}$$

$W_M$ is equal to $W_1$ for process II and to $W_2$ for process III as shown in Fig.1(a). The a.c. conductivity can then be represented as

$$\text{Fig. 2: Three hopping processes contribute to the a.c. conduction.}$$
\[ \sigma_{ac} = \sigma_b + \sigma_{sh} + \sigma_{se}, \]  

(6)

where \( \sigma_b \) is the bipolaron contribution (process I), and \( \sigma_{sh} \) and \( \sigma_{se} \) are the single polaron contributions of processes II and III, respectively. The last two terms in eq.(6) produce a large temperature dependence of the a.c. conductivity due to both a small value of \( \beta \) than that for the bipolaron process and also an increasing number of thermally activated pairs.

Application of the model to experimental data - Fitting eq.(6) to experimental data produces the values for the band gap \( B \), the energy of the bound state \( W_1 \) and \( W_2 \), the bulk dielectric constant \( \kappa \), and the total spatial density of charged defects \( N \). All these are tabulated in Table I.

![Fig.3: Temperature dependence of \( \sigma_{ac} \) in glassy Se (data from Lakatos and Abkowitz (2)).](image)

![Fig.4: Temperature dependence of \( \sigma_{ac} \) in glassy Se\(_{90}\)Te\(_{10}\) (data from Mehra et al. (3)).](image)

![Fig.5: Temperature dependence of \( \sigma_{ac} \) in As\(_2\)Te\(_3\) film (data from Rockstad (4)).](image)
The total conductivity \( \sigma_T = \sigma_{ac} + \sigma_{dc} \) of both the experimental data and calculations (solid curves) are shown in Figs. 3 glassy Se (2), 4 glassy Se_{90}Te_{10} (3), and 5 As_{2}Te_{3} films (4). Quantitative agreement with experiment is fairly good. The dashed and dash-dotted curves, S and B, are contributions from single polarons (the last two terms in eq.(6)) and for bipolarons, respectively. A departure from "bipolaron-like" behaviour at higher temperatures and/or low frequencies which so far has been regarded as quantum-mechanical tunnelling at the band edge (1), (4)-(6), can equally well be accounted for by "single polaron" hopping.

The \( \sigma_{ac}(= \sigma_T - \sigma_{dc}) \) in As_{2}Te_{3} films falls below \( \sigma_{dc} \) at higher temperatures as shown in Fig.5 (dash-two dotted curve; S + B), indicating that \( \sigma_{ac} \) due to single polarons is smaller than \( \sigma_{dc} \). Similar results have been observed in many materials (5), (6). The strong temperature dependence has not been observed in glassy As_{2}Se_{3} (7), suggesting that the contribution of single polarons may be entirely dominated by \( \sigma_{dc} \) in this material.

A large temperature dependence of \( \sigma_{ac} \) can only be observed in materials which have a small negative-\( U_{eff} \) and/or a large energy difference between extended states and the Fermi level.

The physical parameters tabulated in Table 1 estimated from the present model are plausible, and can be supported by values from the Stokes shift of the photoluminescence, drift mobility and d.c. conductivity studies, although the total spatial densities are larger than that from other estimates (8). The values of \( W_1 \) (0.28 eV) and \( W_2 \) (0.33 eV) in Se estimated from drift mobility (9) are smaller than those of the present study. The large Stokes shift of the photoluminescence in Se (10), however, cannot be explained by a small \( W_1 \) and \( W_2 \). The shallow traps estimated from drift mobility in Se thus cannot originate from randomly distributed charged defects.

<table>
<thead>
<tr>
<th>( B(eV) )</th>
<th>( W_1(eV) )</th>
<th>( W_2(eV) )</th>
<th>( U_{eff}(eV) )</th>
<th>( E_p(eV) )</th>
<th>( \kappa )</th>
<th>( N(cm^{-3}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>2.10</td>
<td>0.70</td>
<td>1.10</td>
<td>0.30</td>
<td>0.85</td>
<td>6.0</td>
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<tr>
<td>Se_{90}Te_{10}</td>
<td>1.90</td>
<td>0.61</td>
<td>0.93</td>
<td>0.36</td>
<td>0.79</td>
<td>7.0</td>
</tr>
<tr>
<td>As_{2}Te_{3}</td>
<td>0.95</td>
<td>0.30</td>
<td>0.33</td>
<td>0.32</td>
<td>0.46</td>
<td>10.0</td>
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<tr>
<td>As_{2}Se_{3}</td>
<td>1.80</td>
<td>0.55</td>
<td>0.75</td>
<td>-0.50</td>
<td>0.80</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Conclusions - It has been demonstrated that the combined mechanism of bipolaron and single polaron hopping satisfactorily accounts for all the features observed experimentally in amorphous chalcogenides. The energy levels and densities of charged defects were estimated from the present model for given materials.

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