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ELECTRONS AT THE GLASS TRANSITION

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Abstract: The problem of the freezing-in of localized electrons in structural defects is approached for liquid chalcogenides. The concentration of dangling bonds and the corresponding recombination time are calculated at the glass-transition.

1. Introduction

An interesting aspect of glassy chalcogenides is the high concentration of dangling bonds "frozen-in" at the glass transition. According to different experimental and theoretical arguments, the estimated values range between $10^{17} \div 10^{19}$ cm^{-3}. Such a high concentration of defects, at glass transition temperatures of hundred kelvins, indicates that the recombination rate of dangling bonds decreses very much with temperature, while the concentration remains relatively large. This contrasts with any **classical** picture for the mechanism of activation-recombination of dangling bonds. Indeed Kastner and Fritzsche /1/ have suggested the following **quantum** picture, for the formation of dangling bonds in chalcogenides. A normally bonded chalcogen, with two lone-pair electrons, looses one and puts the other in a covalent bond. So it becomes 3-fold covalently coordinated and positively charged (D^+). The electron lost by the D^+ is captured simultaneously by another chalcogen, that becomes singly coordinated with 4 lone-pairs electrons (D^-). The D^- gains further energy from the lattice distortion and becomes a **double polaron**, as suggested by Anderson /2/. It is argued that the minimum energy of formation E_m is given by the gap width (2 eV) minus the polaron energy (0.5 eV). So we may estimate, say in Selenium, a minimum activation energy of about 1.5 eV. This picture clearly shows that:

(a) D^+-D^- defects are created in pairs and are **not** point-defects. Yet, they have a very complicated structure, corresponding to a large **local** entropy.

(b) Since the recombination involves a transition from covalent to lone-pair electrons, it seems likely that **quantum tunneling** is the leading mechanism, as suggested by Mott and Street /3/.

2. Calculation of the Free Energy of Dangling Bonds

We have tried to include the points (a) and (b) in a self-consistent calculation of the free energy of dangling bonds in chalcogenides. We calculate the recombination rate as given by a phonon assisted tunneling of electrons between D^- and D^+. This yields the following expression

(1) $$\omega_{rec} = \omega(T)\exp(-\gamma L) \quad (\omega(T) \propto T \text{ at high temperatures})$$

where L is the average distance between D^+ and D^-. If M is the total pair-concentration, we write:

(2) $$L \cong M^{-1/3} \quad .$$

Depending on their local configurations, the dangling bonds will have an energy ε, in addition to the minimum activation energy E_m. According to Bacalis et al /4/, we can show that $\varepsilon = \alpha_{\pm}E$, where E is the binding energy of a localized elctronic state, measured from the mobility edge of the valence band (-) and conduction band (+). $\alpha_{\pm}$ are two dimensionless phenomenological parameters of order unit. So we introduce two **unknown** energy distributions $G_{\pm}(E)$ corresponding to **doubly occupied** states (the double polarons in D^-) and to **empty** states (the hole in D^+) respectively. The internal energy per unit volume of the dangling bonds becomes:

(3) $$U = E_m M + \Sigma_\sigma \alpha_{\pm} \int dE\, G_\sigma(E)E \qquad \text{with } \sigma = \pm$$

We stress that

(4) $$\int G_\sigma(E)dE = M \quad \text{(the total pair concentration)}$$

because D^+ and D^- are created and destroyed in pairs. In the calculation of U we have neglected the Coulomb interaction because, in thermal equilibrium, negative and positive effects tend to compensate reciprocally, to first order. For the calculation of the entropy, we adopt an argument /5/, originally proposed for strongly correlated defects in liquids. In the glass, the energy levels in $G_{\pm}$ are stationary, i.e. the intrinsic line-width $\Delta E = \omega_{rec}\hbar$ is very small and does not overlap with other levels. But in the melt we expect ΔE to increase very much, and to overlap with many neighbouring levels.The concentration $G_{\pm}(E)\Delta E$ of dangling bonds whose energy falls in ΔE become **indistinguishable** if we assume, as reasonable, a one-to-one correspondence between energy and local configurations. If we now distribute the defects on the N sites of the lattice, according to the preceding definition of distinguishability, we get an entropy expression which depends **explicitly** on ΔE:

(5) $$S = -K\Sigma_\sigma \int G_\sigma(E)[\ln(\Delta E/N) - 1 + \ln G_\sigma(E)]dE \quad ; \quad \sigma = \pm .$$

According to our model, ΔE is proportional to the recombination rate, that depends exponentially on the average distance L between D^+ and D^- (eqn (1)). L is, in turn, a function of the concentration M of pairs (eqn(2)) i.e. of $G_\pm(E)$ (eqn (4)). The Helmholtz free energy

$$\Phi = U - TS = \Phi[G_\pm(E)] \ ,$$

calculated by means of (5) and (3), becomes a complicated functional of the **unknown** distributions $G_\pm(E)$, containing the recombination rate of dangling bonds in a self-consistent way.

3. Results and Comparison with Experimental Data

We have minimized Φ with a standard variational method and have obtained the following **analytical** results:

(I) The distributions $G_\pm(E)$ are **exponential**:

$$G_\pm(E) \propto \exp(-E/\alpha_\pm KT).$$

(II) The total concentration of dangling bonds follows a **power law** in T:

$$M \propto T^\alpha$$

where α varies smoothly with T and tends to the value 3 (or n, in n-dimensions) at low temperatures.

(III) The time of recombination $\tau_{rec} = 1/\omega_{rec}$ follows an **Arrhenius law**:

$$\tau_{rec} \propto \exp(3E_m/4KT) \ .$$

The result (I) is quite consistent with the photoadsorbtion measurements /4/, indicating the existence of exponential tails of localized states at the top of the valence band and at the bottom of the conduction band. These tails are usually called "Urbach tails". In chalcogenides, it is actually shown that the slope is inversely proportional to the temperature T, down to values close to T_g, at which the tails "freeze-in". The results (II) and (III) show the reason why a large concentration of dangling bonds can be frozen-in the glass: the time of recombination

increases with decreasing of T according to an **Arrhenius law**, but in the meanwhile, the defect-pair concentration M decreases in a much **smoother** way ($M \propto T^{\alpha}$).

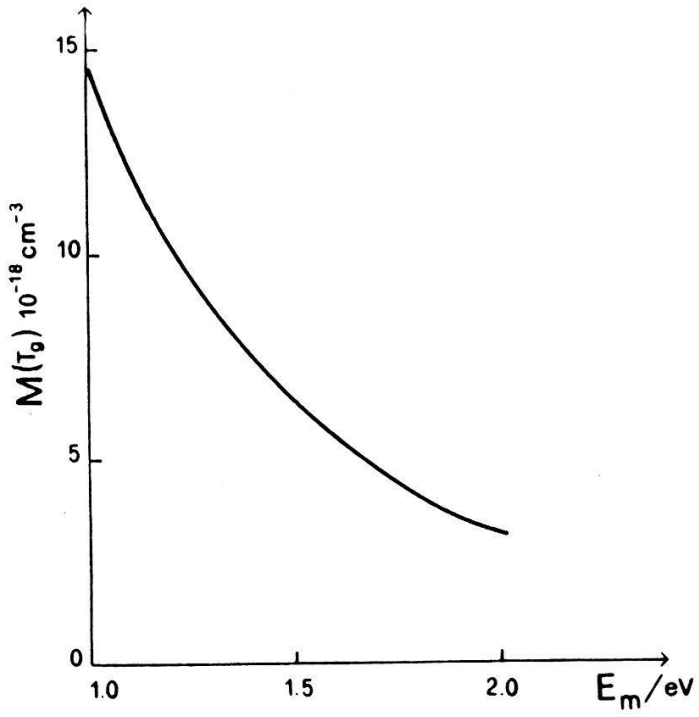

Fig. 1: The concentration M of dangling bonds is plotted for Se at T_g, as a function of the minimum formation energy E_m.

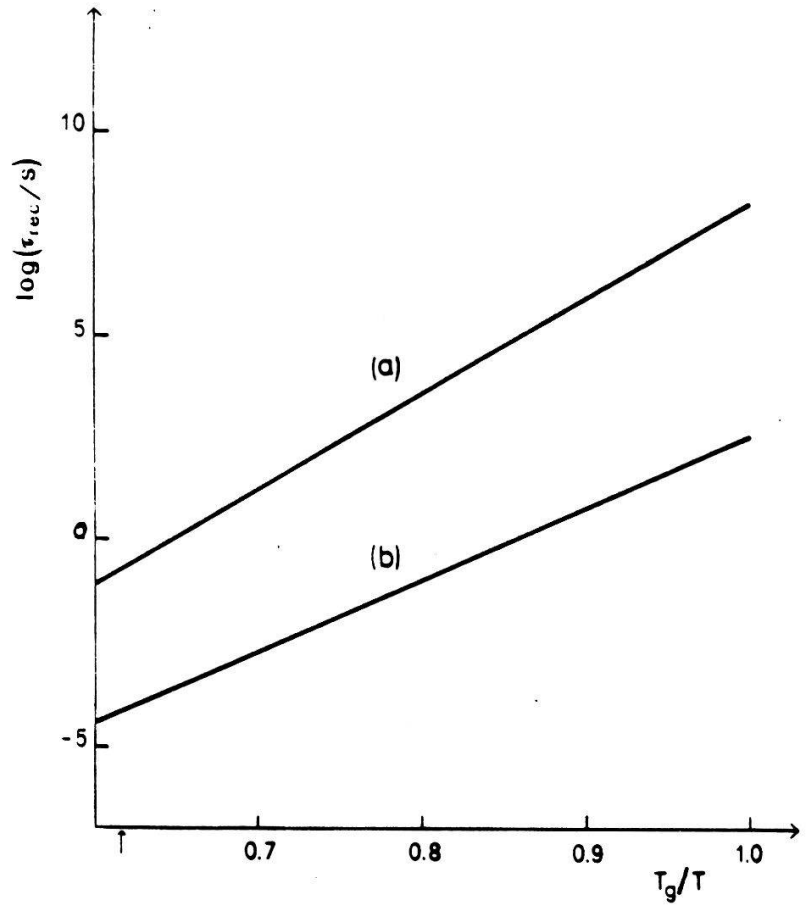

Fig.2: Arrhenius plot of the recombination time of dangling bonds in the undercooled melt of Se for E_m = 2eV (a) and for E_m = 1.5 eV (b).

In the case of Selenium, all the phenomenological parameters can be reasonably estimated and a quantitative calculation can be performed. The results are reported in Figs 1 and 2. In particular, by setting E_m = 1.5 eV, we calculate M ≅ $6x10^{18}$ cm^{-3} and find recombination times of order **hours** at T_g, showing that the dangling bonds are actually frozen-in with the expected **large** concentration.

4. Conclusions

In conclusion, the present results show that **quantum** effects are very important, even in a high-temperature process like the glass transition, as soon as one takes the **electronic** features of the process into account. This has been done, in the present case, for structural defects, like dangling bonds, but the hope is to extend the method to the basic understanding of **all** kinetic processes occurring at the glass transition. A further relevant point is the difference between the present approach to the **electronic** localization in glasses and Anderson localization. We find that the localized electronic states are **non stationary** solutions of the liquid hamiltonian, with **divergingly large** times of recombination. In contrast, Anderson localization refers to **stationary** solutions in a disordered solid. According to Jäckle /6/, this should mark a basic difference in the **residual entropy**. The present approach (glass = frozen-in liquid) implies that the localized electrons **do** contribute to the residual entropy of glasses. Anderson localization (glass = disordered solid) would imply that localized electrons **do not**.

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