

A simple model for the estimation of charge accumulation in amorphous selenium

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ABSTRACT

Based on bond angle an elementary atomic triad model is proposed for the estimation of atomic charge accumulation inside distorted selenium chains. The calculated charges applying this model are in a good correlation with charge accumulations on selenium atoms derived by the Hartree–Fock *ab initio* method. Using this model the distribution of atomic charge accumulation is estimated in amorphous selenium.

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1. Introduction

Chalcogenide glasses contain one or more chalcogen elements, sulphur, selenium or tellurium in combination with elements from IVth, Vth or VIth group of the periodic table of elements. They are very promising materials for various optical and photonic applications (lenses, windows, fibres). Phase change memory uses the unique behavior of chalcogenide glasses. These materials show various changes in structure and in electronic properties during bandgap illumination like photodarkening [1] and photoinduced volume changes [2]. Much effort has been made to understand the underlying mechanisms of these processes on an atomic level, but several open questions still remain open.

Amorphous selenium is a model material for chalcogenide glasses. Continuing our interest in the electronic structure of this material [3] we investigated the charge distribution of amorphous selenium in detail. Charge accumulation has an important influence on electron energy distribution and it plays an important role for the chemical shift in NMR measurements but it has only a secondary influence on hole pairing model leading to photodarkening and volume expansion (see Singh and Tanaka's work [4]) because our model does not contain excited state.

Let us consider an elementary triad of three selenium atoms (i , j , and k) as it is displayed in Fig. 1. They form two sigma bonds between ij and ik atoms with a jik bond angle denoted by φ . The net charges on these atoms depend on the deviation $\Delta\varphi$ from the ideal Se–Se–Se bond, $\Delta\varphi = \varphi - \varphi_0$. We parametrize this relationship by the following simple function:

$$q_i = 2(A\Delta\varphi + B\Delta\varphi^2), \quad (1)$$

$$q_j = q_k = -(A\Delta\varphi + B\Delta\varphi^2), \quad (2)$$

where A and B are two fitting parameters. A similar (not the same) triad model has been developed previously by us for diamond like amorphous carbon [5] and for amorphous silicon [6]. The total charge of this triad is equal to zero. The charge accumulation on atom i inside a chain is a sum of contributions originating from all combinations of this triad containing atom i . Since in a selenium chain each atom is only once at the center and at the end of two triads twice (see Fig. 2) the total charge accumulation on selenium atom i is

$$Q_i = 2(A\Delta\varphi_i + B\Delta\varphi_i^2) - A(\Delta\varphi_{i-1} + \Delta\varphi_{i+1}) - B(\Delta\varphi_{i-1}^2 + \Delta\varphi_{i+1}^2). \quad (3)$$

To test the quality of our local model we calculated the charge accumulation in amorphous Selenium chains applying the full HF *ab initio* scheme. Next, the angles present in the model structures were inserted into Eq. (3) and the resulting charges were plotted against that of the full calculation.

As a mixture of long chain molecules and rings forms the atomic configurations in amorphous selenium, we constructed four different chain models containing 19–41 selenium atoms with varying lengths. At the two ends of the chains hydrogen atoms saturated dangling bonds. Furthermore, in order to avoid any boundary effects we also have built up a ring of 50 selenium atoms. In our structural models bond angles turned out to vary between 70° and 110°. Based on these models single-point restricted Hartree–Fock (HF) *ab initio* calculations with simple STO-3G basis set have been performed using the GAUSSIAN 03 program package [7]. A linear correlation was found between the calculated charge accumulations (HF *ab initio*) and the charge accumulation from our bond-angle model (calculated with Eq. (3)). We concluded that the charge accumulation on selenium atoms in long chains can be traced back to a local effect in the following sense. It is based on a three-atom effect and it can be described by bond-angle distortions which reflect changes in hybridization. In the present case we obtain as the best fit A and B to be equal to -0.45 me/deg

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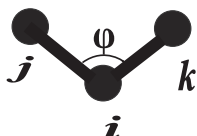


Fig. 1. An elementary triad of selenium atoms.

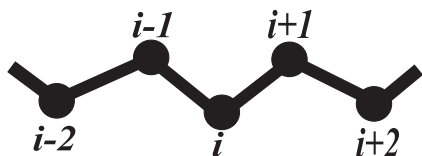


Fig. 2. Selenium chain model.

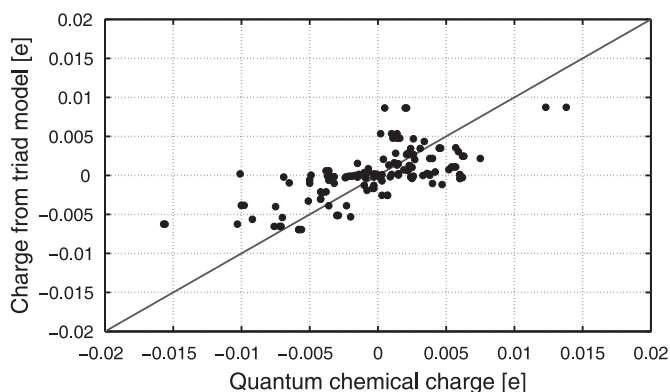


Fig. 3. Comparison of net atomic charges calculated by HF *ab initio* method and by Eq. (3) (symbols).

and -0.0089 me/deg^2 , respectively (see Fig. 3). In our fitting we have chosen the ideal bond angle to be $\varphi_0 = 101^\circ$. Only the quadratic term is sensitive to φ_0 but it has two orders of magnitude smaller prefactor compared to the linear term. Obviously, already the linear term in our triad model provides a quite satisfactory fit. The quadratic term slightly improves the fit.

Finally, to estimate charge fluctuation in a-Se we used our previously constructed defect free atomic configurations [2,8,9]. Applying Eq. (3) we obtained a distribution of charge accumulations in a-Se as displayed in Fig. 4. It is close to a Gaussian distribution with full width at half maximum of 0.02 electrons.

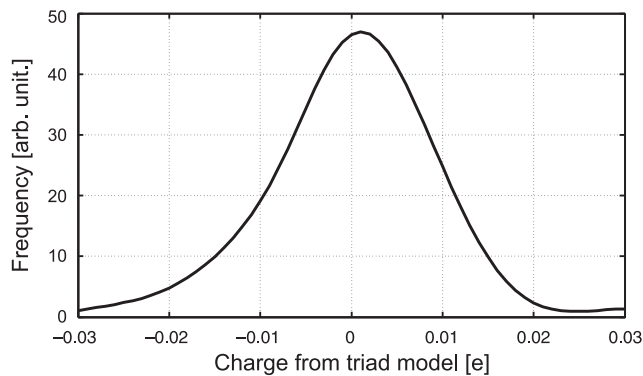


Fig. 4. Distribution of atomic charge accumulations in model amorphous selenium.

In conclusion, we have demonstrated that the total charge accumulation in amorphous selenium primarily depends on the bond-angle deviation from the ideal value. It is thus a local effect. In addition, it does not depend on the bond length. The dependence on the ideal bond angle is quite small, since it only enters the quadratic term in Eq. (3), which has a prefactor that is two orders of magnitude smaller compared to the linear term. This latter term does not depend on the ideal bond angle. Our simple local model presented here provides a useful method for the estimation of charge accumulation. Any large-scale computer calculations are not necessary.

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