

CHARGE DISTRIBUTION IN AMORPHOUS SILICON CLUSTERS. QUANTUM
CHEMICAL STUDY COMBINED WITH RING STATISTICS

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We applied a previously developed quantum chemical method to determine atomic charge distribution in the continuous random network model of amorphous silicon by Wooten and coworkers. A linear relation between bond angle distortions and net atomic charges has been found. The charge distribution displays maxima or shoulders and the location of these can be related to the number of fivefold rings containing the same atom.

1. INTRODUCTION

Charge distribution in amorphous silicon (a-Si) plays an important role in determining 2p core-level spectral or integrated infrared absorptivity.² Recently we elaborated a quantum chemical method for the determination of atomic net charges in geometric models of a-Si.^{3,4} The method, adapted to an IBM PC/AT micro-computer, allows to treat clusters with up to 50 atoms thus size effects can be studied to some extent, as well. In this paper we present results for the continuous random network (CRN) model of Wooten et al.^{5,6} and concentrate on the overall shape of the charge distribution curve. This may be important in determining shapes of infrared absorption bands.

2. METHOD

The method is based on a valence electron effective Hamiltonian using a basis set of atomic sp^3 hybrids.⁷ These are directed along the corresponding Si-Si bond and subsequently orthogonalised on

each atom. Orthogonalisation may result in a deviation of the actual s -character of the hybrids from the standard sp^3 values. Accordingly, geometry distortions are reflected by hybridisation changes. To model the bulk, pseudoatoms were put at the boundary. These possess one (or two) neighbours only and they are represented by one (or two) hybrids, their effective core charges being 1 (or 2). Accordingly, our method yields exactly zero charges for each atom in a finite cluster of the diamond lattice.

We found a simple empirical formula to calculate atomic net charges from bond angle distortions.⁴ We divided the silicon cluster into elementary triads (indicated by heavy lines in Fig. 1) that are inherently neutral. Net charge increments within each individual triad are supposed to be linearly dependent on the deviation of the bond angle from the ideal value (109.47°), $d\theta$,

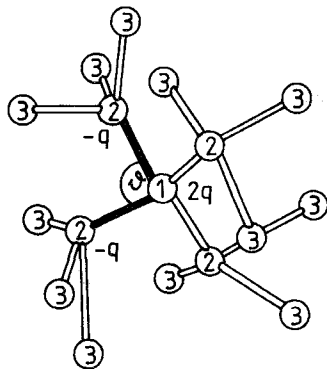


FIGURE 1. Atomic arrangement in a CRN lattice. First and second neighbours of the central atom (1) are denoted by 2 and 3.

$q = A \cdot d\theta$ ($A = -0.69e/^\circ$). The total atomic net charge is a sum of contributions originating from all triads of the type $i=(212)$ and $j=(321)$

$$q_i = \sum q_{i1} + \sum q_{j1} \quad (1)$$

We applied Eq. (1) to calculate net charges on all 216 atoms of the CRN model.

3. RESULTS AND DISCUSSION

The charge distribution curve, as obtained by smoothing the calculated histograms with Gaussian line broadening that corresponds to a full width of 0.0064 electrons at half maximum, is pre-

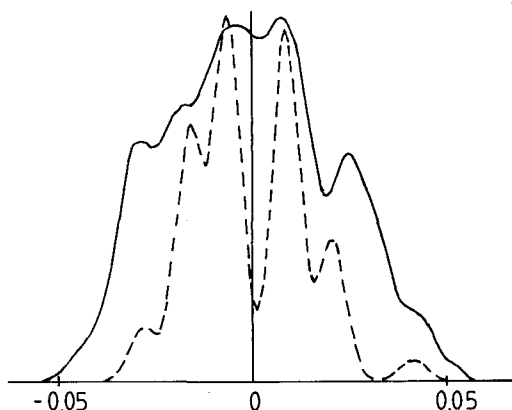


FIGURE 2. Charge distribution in a-Si. Full line: from Eq. (1), dashed line: from fivefold ring statistics.

sented in Fig. 2. The curve has characteristic maxima or shoulders, the highest ones near zero net charge. The rms charge fluctuation is 0.021 electron, this may be compared to values obtained from models by Henderson⁸ (0.021) and Ching et al.⁹

(0.027). Charge distribution curves for the previous

model differ quantitatively from that on Fig. 2, but each curve possesses the same number of maxima (or shoulders) indicating that topological characteristics are independent of the details.

Analysing the distribution of rings, we have found that the number of fivefold and sixfold rings belonging to the same atom (N_5 and N_6) determines charge distribution to a given extent. The charge averages for atoms with 0, 1, 2, 3, 4 and 5 fivefold rings are -0.0227, -0.0157, -0.0053, 0.0094, 0.0212 and 0.0351 electrons, respectively. These values show fair coincidence with maxima on the charge distribution curve. Applying the above Gaussian line broadening method we smoothed the histogram displaying the number of atoms with 0, 1, 2, 3, 4 and 5 fivefold rings (10, 45, 67, 64, 26 and 4, respectively). The fair correspondence between both curves call the attention to the primary importance of ring statistics in determining charge distribution.

Sixfold rings have a smaller, but yet recognisable, effect on the charges. The ranges of N_6 for a fixed N_5 determines the sign of the charge deviation from the average quoted above. For $N_5=0$

negative deviations are obtained if N_6 ranges between 5 and 9 and positive ones if the range is 9-12. Other ranges for $N_5=1, 2, 3, 4$ and 5 are (values for positive deviations in parentheses) 1-8(5-10), 2-7(4-8), 1-5(3-9), 0-5(2-5), 1-2(3), respectively.

As a consequence, we may state that atomic charge distribution in a-Si is determined primarily by bond angle distortions that are dependent on the number of fivefold and perturbed by the number of sixfold rings attached to the same atom.

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