Chalcogenide Letters Vol. 2, No. 5, May 2005, p. 45 - 48

STRUCTURAL MODEL FOR AMORPHOUS ARSENIC

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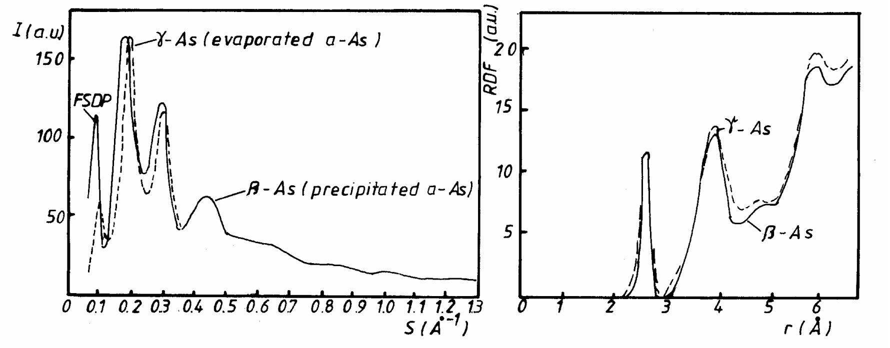
A layer-like model has been demonstrated for the structure of amorphous arsenic.

1. Introduction

The arsenic is the main component of many chalcogenide systems. Arsenic and phosphorus are intermediate between the tetrahedral atoms (germanium, silicium, or carbon) and chalcogenide atoms (sulphur, selenium and tellurium). The structural properties of amorphus arsenic seem to be similar to those of the non-crystalline chalcogenides. That is why the investigation of the structure of amorphous arsenic could be of relevance for the structure of disordered chalcogenides.

2. Crystalline and amorphous aresenic

As stated by Krebs and Steffen [1] and Breitling and Richter [2] the amorphous arsenic can be obtained in two forms: β-As and γ-As. Bulk samples and precipitated amorphous arsenic exhibit a β-type structure while evaporated films are of γ-type. The differences in the X-ray scattered intensities and the corresponding RDF's are evident in figure 1a,b.



a b

Fig. 1. The structure factor (a) and the radial distribution function (b) for the two forms of amorphous arsenic: β and γ arsenic.

The first sharp diffraction peak (FSDP) plays an essential role when the two forms are identified. Moss has shown [3] that during annealing this peak increases and becomes narrow, thus suggesting a transition from γ to β form.

3. Structural model, results and discussion

In order to explain the amorphous structure of arsenic, firstly microcrystalline models were tried. Two types of As-crystal do exist: a rhombohedral phase (Rh-As) and an orthorhombic phase (Or-As). The first one has a “chair-like” configuration of the atoms and the second one exhibits a ”layered” structure. Smith et al. [4] have shown that only for the orthorhombic crystal the special deformation of the lattice gives rise to FSDP. They concluded that a-As is related to the orthorhombic crystal.

Davis et al. [5have built an amorphous arsenic (a-As) model with 533 atoms and computed its minimum free energy configuration. The authors concluded that the model reproduces quite well the experimental RDF. Nevertheless, two unresolved problems still remain: a). the explanation of the differences between β-As and γ-As in the frame of the CRN model and b). the aptitude of the model to reproduce FSDP. In order to explain the FSDP some authors assume the existence of definite molecular species in the material (e.g. As_4 molecules found, also, in the vapour phase).

In modeling the structure of disordered three-fold coordinated arsenic we started from the assumption that disordered folded layers are the main constituents of the non-crystalline phases. This idea seems to have the chance to explain the increase of the internal distance deduced from the position of the FDSP, when one passes from crystal to amorphous phase. In the same time the way seems to be opened to explain the structural differences between β-As and γ-As: in γ-As the disordered layers are highly interconnected and kept together by occasional bonds which, during annealing break and a new equilibrium distance between layers is established. Thus, the new form β-As is obtained. The distance *d* is larger for the relaxed case, as observed.

With the aim to shed more light on the structure of a-As we carried out structural simulations using atomic scale models. The free energy of a hand built model as a disordered layer with 146 atoms was minimized by computer using a Monte Carlo procedure. Bond stretching and bond bending potentials ($\beta/\alpha=1$) were used. An equilibrium distance $r_1=2.51$ Å and a bond angle $\alpha=98^o$ were used.

The main characteristics of the disordered layer with minimum free energy are:

-number of 5,6,7,8 –fold rings are 22,16,11,3, respectively.

-r.m.s. of r_1 is 0.11 Å and r.m.s. of α is 7.87^o.

Now we shall try to prove the validity of the hypothesis regarding the structure with disordered layers for a-As. An important experimental finding in a-As and other glasses with arsenic [6] is that, as a general feature, the distance corresponding to the angular position of FSDP is significantly higher than the interlayer distance in the parent crystals. For a-As the interlayer distance is 5.85 Å, appreciably exceeding that of 5.50 Å for the interlayer distance in orthorhombic arsenic. No reasonable explanation for this difference was given up to day. It is quite improbable that the Van der Waals equilibrium distances between layers in amorphous and crystalline materials would be essentially different. Nevertheless, if one supposes that the effective thickness of the layers are different in the amorphous and crystalline phase, the apparent increase of the interlayer distance can be understood.

In order to determine accurately the thickness of the simulated irregular layer we computed the statistics of the height of the individual As-pyramids. We have obtained the mean value of the heights: 1.63 Å. If one takes into account that the layer thickness in As crystal d=1.25 Å, then the increase in the layer thickness (from c-As to a-As) is 0.38 Å. This increase of the layer thickness correspond to the increase of the interlayer distance and is in excellent agreement with the best experimental value: d= 5.85 – 5.50 = 0.35 Å.

Thus, on the basis of the above calculation, we can furnish a sound argument for the origin of FSDP in a-As, but the problem is now to stack layers in order to obtain a correct three-dimensional structure.

Three identical layers, shifted along the Oz axis by 5.85 Å give rise to a spatial model, which is unsatisfactory as concerning the details of the RDF. To avoid the exact periodicity of the layers which constitute the model, each of them was differently oriented (rotated by $\pi/2$, reflected in the XOY plane). The resulting RDFs (especially for the model with reflection) after correction for their finite size, is in quite good agreement with the experimental RDF for a-As (figure 2)

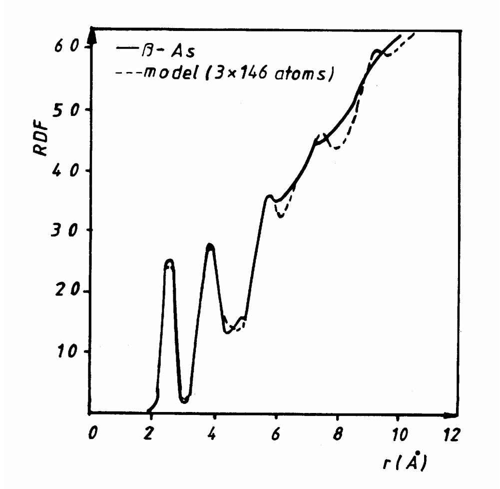


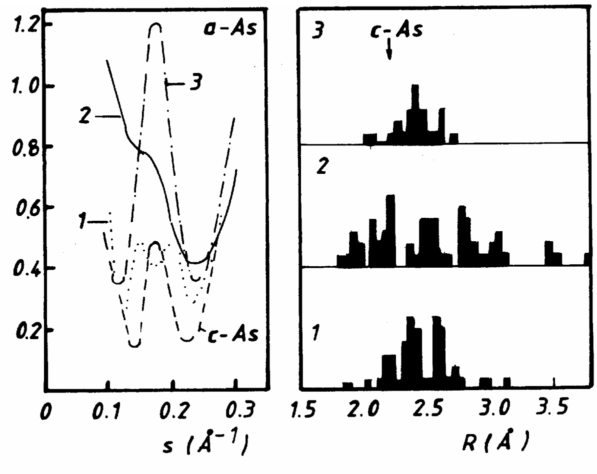
Fig. 2 The radial distribution function of the Popescu’s model with disordered layers (3 × 146 atoms) compared to the experimental function.

The agreement of the experimental and model RDFs seems to be as good as the agreement of the experimental RDF and the RDF for the CRN model devised by Davis et al. A decisive test for the validity is however the aptitude of the model to reproduce the FSDP.

We performed a detailed analysis of several typical models for a-As:
the Greaves-Elliott-Davis model [7], the Beeman’s model (private communication of the coordinates) and our layered model (Popescu's model). Firstly, we calculated the structure factor in the region of the FSDP for the above models. Secondly, we calculated the hole radius distribution (in the models).

In order to determine the radius distribution of the holes in a given computer model we used a Monte-Carlo procedure. Starting from a given position inside the model, the distance d to the nearest atom was calculated. Afterwards, small aleatory movements were given to this arbitrary position and were retained only those moves which led to higher radius of the hole. Finally the maximum radius was obtained. By repeating the procedure at different starting positions inside the model, the complete distribution of the holes was obtained.

While FSDP reflects the degree of layering of the model, hole radius distribution (HRD) accounts for the layer packing characteristics. Figure 3 shows the structure factor in the FSDP range for various models of a-As and for crystalline As (c-As).



a b

Fig. 3. The FSDP region (a) and the hole radius distribution (b) in three models for a-As: 1. Beeman’s model; 2. GED’s model; 3. Popescu’s model.

A significant correlation is evidenced between the height of the FSDP and the width of the HRD. If no layers are developed in the model, the FSDP is lacking (see the GED model). The Beeman's model exhibits a bimodal distribution of hole radii and this feature is correlated with the splitting of the FSDP. The Popescu's model with well-correlated layers shows a very strong FSDP. The peak developed by the crystal in the region of FSDP has low intensity. The r.m.s. of HRD in the GED model is large (not yet computed from the data given in figure 3 !) while for the Popescu’s model is narrow. We must point out that the careful investigation of the Beeman’s model (633 atoms) has evidenced some compressed regions with the tendency to raise the first coordination sphere and regions with lower density (normal coordination sphere: N=3). This inhomogeneity seems to be responsible for the split FSDP.

4. Conclusion

Our modelling investigation and the experimental data converge in supporting a layer-like structure for amorphous arsenic.

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