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RMC MODELLING OF $Ge_{15}Te_{85}$ - SHORTCOMINGS AND CHALLENGING PROBLEMS

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The RMC modeling of Ge-Te alloy has been carried out. In spite of the large number of iterations, some discrepancies between the calculated curves and the experimental ones still remain. Further relaxation with a Lennard-Jones type potential gives significant improvement only for the first coordination peak in RDF. The causes of the more or less good fit are discussed and suggestions for further improvement of the model are given.

1. Introduction

The amorphous chalcogenides are important for various optoelectronic applications. The amorphous binary Ge-Te alloys are phase-change ovonic materials and show switching properties [1]. The amorphous chalcogenides are also used in optical phase change recording [2]. $Ge_{15}Te_{85}$ is one of the most extensively studied alloy that can serve as a relatively simple model for systems of high applicative interest, as e.g. Ge-Sb-Te, used in phase change memories. Despite considerable experimental effort [3,4] the structure of $Ge_{15}Te_{85}$ is still challenging. The local atomic environment in amorphous $Ge_{15}Te_{85}$ was recently determined by Jovari and Kaban [5]. They found that the average coordination number of amorphous $Ge_{15}Te_{85}$ alloy is larger than 2.4, the rigidity percolation threshold, but less than 2.67, the topological threshold. The tellurium coordination number was found to be larger than 2. Moreover, the Ge-Te correlations extend up to ~30 Å.

In this paper we report the results on the RMC modeling of $Ge_{15}Te_{85}$ alloy and investigate the atomic scale configurations characteristic to the model. We observe significant deviations from the crystallo-chemistry of the Ge-Te crystalline configurations. The possible improvement of the modelling procedure is discussed.

2. Experiment and model

X-ray diffraction experiments were performed at the BW5 experimental station at HASYLAB, Hamburg. Scattered intensity on powdered amorphous sample was measured in the range 0.5 – 20 $Å^{-1}$.

The model developed by us consists in a cluster of atoms (20 000) with 3000 Ge atoms and 17000 Te atoms. The density used in Reverse Monte Carlo procedure was taken 0.0282 $Å^{-3}$ [6]. Minimum distances between Te-Te, Ge-Te and Ge-Ge pairs were 2.5, 2.3 and 3.5 Å, respectively.

3. RMC modeling results

Fig. 1 shows a comparison between the experimental diffraction curve [7] and the curve calculated form the RMC model of the alloy.

One observes significant deviations of the fit, especially for the first two maxima in the structure factor, and deviations for several peaks in the fit of the radial distributions function calculated from the model and from the experimental structure factor (Fig. 2).

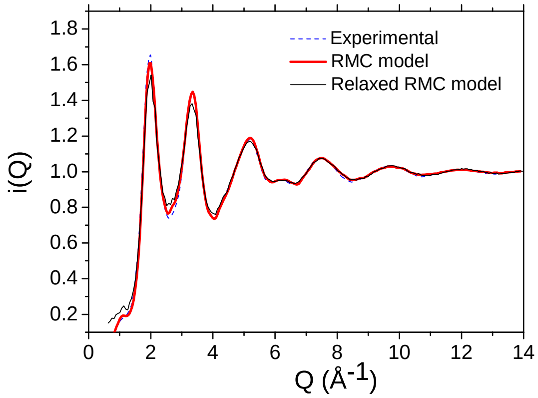

Fig. 1. The diffraction pattern of the Ge-Te alloy compared to the structure factor got from the RMC model

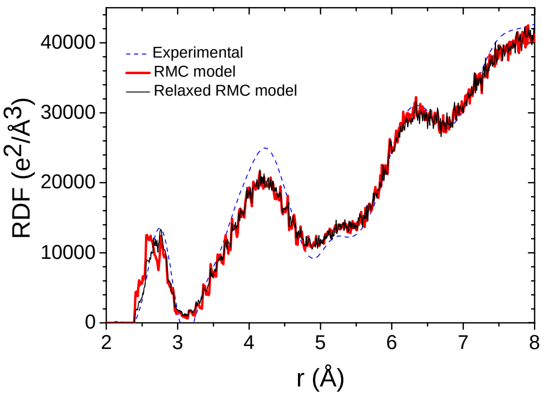

Fig. 2. The radial distribution curve for $Ge_{15}Te_{85}$ compared with the pair distribution function of the model (for the first peak the average position is 2.70 Å)

The above remarked deviations lead us to suppose that serious inconsistencies in modelling do exist.

We have analysed various local configurations of the atoms in the model. Figure 3 shows two typical configurations.

*Fig. 3. a. RMC model $E_{total\ /atom}$=4.7*10^{-5} dynÅ Ge coordination: 2.53 Å, 2.71 Å, 2.74 Å, 2.63 Å b. RMC + Lennard Jones relaxation : 17 500 iterations; $E_{total/atom}$ =2.3*10^{-5} dynÅ; Ge coordination: 2.53 Å, 2.67 Å, 2.76 Å, 2.63 Å*

Fig. 4. Two local configurations in the Ge-Te model: a. RMC model $E_{total/atom}=0.67*10^{-5}$ *dynÅ*
b. RMC + after relaxation with Lennard-Jones potential: 17500 iterations;
$E_{total/atom}=0.606*10^{-5}$ *dynÅ*

The configurations obtained by RMC modeling of Ge-Te alloy are characterized by a mixture of three-fold and four-fold coordinated germanium and two-fold and three-fold coordinated tellurium . In case “A”, shown on Fig. 4, the germanium coordination is four, an usual coordination for the covalent germanium. In the same case tellurium takes the coordination 1 because the second tellurium atom is situated at a distance of 3.35 Å, far from the covalent Te-Te bonding distance of 2.74 Å. The consequence of the deviation of the bonding distances from the correct crystallochemical distance is the profound deviation of the first peak in RDF from the shape and position determined experimentally.

Fig. 5 compares the first peak in RDF with that obtained from the RMC model. The differences are very large. Not only the position of the peaks does not match, but the RMC peak shows an abrupt profile on the side of low distances. The cut-off is due to the distance constraints in the model, but the difference in position cannot be explained.

Therefore, we have tried to improve the agreement between the model and the experiment by introducing a new simulation step, achieved in the frame of the Lennard-Jones theory of interaction. The Lennard-Jones interaction forces have been introduced in the model under the form:

$$V_{LJ} = \quad (S/R)^{12} - (S/R)^{6}$$

Where $S= r_o \times 0.89$ where r_o is the average distance between the atoms: 2.70 Å and R is the distance from a central atom picked up due to random process of simulation.

The calculation of the structure of minimum energy with Lennard-Jones potential was carried out by a Monte-Carlo-Metropolis procedure. The minimum of the potential was centered on the distance r_l=2.70 Å. The calculation of the free local energy (see Fig. 4) the following parameters were used: equilibrium distance 2.746 A (obtained from the experimental curve and the mean equilibrium angle between bonds was taken 100.75°. After 17500 random iterations we have calculated the parameters of the model. Figure 3 B shows the differences in local coordinations when the relaxation with Lennard-Jones potential is considered. The abnormally large distances got in thre RMC modelling (3.35 A) tends to decrease, approaching (3.15 A) the correct bonding distance. In the same time the comparison between the profile of the first peak in RDF before and after relaxation shows an obvious improvement by LJ relaxation (see Fig. 5).

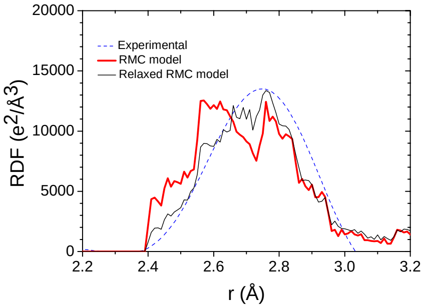

Fig. 5. First coordination sphere in $Ge_{15}Te_{85}$*:*
--- experiment _____ RMC model - relaxed RMC model

Furthermore, in order to see how the additional relaxation by Lennard-Jones (LJ) potential could improve the fit between the experimental and modeling diffraction curves, we have represented in Fig. 6 and 7, at a larger scale, the experimental curve, the curve got from RMC modeling and the curve got after 17500 relaxation steps with LJ potential. For evidencing the details and differences we have represented the curves for different ranges of the scattering vector.

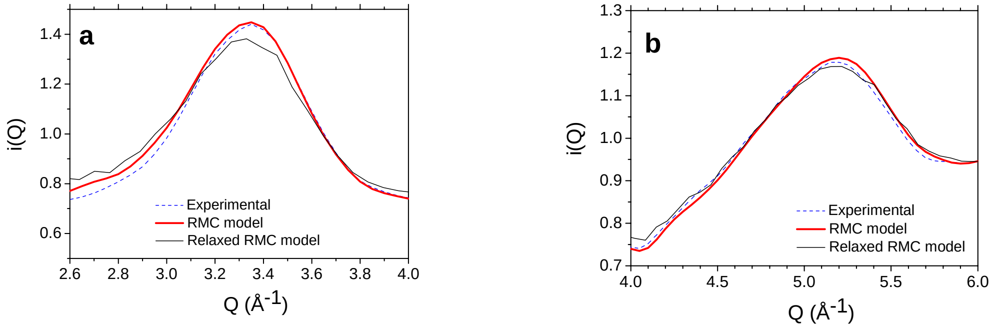

Fig. 6. Regions of the diffraction pattern of $Ge_{15}Te_{85}$ alloy. A comparison between experimental curve, the curve got after RMC modelling and the curve obtained after an additional LJ relaxation.

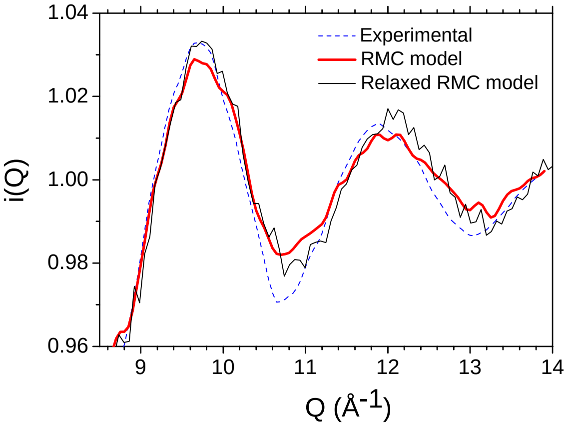

Fig. 7. The comparison between the diffraction pattern for the model, before and after relaxation with LJ potential, and the experimental curve.

For the maxima situated at large scattering angles the LJ relaxation seems to give better agreement with the experiment even for a small number of iterations, while for the low scattering vector, specially for the first diffraction maximum the LJ relaxation determines a worsening of the fit. A better fit is got after LJ relaxation in the regions illustrated by Fig. 6b and 7.

We must remark that the first maxima in the structure factor of the amorphous materials are related to the ordering of the atoms at distances larger than the first coordination spheres, while the details at large scattering angles are related to the first coordination sphere, namely to the bonding distances between atoms.

4. Discussion

The imperfect fit of the experimental results for the structure of Ge-Te alloy to the RMC data, speaks in favour of some shortcomings of the RMC method. The problem seems to consists in the impossibility of the RMC method to take into account the medium and long range ordering in the disordered networks. At the limit we must admit that the method does not work for crystalline materials. It is not possible to model the crystal when only the X-ray diffraction diagram is used for the fit. A relaxation with the most simple short range interaction force Lennard-Jones force, can improve the fit of the RMC curves with those got from experiment. Nevertheless, the results are not spectacular. We believe that the reason is the same: the long range and directional forces are not taken into account. We suggest a combination of forces applied to local configurations through a more complicated relaxation process. The starting configuration could be the final configuration obtained by RMC simulation. The worsening of the fit for the structure factors, when the LJ simulation is carried out could be related to the void structure, usual for the covalent networks. Earlier we have demonstrated on the case of amorphous germanium, that filling of the voids with simulated atoms determines strong decrease of the first peak in the structure factor calculated from the model. In our LJ simulation, what happens is probably the vanishing of the void structure and some local compaction of the model. That is why, in order to have a good modelling of the alloy we must take into account the second and third non-central order interactions, that are able to preserve the atomic-scale voids present in covalent or partially covalent materials.

5. Conclusions

The RMC is an attractive method for the simulation of the structure of amorphous materials. Nevertheless, it is necessary to take care when the structural data are interpreted due to some obvious shortcomings, e.g. bad reproducing of the first peak in RDF. Methods for improving are suggested.

Acknowledgements

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