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# Structural change of crystalline and amorphous-Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> by reverse Monte Carlo analysis of x-ray diffraction data and extended x-ray absorption fine structure data

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## Abstract

Reverse Monte Carlo analyses of crystalline and amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> thin films were carried out using x-ray diffraction data and three spectra from extended x-ray absorption fine structure measurements. To produce a crystal model, we employed a large system with 12 800 Ge, 12 800 Sb and 32 000 Te atoms. The obtained model for the crystal structure was used for the initial configuration of the amorphous model. As a result of a series of reverse Monte Carlo analyses with various constraints, we found that the partial pair distribution function in the amorphous state with the largest deviation from the crystal state is a Ge–Sb pair and the distance is less than 2.7 Å. This suggests that Sb atoms in amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> thin film have a four-coordinate within 3.2 Å.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Reverse Monte Carlo (RMC) analysis is a general method for three-dimensional (3D) structural modelling based on experimental data [1], and in particular an established technique for analysing local structure and revealing the characteristic configuration for disordered materials [2–5].

RMC analysis has also been applied to crystalline structure for refinements. In particular, it can be used for analysing the diffuse scattering of powder and single-crystal diffraction data [7–13]. The RMC method can produce a model of a multi-component system using many different sorts of experimental data simultaneously [14]. The result provides partial radial distribution functions and partial structure factors.

RMC modelling has been applied yet more to extended x-ray absorption fine structure (EXAFS) spectra [15–18]. The first RMC analysis for EXAFS spectra was performed for amorphous and crystalline silicon by Grumant and McGreevy [15]. An EXAFS spectrum provides the local atomic information, while x-ray diffraction (XRD) data have information on the long-range order of the structure. Many RMC analyses have been performed for combinations of XRD and EXAFS data or for neutron diffraction and EXAFS data [16–18]. The many contributions made through the use of the RMC method and the RMC advantages of the method are described in McGreevy's review [19].

There are, however, not so many examples of RMC analysis of a three-component disordered system such as a ternary alloy, because it is very difficult to determine the partial structures of disordered materials consisting of similar species. Therefore it is an interesting question as to whether it is possible or not to analyse the structure of a disordered ternary alloy using XRD and EXAFS data using RMC methods. We think that  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin film, which has recently attracted a great deal of attention, is a good choice for this purpose.

Amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  film (GST) is known to be a material with a component of the  $\text{GeTe-Sb}_2\text{Te}_3$  pseudo-binary alloy system [20–23, 25, 26]. It has a characteristic of undergoing a large optical change when subjected to a laser beam pulse of less than 50 ns, accompanied by quick structure changes from the amorphous phase to the meta-stable crystalline phase and vice versa. Its commercial uses now include phase-change optical memory and disk media [20].

Through XRD experiments, Yamada and Matsunaga have determined the structure of the crystalline phase to be NaCl type with vacancies [21, 22]. In the structure, Te atoms occupy all positions on a face-centred cubic (FCC) sub-lattice of the lattice, and Ge, Sb and vacancies randomly occupy other FCC sub-lattice positions in the ratio 2:2:1. Kolobov *et al* have shown that the crystalline structure is a distorted rock salt [23].

Although many investigations into the structure of amorphous GST have been performed, the structure of the amorphous phase has remained unknown but has been assumed to possess a randomized NaCl-type structure. Kolobov *et al* [23] have opinions that there are two kinds of Te–Ge bonds; specifically, a shorter and strong Te–Ge bond and a longer and weak Te–Ge bond, and that they correspond to octahedral and tetrahedral sites in the crystal, respectively. Their explanation of the reasons why structure changes in GST are fast and stable is that the crystallization–amorphization process does not require the rupture of strong covalent bonds, that the transition is diffusionless and also that the Te sub-lattice is partially preserved, as is the local structure around Sb atoms. These reasons are also taken into account for why the transition can easily be reversed. Very recently, Kolobov *et al* [26] demonstrated that GST can be rendered amorphous by the application of high pressures (about 20 GPa).

The aim of the present work is to find the closest models of the amorphous structure and the crystalline structure of GST by RMC analyses. This analysis is based on the as-yet unproven deduction that the structural change in GST is almost diffusionless. For this purpose we first carry out RMC analysis of crystalline GST film to create an initial configuration for amorphous GST film. Using the results thereof, we then perform RMC analyses of amorphous GST film with various severe constraints.

## 2. Preparation and RMC analysis

XRD and EXAFS measurements of the crystalline  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (c-GST) film and the amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (a-GST) film were performed on the BL19B2 beam line of SPring-8. Both samples were provided by Matsushita Electric Industrial Co. Ltd. The powder samples for XRD measurements were prepared by scraping off the GST films from the glass substrates using a knife edge. These samples were put in glass capillaries. The samples for EXAFS measurements

were formed in a film with a thickness of about 200 nm on organic film sheets. These samples were cut into square pieces about 10 mm in size. Appropriate numbers of these pieces were stacked to optimize the total thickness of samples. XRD measurements were carried out by using a Debye–Scherrer camera on the BL19B2 beam line of SPring-8. The incident x-ray energy was 29 keV. EXAFS measurements were carried out on the K-edges of Ge, Sb and Te in transmission mode at room temperature.

The total structure factors of XRD  $F(Q)$  and EXAFS spectra  $\chi(k)$  were estimated from the experimental data by standard means. At first,  $F(Q)$  was converted into the radial distribution function (RDF) by Fourier transformation. Secondly, noisy data of the RDF in the range of a distance lower than about 2 Å were subtracted from the spectrum. Finally, the modified RDF spectrum was reconverted into  $F(Q)$ . This process is similar to the MCGR [28] method.  $\chi(k)$ s were estimated by extracting the contribution of the first-nearest-neighbour pairs from EXAFS spectra using the Fourier filter method [27]. These data were prepared as an experimental structure factor and EXAFS spectra of Ge, Sb and Te for RMC analyses.

The number densities of the amorphous sample were estimated by using the critical angle for the total x-ray reflection to be about  $0.0325 \text{ \AA}^{-3}$ . We assumed that the number density of the crystal film does not change and is the same value as that of the amorphous film, judging from the results of the rough estimation.

In order to make an initial configuration for a model of a-GST, we started RMC modelling of c-GST using the convolution technique for powder crystalline materials [6, 7]. When a finite model crystal is Fourier transformed to obtain the corresponding structure factor  $F^M(Q)$ , an oscillatory noise arises in the  $F^M(Q)$  over the  $Q$  range, which is caused by the finite size of the model. Therefore, in advance, we added to the experimental structure factor  $F^E(Q)$  the oscillatory noise corresponding to the model size. This was done by convoluting  $F^E(Q)$  with the Fourier transform of a truncation function  $m(r)$ :

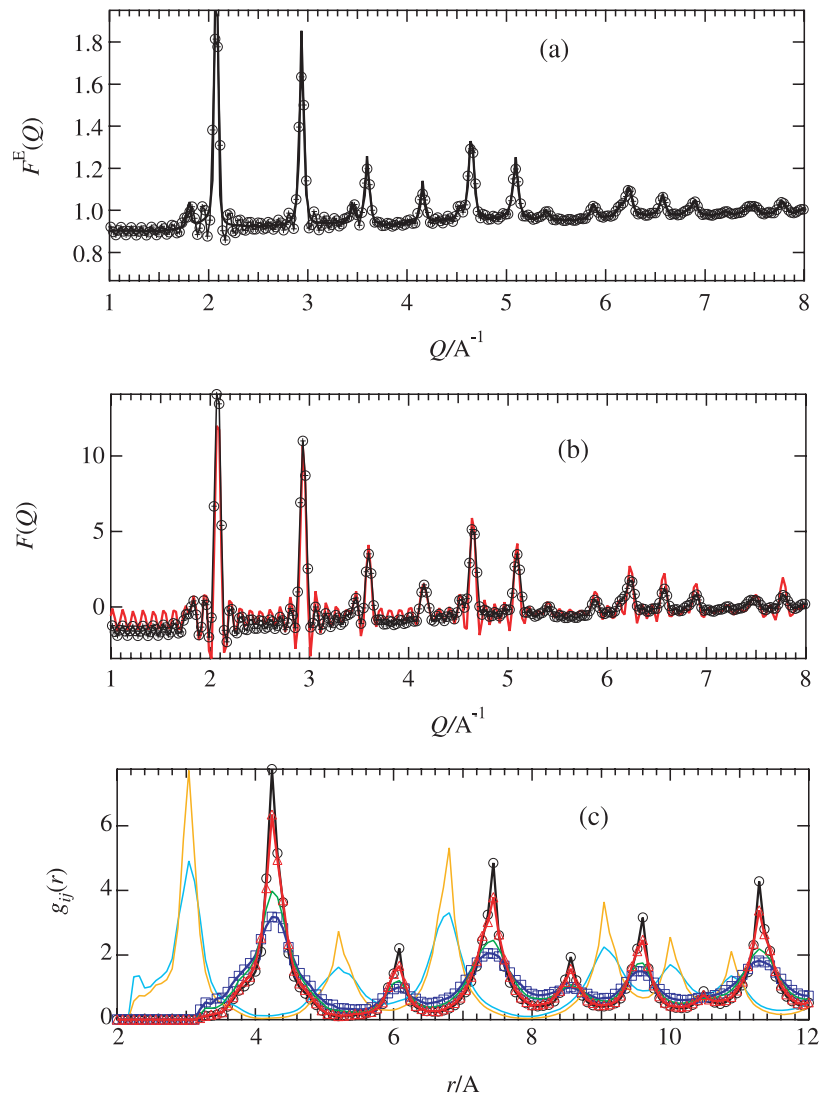
$$m(r) = \begin{cases} 1, & \text{for } r < L/2 \\ 0, & \text{for } r > L/2, \end{cases}$$

where  $L$  is the size of the box in the model. A better RMC analysis for powder crystalline materials has been developed by Mellergård and McGreevy [29], however we consider that the normal RMC method is adequate for this study. The observed and the convoluted  $F^E(Q)$  are plotted in figure 1(a). We used the convoluted  $F^E(Q)$  instead of the measured one.

In order to reduce the convolution effect, we set, as an initial RMC configuration for c-GST, 12 800 Ge, 12 800 Sb and 32 000 Te atoms on a NaCl-type perfect lattice where all Te atoms are on Cl sites and Ge, Sb and vacancies are on Na sites at random. The three-dimensional atomic configuration is drawn in the left-hand picture in figure 2. We started an RMC program with the same maximum size of random movement,  $\delta$ , for each atom (0.1–0.5 Å), which is one of the RMC parameters to be set. This corresponds approximately to a jump length for one RMC step.

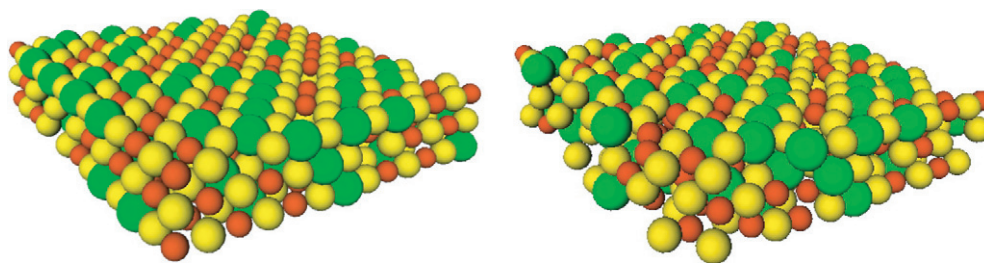
Considering the local atomic fluctuations and the existence of vacancies, we set the closest distance  $r_c$ , which is one of the RMC parameters and represents a restricted minimum separation within each of six kinds of pairs, Te–Te, Te–Ge, Te–Sb, Ge–Ge, Ge–Sb and Sb–Sb, to be 3.20, 2.24, 2.24, 3.20, 3.20 and 3.20 Å, respectively. The value 2.24 was determined by the fact that the Fourier transformation of  $F^E(Q)$  does not have any significant spectrum below that distance. As it is thought that the lattice constant of c-GST is about 6.02 Å [23], it is reasonable that the largest distances of Te–Te, Ge–Ge, Ge–Sb and Sb–Sb pairs will be no less than 3.20 Å.

Although not shown here, the height of the first two peaks in  $F^M(Q)$  of the initial configuration were lower than those in  $F^E(Q)$ . We confirmed that the first short peaks do not



**Figure 1.** Total structure factors of the c-GST sample. (a) The measured data (bold line) and the convoluted one (line with symbol) are plotted. (b) The obtained model structure factor and the experimental one after 16 000 RMC accepted moves. The bold red line represents the RMC result. (c) The corresponding partial distribution functions. The black line denotes the Te–Te radial distribution function, blue denotes Ge–Ge, red denotes Sb–Sb, light blue denotes Te–Ge, yellow denotes Te–Sb and light green denotes Ge–Sb.

depend on the model size. We do not refer to this fact in the present work, because the model structure was fitted quickly to  $F^E(Q)$ . A typical result after 16 000 RMC accepted moves is shown in figures 1(b) and (c). The obtained peak positions and peak height of  $F^M(Q)$  agreed well with  $F^E(Q)$  except for the small oscillation noise. Considering the number of RMC moves, the obtained structure factor has insufficient relaxation. That this RMC process plays the role of a small thermal relaxation provides an explanation for the experimental structure factor of c-GST. This shows that the initial perfect lattice is not far from the structure of c-GST. As the model's lattice constant estimated from the half box length is 6.048 Å (which is close



**Figure 2.** Three-dimensional atomic view of the initial NaCl-type structure (left-hand side) and the relaxed structure by RMC moves (right-hand side). Only a small part of the model configuration is drawn as balls with appropriate sizes (a yellow coloured ball stands for Te, red for Ge, and green for Sb). This picture (the right-hand side) corresponds to the partial radial distribution functions in figure 1.

to 6.02), the number density of the crystal model is not unreasonable. Although the partial radial distribution functions have rather broad peaks, the centres of the peaks are still in the perfect crystal positions. The first-nearest-neighbour distances  $R_{\text{NN}}$  between Te and Ge atoms and Te and Sb atoms were about 3.0 Å.  $R_{\text{NN}}$  for Ge–Ge, Sb–Sb and Ge–Sb pairs were about 4.2 Å. These values are consistent with those of previous papers [20, 22, 23]. The 3D atomic configuration of this state is drawn in figure 2 (right-hand side). We stopped the RMC program at this point. Therefore the values of  $r_c$  are not particularly important for analysis of c-GST with the present step. The average displacement  $\sqrt{\langle u^2 \rangle}$  of each atom from its initial position was 0.25 for Te, 0.48 for Ge and 0.28 Å for Sb. We believe that the reason why Ge atoms have such a large displacement but the same  $\delta$  is that the Ge atoms' contribution (x-ray scattering factor) to the total structure factor is not so large in comparison with that of other atoms. We also calculated the translational order parameter  $P_{\text{FCC}}$  to the vector  $2\pi/l(-1, 1, -1)$ , where  $l$  is the unit cell size, which represents an index of the deviation from the original FCC sub-lattice. The values of  $P_{\text{FCC}}$  for Te, Ge and Sb atoms are 0.93, 0.84 and 0.93, respectively. Ge atoms are thought to be very close to the original positions on an FCC sub-lattice.

As we do not have other experimental data for c-GST, we cannot determine how the crystal structure should be relaxed. We cannot analyse the structure of the crystalline phase of GST thin film in detail any further in the present work. Finally, we set the configuration corresponding to the structure in figure 1(c) to an initial configuration for a-GST. Notice that it is possible to fit the model structure factor to the experimental data precisely if a very small  $r_c$  and large  $\delta$  values are selected, however the obtained model might be almost physically unrealizable.

For the structure of a-GST, we used XRD data,  $F^{\text{E}}(Q)$ , and EXAFS spectra  $\chi^{\text{E}}(k)$  for all components, that is, Te, Ge and Sb. To emphasize the high- $k$  region of the signals, we used EXAFS signals weighted by  $k^3$  instead of  $\chi(k)$ . We also calculated the coefficients for all EXAFS signals to Fourier transform the model partial radial distributions using the software package 'FEFF'. The coefficients are functions of  $k$  and  $r$ . We set the intervals  $\Delta k$  and  $\Delta r$  to be  $0.051 \text{ \AA}^{-1}$  and  $0.08 \text{ \AA}$ , respectively. We used the same x-ray scattering factors for all atoms as for the crystal data (shown in [24]). The system size was the same as the case for c-GST, that is, 12 800 Ge, 12 800 Sb and 32 000 Te atoms.

The aim of the present work is not to create a precise model of amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin film, but to analyse the quick structural change from its crystalline phase to its amorphous phase of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin film. For the purpose, we have to look for the most severe conditions to reproduce the four experimental structural data by the RMC method. We do not wish to get the best-fit model, because a best-fit model is not always a physically correct model. We wish to get better fits using a close but reasonable model of the amorphous phase to the crystal

**Table 1.** The closest allowed approaches,  $r_c$ , of three kinds of pairs, Ge–Ge, Ge–Sb and Sb–Sb, used for a series of RMC analyses of a-GST. The values of  $r_c$  for the others are set to be 3.2 for Te–Te, 2.24 for Te–Sb and 2.24 for Te–Sb. The unit of length is Å. The last two rows represent  $\chi^2$  for all data, and for the Ge EXAFS spectrum only. These can be regarded as the fitness indices.

	No 1	No 2	No 3	No 4	No 5	No 6	No 7	No 8	No 9	No 10
Ge–Ge	2.24	3.2	3.2	2.56	2.56	2.24	3.2	3.2	2.56	2.24
Ge–Sb	2.24	3.2	3.2	3.2	3.2	2.56	2.56	2.56	2.56	2.24
Sb–Sb	2.24	3.2	2.56	3.2	2.56	3.2	3.2	2.56	3.2	3.2
$\chi_T^2$	1.7	2.0	1.9	1.8	1.8	1.7	1.7	1.7	1.7	1.7
$\chi_{Ge}^2$	1.9	10.1	9.3	7.9	7.4	4.7	4.0	4.3	3.7	2.6

structure of GST. So we prepared ten kinds of samples for the RMC parameters, which are listed in table 1.

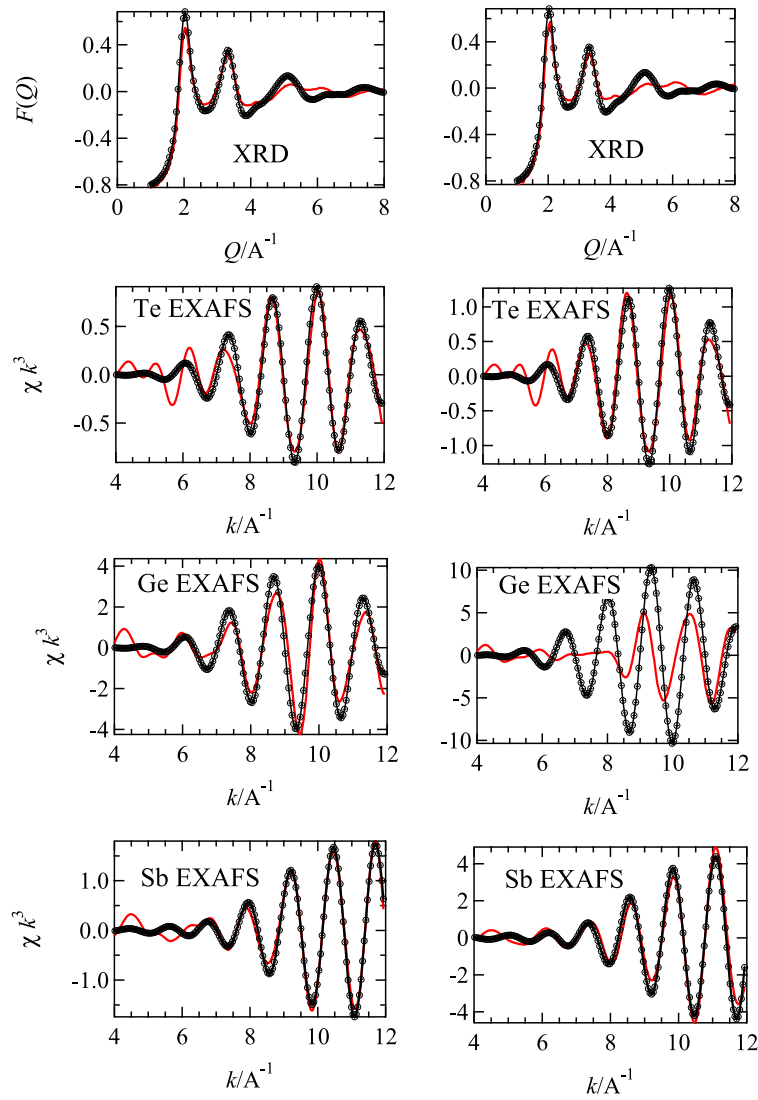
### 3. Results

We started all RMC runs with the same values of  $\delta$  (0.3 Å) for each atom from the same initial configuration, which is shown in figure 1(c). That is, all atoms move at random with the above maximum size of movement  $\delta$  to reproduce  $F^E(Q)$  and three  $\chi^E(k)k^3$ s with different parameters  $r_c$ . Other parameters were set to be the same value for all cases. There are only three kinds of values in table 1. The value 2.56 was tentatively selected as a middle point between 2.24 and 3.2. It can be readily seen that sample no. 1 is the easiest case and no. 2 is the hardest case to be fitted among these ten samples. The conditions for sample no. 2 are the same as those for the RMC run for c-GST.

After more than 500 000 (acceptance) steps, as we expected, we found that, under the conditions, the experimental data were easily fitted for sample no. 1 while sample no. 2 did not provide an acceptable fit. In the last two rows of the table 1 we show  $\chi^2$  after about 500 000 steps as the indices for the fitness. The values of  $\chi^2$  are relative values and depend on the experimental error.

The results for two samples are shown in figure 3. For all the cases including the cases shown later, we ran RMC analysis for more than 500 000 (acceptance) steps and confirmed that  $\chi^2$  for the fitness was not improved any further. In figure 3, total structure factors for XRD and the Te, Ge and Sb spectra of EXAFS for the model and measured data are plotted. During RMC analyses, the amplitudes of the structure factors and EXAFS spectra are renormalized and the constant backgrounds are also subtracted in order to construct correct  $g_{ij}(r)$ s. Therefore the scale of the vertical axis may be different in each figure.  $F^M(Q)$  and  $\chi^M(k)k^3$  for Te and Sb for both samples have almost the same behaviours.

The obvious disagreement with the experimental data appears in the Ge EXAFS spectrum.  $F^M(Q)$  and other  $\chi^M(k)k^3$  seem to be in agreement with the experimental ones. Even after 1000 000 s acceptance RMC steps the fitness was not improved any more. The conditions, which are listed in table 1, are mainly determined to resolve this disagreement. Sample nos 3, 4, and 5 are cases in which the  $r_c$  of Ge–Ge and Sb–Sb pairs are set smaller than those for sample no. 2. These cases had, to greater or lesser degrees, the same sort of disagreement in Ge spectrum as in sample no. 2. Those results are not shown here. For all cases, the small differences in  $r_c$  do not significantly affect the XRD pattern and EXAFS spectra of Te and Sb. Sample nos 6 to 9 are cases in which the  $r_c$  values for Ge–Sb pairs are set to be smaller than those for sample no. 2. These four results showed better improvements for the Ge spectrum, and the fitness is reasonably acceptable. Sample no. 10 produced a good model that is in agreement

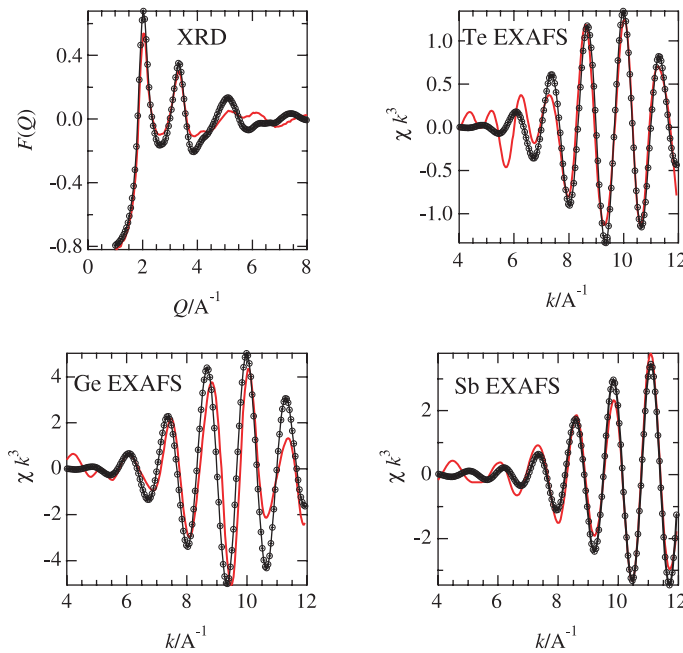


**Figure 3.** The comparisons with  $F^E(Q)$ ,  $F^M(Q)$ ,  $\chi^E(k)k^3$  and  $\chi^M(k)k^3$  of two models for a-GST. The left-hand side figures are for sample no. 1; the right-hand side for sample no. 2. The black lines with symbols represent experimental data and the bold red lines are for the RMC model.

with the four experimental data. We can see from table 1 that  $\chi_{\text{Ge}}^2$  approximately decreases with decreasing  $r_c$  for the Ge–Sb pair. We think the models for sample no. 1 and sample nos 6 to 10 are structural models which account for the experimental data. The most severe condition in the  $r_c$  constraint for a reasonable model in comparison with the nearest-neighbour distance in the crystalline state is sample no. 7. The model that we are looking for can exist in conditions near the conditions of this case. The model can be thought of as the closest model of a-GST to the structure of c-GST. The results for sample no. 7 are shown in figure 4.

Next, we carried out RMC analyses, again starting from the same initial configuration with other constraints in which the parameter  $\delta$  is set to be zero. When  $\delta$  for a Ge atom is set to be zero, Ge atoms do not move at all from the initial condition. We call this additional condition

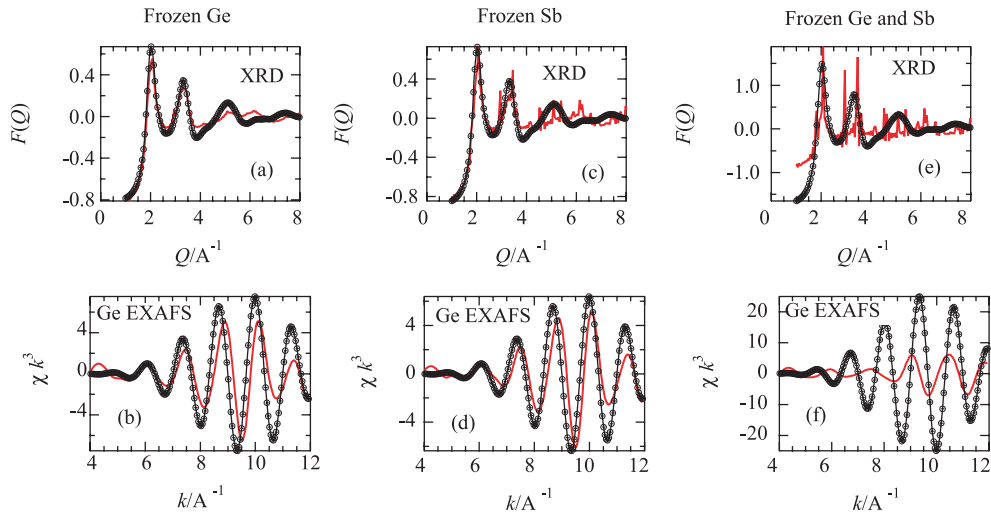




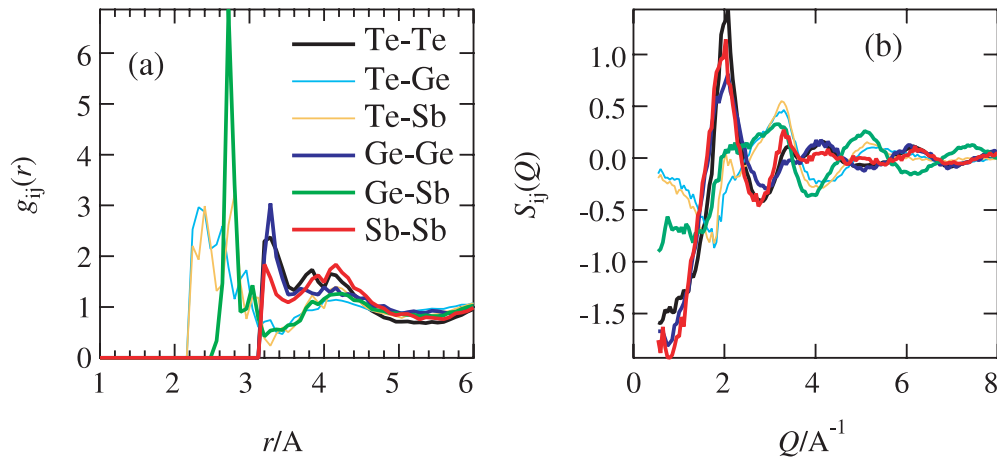
**Figure 4.** The RMC results for sample no. 7 for a-GST. The black lines with symbols represent experimental data and the bold red lines are for the RMC model.

*frozen* Ge here. When  $\delta = 0.3 \text{ \AA}$ , Ge atoms move freely, although the maximum movement per jump is restricted. In this condition, the constraint may be called *free* Ge. All the conditions appearing in table 1 are *free* atom conditions. We applied *frozen* Te, *frozen* Ge, *frozen* Sb and *frozen* Ge and Sb conditions to sample no. 7 and started RMC analyses again from the same initial configuration that is shown in figure 1(c). The results of these RMC analyses were as follows:  $F^M(Q)$  for XRD does not provide the overall features of amorphous structure and shows many Bragg peaks corresponding to the sub-lattice of a crystalline structure. This is taken to mean that the model was not fitted to XRD data. However, three EXAFS spectra were comparably reproduced. For the condition of *frozen* Ge, the obtained spectrum did not change significantly in comparison with the results for conditions in which all atoms are *free*. That is, the results were almost the same as shown in figure 4. For the conditions of *frozen* Sb and *frozen* Ge and Sb, we have Bragg peaks in the  $F^M(Q)$  of XRD. The results for  $F^M(Q)$  and  $\chi^M(k)k^3$  are shown in figures 5(a)–(f). The clear inference from these figures is that if the relative distance between Ge and Sb atoms does not change, the EXAFS spectrum of Ge cannot be reproduced correctly.

Finally we show, in figures 6(a) and (b), the resultant partial radial distribution functions and partial structure factors for sample no. 7 for the condition of all *free* atoms. We can see the fine structures between 2.0 and 3.0  $\text{\AA}$  of  $g_{ij}(r)$  which reflect the EXAFS spectra. From figure 6(a), there seem to be longer and shorter pairs not only for Te–Ge, as Kolobov *et al* mentioned [23], but also for Te–Sb pairs within the first shell and for Te–Te and Sb–Sb pairs between 3.2 and 4.5  $\text{\AA}$  approximately. It is very surprising that there is a distinctive peak in  $g_{\text{GeSb}}(r)$  at 2.7  $\text{\AA}$ , because there has been no experimental evidence showing a strong bond for Ge–Sb pairs in this alloy system.  $S_{\text{GeSb}}(Q)$  does not show a sharp first peak like  $S_{\text{TeTe}}(Q)$ ,  $S_{\text{GeGe}}(Q)$  and  $S_{\text{SbSb}}(Q)$ . It has a characteristic shape, suggesting the formation of a molecule or



**Figure 5.** The RMC results (XRD and Ge EXAFS) for sample no. 7 with the addition of the conditions of *frozen Ge*, *frozen Sb* and *frozen Ge and Sb* for a-GST. The black lines with symbols represent experimental data and the bold red lines are for the RMC model.



**Figure 6.** The  $g_{ij}(r)$  and  $S_{ij}(Q)$  obtained from the result for sample no. 7. The corresponding  $F^M(Q)$  and  $\chi^M(k)k^3$ s are shown in figure 4.

chain-like cluster. It is also very interesting that the coordination distance between Ge and Sb atoms became shorter from 4.2 Å to less than 2.7 Å. It is clear from a series of RMC analyses that the Ge EXAFS spectrum is responsible for this shorter bond.

#### 4. Discussion

From a series of analyses, it is an obvious fact that most atoms have to move more or less when the structure changes from a crystalline to an amorphous state. We have not shown the best-fit case. If we pursue the best-fit models for the experimental data for amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin

film, we would have to explain the severe situation of the shorter distances of Te–Te and Sb–Sb pairs.

We think that the bonding between Ge and Sb atoms governs the structural change from the crystalline phase to the amorphous phase of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin film. We calculated the average coordination number around each atom  $i$ ,  $N_c^i$ , for sample no 7. The coordination distance for the first shell was determined to be 3.20 Å from the partial radial distribution functions. The values of  $N_c^{\text{Te}}$ ,  $N_c^{\text{Ge}}$  and  $N_c^{\text{Sb}}$  were 2.3, 3.7 and 3.8, respectively. These values are not too high for the coordination number of this system [30]. We also calculated the coordination numbers corresponding to the  $g_{\text{GeSb}}(r)$  at 2.7 Å, and it was about 1. Therefore the present result suggests that Sb has a four-coordinate within 3.2 Å distance because of a Ge atom nearby. This result is in conflict with that of a recent EXAFS study by Baker *et al* [30]. They applied bond constraint theory to the results obtained from  $k^3$ -weighted EXAFS spectra and say that the Ge–Sb pair could not be fitted using either Ge or Sb data. The average coordination numbers up to  $\sim 4.5$  Å, which are not shown here, do not change significantly in comparison with those of c-GST, while the coordination numbers within the first shell become lower. We can calculate the coordination number distributions and average coordination numbers for each pair. But this would be premature in the present work. In Kolobov *et al*'s model, Ge atoms mainly relax and move to the special sites. The present result is consistent with their model at that point. Their model does not tell us about significant features of the Sb–Ge pair. The present result for Sb–Ge pairs should be verified with complementary data such as neutron diffraction. Similar RMC analyses of a-GST thin film, adding neutron diffraction data, are necessary to establish the fine structure more clearly. The concrete 3D model for the structural change from crystal to amorphous GST thin film will be constructed using simultaneous fitting with more experimental data.

## 5. Conclusions

Considering the known information, we have constructed a model of the crystalline structure of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin film using RMC analysis with x-ray powder diffraction data, which was given as a well-relaxed NaCl-type structure. Taking over the structural properties, we can construct the closest model of the amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin film to the crystal structure using RMC analyses with a XRD and three EXAFS spectra data. We demonstrate that if EXAFS spectra are sensitive in the components system, the combination of XRD and EXAFS data is useful for a structural analysis of the ternary alloy. From a series of RMC analyses with various constraints, we found that the pair with the largest deviation from the crystal state is the Ge–Sb pair, and the distance is less than 2.7 Å. This is mainly responsible for the Ge EXAFS spectrum.

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## References

- [1] McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
- [2] Nield V M, How M A and McGreevy R L 1991 *J. Phys.: Condens. Matter* **3** 7519
- [3] Arai T and McGreevy R L 1999 *Phys. Chem. Liquids* **37** 455

- [4] Arai T and McGreevy R L 1998 *J. Phys.: Condens. Matter* **10** 9221
- [5] Wicks J D and McGreevy R L 1997 *Phase Transit.* **61** 195
- [6] McGreevy R L and Zetterström P 2003 *Curr. Opin. Solid State Mater. Sci.* **7** 41
- [7] Nield V M, Keen D A, Hayes W and McGreevy R L 1992 *J. Phys.: Condens. Matter* **4** 6703
- [8] Nield V M, Keen D A, Hayes W and McGreevy R L 1993 *Solid State Ion.* **66** 247
- [9] Montfroy W, McGreevy R L, Hadfield R and Andersen N H 1996 *J. Appl. Crystallogr.* **29** 285
- [10] Nield V M, Keen D A and McGreevy R L 1995 *Acta Crystallogr. A* **51** 763
- [11] Proffen T and Welberry T R 1997 *Z. Kristallogr.* **212** 764
- [12] Welberry T R, Proffen T and Bown M 1998 *Acta Crystallogr. A* **54** 661
- [13] Keen D A, Tucker M G and Dove M T 2005 *J. Phys.: Condens. Matter* **17** S15
- [14] Arai T and McGreevy R L 2005 *J. Phys.: Condens. Matter* **17** S23
- [15] Gurman S J and McGreevy R L 1990 *J. Phys.: Condens. Matter* **2** 9463
- [16] Wicks J D and McGreevy R L 1995 *J. Non-Cryst. Solids* **192/193** 23
- [17] Winterer M 2000 *J. Appl. Phys.* **88** 5635
- [18] Winterer M, Delaplane R and McGreevy R 2002 *J. Appl. Crystallogr.* **35** 434
- [19] McGreevy R L 2001 *J. Phys.: Condens. Matter* **13** R877
- [20] Yamada N, Ohno E, Nishiuchi K, Akahira N and Takao M 1991 *J. Appl. Phys.* **69** 2849
- [21] Yamada N and Matsunaga T 2000 *J. Appl. Phys.* **88** 7020
- [22] Matsunaga T and Yamada N 2002 *Japan. J. Appl. Phys.* **41** 1674
- [23] Kolobov A V, Fons P, Frenkel A I, Ankudinov A L, Tominaga J and Uruga T 2004 *Nat. Mater.* **3** 703
- [24] Prince E (ed) 2004 *International Tables for Crystallography* vol C *Mathematical, Physical and Chemical Tables* 3rd edn (Berlin: Springer)
- [25] Sato M, Matsunaga T, Kouzaki T and Yamada N 2004 *Mater. Res. Soc. Symp. Proc.* **830** 245
- [26] Kolobov A V, Haines J, Pradel A, Ribes M, Fons P, Tominaga J, Katayama Y, Hammouda T and Uruga T 2006 *Phys. Rev. Lett.* **97** 035701
- [27] Stern E A, Sayers D E and Lytle F W 1975 *Phys. Rev. B* **11** 4836
- [28] Pusztai L and McGreevy R L 1997 *Physica B* **234–236** 357
- [29] Møllergård A and McGreevy R L 2000 *Chem. Phys.* **261** 267
- [30] Baker D A, Paesler M A, Lucovsky G, Agarwal S C and Taylor P C 2006 *Phys. Rev. Lett.* **96** 255501