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Si₂Te₃ Dimer Orientation Structure

Faculty Sponsor

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Abstract

Experimental material data can often be lacking; reasons include lack of interest, as well as lack of feasibility. This lacking can be made up for through computational modeling, which is less costly and time consuming than experimental testing. The aim of this study was to examine the unique structure of Si_2Te_3 and to determine possible phase transitions that result from the orientation behavior of the silicon dimers that comprise the compound. Results showed the continuation of near absolute zero behavior up to a sudden phase transition occurring around 50°K . This was followed by a more gradual phase transition starting at 200°K that continued until the sudden transition at 623°K noted by prior research that renders the study's implemented model physically irrelevant. A degree of dimer organization was maintained at all temperatures up to the model limit of 623°K .

Introduction

There is a near limitless amount of possibilities when it comes to the design of material research experiments. However, due to the finite resources and time available to researchers, experiments must be chosen pragmatically; the costs and projected benefits of experimental research into a given material must be weighed in order to make a proper choice of study. For this purpose computational physics proves invaluable. Simulating physical phenomena in material provides a resource light alternative to experimental research that can provide insight into potential discovery. It effectively produces strong hypotheses to motivate experimental research. This study was founded on a similar motive. The behavior of silicon dimer orientations in Si_2Te_3 is poorly studied in experimental research. This dissatisfaction is further compounded by a disagreement between experimental and computational studies concerning the composition of dimer orientations [1-3]. The perceived lacking in experimental research and the disagreement with recent computational research provides the basis for this study is motivated.

Si_2Te_3 naturally forms in a unique configuration consisting of a hexagonal lattice of tellurium atoms, with two out of every three hexagons being filled with a pair of bonded silicon atoms [2,3]. This silicon pair, called a dimer, can occupy one of four different orientations as shown in Figure 1. These lattices then stack to form multilayered structures. This structure is fairly unique, making research lack commonality with other materials.

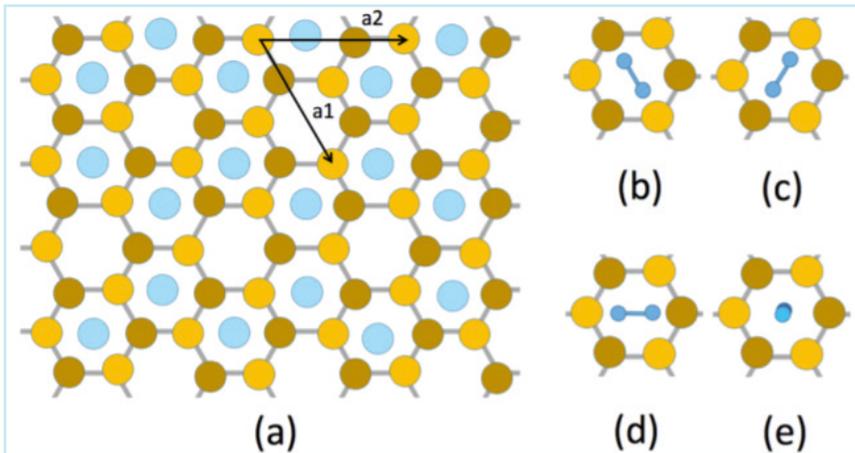


Figure 1: (a) A diagram of a Si_2Te_3 lattice. (b-d) The three in-plane dimer orientations. (e) The out-of-plane dimer orientation. [1]

X-Ray and electron diffraction experiments indicate an equal distribution of the four orientations among all dimers [3]. However, recent computational research has indicated a temperature dependence of the orientation distribution that doesn't align with the diffraction experiments [1]. It is most likely that the highly perturbative nature of the experimental methods excites the dimers and leads to this discrepancy. It is this discrepancy and computational research that this study is based upon. The goal is exploratory; to study the distribution of dimer orientations at various temperatures up to the phase transition temperature of 623° K where the dimers disassociate, and the silicon atoms cease to pair.

Methods

Application of Monte Carlo

The dimer orientation behavior of a single sheet of Si₂Te₃ was determined through the Metropolis Monte Carlo method. It is a statistical method used to find the average behavior of a system through a statistical sampling of system states. The set of all system states is treated as a Markov chain, with the probability of transitioning from one state to a neighboring perturbation being equal to the ratio of the weights of the two states. The sampled states were chosen by attempting random perturbations of the state and accepting the new perturbed state based on the transition probability in the Markov chain. The weighting function for the states was chosen in the study by treating the Si₂Te₃ system as a canonical ensemble. Due to this choice, any measurable calculated using this method is an approximation of the expectation value of the measurable. [4]

Choice of measurables

Two aspects of the dimer layout were chosen for examination. The first was the total system energy or Hamiltonian. Since the stored energy in the system comes exclusively from the interaction of neighboring mismatched dimer orientations, this serves as a rough benchmark for the disorder present in a given state. The second aspect was the layout of connected regions of like orientations. The ability of the dimer orientations to organize into distinct regions is a significant indicator of order and contains information the Hamiltonian does not detail, thus warranting observation. The specific observables measured for the simulation were the Hamiltonian, the number of major connected regions, the average region size by orientation, and the average centers for connected regions. Major regions were chosen to be those large enough to not be considered minor chance fluctuations, and thus required to contain at least 5% of the total number of dimers.

There were three metric scenarios considered for comparison. The first was the completely ordered scenario; here all dimers are aligned in parallel. This is the simplest scenario that occurs at 0° K and similar low temperatures. The second is the completely disordered scenario where all dimers are equally likely to be in any state. The last scenario is the disordered scenario where all dimers are equally likely to be in any in-plane orientation. This last scenario was included for comparison due to the much larger energy contribution the out-of-plane (OOP) orientation caused when interacting with in-plane orientations [1].

Results

For the simulation a ten-by-ten Si₂Te₃ lattice was used. Larger lattices showed identical behavior but ran at exponentially higher times to produce similar quantities of data. The measurables of the metric scenarios are shown in Table 1 and were used to benchmark the system behavior at various temperatures.

	Hamiltonian (meV)	Major regions	Average region size of present orientations (% of all dimers)
Ordered	0	1	100%
Disorded	1674	2.17	2.2%
Mostly Disordered	350	3.7	2.65%

Table 1. Measurable values of the three metric scenarios.

The Hamiltonian was determined over the range of relevant temperatures and experienced a sudden rise between 30° K and 70° K, followed by a period of constant growth before accelerating again gradually starting at 200° K. This is shown in Figure 2.

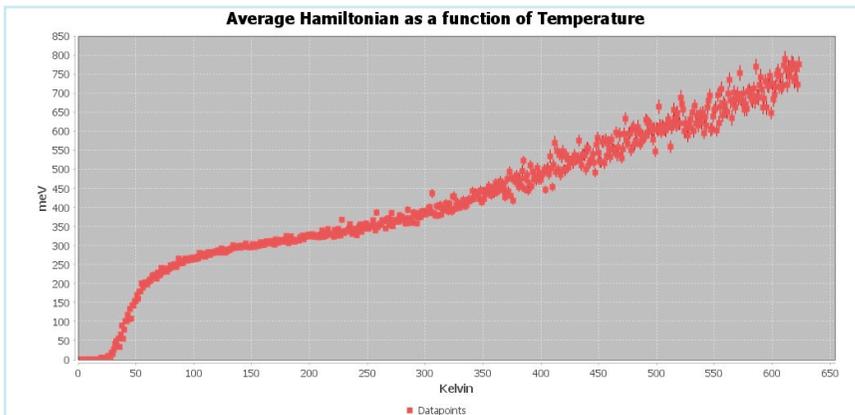


Figure 2. System Hamiltonian behavior over temperature

The number of major regions showed a similar sudden transition in behavior between 30° K and 70° K, but no additional behavior past 200° K. This is shown in Figure 3.

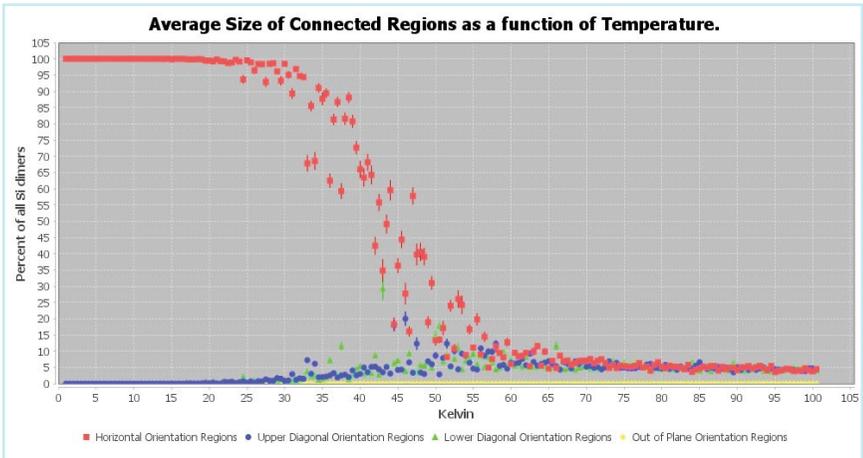


Figure 3: System major region count over temperature

The sudden behavior change between 30° K and 70° K is continued in the average region size behavior; during this temperature range misaligned orientations begin to be prevalent. Similarly at 200° K the out of plane orientation starts to become prevalent, but not prior. Two graphs of the behavior are shown in Figures 4 and 5; 5 contains a higher temperature resolution calculation of the 30° K to 70° K range.

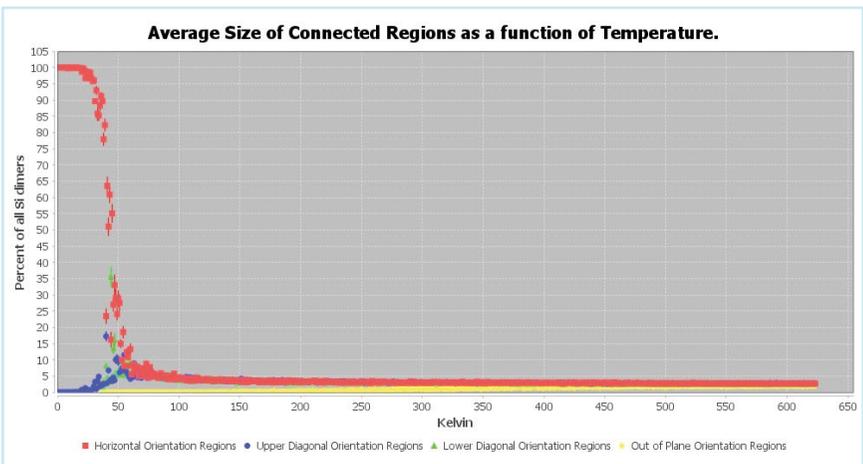


Figure 4: System region size behavior over temperature

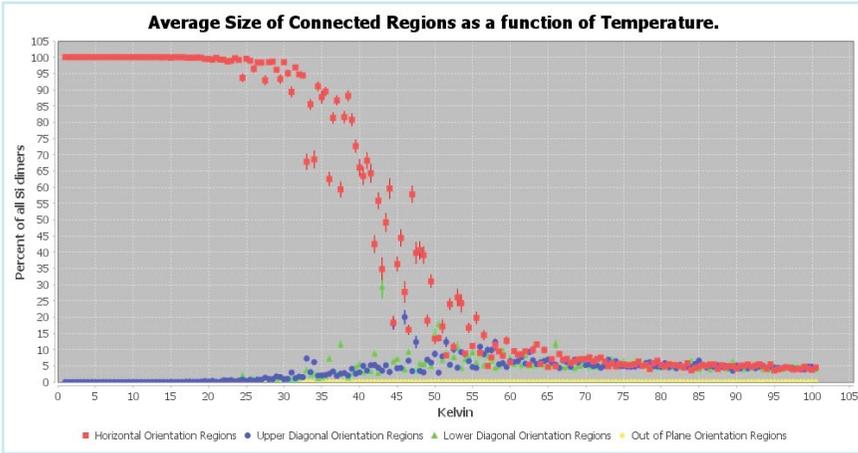


Figure 5: System region size behavior over temperature

Additional unexpected behavior was found when measuring the average connected region centers. When perturbations in the ordered metric scenario begin to be prevalent, they usually are clustered around the sides of the lattice. This similarly occurs for the OOP orientation when it becomes prevalent at around 200° K. After each of these initial periods of growth from the side perturbations become more prevalent in the middle of the lattice. This first insulating effect is shown in Figure 6, and second one in Figure 7.

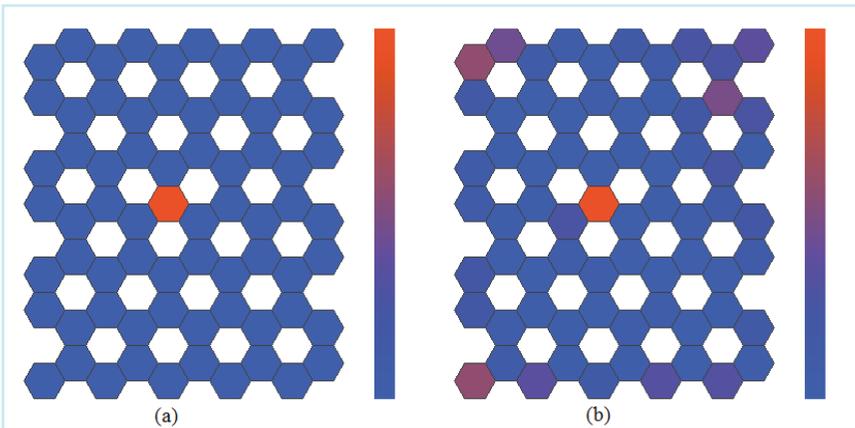


Figure 6: Heatmaps of region centers over the course of Monte Carlo sampling at various temperatures. (a) 10° K, 100 counts (b) 35° K, 55 counts.

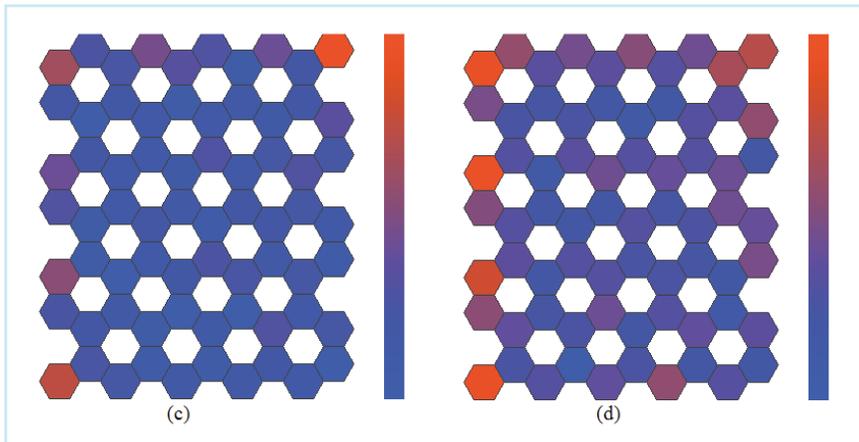


Figure 6 (continued): Heatmaps of region centers over the course of Monte Carlo sampling at various temperatures. (c) 50° K, 65 counts (d) 60° K, 55 counts. (c) 50° K, 65 counts (d) 60° K, 55 counts

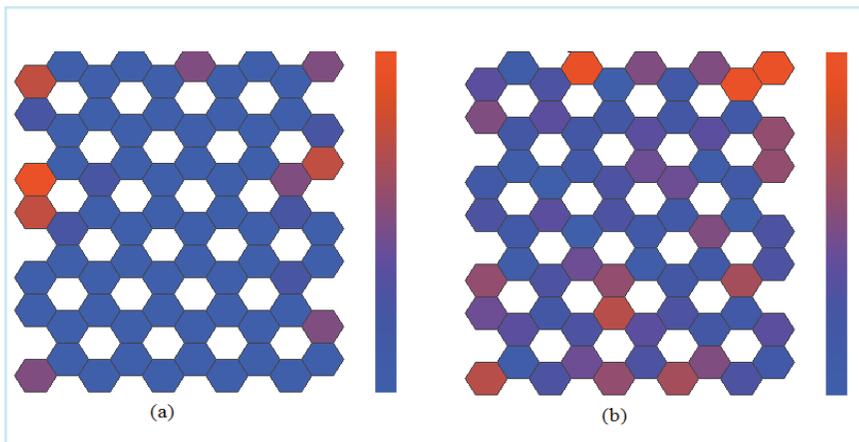


Figure 7. Heatmaps of out of plane (O.O.P.) orientation region centers over the course of Monte Carlo sampling at various temperatures. (a) 225° K, 4 counts (b) 585° K, 14 counts

Discussion

Two phase transitions can be observed: one centered at 50° K and another gradual transition starting at 200° K. The ordered, or 0° K, scenario is maintained closely up to the sudden first transition. This first transition occurs due to the temperature being high enough to allow misalignments to become commonplace. Additionally, the second transition occurs when the temperature is high enough that the OOP dimer orientation, which requires the most energy, can occur, although not frequently. Both the

completely disordered and in-plane disordered scenarios are not reached at any temperature. Some measurables are reached, such as the Hamiltonian, but never all. This implies that at all temperatures up to the known dimer dissociation transition at 623° K the dimer orientations never truly randomize. Additionally, these phase transitions are accompanied by an insulating effect where in the early stages of each transition perturbations in the status quo mostly appear on the edges of the lattice.

Two primary sources of error can be identified as part of the Monte Carlo method. The first is the standard deviation in the measurable that is averaged from the sampled states. This was dealt with by increasing the sampling size, but the downside of increased calculation time made large lattice calculations time consuming. The second error source is from domain boundaries. Since the sampled states are more likely to perturb towards the lower energy states of their neighbor perturbations, it is possible for sampled points to become trapped in a local minimum. This can cause multiple identical Metropolis Monte Carlo simulations to return measurables with very small standard deviations, despite having large differences between them. This is the error source causing the large spread observed in the later temperatures of Figure 2 and 3, as well as the phase transition shown in Figure 5. In this case the only solution would be to increase the lattice size in order to make local minimum trapping less likely. Since the spread caused by this was not enough to obscure the overall behavior, this was not an issue of concern in the study. In future work comparing the results to experimental data, quantitative fits of these curves will be necessary, and thus greater precision that was not needed here will be required.

Conclusion

Two proposed phase transitions for Si₂Te₃ in the low temperature range have been calculated using statistical methods. Since the orientation of a dimer causes a perturbation in the surrounding tellurium lattice, and thus affects the expansion of the material, it is possible that these transitions can be observed on the macro level by a varying coefficient of thermal expansion due to the varying prevalence of orientations and a non-uniform expansion throughout the material due to the insulating effect [1]. Since the results are concerning a single layer of Si₂Te₃, additional study is required to determine similar behavior in multilayer samples.

There were three metric scenarios considered for comparison. The first was the completely ordered scenario; here all dimers aligned in parallel. This is the simplest scenario that occurs at 0° K and similar low temperatures. The second is the completely disordered scenario where all dimers equally

likely to be in any state. The last scenario is the disordered scenario where all dimers was equally likely to be in any in-plane orientation. This last scenario was included for comparison due to the much larger energy contribution the out-of-plane (OOP) orientation caused when interacting with in-plane orientations [1].

Funding

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