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Role of vacancies in the high-temperature pseudodisplacive phase transition in GeTe

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To date, the high-temperature phase transition $R3m$-$Fm\bar{3}m$ in GeTe is commonly believed to be second-order displacive with an anomalous volume contraction at the phase transition temperature, T_{PT}, from diffraction measurements. Three main results are here reported: (i) the phase transition is accompanied by latent heat absorption, (ii) in the high-resolution x-ray-diffraction powder pattern the cubic phase appears before the merging of the rhombohedral peaks, and (iii) the cubic phase possesses a larger amount of germanium vacancies than the rhombohedral phase. From results (i)–(iii) we conclude that the phase transition is not purely second-order displacive and that the volume contraction observed at T_{PT} can be explained with the formation of vacancies in the cubic phase.

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According to previous neutron scattering [1–3] and x-ray diffraction studies [4], crystalline GeTe is rhombohedral ($R3m$) at ambient conditions and it undergoes a second-order displacive phase transition to cubic $Fm\bar{3}m$ between 600 and 750 K depending on the carrier concentration. The phase transition is accompanied by a contraction of the unit cell volume [1], which is unexpected for a purely displacive phase transition [3]. Recently, extended x-ray-absorption fine-structure spectroscopy and Raman spectroscopy [5], pair distribution function [6], and time-domain terahertz spectroscopy [7] studies have questioned the pure displacive character of the phase transition which can be better described as being of an order-disorder type. The misinterpretation of the nature of the phase transition was attributed to the "pitfalls of averaging effects" of diffraction, which probes the ensemble average structure, but is insensitive to random local distortions [5]. The renewed interest in the structure is well explained by the exceptional properties of GeTe in the field of phase change materials for data storage [8–11] and as a thermoelectric [12,13]. Furthermore, GeTe was reported to be the first example of a diatomic narrow-gap semiconductor with a displacive transition to a ferroelectric phase [14]. The structure and the exceptional properties in GeTe have been rationalized in terms of resonant bonding effects [15–17] which arise from the three p-electrons forming six covalent bonds in an ideal or slightly distorted octahedral coordination [18,19]. Resonant bonding effects result in anomalously large Born effective charges and dielectric constants in GeTe [18].

In this work we investigate the nature of the phase transition by means of differential scanning calorimetry (DSC). We further explore the structure of GeTe from 115 to 888 K by means of high-resolution x-ray diffraction carried out at BL44B2 [20] at SPring-8. The use of x-rays instead of neutrons is motivated by the lower instrumental peak broadening, which allows a better inspection of subtle structural changes such as the present phase transition.

Overall, the present study shows that the phase transition is not purely second-order displacive and that the cubic structure is more cation-defective than the rhombohedral phase, which explains the volume contraction at the phase transition temperature, T_{PT}. Details on the experiments and refinements are given in the Supplemental Material [21]. References cited in the Supplemental Material include Refs. [22–24].

I. DSC MEASUREMENT

According to the classical thermodynamic classification of phase transitions, in a second-order phase transition the first derivatives of the free energy with respect to temperature and pressure are continuous, whereas a discontinuity occurs in the second derivatives. At constant pressure, these derivatives correspond to entropy and heat capacity:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_P = \frac{-C_P}{T}. \tag{1}$$

At T_{PT}, $\Delta G = \Delta H - T\Delta S = 0$, hence,

$$\Delta S = \frac{\Delta H}{T}. \tag{2}$$

Since in a second-order phase transition there is no discontinuity in the entropy curve, $\Delta H = 0$; i.e., no latent heat can be associated with the phase transition. Calorimetric techniques can be used to assess the type of the phase transition. The DSC analysis conducted on 82.83 mg of GeTe between 303 and 848 K at 10 K/min under the argon atmosphere reveals a small endothermic/exothermic peak upon warming/cooling between 645 and 665 K (Fig. 1). This temperature corresponds to the transition $R3m$-$Fm\bar{3}m$ as seen by diffraction (see below). From this simple measurement, it can be concluded that a small energy barrier exists between the rhombohedral and cubic phases; i.e., the phase transition is of a first-order type and not of a second-order type as it is commonly believed. The

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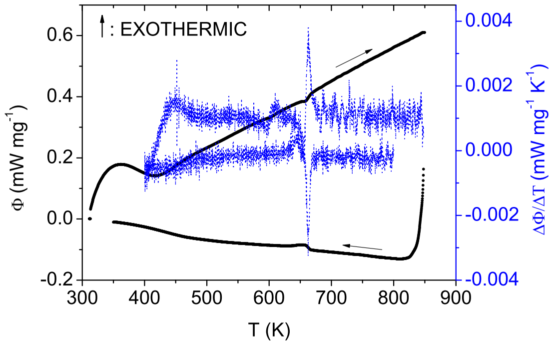

FIG. 1. DSC signal and its derivative as a function of temperature. The slope is different from zero due to the sample heat capacity.

energy barrier between the two phases is 2.9 meV per formula unit of GeTe.

II. HIGH RESOLUTION POWDER X-RAY DIFFRACTION

High-resolution x-ray powder diffraction patterns were collected at BL44B2 [20], SPring-8. Profile fittings and Rietveld refinements were carried out in JANA2006 [25]. A discontinuity in the cell volume expansion is found in proximity to the phase transition temperature in accordance with previous neutron studies [1,3] (see Fig. S3 in Ref. [21]). Also, when the refinements are carried out on a single phase, the increase of ADPs with temperature exhibits a "kink" at T_{PT} [1,3] and the R factors increase close to T_{PT} [1]. If the phase transition is purely displacive the rhombohedral distortion will gradually decrease with temperature until the cell becomes cubic. This is mathematically represented by the angle of the rhombohedral primitive cell, α_R, that becomes 60° when the structure is cubic. In this scenario, Bragg diffraction peaks that split in the powder pattern when the structure is rhombohedral gradually approach in 2θ and completely overlap when the structure is cubic. In fact, the rhombohedral peaks gradually approach and the rhombohedral angle approaches the theoretical values of 60° (see Table S2 in Ref. [21]). However, as shown in Fig. 2, a peak belonging to the cubic phase appears at $T = 631$ K before the rhombohedral peaks overlap, i.e., at $\alpha_R = 59.315(8)^\circ$. Between 631 and 692 K the intensity of the cubic peaks increases at the expense of the rhombohedral peaks, which continuously approach in 2θ. At $T > 692$ K only the cubic peak persists. This infers that the transition $R3m$-$Fm\bar{3}m$ represents a discontinuity which rules out the purely displacive character of the phase transition. The structural model including the sole $R3m$ phase (model 1, see Sect. S4 in Ref. [21]) cannot properly fit the powder data between 631 and 692 K given the simultaneous presence of the cubic and rhombohedral phases. Therefore a second structural model including the cubic phase (model 2) was also tested, leading to a substantial improvement of the R factors between 631 and 692 K. The kink in the ADPs curves close to T_{PT} (Fig. 3) is likely an artifact due to the presence of two phases and to the appearance of anisotropic strain, which unavoidably worsen the Rietveld fitting. Such a kink is smoothed out (even canceled for the Te atom) when a structural model including two phases is used to correctly describe the presence of the cubic and rhombohedral phases (Fig. 3).

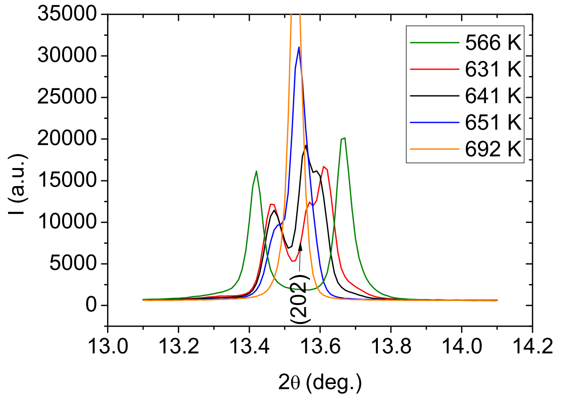

FIG. 2. "Merging" of the $(104) + (1,-1,-4)$ and $(2,-1,0)$ peaks in the hexagonal setting. The (202) cubic peak appears before the rhombohedral reflections overlap and increase in intensity until only the cubic phase is present.

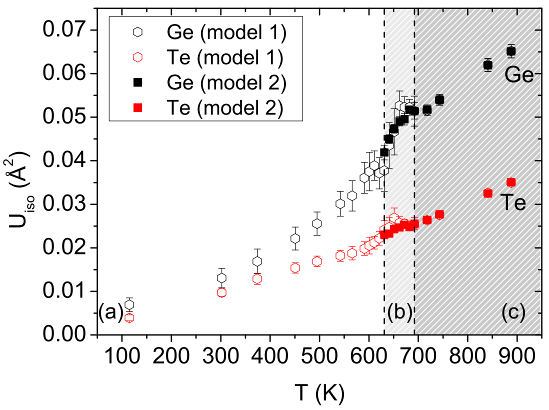

FIG. 3. Isotropic ADPs from a single-phase ($R3m$) refinement (model 1 as reported in Ref. [21]) and from a double-phase refinement (model 2 as reported in Ref. [21]), i.e., including both rhombohedral and cubic phases in the refinement between 631 and 692 K (b), and only the cubic symmetry for $T > 692$ K (c). Details and numerical values are reported in Tables S1–S5 in Ref. [21].

III. OCCUPANCY OF GERMANIUM IN THE TWO PHASES

Like other IV–VI narrow-gap semiconductors [26–28], GeTe is nonstoichiometric due to vacancies of the cation, here germanium [29]. The relative amount of vacancies of Ge with respect to tellurium can be determined through the refinement of the site occupation factor. In the rhombohedral phase the site of Ge is statistically fully occupied (Fig. 4). A clear decrease of the occupancy of Ge occurs in the cubic phase. A large amount of vacancies have been also observed in the phase change material $\mathrm{Ge_2Sb_2Te_5}$ in the cubic phase [9,30–32]. Also, it has been shown that the introduction of vacancies reduces the number of antibonding states close to the Fermi energy in $\mathrm{Ge_1Sb_2Te_4}$ by removal of energetically unfavorable antibonding Ge-Te and Sb-Te interactions [33], although an increase of carrier concentration has been observed in $\mathrm{Ge_1Sb_2Te_4}$ upon the transition from the cubic to the rhombohedral phase [34]. Hence, the present findings call for further high-temperature

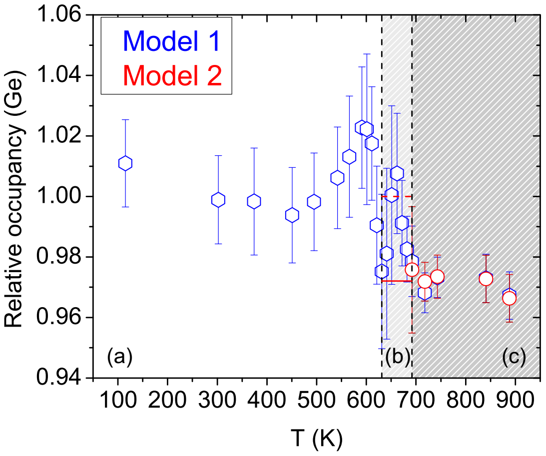

FIG. 4. Relative occupancy of Ge with temperature. In panel (a) only the rhombohedral phase is present, and if occupancy (Ge) is freely refined, it does not significantly deviate from unity. In panel (b) the two phases coexist and the occupancy of Ge in the rhombohedral phase was constrained to unity (dashed line) to avoid overparametrization, whereas the occupancy of Ge in the cubic phase was constrained to the averaged value obtained at $T > 692$ K (continuous line), i.e., when only the cubic phase is present. In panel (c) only the cubic phase is present. A decrease of occupancy (Ge) occurs at T_{PT}. The standard uncertainties from the Rietveld refinement are increased for the Berar's correction factor (see Sec. S4 in Ref. [21]). The averaged values and the root-mean-square deviations at $T < 631$ K and $T > 692$ K are 1.003(14) and 0.972(6), respectively.

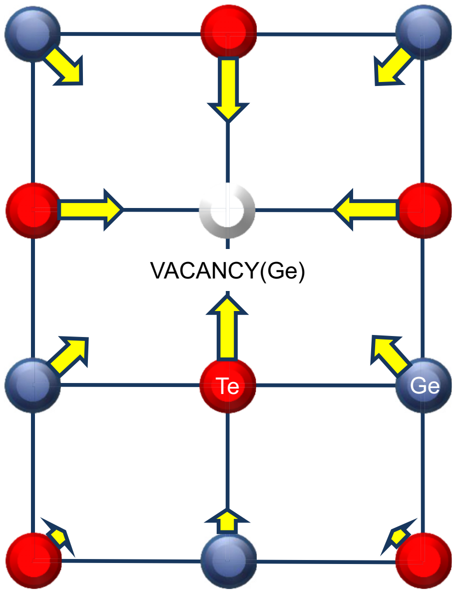

FIG. 5. Local distortions caused by the presence of a vacancy. The increased amount of vacancies in the cubic phase causes a lowering of the averaged unit cell volume at T_{PT}.

charge carrier measurements and theoretical calculations to check whether the number of antibonding states in cubic GeTe is higher than that in rhombohedral GeTe, thus explaining the higher amount of vacancies in cubit GeTe. The "anomalous" volume contraction at the phase transition can be well linked to the higher amount of germanium vacancies in the cubic phase than in the rhombohedral phase. In SnTe, the cell parameter decreases with increasing the carrier concentration and the amount of vacancies of Sn in a linear Vegard lawlike correlation [35]. It is, in fact, expected that the presence of a cation vacancy causes a local displacement of the atoms towards the vacancy (Fig. 5). Such distortion gradually decreases for atoms belonging to successive coordination shells. As a consequence, in GeTe, the volume of the average cell decreases in proximity to T_{PT}. The weak endothermic peak observed at T_{PT} might be related to the formation of germanium vacancies, the cubic phase having around 3% more vacancies than the rhombohedral phase. Hence, the formation energy of a vacancy is estimated to be 0.097 eV, which, however, is remarkably lower than 0.25 eV as calculated from theoretical calculations [36]. The question then arises on the mechanism of the vacancy formation. It is well established that rhombohedral GeTe possesses a submicron herringbone structure with the rhombohedral domain twinning along specific combinations of (100) and (110) planes [37]. We *speculate* that vacancies could form at the twin boundaries. Further experiments, e.g., using multitemperature transmission electron microscopy, will possibly shed light on the mechanism of vacancy formation.

The present study study reveals important aspects of the nature of the phase transition which were not scrutinized by precedent studies. Although being close to a second-order displacive type, the phase transition $R3m$-$Fm\bar{3}m$ possesses a small energy barrier and it is not continuous. We attribute such discontinuity to the formation of vacancies in the cubic phase, which causes a decrease of the unit cell volume at T_{PT}. This adds an important insight into the ongoing debate on the nature of high-temperature phase transition. The mechanism of vacancy formation and whether the high-temperature cubic phase is statically or dynamically disordered in analogy to SnTe [27,38–40], PbS, PbSe, and PbTe [40–43] will be the subject of future studies.

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