Phase-Change Thin Film and Incredibly Large Optical Nonlinearity

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Abstract

Super-resolution near-field structure, Super-RENS has provided an incredibly large optical nonlinear effect in phase-change materials at high temperature. However, the resolution mechanism with such a large nonlinear effect has not been identified yet. Since 2004, we have engaged in understanding the phenomenon step by step, using physical and chemical analysis. It has experimentally been cleared that the large nonlinearity occurs at a boundary of two crystalline phases at more than a specific temperature. We present the most up-to-date model and discuss the incredible phenomenon.

Keywords: Super-resolution near-field structure (super-RENS), ferroelectrics, ferroelectric catastrophe, chalcogenides, GeSbTe, AgInSbTe, strain force, 2nd phase transition.

INTRODUCTION

In *E*PCOS04*, we presented a super resolution model for *super-RENS* optical disk under *ferroelectric catastrophe* by the experimental evidence of *2nd-phase transition* [1]. Recently, it was also confirmed by *Kolobov et al.* that $Ge_2Sb_2Te_5$ is a ferroelectric material, in which a Ge atom position is sifted in between octahedral and tetrahedral coordination in a unit Te cell [2]. As a result, the electronic polarizability of the Ge atom is varied to give the difference of refractive index in between the crystal and the quasi-amorphous. On the other hand, Sb-based alloy, for example, AgInSbTe, also shows nearly the same as or much higher super resolution effect than that of $Ge_2Sb_2Te_5$. Therefore, more generalized super resolution model is required. In this paper, we discuss a new super resolution model under the *Peierls distortion* of chalcogenides, in which metal characteristics transits into dielectric ones under pressure.

PEIERLS DISTORTION

Peierls distortion is a phenomenon that one crystalline phase transits into another under high pressure, in which the metallic properties are lost and dielectric properties are raised instead [3]. For example, let's think about a crystalline phase consisting of a *rhombohedral* lattice with a lattice parameter a. The first *Brillouin zone* is made of in between $-\pi/a$ and π/a in reciprocal lattice. As applying a compressive stress to the phase to transform into a cubic lattice, a new sub-*Brillouin zone* is generated such as in between $-\pi/2a$ and $\pi/2a$. As compressing the phase, the new band couples with the original one to generate a new energy band, as shown in **Fig. 1**. This is called *Peierls distortion* or *transition*. Therefore, in inducing *Peierls distortion*, a high compressive stress of ~ *GPa* order is required. *Peierls* already indicated in 1950s that V group metals and IV-VI group alloys might generate the transition. Actually, several experimental and theoretical works have been done [4,5].

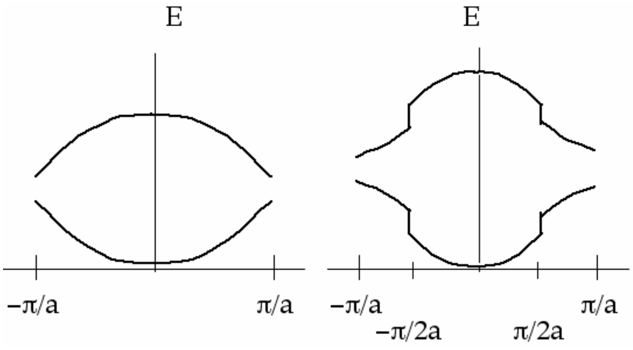

Fig.1 Energy band gap change by Peierls transition
Left: original and right: coupled with sub-band induced by the transition

Let's start from pure antimony, Sb. Sb crystal consists of a *monocrinic* lattice called *A-7*. The 3-D lattice structure is shown in **Fig. 2**. *A-7* usually belongs to *hcp* group, but actually is made of a network sheet of Sb atoms as shown in **Fig. 3**. A bonding energy between the network sheets is very weak in comparison to the energy in the sheet consisting of 3σ bonds. That is, the first Brillouin zone in band energy in Sb almost depends on the σ bonds. However, as increasing compressive pressure, the space between the sheets is crashed and gradually the Sb atoms feel the covalent energy from the neighbor sheet. Finally, as a result, a *simple cubic* (*sc*) phase is newly generated. This image is depicted in **Fig. 4**. The transition from A-7 to sc was experimentally confirmed, and it occurs under a volume reduction of more than 0.5%. *Seifert et al.* calculated the band energies before and after the transition [6] and found a band gap in the *sc* phase. It means that the metallic phase transits into dielectric because of the band gap as shown in **Fig. 5**.

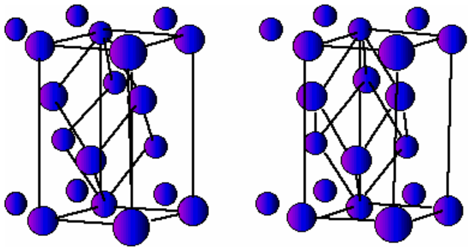

Fig.2 3 dimensional A-7 structure of Sb
Try to catch the left image by your right eye and to catch the right image by your left eye

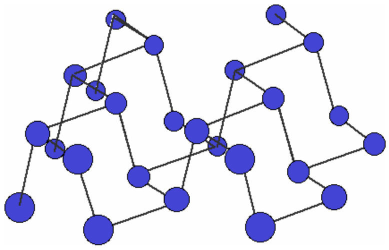

Fig.3 Network connection of Sb atoms in A-7 structure

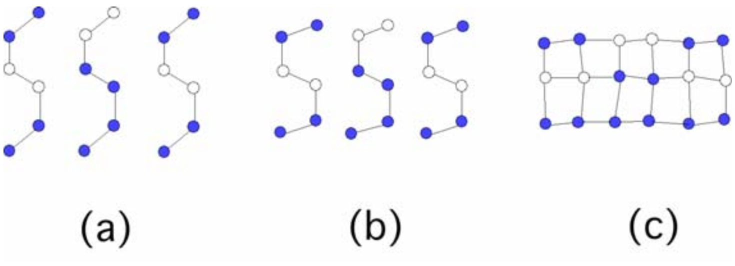

Fig.4 Compressing image of A-7 to sc structure, (a) -> (b) -> (c)

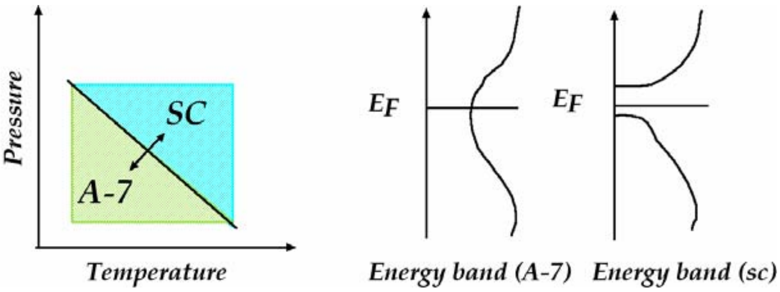

Fig.5 As increasing temperature or increasing pressure, A-7 transits to sc and a band gap is generated at Fermi level

INTERNAL STRESS IN OPTICAL DISK

So, How much pressure is induced in phase change disk actually? *M. Wuttig et al*. have already estimated the internal pressures in GeSbTe (*GST*) and AgInSbTe (*AIST*) [6,7] at the temperature range of 135 °C to 275°C. In case of $Ge_2Sb_2Te_5$, the density of the as-deposited one was 5.87 g/cm^3. After the first phase transition, the phase transited to a *fcc* phase with a density of 6.28 g/cm^3, then finally reached a *hcp* phase with a density of 6.40 g/cm^3. The transition from the *fcc* to *hcp* in the actual mulilayered structure with ZnS-SiO_2 layers was observed by differential Scanning calorimetry (DSC) [8]. According to the results, 0.8% of volume reduction may occur in the disk. The volume reduction in AIST was roughly estimated as 0.5~0.6% as well. However, we have to notice the internal stress is not compressive, but oppositely tensile. As mentioned in *E*PCOS04*, because of the volume reduction at the first phase transition, the phase change film itself wants to crash the volume, but oppositely the dielectric layers must endure the force. So, a very huge stress is left after the 1st phase transition. As increasing temperature further, then the internal stress is gradually modified because the thermal expansion rate of the phase change film is bigger than that of the ZnS-SiO_2. For example, in case of $Ge_2Sb_2Te_5$, the internal pressure shifts towards tensile up to *150 MPa*, but it turns back towards compressive at more than 250°C. Therefore, the Peierls transition never occurs at low temperature in the phase change optical disk, but may occur at a high temperature.

WHAT MAY INDUCE PEIERLS TRANSITION?

The important key to trigger the Peierls transition is a compressive stress below the melting point. Let's think about a simple tube filled with a phase change material in crystal as shown in **Fig. 6**. Hence, the area set at *S*. As laser heats up a central area above the melting point, then a molten region is born in the crystalline tube. The thermal expansion rate of the molten area depends linearly on temperature and it is estimated as 6.53-6.7*10^{-4}T(°C) for Sb, 5.70-3.5*10^{-4}T(°C) for Te, and 5.6-5.5*10^{-4}T(°C) for Ge, respectively. On the other hand, that of the solid also depends on temperature, but it value for $Ge_2Sb_2Te_5$ is about 1.8*10^{-5}T(K). According to the comparison, the molten area's expansions of Te and Sb are 12 and 24 fold bigger than that of the solid crystal $Ge_2Sb_2Te_5$ at 600°C, respectively. According to the result, we can estimate the internal pressure at 600 °C with the Yong's modulus ***E***:

$$\sigma + = \mathbf{E}\ \Delta lS/lS = 50\text{x}\ (0.28\text{-}0.048) = 11\ GPa.$$

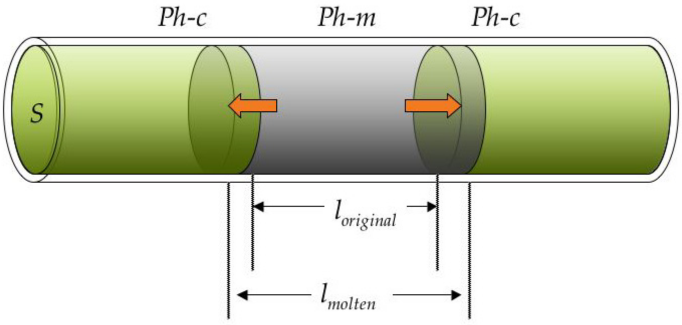

Fig. 6 Simple model to induce a high pressure to solid phase (Ph-c) from molten phase (Ph-m) The tube 's cross-section is S.

Hence, the value of the molten expansion rate of $Ge_2Sb_2Te_5$ was roughly estimated as the composition ratio. It should be notified that the internal pressure σ+ more increases as the Sb composition becomes rich. Therefore, once a molten area is generated in the tube in the model, more than 20% volume expansion is expected, which is enough to realize *Peierls transition* to the surrounding solid phase to transit A-7 to sc structure in Sb alloys.

SUMMARY

Peierls distortion induced in the phase change optical disk probably becomes a source of super resolution when the film is sandwiched by dielectric films with a low thermal expansion. Once a molten area is born in the solid phase, a high pressure of more than 10 *GPa* is generated, which becomes a trigger for the *Peierls transition*.

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