

Review

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Orbital-selective electronic excitation in phase-change memory materials: a brief review

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Abstract: Ultrafast laser-induced phase/structural transitions show a great potential in optical memory and optical computing technologies, which are believed to have advantages of ultrafast speed, low power consumption, less heat diffusion and remote control as compared with electronic devices. Here, we review and discuss the principles of orbital-selective electronic excitation and its roles in phase/structural transitions of phase-change memory (PCM) materials, including $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ and GeTe phases. It is demonstrated, that the mechanism can influence the dynamics or results of structural transitions, such as an ultrafast amorphization of $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ and a non-volatile order-to-order structural transition of GeTe. Without thermal melting, these structural transitions have the advantages of ultrafast speed and low power consumption. It suggests that the orbital-selective electronic excitation can play a significant role in discovering new physics of phase change and shows a potential for new applications.

Keywords: first-principles calculations; light-matter interaction; non-thermal phase transition; optical memory; orbital selective.

Dedicated to Professor Richard Dronskowski on the occasion of his 60th birthday

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1 Introduction

Recently, optical memory and computing technologies have attracted a lot of attention [1–3]. As compared with current electronic devices, optical memory or computing has intrinsic advantages including low power consumption, fast speed, less heat diffusion and remote controllability [4]. Optical phase-change memory (PCM) [5–7] is one of these technologies. The key physical processes of optical PCM are the laser-induced phase transitions in PCM materials [8–16]. Generally, a PCM material has two states including amorphous and crystalline states with significant optical contrast to realize binary (0/1) data storage. For example, the crystalline phase often has a high optical reflectivity while the amorphous phase possesses a low reflectivity. The recording and erasing processes of information can be optically controlled, because the reversible phase changes between the two states can take place under suitable laser irradiation conditions. Also, both the crystalline and amorphous phases are stable at room temperature, which enables a non-volatility of data.

In general, the role of optical excitation in the structural transition was usually regarded as a pure thermal heating effect until theoretical studies revealed a possible non-thermal effect of electronic excitation [17, 18]. For the mechanism based on thermal heating, a shorter but strong laser pulse melts the crystal and quenches it into an amorphous phase while a longer but weak laser pulse anneals the amorphous phase and recrystallizes it [14]. For the non-thermal mechanism, the electronic excitation directly softens specific chemical bonds and thereby leads to a solid-to-solid amorphization without melting [18]. Naturally, such a kind of mechanism should rely on new physical rules and bring about new phenomena. Therefore, optically induced non-thermal phase/structural transitions gain broad interest owing to the potential new physics and applications.

An important rule for the optical excitation is an orbital-selective electronic transition. Although the light irradiation seems homogeneous in a relatively large area, the response of the atoms in a material has been revealed to

be element and orbital dependent by first-principles calculations [19–21]. It is demonstrated that the selective excitation is a critical rule to control non-thermal phase/structural transitions induced by laser excitation [21]. Moreover, the selective excitation is also identified as the origin of some new types of phase/structural transitions [20]. Therefore, the topic should lead new research interests.

Here, we review and discuss the role of orbital-selective excitation in the ultrafast laser-induced phase/structural transitions. We take two recently reported popular PCM materials ($\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ and GeTe alloys) as examples [12, 22], show the basic principle of orbital-selective excitation and how it can influence the phase-change dynamics and results. The method to analyze the electronic orbitals of materials and the corresponding tools are also presented. Finally, outlooks are suggested including the potential advantages of the new type of phase/structural transitions in applications, the inspirations of utilizing the mechanism to control the ultrafast laser-induced phase/structural transitions, the possibility to extend the mechanism to several other material systems, the main problems and the possible solutions of these problems.

2 Principles of orbital-selective excitation

From the point of view of molecular orbital theory, the energy band of a material is composed of different atomic or hybridized atomic orbitals. These orbitals are often mainly located in different energy ranges. Particularly, the valence band maximum (VBM) and conduction band minimum (CBM) often are contributed by different orbitals. If a material is composed of different elements, the difference between the VBM and CBM should be remarkable. For example, Figure 1 shows the orbital-decomposed partial density of states (PDOS) of the $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ alloy calculated by first-principles calculations [21]. The top part of the valence band is dominated by Te-5p orbitals (just below 0 eV) while the bottom part of the conduction band (just above 0 eV) is mainly dominated by the Sc-3d orbitals. Moreover, the Sc-3d orbitals are split into t_{2g} (d_{xy} , d_{yz} , and d_{zx}) and e_g (d_{z^2} and $d_{x^2-y^2}$) orbitals where the distribution of the t_{2g} orbitals is significantly greater than that of the e_g orbitals. In other words, under laser excitation, the electronic transition from the valence to the conduction band means that the electrons are mainly transferred from Te-5p to Sc-3d- t_{2g}

orbitals. Such a kind of orbital-resolved electronic transition upon optical excitation is called orbital-selective electronic excitation here. Laser pulses with different parameters can result in different electronic occupations in the energy space, but the orbital selectivity should still exist. Furthermore, it can be expected that the quantum selection rule of electronic transitions may also lead to orbital-selective excitation in some cases. Note that the analysis tool, the **LOBSTER code**, developed by Prof. Richard Dronskowski and his colleagues has played an important role in the analyses of the orbital-decomposed PDOS [23–26].

3 Influences of selective excitations on phase/structural transitions

The orbital-selective excitation makes the response of a material to optical excitation inhomogeneous on the atomic scale. As a result, the structural transitions should have new dynamics beyond that of the homogeneous thermal melting. For example, Figure 2a shows the time evolution of the bond angle distribution of the $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$

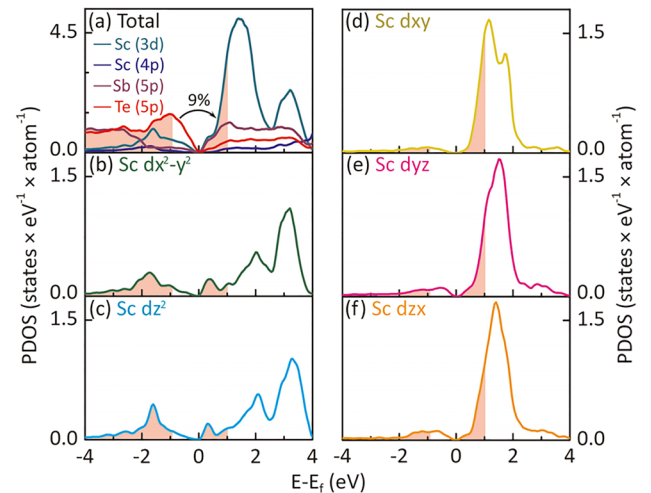


Figure 1: Orbital-decomposed partial density of states (PDOS) of the $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ alloy. (a) Total PDOS of Sc, Sb, and Te. (b)–(f) The d states of Sc decomposed into $d_{x^2-y^2}$ and d_{z^2} , d_{xy} , d_{yz} , and d_{zx} orbitals, respectively. Shaded areas indicate the electronic occupation of a 9% valence electron excitation. The data is calculated by first-principles calculations based on density functional theory (DFT) and then analyzed by the LOBSTER code. Reproduced with permission (ref. [21]). Copyright 2020, Published by Nature Publishing Group under a creative commons attribution 4.0 international License (CC BY 4.0).

alloy in the 9%-valence electron excitation time-dependent density functional theory molecular dynamic (TDDFT-MD) simulation [27]. At about 0.9 ps, the bond angle distribution shows a splitting of 60, 90 and 130° which agrees with the bond angles of 60, 90 and 120° for the d - t_{2g} orbitals, as shown in Figure 2b–e. Note that the bond angle splitting is absent in the ground-state MD of thermal melting. Therefore, it is evidenced that the orbital-selective excitation indeed governs the structural transition under the excitation, which leads to an ultrafast (within 1 ps) solid-to-solid amorphization of the $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ alloy. The schematic picture of the amorphization is presented in Figure 3. The strong Sc–Te bonds make the adjacent Sb–Te bond weaker than normal Sb–Te bonds. The excitation-induced distortion of bond angles further weakens the adjacent Sb–Te bonds and leads to fast amorphization. The integration of crystal orbital Hamilton population (ICOHP) in Figure 3c is used to estimate the strength of chemical bonds. The ICOHP is also analyzed by the LOBSTER code.

The orbital-selective excitation can also result in new structural transitions under specific conditions. For example, first-principles calculations based on DFT and TDDFT-MD simulations revealed a non-volatile order-to-order structural transition in rhombohedral r-GeTe [20]. For r-GeTe, the top part of the valence band and the bottom part of the conduction band are mainly contributed by Te- p and Ge- p orbitals, respectively [22]. In other words, orbital-selective excitation also works since the electrons are transferred from Te- p to Ge- p orbitals under a band edge optical excitation. Different from the case of the $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ alloy, the electronic transition takes place just

in p orbitals and thereby does not lead to a notable change of bond angles. However, the structure of r-GeTe is symmetric in the in-plane (xy) direction but not in the out-of-plane (z) direction. Then, the excitation induced atomic forces are operative only in the z direction since the forces in the xy directions are cancelled to zero. In fact, r-GeTe shows a spontaneous ferroelectric polarization in the z direction, as shown in Figure 4a and b. Under the optical excitation with a proper intensity (such as 1.9% valence electrons in this case), the atomic forces acting on Ge and Te have opposite directions which drive the coherent atom movement along the z axis with opposite directions, that is, corresponding to the A_{1g} mode. As a result, the polarization can be switched to the opposite direction, as shown in Figure 4c and d. Because the polarization switching requires a coherent motion of Ge and Te atoms, the subsequent de-coherence induced by electron-electron, electron-phonon and phonon-phonon couplings can prevent the backward switching. The switching is completed within 1 ps in the simulation. Therefore, a non-volatile order-to-order structural transition as well as ferroelectric switching are achieved by orbital-selective electronic excitations.

4 Conditions for the effectiveness of selective excitation

Obviously, the orbital-selective excitation and its influence on phase/structural transitions are condition dependent. Specific materials, laser parameters and environments are needed to make the orbital-selective excitation effective in the phase/structural transition. Here, we try to summarize the conditions. First, the material should be a compound with different elements. As such, the orbitals of the valence and conduction bands could be more differentiated. Second, breaking structural symmetry are required to produce directional forces upon excitation, and thereby lead to possible order-to-order structural transitions. Third, the duration of the laser pulse should be short enough, such as 100 fs, to guarantee that the non-thermal mechanism works. Generally, a long laser pulse in the nanosecond range, can easily melt the material due to heat accumulation. Fourth, the photonic energy of the laser should match the energy of the BAD of the electronic transitions between different orbitals. Fifth, the temperature has to be carefully controlled because it influences coherent motions of atoms and electron-phonon coupling, and thus will influence the transition. Therefore, a relatively low temperature is favorable for orbital-selective excitation.

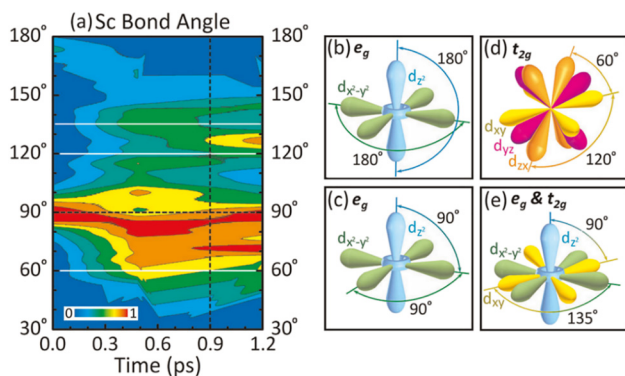


Figure 2: (a) Time evolution of bond angle distribution (BAD) of Sc during the 9%-excited time-dependent density functional theory molecular dynamic simulation. Color bar indicates the normalized intensity. (b)–(e) Schematic pictures of the bond angles of d orbitals. Reproduced with permission (ref. [21]). Copyright 2020, Published by Nature Publishing Group under a creative commons attribution 4.0 international License (CC BY 4.0).

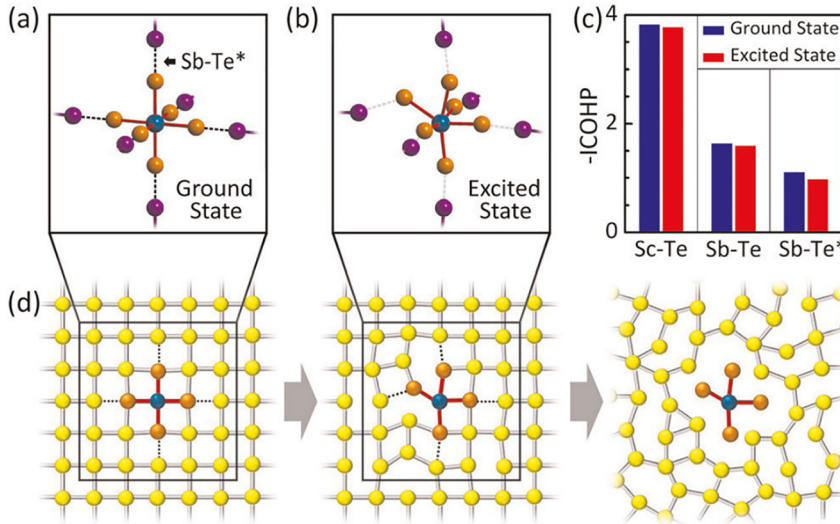


Figure 3: (a)–(b) Schematic Sc-centered motifs. (c) Integration of crystal orbital Hamilton population (ICOHP) of Sc–Te and Sb–Te bonds. (d) Schematic pictures of the amorphization of the $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ alloy.

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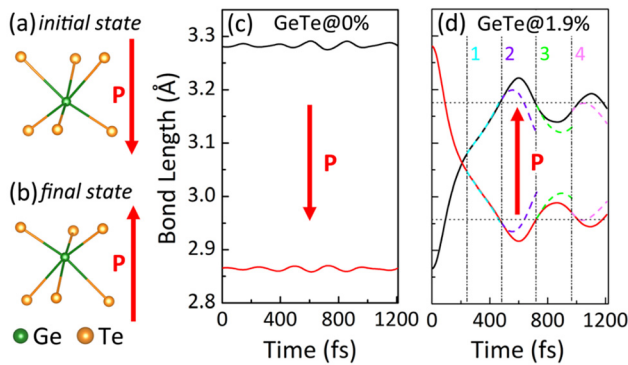


Figure 4: (a)–(b) Structure motifs of rhombohedral *r*-GeTe with opposite ferroelectric polarization directions. (c)–(d) Time evolutions of bond lengths of *r*-GeTe during TDDFT-MD simulations at ground state and excited state, respectively.

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5 Conclusions and outlooks

In summary, we review and discuss the basic principles of orbital-selective electronic excitation and its roles in phase/structural transitions of PCM materials, such as $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ and GeTe alloys. It is shown that the orbital-selective excitation should be one of the important mechanisms for optical excitation. First-principles calculations have demonstrated that the mechanism can indeed influence the dynamics or the results of phase/structural transitions, such as the ultrafast amorphization of the ternary alloy $\text{Sc}_{0.2}\text{Sb}_{1.8}\text{Te}_3$ and the non-volatile order-to-

order structure transition of the binary GeTe. Without thermal melting, these transitions have the advantages of ultrafast speed and low-power consumption. Such a mechanism can inspire us to better control the structure transitions by manipulating the material, the laser parameters, and the environmental temperature. We believe that the orbital-selective excitation can be extended to other fields, such as optically controlled ultrafast ferroelectric switching. At present, the main problem is that the dynamic and atomic picture of ultrafast laser-induced phase/structural transitions is not easy to be detected by experiments. The non-thermal phase/structural transition requires suitable conditions considered together from the material, laser and environment side. A combination of experimental studies and first-principles calculations should be a possible approach. Particularly, the high-throughput calculations and machine-learning technology may provide new opportunities to study the problems in the near future [28, 29].

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References

- Feldmann J., Youngblood N., Karpov M., Gehring H., Li X., Stappers M., Le Gallo M., Fu X., Lukashchuk A., Raja A. S., Liu J., Wright C. D., Sebastian A., Kippenberg T. J., Pernice W. H. P., Bhaskaran H. *Nature* 2021, 589, 52–58.
- Feldmann J., Youngblood N., Wright C. D., Bhaskaran H., Pernice W. H. P. *Nature* 2019, 569, 208–214.
- Ríos C., Stegmaier M., Hosseini P., Wang D., Scherer T., Wright C. D., Bhaskaran H., Pernice W. H. P. *Nat. Photonics* 2015, 9, 725–732.
- Burr G. W. *Nature* 2019, 569, 199–200.
- Chen N.-K., Li X.-B. *Chin. Phys. B* 2019, 28, 104202.
- Li X.-B., Chen N.-K., Wang X.-P., Sun H.-B. *Adv. Funct. Mater.* 2018, 28, 1803380.
- Ovshinsky S. *Phys. Rev. Lett.* 1968, 21, 1450–1453.
- Chen N.-K., Li X.-B., Wang X.-P., Tian W. Q., Zhang S., Sun H.-B. *Acta Mater.* 2018, 143, 102–106.
- Chen N.-K., Li X.-B., Wang X.-P., Xia M.-J., Xie S.-Y., Wang H.-Y., Song Z., Zhang S., Sun H.-B. *Acta Mater.* 2015, 90, 88–93.
- Ding K., Wang J., Zhou Y., Tian H., Lu L., Mazzarello R., Jia C., Zhang W., Rao F., Ma E. *Science* 2019, 366, 210–215.
- Kolobov A. V., Fons P., Frenkel A. I., Ankudinov A. L., Tominaga J., Uruga T. *Nat. Mater.* 2004, 3, 703–708.
- Rao F., Ding K., Zhou Y., Zheng Y., Xia M., Lv S., Song Z., Feng S., Ronneberger I., Mazzarello R., Zhang W., Ma E. *Science* 2017, 358, 1423–1427.
- Simpson R. E., Fons P., Kolobov A. V., Fukaya T., Krbal M., Yagi T., Tominaga J. *Nat. Nanotechnol.* 2011, 6, 501–505.
- Wuttig M., Yamada N. *Nat. Mater.* 2007, 6, 824–832.
- Xu M., Mai X., Lin J., Zhang W., Li Y., He Y., Tong H., Hou X., Zhou P., Miao X. *Adv. Funct. Mater.* 2020, 30, 2003419.
- Zhang W., Mazzarello R., Wuttig M., Ma E. *Nat. Rev. Mater.* 2019, 4, 150–168.
- Li X.-B., Liu X. Q., Han X. D., Zhang S. B. *Phys. Status Solidi B* 2012, 249, 1861–1866.
- Li X.-B., Liu X. Q., Liu X., Han D., Zhang Z., Han X. D., Sun H.-B., Zhang S. B. *Phys. Rev. Lett.* 2011, 107, 015501.
- Chen N.-K., Han D., Li X.-B., Liu F., Bang J., Wang X.-P., Chen Q.-D., Wang H.-Y., Zhang S., Sun H.-B. *Phys. Chem. Chem. Phys.* 2017, 19, 24735–24741.
- Chen N.-K., Bang J., Li X.-B., Wang X.-P., Wang D., Chen Q.-D., Sun H.-B., Zhang S. *Phys. Rev. B* 2020, 102, 184115.
- Wang X.-P., Li X.-B., Chen N.-K., Bang J., Nelson R., Ertural C., Dronskowski R., Sun H.-B., Zhang S. *npj Comput. Mater.* 2020, 6, 31.
- Chen N.-K., Li X.-B., Bang J., Wang X.-P., Han D., West D., Zhang S., Sun H.-B. *Phys. Rev. Lett.* 2018, 120, 185701.
- Dronskowski R., Bloechl P. E. J. *Phys. Chem.* 1993, 97, 8617–8624.
- Deringer V. L., Tchougreff A. L., Dronskowski R. *J. Phys. Chem. A* 2011, 115, 5461–5466.
- Maintz S., Deringer V. L., Tchougreff A. L., Dronskowski R. *J. Comput. Chem.* 2016, 37, 1030–1035.
- Nelson R., Ertural C., George J., Deringer V. L., Hautier G., Dronskowski R. *J. Comput. Chem.* 2020, 41, 1931–1940.
- Runge E., Gross E. K. U. *Phys. Rev. Lett.* 1984, 52, 997–1000.
- Chen N.-K., Huang Y.-T., Li X.-B., Sun H.-B. *Chin. J. Lasers* 2021, 48, 0202001.
- Liu Y.-T., Li X.-B., Zheng H., Chen N.-K., Wang X.-P., Zhang X.-L., Sun H.-B., Zhang S. *Adv. Funct. Mater.* 2021, 31, 2009803.