Ab initio molecular-dynamics simulations of electronic and structural properties of liquid semiconductors

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The solid Te is a typical semiconductor, which has the trigonal structure consisting of infinite twofold-coordinated helical chains of covalently bonded atoms. Under pressure, the crystalline Te undergoes four structural phase transitions at room temperature; which are accompanied by discontinuous increase in coordination number from two at ambient pressure to eight at 27 GPa. It is interesting to investigate the structural and bonding properties of liquid states under pressure in connection with the pressure-induced structural change in the crystalline states.

Recently, Funamori and Tsuji [1] investigated the structure of liquid Te under pressure up to 22 GPa by synchrotron X-ray-diffraction techniques. They found that the nearest-neighbor distance increases with increasing pressure in spite of the volume contraction, and has maximum at about 6 GPa, while the coordination number increases monotonically. It is of great interest to consider the microscopic origin of these anomalous pressure dependences in connection with the change in the chain structure. Furthermore, the investigation of electronic structures and bonding properties is essentially important to understand such pressure-induced structural changes in compressed liquid chalcogenides. For these purposes, we have carried out *ab initio* molecular-dynamics (MD) simulations of liquid Te under pressure up to 47 GPa [2,3].

The calculated results of the structure factors and the pair distribution functions are in good agreement with the experimental mesurements. From the results of our *ab initio* simulations as well as the experimental observations [1], it is clarified that there are two stages in the compression process of liquid Te. In the first stage under pressure up to about 6 GPa, the elongation of the nearest-neighbor distance is induced by forming a weak covalent bonding state between two Te atoms. Our analyses including the overlap populations and the maximally localized Wannier functions reveal that the lone-pair electronic state around each Te atom becomes a weak covalent bonding state with a highly asymmetric spatial distribution between two Te atoms. The first stage is considered as the stage in which the number of weak covalent bonds increases. When such weak bonds are formed, the original covalent bonds will elongate and weaken due to the charge neutrality around each atom, which would be the main reason for the expansion of the nearest-neighbor distance. In the second stage for further compression, the anisotropy of atomic configuration around each Te atom is reduced with increasing pressure. From the resemblance between the spatial distributions of the electronic wavefunctions at 12 and 47 GPa, it is concluded that, in the second stage, new bonds are no longer formed, and the electronic states around Te atoms have a weak pressure dependence.

References

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