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Peierls transition in sodium under high pressure: a first-principles study

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Abstract
We have used first-principles calculations to investigate the electronic structure of the new oP8 phase of sodium which was experimentally reported recently (Gregoryanz *et al* 2008 *Science* **320** 1054). Our results show the transition from I-43d to oP8 structure, which happens at room temperature, can also happen at 0 K. The I-43d structure will change to the oP8 structure at about 155 GPa and 0 K, rather than the CsIV structure at 190 GPa and 0 K, as the previous studies (Neaton *et al* 2001 *Phys. Rev. Lett.* **86** 2830) predicted. It is also found that the oP8 structure forms a new nonequilateral triangle Na_3 structure and mainly distributes charge accumulation in the voids of the structure, rather than within the Na_3 triangles. Electronic density of states analysis shows that the oP8 structure opens a deeper pseudogap close to the Fermi level through symmetry breaking of the structure compared with that of the I-43d structure. Together with its unusual charge density distribution, it is found that the Peierls mechanism works for the transition to the oP8 structure. Differing from previous results about the Peierls mechanism of light alkali metals, the unit which produces a one-dimensional charge density wave is the Na_3 cluster instead of the pairing mechanism.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

At ambient conditions, the light alkali metals lithium and sodium have simple structures and behave like free-electron crystals. However, they are not simple metals any longer under higher pressures. It was first predicted by first-principles calculations [2, 3], and later confirmed by experiment [4–6], that lithium and sodium undergo a sequence of symmetry-breaking transitions driven by the Peierls mechanism. This Peierls transition opens a pseudogap close to the Fermi level through symmetry breaking of the structure, which reduces the one-electron energy sum and makes the new structure more energetically favorable. The Peierls transition plays an important role in the high pressure phase transitions of light alkali metals, brings more new structures, even changes the electronic structure of liquid metals and leads to an unusual negative melting curve in sodium and lithium as reported recently [7, 8]. For sodium, previous experiments [5, 9–11] have shown that it transforms first from the bcc to the fcc phase at 65 GPa, and then to a more complex cubic structure, I-43d, at 103 GPa. This I-43d structure, which also appears in lithium at 42 GPa, was widely reported as a broken-symmetry structure [4, 12, 13]. The recent x-ray single-crystal synchrotron diffraction studies of sodium as a function of pressure and temperature (up to 130 GPa at 500 K and up to 150 GPa at room temperature) [1] have indicated that sodium exhibits six different structures in this region. It has also been shown that the I-43d structure changes to a simple primitive orthorhombic structure at 118 GPa and a temperature below 275 K, which was called oP8 for short in their paper. We noticed that the new oP8 structure has a lower symmetry than that of the I-43d structure. This symmetry-decreasing transition in alkali metals under high pressures is often accompanied by an apparent change of electronic structure which is possibly related to the Peierls transition. To verify such a conjecture, our current studies mainly focus on the electronic structure of the new oP8 structure to see what happens with this decrease in symmetry.

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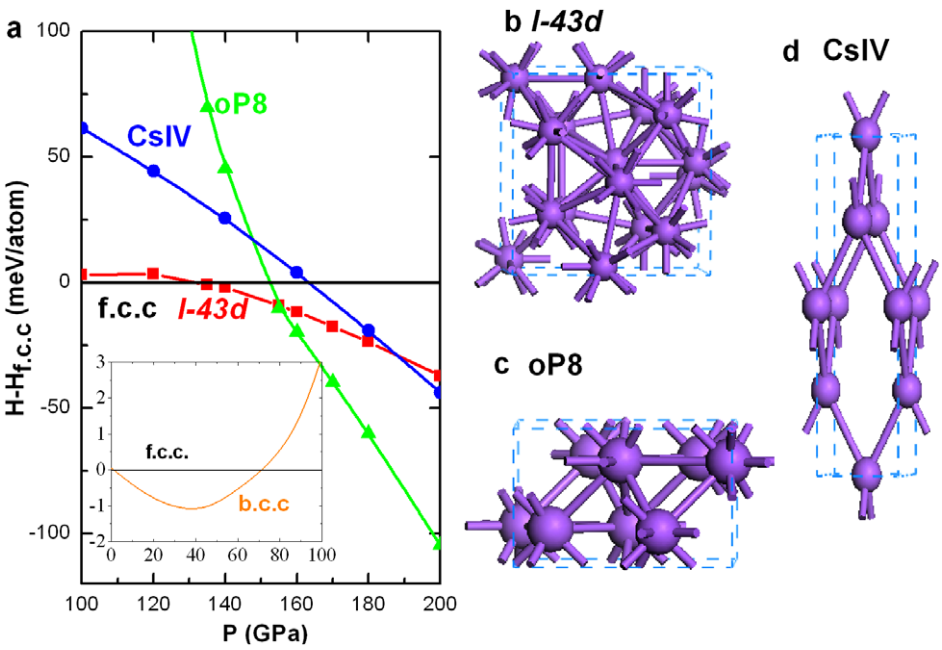

Figure 1. (a) Enthalpy difference $H - H_{\mathrm{fcc}}$ (meV) versus pressure (GPa) for competitive structures of dense sodium. The inset illustrates the low pressure bcc–fcc transition. The three crystal structures of sodium at 155 GPa described in the text are shown in (b), (c) and (d), respectively. The I-43d (b) is a distorted $2 \times 2 \times 2$ superstructure of bcc and has space group I-43d with 16 atoms. The oP8 (c) is a simple orthorhombic structure with 8 atoms per unit cell. Its space group is $Pnma$. The CsIV (d) is a tetragonal structure, which has 4 atoms in its conventional cell and belongs to the space group of $I4_1/amd$ symmetry.

2. Computational details

All electronic structure calculations in this work were performed within the density function theory, using the local-density approximation (LDA) [14]. A plane-wave ultrasoft pseudopotential method, such as implemented in the CASTEP code [15], was employed. As the result would be affected by increasing core overlap at high densities, we treated the 3s 2p and 2s electrons as valence electrons and incorporated only the tightly bound 1s state into an effective frozen core. The self-consistent calculations converged when the energy threshold was lower than 10^{-6} eV/atom. In order to reduce the influence due to the choice of the plane-wave basis and k points, as well as to guarantee the computational precision, a cutoff energy was set to 410 eV in all calculations. Moreover, a k-point spacing smaller than 0.03 Å^{-1} was individually adjusted in reciprocal space, not only to the size of each computational cell of the crystallographic structures but also to its variation at a given compressed volume. To calculate the phonon dispersion curve, the PHONON software [16] with the *ab initio* force-constant method was used [17]. For the oP8 structure, we built a $2 \times 4 \times 2$ supercell with 128 atoms for the frozen phonon calculations and used a finite atomic displacement of 0.03 Å.

3. Results and discussion

The oP8 structure was reported at room temperature. Hence, we first investigate its phase stability at 0 K. We calculated the enthalpies of sodium in different structures relative to its fcc phase for pressures up to 200 GPa. The results are shown in figure 1(a). The different crystal structures are shown in figures 1(b)–(d). Both I-43d and oP8 structures have been found experimentally. After the I-43d structure, it is unknown which structure the I-43d structure will change to with increasing pressure. Previous theoretical studies [3, 12, 13] predicted that it would change to the CsIV structure at about 190 GPa. Our enthalpy calculations show that above 1 GPa the bcc structure emerges with the lowest enthalpy, but it is actually unstable and transforms to fcc at 71 GPa (see the inset to figure 1(a)). The I-43d structure appears at 130 GPa against the fcc structure. Above 190 GPa, the enthalpy of the CsIV structure is lower than that of the I-43d structure. All the enthalpy calculations above are consistent with the previous LDA study for sodium [3]. However, our results show that the oP8 structure at room temperature has the lowest enthalpy in the pressure range from 155 to 200 GPa at 0 K. Our phonon dispersion calculations also indicate that the oP8 structure is stable dynamically up to 200 GPa in the range of our calculations at 0 K. Figure 2 shows phonon dispersion curves of the oP8 structure at 160 GPa. In the view of thermodynamics and phonon dispersion behavior, the new oP8 structure should be stable at 0 K. The I-43d structure should change to the oP8 structure at 155 GPa and 0 K, just like what happens at room temperature.

Since the oP8 structure is the most stable structure under pressures above 155 GPa, we first study its electronic structure and compare it with that of I-43d. Its band structure and the total density of states at 155 GPa are shown in figure 3. It is noted that the new oP8 phase is still a metal even though a pseudogap close to the Fermi level is opened. The total and partial electronic density of states of the oP8 and I-43d structure of sodium under a pressure of 155 GPa are shown in

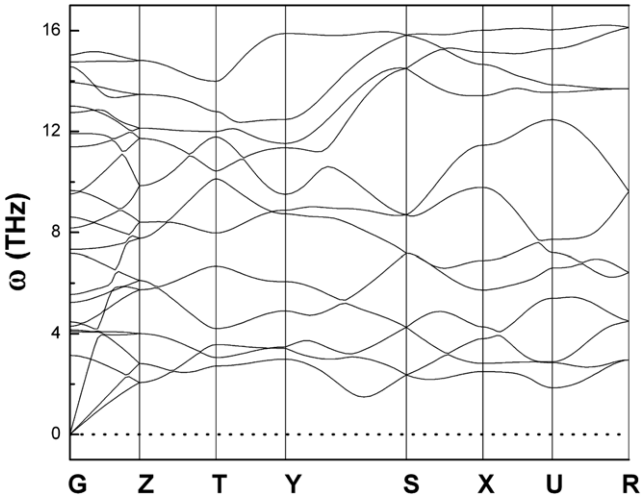

Figure 2. The phonon dispersion curves of the oP8 structure in sodium at 160 GPa and 0 K.

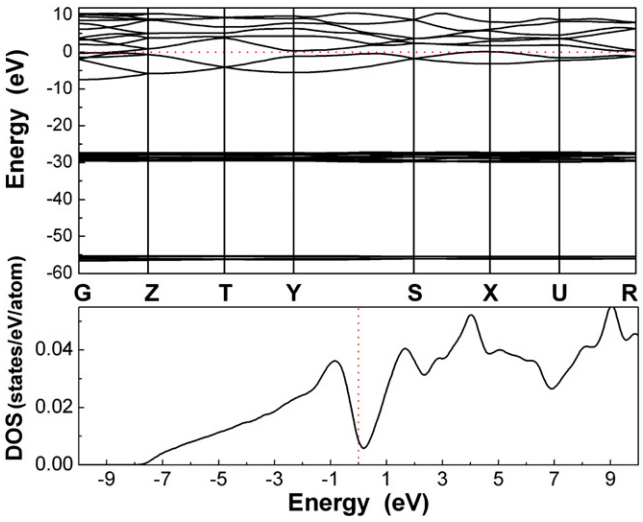

Figure 3. The total electronic DOS and band structure of the oP8 structure in sodium at 155 GPa.

figure 4. It is found that both oP8 and I-43d structures open a pseudogap close to the Fermi level, but the oP8 structure brings more p states below the Fermi energy, leading to an energy decrease. The one-electron energy sum is reduced and the oP8 structure gains more band energy eventually.

We study the structural change of oP8 in detail with increasing pressure. It is found that the relative positions of atoms in the (010) direction are not changed, but distorted more and more in the (010) plane with the increase in pressure. If the relative positions of atoms in the (010) plane are undistorted, we get a higher symmetry structure with the orthorhombic space group $Cmcm$, which is called the undistorted structure for short. Figure 5(a) shows the (010) plane of the undistorted structure containing a parallelogram unit Na_4, which can change to the oP8 structure through the distortion of atoms in the (010) planes. This distortion leads to the new nonequilateral Na_3 triangle structures (shown in figure 5(b)) in the (010) plane of the oP8 structure, forming

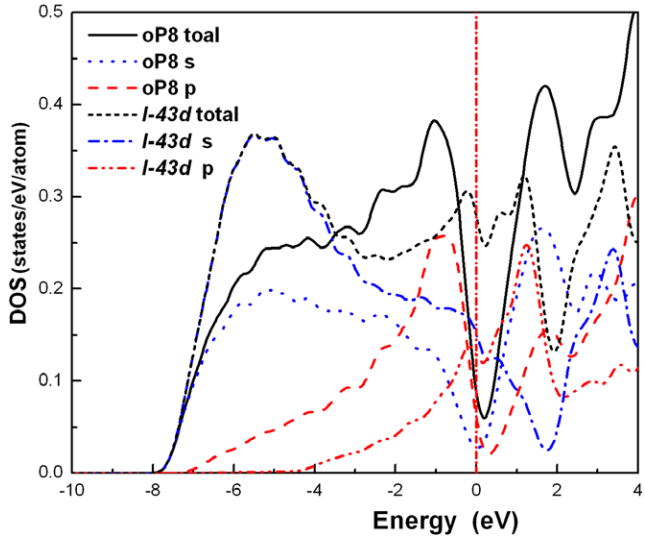

Figure 4. The total and partial electronic DOS of oP8 and I-43d structures in sodium at 155 GPa.

a one-dimensional structure with these Na_3 units. The total electronic density of states of the undistorted and distorted structures were calculated at 155 GPa, which are shown in figures 5(c) and (d). It can be seen clearly that the undistorted structure does not have a pseudogap: the distortion of atoms in the (010) planes contributes to a pronounced minimum in the DOS close to the Fermi level. This distortion leads to the lowering of the band energy and also increases the repulsion between atoms. If the lowering of the band energy is sufficient to overcome the cost in increased repulsion associated with this distortion, the lower symmetry structure can exist stably. This is mainly the typical Peierls mechanism found in alkali metals. Based on the above analysis, the oP8 structure is also a broken-symmetry structure just like the I-43d structure. The Peierls mechanism works in the high pressure phase oP8 of sodium.

The charge density in the (010) planes of the oP8 structure at 155 GPa is shown in figure 6. The charge mainly accumulates in the voids of the structure, rather than within the Na_3 triangles, forming a clear one-dimensional conducting channel with many Na_3 units. The valence electrons are forced to some degree away from regions of significant core overlaps into the interstitial space. This is the exclusionary effect of atomic cores on valence orbitals, which was pointed out by Neaton and Ashcroft [2] who showed how it could lead to the pairing mechanism in the α-Ga structure in lithium. A similar Li_3 structure has been reported in previous theoretical predictions [18]. However, in that paper, the Li_3 unit does not form a one-dimensional charge density wave and the Peierls mechanism does not appear. Our result is different from previous studies in the Peierls transition of the light alkali metals in that three-atom units instead of a pairing mechanism form a one-dimensional charge density wave.

4. Conclusion

In summary, the total energy, lattice dynamics and electronic structure of the oP8 structure in sodium recently reported experimentally [1] have been studied using *ab initio*

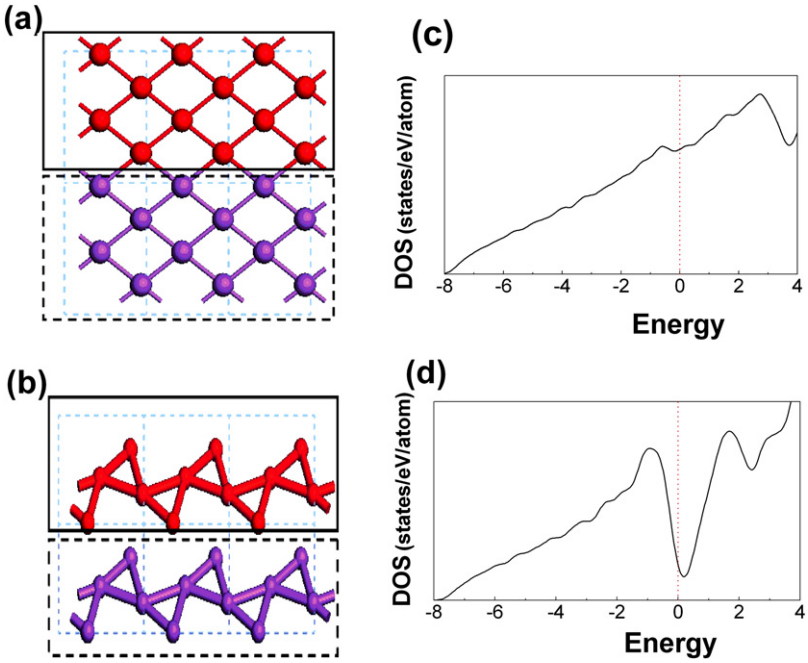

Figure 5. (a) and (b) are the (010) plane of undistorted and distorted structures of sodium at 155 GPa, while (c) and (d) are the corresponding total electronic DOS. The atoms included in the solid and dashed line pane show the corresponding atoms of the undistorted and distorted structures.

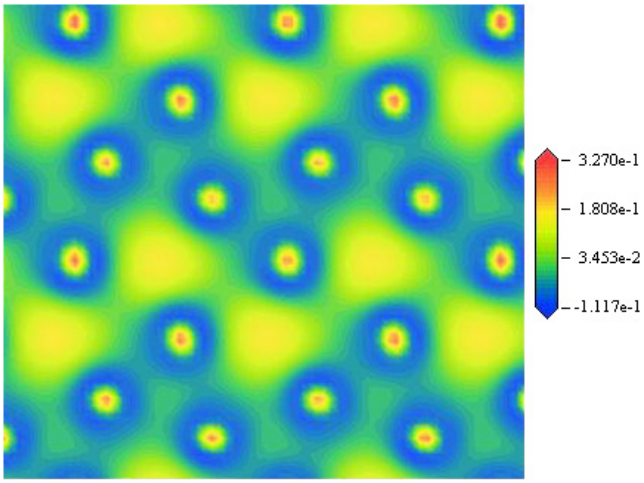

Figure 6. The charge density of the oP8 structure of sodium at 155 GPa in the (010) plane, plotted passing through the four atoms.

calculations. It has been shown that the transition from the *I*-43*d* structure to the oP8 structure observed at room temperature can also happen at 0 K. The Peierls mechanism works in this oP8 structure and it forms a one-dimensional charge density wave with many new Na_3 units instead of the pairing mechanism, which is different from the previous Peierls mechanism found in the light alkali metals.

Acknowledgments

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