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## LETTER TO THE EDITOR

# The low-temperature phase of sodium: an intermediate orthorhombic distortion?

Hema Sankaran, Surinder M Sharma and S K Sikka

High Pressure Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India

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**Abstract.** We have shown through first-principles total-energy calculations on sodium that at low temperatures there is a nearly-zero barrier path of continuous orthorhombic deformations leading from the body-centred cubic (BCC) to the more stable hexagonal close-packed (HCP) structure. The observed diffraction patterns may now be explained without the aid of stacking faults that are needed to account for deviations from the calculated pattern if a 9R structure is assumed.

Sodium undergoes a transition from the body-centred cubic structure to a close-packed structure when cooled below 36 K [1]. Only a portion of the sample transforms [1–4] and the final structure is dependent on the history of the sample [2]. The low-temperature phase has been variously interpreted as a hexagonal close packed structure (HCP) [1] and a 9R structure [3–5]. Recent single-crystal neutron diffraction experiments [6] show unambiguously the existence of an HCP phase at low temperatures. However, the diffraction spectrum differs from the pattern calculated on the basis of a mixture of BCC, HCP and 9R phases. A qualitative explanation is possible by assuming stacking faults in the 9R structure, though a percentage probability of deformation faults as high as 20% is required [7]. Alternatively the double twin faults also give a qualitative agreement between the spectra for a 9.3% probability of fault occurrence per layer [3]. We shall show below that a simple explanation, without an *ad hoc* invocation of stacking faults, is possible. The same explanation may be valid for Li, where a similar situation exists.

We have performed first-principles total-energy calculations for Na and found that there exists an ensemble of intermediate orthorhombic structures through which the system must necessarily pass while going from the BCC to the HCP structure. This ensemble provides a natural basis for our interpretation of the observed results.

A close look at the BCC and HCP structures shows that the atomic arrangement in  $(\bar{1}10)_{\text{BCC}}$  and  $(001)_{\text{HCP}}$  planes are quite similar. As seen from figure 1, minor adjustments by means of a strain,  $\epsilon_1(001)\langle 001 \rangle$ , leading to an increase of  $\theta$  from  $109.47^\circ$  (BCC) to  $120^\circ$  (HCP), and a second strain,  $\epsilon_2 [110]_{\text{BCC}}\langle 110 \rangle_{\text{BCC}}$ , displacing atoms in adjacent  $\bar{1}10_{\text{BCC}}$  planes through a relative distance of  $(1/6)\langle 110 \rangle_{\text{BCC}}$  bring the BCC to a hexagonal structure. Under the constraint of constant volume and fixed spacing,  $d_{110}$ , between the  $(\bar{1}10)_{\text{BCC}}$  planes, the hexagonal structure thus obtained

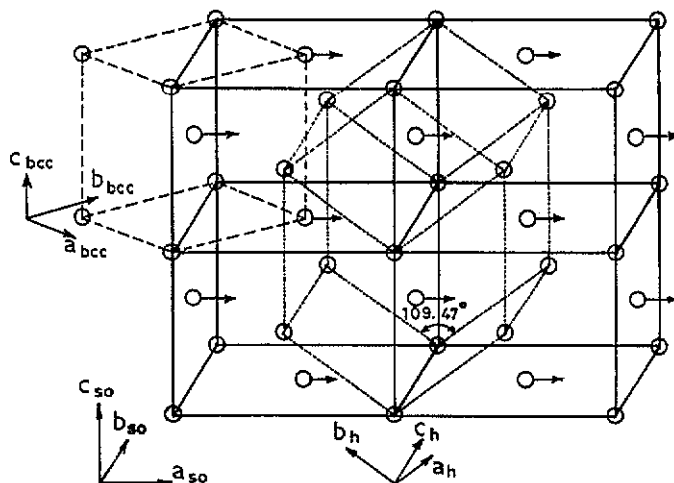


Figure 1. The choice of various unit cells. The orthorhombic unit cell (bold lines) was used for our LMTO calculations. Four such cells have been drawn to show the original BCC cell (dashed lines) and a hexagonal cell (dotted lines). An HCP structure is obtained when the angle  $\theta$  increases from  $109.47^\circ$  to  $120^\circ$ , and the atoms marked with arrows move by  $a_{SO}/6$  in the direction shown.

has a  $c/a$  ratio of 1.565. An additional adjustment, either by a change in volume across the transition, and/or a change in the  $d_{110}$  spacing, is required to attain the final  $c/a$  ratio of the HCP structure. Thus, three quantities—the angle  $\theta$ , the displacement  $x$  of atoms, and the  $d$  spacing between  $\bar{1}10$ —are the parameters that bring about this structural transition. The strain,  $\epsilon_1$ , is related to the elastic constant,  $(c_{11} - c_{12})/2$ , and  $\epsilon_2$  corresponds to the zone-boundary phonon mode  $TA_1[\bar{1}10]_{BCC}(110)_{BCC}$ . Our earlier experience of similar situations in Si ( $\beta$ -Sn to primitive hexagonal) [8] and Hg and Cd Hg alloys [9] (BCC to HCP) showed that generally these two strains are coupled. A Landau-type free-energy functional [10] can be written down with the coupled strains as two order parameters. Minimization of the free-energy functional with respect to one of the strains shows that Devonshire's theory of first-order martensitic transformation is applicable to the system. The phase transition may thus proceed without the complete softening of either the elastic constant,  $(c_{11} - c_{12})$ , or the zone-boundary phonon mode, a feature similar to that suggested for Li by Gooding and Krumhansl [11].

Using the procedure outlined by Andersen [12], the total-energy differences from the reference BCC structure for HCP and all intermediate distorted structures were computed (see also [13]). The various intermediate distorted structures result from the application, in various amounts, of one or more of the deformations  $x$ ,  $\theta$  and  $d_{110}$ . The linear muffin-tin orbital method (LMTO) [14] was used to solve the energy-band problem. Correction to the spherical approximation for electrostatic energy was incorporated by algebraically adding the Ewald energy differences. All calculations were carried out on a simple-orthorhombic (SO) four-atom super cell with  $a_{SO}$  along  $\langle 110_{BCC} \rangle$ ,  $b_{SO}$  along  $\langle \bar{1}10_{BCC} \rangle$  and  $c_{SO}$  along  $\langle 001_{BCC} \rangle$  (figure 1). This enabled us to describe BCC, HCP, and the various intermediate distorted structures in the same unit cell, with an appropriate choice of axial ratios and atom positions. The difference in convergence of the structure constants that may arise with different choices of the Brillouin zone was thus eliminated. Since the change in volume across the transition

is negligible in sodium (0.25% [1]) all calculations were carried out at the transition volume of  $255a_0^3$  per atom. Calculations were carried out at 96  $k$  points in the irreducible wedge of the Brillouin zone. Self-consistency of the sum of eigenvalues was carried out to six significant digits; the precision in energy differences was thus better than 0.01 mRyd.

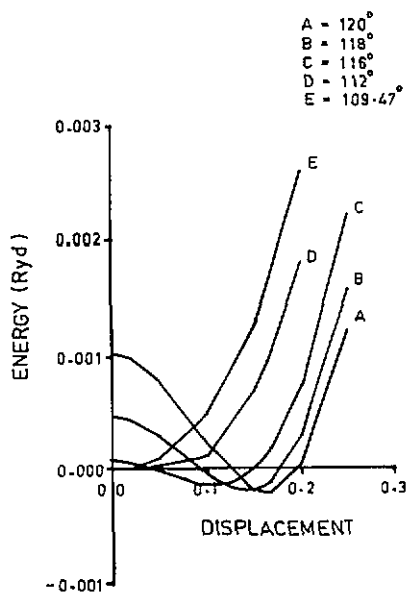


Figure 2. Energy differences as a function of displacement,  $x$  (in fractional units of  $a_{SO}$ ), of the atoms. Curves A to E are for different angles,  $\theta$ .

Several interesting features emerge from the calculations. Figure 2 shows the total energy differences as a function of the displacement  $x$  for various angles  $\theta$ . The lowest energy configuration shifts continuously from  $x = 0$  (equilibrium BCC position) at  $\theta = 109.45^\circ$  to  $x = 0.1667$  (relative displacement of alternate  $\bar{1}10$  BCC planes by  $(1/6)(100)$ ) at  $\theta = 120^\circ$ . This is a clear demonstration that the two strains,  $\epsilon_1$  and  $\epsilon_2$ , are coupled. The energy for the HCP configuration is lower, indicating the possibility of a transition from the BCC to the HCP structure at sufficiently low temperatures. We remark that this result is consistent with that of Moriarty and McMahan [15]. Our calculation yields an energy difference of 0.2 mRyd per atom for the two structures, which is larger than the measured value [16]. However, in view of the transition path that we propose, it is indeed doubtful whether it is the true energy difference between the two structures that has been measured in the experiments. We further note that the energy difference for the BCC and HCP structures that we have calculated is comparable to the energy difference ( $\sim 0.3$  mRyd) reported recently for BCC and FCC structures [17].

Our calculations also show (in contrast to [18]) that  $d_{110(\text{BCC})}$  is an important variable. As seen in figure 3, at a fixed angle ( $\theta = 120^\circ$ ), an increase in  $d_{110}$  from  $11.3a_0$  to  $12.09a_0$  results in an initial decrease in energy and then a subsequent increase. The minimum energy is attained for  $d = 11.604a_0$ , which corresponds to a value of  $c/a$  of 1.628 for the HCP cell, which is in good agreement with the

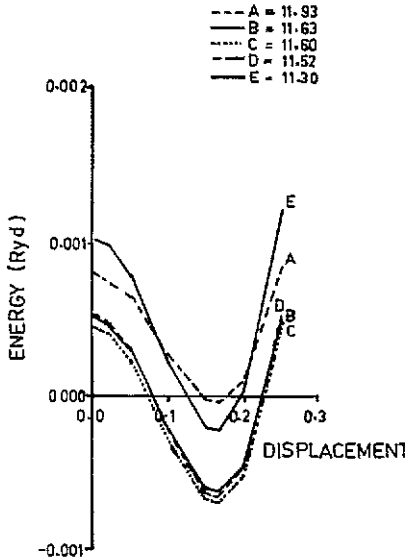


Figure 3. The effect of changes in the spacings of the  $110_{\text{BCC}}$  planes. Energy differences are plotted as a function of  $x$ . All curves A to E for  $\theta = 120^\circ$  (hexagonal), but for different spacings between the  $110_{\text{BCC}}$  planes (expressed in  $a_0$ ).

observed value. Though the energy of the HCP structure is lower than that of the BCC structure, there exists a barrier of 0.25 mRyd per atom. Having generated the hypersurface,  $E(x, \theta, d)$  ( $E$  being the difference in the total energy with respect to the BCC structure), we found that there is a path on this surface, leading from the BCC to the HCP structure, along which the barrier is vanishingly small. This path is a function of  $x$ ,  $\theta$  and  $d$ , or alternatively, a function of  $x$  and of the axial ratios  $(b/a)_{\text{SO}}$  and  $(c/a)_{\text{SO}}$ . The path may be approximately described by the following equation:

$$(b/a)_{\text{SO}} = m_1(c/a)_{\text{SO}} + m_2x + c$$

where  $m_1 = 0.57743$ ,  $m_2 = 0.16149$  and  $c = 0.58428$ . Thus, when sodium transforms from BCC to HCP, the various intermediate distorted structures, (corresponding to the various  $(x, \theta, d)$  points along this path) should be realized. The transition in Na is, however, known to be of first order. This may be due to quantum fluctuations (the zero-point energy in Na is 1.1 mRyd per atom [19]) that perhaps initiate the transition before the barrier vanishes. It is also possible that at the finite temperature that is due to the entropy difference between the two structures, the barrier is still non-zero, though of small value.

In view of these results, we feel that, instead of the elaborate sequence of hexagonal layers of the 9R structure with a high probability of stacking faults, an explanation of the diffraction patterns may be based on the relatively simple and plausible mechanism of continuous deformation through intermediate orthorhombic structures corresponding to the low-barrier path seen from the calculations. These distorted structures have the space-group symmetry  $Cmcm$  (number 63 in [20]) with atoms in  $4c$  positions. The axial ratios lie between the limits  $b/a = 1.414$  to  $1.732$  and  $c/a = 1.414$  to  $1.628$ , and the atomic parameter,  $y$ , ranges from 0.25 to 0.333. The distribution of the various intermediate states in the sample being studied would depend

on (i) how the three parameters were being altered at the microscopic level during the experiment, and (ii) inhomogeneous microstructural variations. This explains the variations in the diffraction patterns in different reports. We have computed the diffraction pattern expected from a mixture of BCC, HCP and intermediate orthorhombic structures. A comparison of this with the published experimental data [3] shows fairly good agreement. Since the observed intensity profile is not known to us, we could not carry out a Rietveld-type analysis to evaluate the true proportions of the various intermediate states seen. The broadening of the peaks will emerge naturally as a consequence of the range of intermediate cells seen.

A close examination of the published experimental data suggests that the system is evolving from the BCC to the HCP structure. Diffraction data [3] show that the *hhl* peaks (common to both HCP and 9R structures) are not shifted at all. Of the twelve 'pure 9R' peaks (i.e. those expected for a 9R structure, and not for an HCP structure) expected in the region studied, only eight are observed, and all are shifted from their expected positions. It is interesting to note that all shifts are towards HCP peak positions—e.g. 104 and 105 shift in equal and opposite directions towards 104.5 ( $101_{\text{HCP}}$ ). Similarly, 108 and 1010 are equally displaced towards 109 ( $102_{\text{HCP}}$ ) and 1013 and 1014 towards 1013.5 ( $103_{\text{HCP}}$ ). Because of the different variants, the interpretation of the single-crystal data is not straightforward. However, these features have a natural explanation in the existence of intermediate orthorhombic structures.

It has long been observed in Zr and Ti alloys [21] (which exhibit the martensitic BCC-HCP transition), that if they are cooled rapidly, they then show instead a BCC-orthorhombic transition. This is a clear indication that an orthorhombic distortion is necessary while transforming from the BCC to the HCP structure. Very recently, an intermediate orthorhombic phase was identified in high-pressure experimental diffraction studies of the simple-cubic to HCP-like transition in CsI [22]. It is also interesting to note the recently reported results of molecular dynamics calculations for the BCC-HCP transition [23]. It was seen that, depending on the potentials used, various metastable intermediate structures were obtained, and that at low enough temperatures the HCP structure was most favoured. We would like to add in conclusion that a similar picture may be valid for Li too. The low-temperature phase, whether it be HCP, 9R or FCC can be attained through intermediate orthorhombic distortions, and these may well be the cause for the shifts and broadening of the diffraction peaks. In conclusion, we suggest that a Rietveld type of analysis of the diffraction patterns should be carried out to test our proposal more quantitatively.

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