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**Pressure effects on the martensitic transformation in metallic sodium**

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Na has been shown to undergo a partial martensitic transformation from the bcc lattice to a combination of the 9R lattice and a trigonal or hexagonal lattice below 35 K, somewhat similar to that of lithium, which transforms to a 9R lattice plus an fcc lattice. Recent neutron-scattering experiments on Li under hydrostatic pressure showed a pronounced increase in the transition temperature from 75 to about 90 K at a pressure of 6.5 kbar. Similar experiments on Na, however, show a *decrease* in the transition temperature with pressure, actually suppressing the 9R transition at 1 kbar to 15 K.

Recent neutron-scattering experiments on polycrystals<sup>1-3</sup> and single crystals<sup>4</sup> have shown that both Li and Na partially transform martensitically at low temperatures from the bcc structure to other structures encompassing close-packed lattices with a high density of stacking faults (Li below 78 K and Na below 35 K). Li was observed to be preponderantly bcc and 9R (Sm type) with a small amount of the fcc phase which, on heating, grew in size at the expense of the 9R phase, but subsequently reverted to 100% bcc phase near 200 K and above. Na, on the other hand, was observed<sup>2</sup> to coexist as three phases—bcc, faulted 9R, and a highly faulted hexagonal or rhombohedral phase below 35 K. On warming, the 9R phase, and subsequently the hexagonal phase, transformed back to the bcc phase.

In the case of lithium it was shown<sup>5</sup> that the effect of hydrostatic pressure was to increase the transition temperature appreciably. The present experiment was planned to determine if sodium exhibited similar behavior under pressure. In the meantime, we became aware of the results of acoustic emission measurements<sup>3,6</sup> in polycrystalline Na which showed a pronounced decrease in transition temperature as the pressure was increased by modest amounts.

The experimental conditions for the experiment were similar to those reported for Li.<sup>5,7</sup> The measurements were made at the Intense Pulsed Neutron Source (IPNS)

at Argonne National Laboratory on the Special Environment Powder Diffractometer (SEPD) with the identical He-gas pressure source and pressure vessel. As in the Li experiment, Cd masks were used to eliminate lines due to the Al pressure vessel.

To ensure the lowest temperature possible with such a massive cell and high-pressure line, a 12-W closed-cycle refrigerator (Displex model 208) was used, whereas the previous Li experiment utilized the standard 2-W Displex, model 202. Not only was a lower temperature reached (about 12 K), but the equilibration times were considerably shortened. Two sensors were used to record the temperature, one on the Displex cold-tip adjacent to the pressure vessel and the other at the base (opposite end) of the pressure vessel. There was generally about a  $\frac{1}{2}$ -K difference between the two sensors and it was believed that the lower sensor more nearly represented the sample temperature.

Two different runs were made on Na at IPNS a few months apart. The first was on a polycrystalline rod (sample 1) which showed a substantial amount of preferred orientation, even after being cut into small pieces. Nevertheless, the studies confirmed the results of Chernyshov and co-workers,<sup>3,6</sup> in that at 1.8 kbar the transformation occurred at about 18 K, appreciably lower than 35 K. The transformed structure still appeared to be 9R, although a small amount of the hexagonal phase cannot be

ruled out. At atmospheric pressure the sample had transformed between 30 and 35 K. Several runs were made at lower pressures in order to determine  $T_c$  versus pressure. The procedure was to warm the sample until a single bcc phase was formed, and then set the pressure and lower the temperature. The actual pressure during the run at a fixed temperature was monitored, for there was generally a slight pressure drop with lower temperature. Because of the preferred-orientation effects it was not possible to determine the transformed fraction reliably.

The second set of experiments a few months later was with a sample that had been extruded into wire, cut up into short sections, rolled into little balls and placed in a vanadium can in the Al-pressure vessel. The sample prepared in this way was evaluated on the powder spectrometer at the Missouri University Research Reactor Facility and showed very little, if any, preferred orientation effects. At 4 kbar only the bcc phase was observed; however, the lowest temperature attained in this case was only 18 K. The Na-sample temperature was then raised above the melting point of fcc He and the pressure lowered to

about 1.07 kbar. The temperature was lowered in 2-K steps and the transformation was observed to occur between 16 and 15 K (as measured by the lower sensor), see Fig. 1. The transformed structure was clearly 9R, but only about 20% or less of the bcc phase transformed.

One must also be aware of the diffraction lines due to solid He when one is below the liquidus curve. Lines due to both fcc and hcp  $^4\text{He}$  phases have been observed and they can overlap some of the Na lines. However, with care they can be distinguished.

Runs were made at other lower pressures, again varying the temperature while maintaining a nearly fixed pressure. The results of the two sets of runs are shown in Fig. 2. The results of the second set of experiments lie below the first set of experiments; at a pressure of 0.2 kbar  $T_c$  had dropped to between 25 and 26 K. The lower values of  $T_c$  are thought to reflect cold-work effects due to the method of sample preparation. Nevertheless, the results show that the application of hydrostatic pressure dramatically lowers the transformation temperature and the transformed fraction in Na, whereas in Li hydrostatic pressure appreciably increased the transformation temperature.

Although many neutron-scattering runs were made at various temperatures and pressures, the data were insufficient to determine the compressibility curves of the bcc phase as a function of temperature. Since most of the data were obtained at low temperatures, those runs in the vicinity of 20 K ( $\pm 5$  K) were selected and the lattice constants of the bcc phase as a function of pressure were determined and plotted in Fig. 3. The straight line through the data is only to guide the eye. One notes that the effect of sample preparation had little effect on the compressibility as compared to the measurable differences observed in the transformation temperatures of the two samples.

If one compares the lattice constants and volume changes at the transformation temperature and pressure of the scans shown in Fig. 2, there appears to be a very slight change in volume between the bcc and 9R phases:  $\alpha(\text{bcc}) = 4.212 \text{ \AA}$ , volume per atom =  $37.36 \text{ \AA}^3$ , and

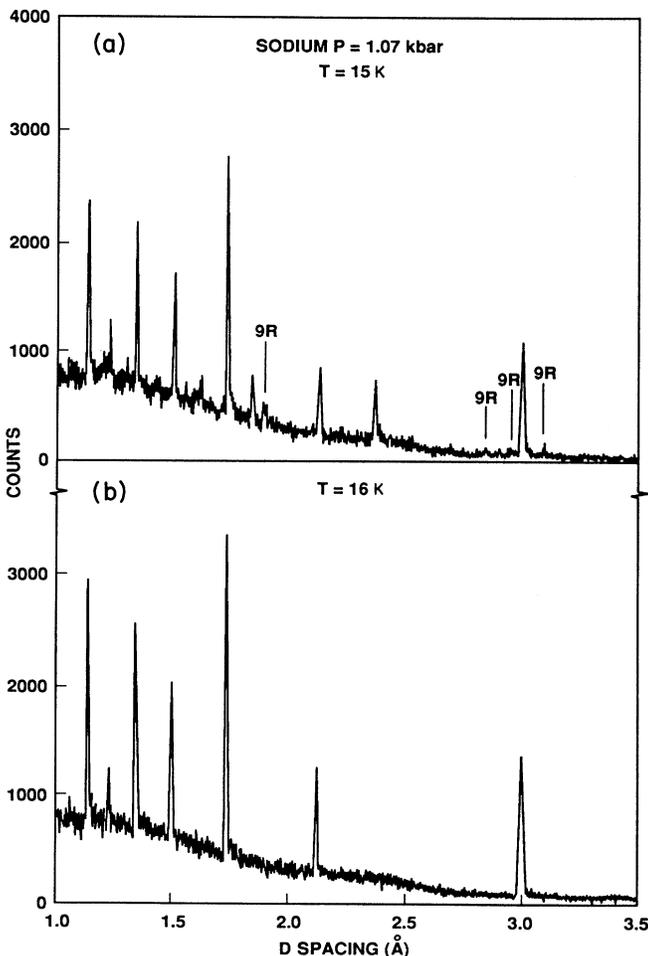


FIG. 1. Neutron-diffraction patterns of sample 2 above (16 K) and below (15 K) the martensitic transformation at 1.07 kbar. The extra unmarked lines in the 15-K pattern are due to the hcp  $^4\text{He}$  phase.

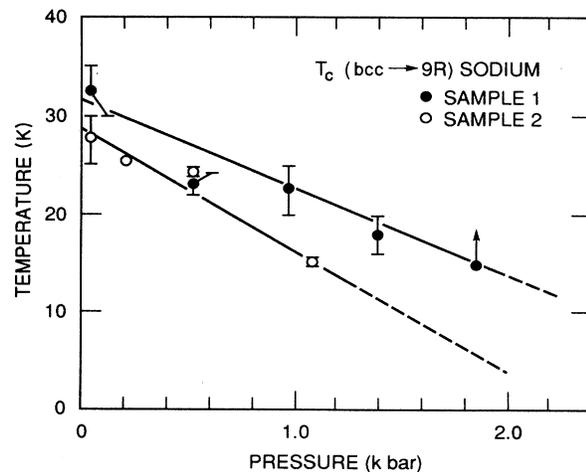


FIG. 2. Phase boundaries for bcc and 9R structures for the two sample preparations.

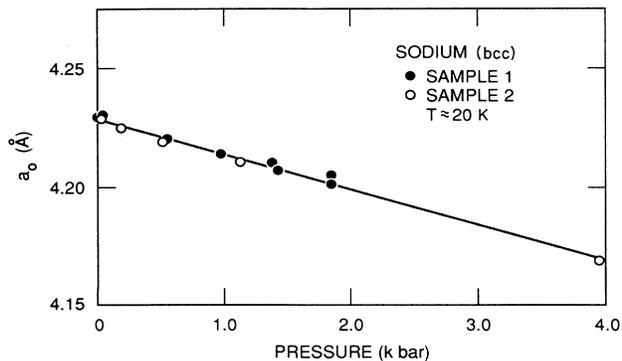


FIG. 3. Variation of bcc-lattice constant vs pressure near 20 K for the two sample preparations.

$a(9R) = 3.763 \text{ \AA}$ ,  $c(9R) = 27.59 \text{ \AA}$ , volume per atom  $= 37.60 \text{ \AA}^3$ , but it may well be within experimental error. The  $9R$  lattice constants were based on the (009) and (110)  $9R$  reflections, since the ( $hhl$ ) type of reflections have been shown<sup>2</sup> to be free of shifts due to stacking faults.

Several theoretical groups (see Ref. 4 and Vaks *et al.*<sup>3</sup>) have made nearly-first-principles total-energy calculations of the alkali metals as a function of volume (i.e., pressure) at absolute-zero temperature (effectively). Most show that, in general, close-packed structures (fcc, hcp,  $9R$ , etc.) are more stable than bcc. They often differ in the type of close-packed lattice that is most stable, but the energy differences are extremely small [only a few K in the

case of Na (Ref. 8)] and are undoubtedly dependent on the approximations made in the various approaches. The experimental observation of the coexistence of several phases, including the bcc phase, indicates that the differences in total energies should be small. The results presented here, however, are consistent with several theories which predict that Na will transform back from a close-packed lattice (hcp) to bcc at a pressure of about 10 kbar, which is considered in agreement with the extrapolated 2–3 kbar observed in the neutron scattering and acoustic emission measurements.

It is not possible from these experiments to readily determine the effects of pressure on the stacking-fault densities or to what extent the presence of the hexagonal phase has been affected. These questions will best be answered by single-crystal experiments under pressure at low temperature.

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