Ultrasonic study of the martensitic phase transformation in sodium

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A gated coherent phase-sensitive ultrasonic technique was employed to measure the ultrasonic velocity and attenuation in single crystals of sodium in the vicinity of the martensitic phase transformation temperature. In order to minimize strains, electromagnetic acoustic transducers were used to generate and receive the acoustic signals. Acoustic waves associated with the elastic constants C_{44}, C_{11}, $C'=(C_{11}-C_{12})/2$, and $C_n=(C_{11}+C_{12}+2C_{44})/2$ were studied for temperatures between 4.2 and 90 K and for frequencies between 6 and 8 MHz. No premartensitic effects were observed for any of the modes studied. The transition was abrupt and was always accompanied by a large increase in the attenuation. The velocity of the waves associated with the elastic constants C_{44} and C_n decreased at the transformation temperature while the velocity associated with C' and C_{11} increased as a result of the transformation. During the reversion process, the crystals underwent a structual reorientation. The results are compared with neutron scattering studies in sodium and previous ultrasonic measurements in lithium.

INTRODUCTION

The martensitic phase transformation in sodium has been extensively studied by a variety of experimental techniques over the last 30 years. All of these studies, with the exception of the neutron scattering studies,[1,2] were performed using polycrystalline samples. X-ray diffraction experiments[3] first showed that sodium partially transforms from a body-centered-cubic structure to a hexagonal close-packed structure. Later experiments included studies of electrical resistivity,[4] change in volume,[5] specific heat,[6] microscopy,[7] and mechanical properties.[8] Although transformation temperatures of approximately 36 K were reported in all these studies, there was disagreement on the amount of the metal that transforms. Specific-heat, resistivity, and microscopy studies indicated that as much as 50% of the metal transforms, in contrast to the original x-ray work of Barrett,[3] who showed that as little as 5% transforms. More recent neutron scattering studies on single crystals indicate that as little as 1% of the sodium transforms, and that the bcc phase maintains the original orientation at low temperatures. In more recent studies of the de Haas–van Alphen effect in small sodium samples at liquid-helium temperatures, Perz and Schoenberg[9] found that careful sample preparation and rapid cooling inhibited the transformation altogether. Similar results were observed by Elliott and Datars.[10]

The martensitic phase transformation in lithium has also been extensively studied. For this metal, however, there is general agreement that the transformation is extensive and as much as 80% of the metal transforms. Previous ultrasonic studies in lithium performed in this laboratory[11] showed that the transformation has a profound effect on the ultrasonic attenuation and velocity. The present study in sodium was undertaken to determine whether any premartensitic effects are present and whether, by careful sample preparation and rapid cooling, the transformation can be inhibited. The measurements were also undertaken in order to compare the results with those of our previous ultrasonic studies in lithium and with the results of the recent neutron scattering studies in sodium.

EXPERIMENTAL DETAILS

The single crystals were oriented along the [110] or [100] directions. Laue transmission photographs yielded extremely sharp and well-defined spots, indicating that the crystals were of high quality. Residual resistance ratios between room temperature and 4 K were typically 2000. The acoustic specimens were typically 5 mm thick and 16 mm in diameter. The ultrasonic signals were generated and detected by electromagnetic acoustic transducers, because these transducers eliminate the need for acoustic bonds on the surface and thus avoid straining the sample. A solenoid-type coil which generates linearly polarized waves and which can be rotated to vary the polarization direction was used for the transmitter, while a pancake-type coil which is sensitive to all polarizations was used for the receiver. The static magnetic field employed was typically in the range of 10 to 13 kG; by changing the direction of the magnetic field, $\hat{\mathbf{H}}$, either longitudinal, $\hat{\mathbf{H}}\perp\hat{\mathbf{q}}$, or transverse waves, $\hat{\mathbf{H}}\parallel\hat{\mathbf{q}}$, could be generated. $\hat{\mathbf{q}}$ is the direction of propagation. Measurements were made using a gated coherent phase-sensitive ultrasonic detection system at frequencies between 6 and 8 MHz, a technique described in detail in earlier publications from this laboratory.[11]

All experimental runs were done in a liquid-helium throttling Dewar. By regulating the throttling rate and the power input to the heater on the sample holder, it was possible to vary the temperature over the range of 4.2 to 90 K. The sample rested in a brass ring and no other mechanical contract was employed in order to avoid straining the sample.

RESULTS AND DISCUSSION

A typical plot of the temperature dependence of the fast shear velocity, associated with the elastic constant

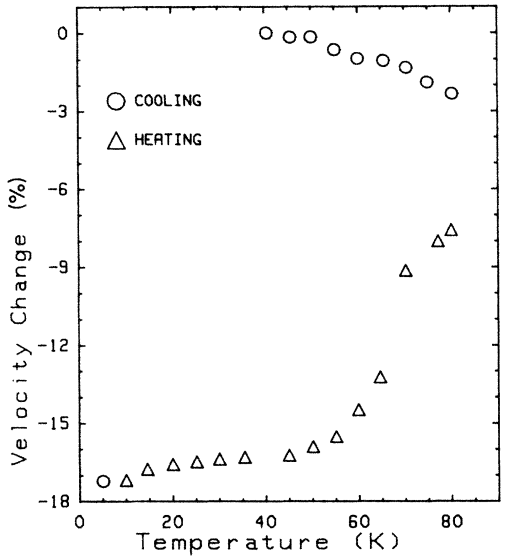

FIG. 1. Temperature dependence of the velocity of the shear wave corresponding to the elastic constant C_{44}, in sodium.

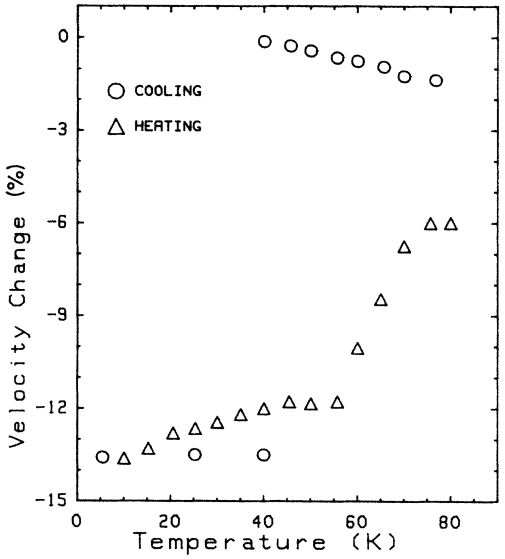

FIG. 3. Temperature dependence of the velocity of the longitudinal wave corresponding to the elastic constant C_n, in sodium.

C_{44}, is shown in Fig. 1. The sample was cooled from 90 K. At the transition temperature, T_m, an abrupt decrease in the velocity (typically 12–15 %) occurred. The velocity then remained relatively constant as the temperature was lowered to 5 K. During the heating cycle, the velocity increased in the temperature range between 50 and 75 K and then exhibited the normal temperature dependence; that is, the velocity decreased as the temperature increased. The corresponding temperature dependence of the ultrasonic attenuation for this mode is shown in Fig. 2. At T_m, an abrupt increase in the attenuation occurred (typically 11 to 23 dB/cm). The attenuation then decreased as the temperature was lowered to 5 K. During the heating cycle, a large decrease in the attenuation was typically observed for temperatures greater than 50 K, the reversion temperature T_r. However, the attenuation for a given temperature above T_r was higher than the initial value of the attenuation at that temperature.

The temperature dependence of the velocity and ultrasonic attenuation for longitudinal waves associated with the elastic constant C_n is shown in Figs. 3 and 4, respectively. Typical echo trains for the longitudinal waves measured at temperatures above and below T_m, as seen in Fig. 5, illustrate the change in velocity and attenuation before and after the transformation. The temperature

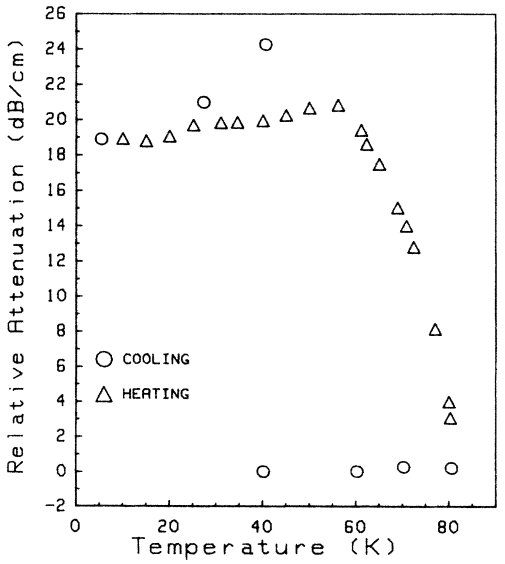

FIG. 2. Temperature dependence of the attenuation of the fast shear wave in sodium.

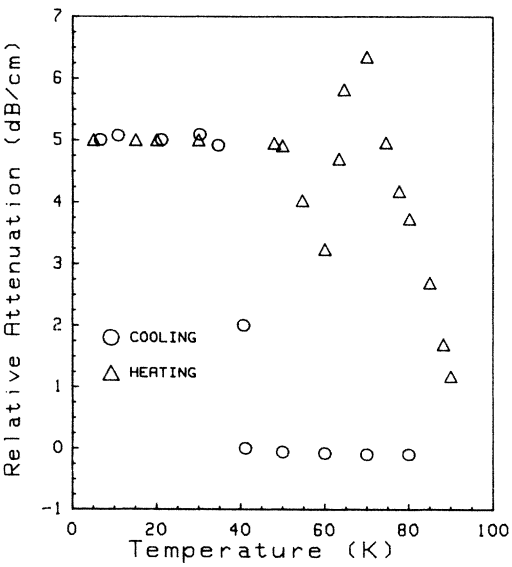

FIG. 4. Temperature dependence of the attenuation of the longitudinal wave in sodium.

dependence of the velocity was similar to that observed for the shear mode, as was the temperature dependence of the attenuation, except that a minimum at 60 K was observed. The temperature dependence of the slow shear mode was also studied; however, because of the extremely high attenuation, greater than 80 dB/cm, no signals could be observed below T_m. During the heating cycle, however, signals reappeared for temperatures near 60 K and the velocity was found to be larger than the pretransformation velocity at this temperature. This feature and the observed temperature dependence in the reversion region indicate that the velocity increased at T_m, which is similar to the results observed in lithium. Similar results were obtained for the longitudinal mode associated with the elastic constant C_{11} for measurements made on a crystal oriented along the [100] direction. Again, for this mode the velocity increased at T_m, along with a large increase in the attenuation.

For all the modes studied, no pretransformation effects in either the velocity or attenuation were observed, and in all cases the velocity and attenuation changed abruptly at T_m. The same effects were observed whether the sample was slowly or rapidly cooled through T_m. Typical changes in velocity and the ultrasonic attenuation are shown in Table I. The behavior of the attenuation and velocity is quite similar to the corresponding values obtained in lithium. The transformation temperatures determined in this study were between 40 and 43 K. Since the same was not in good thermal contact with the probe to avoid straining the sample, the actual temperature is estimated to be 35 K and in good agreement with previously reported values of this quantity. The transformation temperature in sodium is rather well defined, in contrast to lithium, where a range of transformation temperatures between 61 and 82 K was observed.

After each run, the sodium sample was x-rayed. Of the six samples studied, only one crystal retransformed back to a single bcc crystal with the same orientation. The other five underwent a structural reorientation as a result of the retransformation and showed several large grains. These results are consistent with the earlier work of Stedman[1] in that all but one of his crystals underwent a structural reorientation after the transformation, but different from lithium studies in which the crystals returned to the original [110] orientation after transformation. This "memory" effect in lithium and the absence of the effect in sodium is surprising, since in lithium a large fraction of the crystal transforms, while in sodium typically less than a few percent is expected to transform.

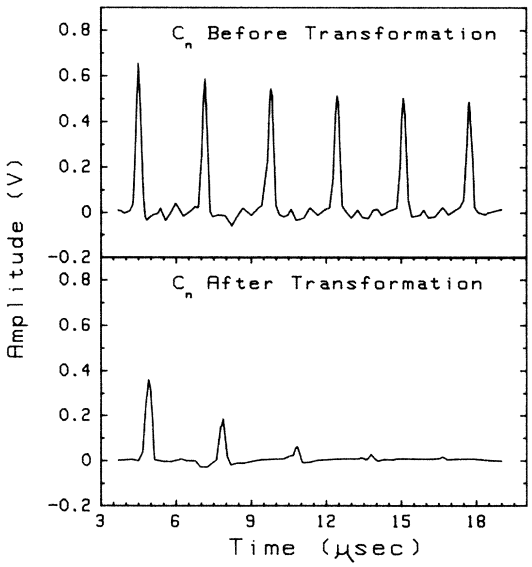

FIG. 5. Echo trains for the longitudinal wave in sodium, before the transformation (77 K) and after the transformation (30 K).

TABLE I. The ultrasonic velocity and attenuation changes at T_m.

Run	Mode	$\Delta V/V$ (%)	Relative attenuation (dB/cm)
2	C_{44}	−15.2	
3	C_{44}	−12.1	16
4	C_{44}	−14.2	11
5	C_{44}	−17.2	23
2	C'		>80
6	C_n	−13.6	10
7	C_n	−7	
8	C_{11}	12	11

The temperature dependence of the velocity for the longitudinal and shear modes in lithium[11] is shown in Figs. 6 and 7, respectively. The temperature dependence is very similar to that observed in sodium, as in the change at T_m. However, since lithium generally does not undergo a structural reorientation upon reversion, the velocity has the same value as before the transformation at high temperatures, which is not the case in sodium. The alkali metals have large elastic anisotropy so the velocity is a strong function of crystallographic orientation. Generally, after the transformation the sodium is a polycrystal so it is not surprising that the velocity does not return to its original value.

Based on the neutron results, the large changes in the ultrasonic velocity and attenuation as the sodium transforms are surprising. The magnitude of the velocity changes in sodium is comparable to that in lithium and is unexpected since only a small fraction of the bcc structure transforms in sodium, in contrast with lithium, where a much larger fraction of the crystal transforms. In addition, neutron studies show that the bcc structure in sodium below T_m has the same orientation. While the individual elastic constants undergo large changes at T_m, the appropriate linear combination of the elastic constants after the transformation, assuming the crystal is cubic with the same orientation, generally lead to a bulk modulus which is not significantly different from the value above T_m. This feature is consistent with isothermal compressibility data[12] which indicate that the compressibility is not strongly affected by the transformation.

Some features of the present study are consistent with the neutron diffraction experiments. Blaschko and

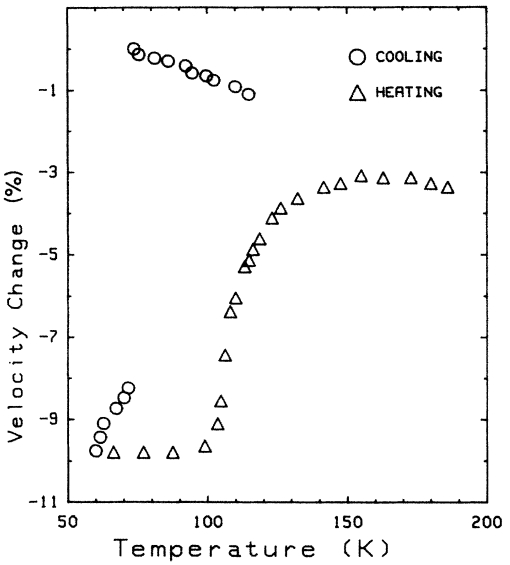

FIG. 6. Temperature dependence of the velocity of the longitudinal wave corresponding to the elastic constant C_n, in lithium.

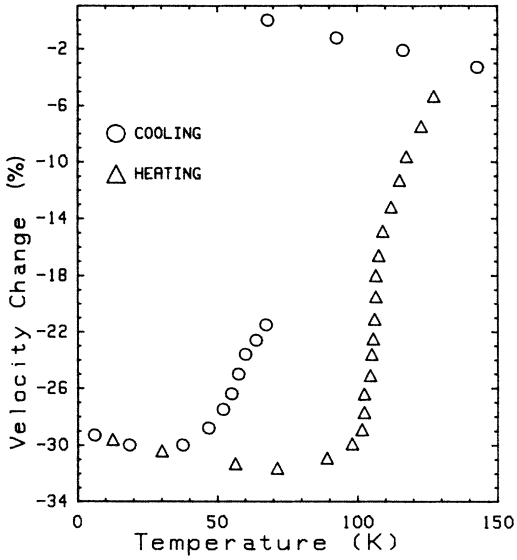

FIG. 7. Temperature dependence of the velocity of the fast shear wave corresponding to the elastic constant C_{44}, in lithium.

Krexner[2] used a neutron scattering technique to study the bcc-hcp transformation in sodium. Their experiment focused on pretransformation effects. No anomalous behavior was observed for the longitudinal and fast transverse-acoustic branches in the [110] direction or for the low-frequency modes in the slow transverse-acoustic branch. This is consistent with the temperature dependence of the velocity above T_m observed in the present study. However, for the slow transverse-acoustic branch, premartensitic effects were observed for high-frequency modes near the Brillouin-zone boundary. It should be noted, however, that the crystal used was of rather poor quality. The mosaic width of the sample was approximately 1° and was not affected by the transformation even if cycled through the transition temperature several times.

The study by Stedman shows that the mosaic width of the crystals increased from less than 0.1° between 1° and 2° at T_m, which corresponds to very large distortions. No marked frequency shifts and no broadening of phonon peaks were observed by Stedman as the transition temperature was approached from above or in the partially transformed crystals. While no marked shift of the phonon frequency peaks was observed, the integrated intensity fell to 0.3 of its original value. Stedman suggests that the mosaic misorientation leads to a blurring of reciprocal space which complicates the neutron scattering process since the phonons do not have well-defined q vectors. The large mosaic structure certainly can account for the large attenuation changes that were observed, but it is not clear that it can explain the large changes in velocity.

In summary, the absence of premartensitic transformation effects observed in the present study is consistent with the low-frequency data obtained in the neutron studies. In view of the extreme care used in handling the samples and methods to excite the acoustic waves and cool the sample, the large attenuation observed indicates that the transformation is difficult to inhibit and after the transformation the crystal is highly distorted. The results are very similar to those obtained in lithium. The reorientation effects observed in sodium are consistent with earlier studies.

ACKNOWLEDGMENTS

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