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Brief Reports

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Absence of a martensitic phase transformation (even an embryonic phase) in potassium as determined by an ultrasound study

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The temperature dependence and magnetic-field dependence of the nonlocal generation of ultrasound were measured between 1.8 and 25 K in high-quality potassium single crystals. The wave associated with the elastic constant C', which is extremely sensitive to any structural phase transformation, was studied. These electromagnetic-generation experiments clearly show that no anomalies in the elastic behavior occur, either in the bulk or within the skin depth. These measurements lend no support to the existence of a martensitic phase transformation or to the existence of an embryonic martensitic state in stress-free bulk potassium single crystals or within the skin depth of these crystals.

In a recent paper Wilson and dePodesta[1] suggested that many of the low-temperature anomalies in the physical properties of potassium that have been reported may be associated with the presence of embryonic martensites. They suggest that a model based on a precursor martensitic state is more consistent with these anomalies than with the charge-density-wave model proposed by Overhauser.[2] Later Blaschko[3] and his collaborators, using neutron-scattering techniques, reported experimental evidence of a tendency toward a low-temperature lattice instability in potassium. The important features of these experiments which impact on the present experiment are the presence of Huang diffuse scattering below 70 K and the irreversible change in the mosaic structure. The neutron-scattering results for potassium reported in Ref. 3 are controversial,[2] as are the results obtained by the same group in lithium[4] and sodium[5] which are known to undergo a martensitic phase transformation. In Li and Na, the observed temperature-dependent diffuse scattering is ascribed to the formation of an intermediate defect structure. The interpretation of the results, as well as the interpretation of the observed anomalous softening of the TA [110] branch near the zone boundary, are controversial.[6,7] A more recent study by Blaschko[8] in lithium single crystals indicates that the elastic diffuse scattering effects and the dip in the phonon curve near the reduced wave $\frac{1}{3}$ [110] previously reported are present only in crystals that had been cycled through the transformation. Even these results are questionable.[9]

It is well known that the martensitic phase transformation can have a profound effect on the physical properties of crystals including transport, thermodynamic, and structural properties. In many metallic alloys which undergo a first-order martensitic phase transformation, a variety of precursor effects occur as the samples are cooled toward the transformation temperature. In NiAl, in particular, anomalous changes occur in the phonon spectra,[10] elastic behavior,[11–13] thermal expansion,[14] and microstructure[15] (quasiperiodic "tweed" phases). We recently completed a study of the elastic behavior of NiAl alloys[13] of various compositions, in which an anomalous behavior in the ultrasonic velocity and attenuation was observed. These effects are most pronounced for C', which also softens as the sample is cooled, a clear signature of a lattice instability. The attenuation increases dramatically near M_s, and no evidence of C' waves can be detected at or below M_s. We have also done similar studies in lithium[16] and sodium[17] which undergo a martensitic transformation near 75 and 36 K, respectively. To avoid straining the samples and to eliminate the problem associated with bonding transducers to the sample, an electromagnetic generation technique was used to both generate and detect the ultrasonic signals in lithium and sodium. This technique has been described in detail elsewhere.[16]

In lithium and sodium no precursor effects were observed as the transformation temperature was approached. 20 Li single-crystal samples and 6 Na single-crystal samples were studied. Both the attenuation and velocity were measured for waves associated with the three independent elastic constants. The results of these studies showed that the ultrasonic technique is excellent for studying phase transformations and is an extremely sensitive probe, particularly for waves associated with the

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elastic constant C', which corresponds to the slow transverse mode. Typical results for the slow shear wave associated with the elastic constant C' in lithium are shown in Figs. 1 and 2 for the attenuation and the velocity, respectively. The data indicate that the transformation occurs very abruptly and the attenuation changes are large. No premonitory effects are present in either the attenuation or the velocity as the sample is cooled. If an intermediate defect structure were present prior to transformation, the attenuation would increase. The attenuation actually decreases as the transformation is approached while the velocity increases in a normal manner. The small signals observed below M_s are associated with multiple reflections of a fast transverse mode. In lithium the fast transverse velocity is approximately three times the slow transverse velocity. The temperature dependence of the velocity and of the attenuation for the fast shear mode and the longitudinal mode show similar behavior. Similar results were obtained in Na, however, no evidence of the C' wave was obtained below M_s. The studies in lithium and sodium show that the phase transformation occurs very abruptly and no premartensitic effects are present in the velocity, the attenuation, or the generation amplitude for any of the three independent elastic constants. The sensitivity of the ultrasonic technique to defects and microstructure can also be seen by examining the behavior of the velocity and the attenuation in the reversion region. Below 130 K, defects and stacking faults are still present. In Fig. 1, the attenuation is about 2 db/cm at 120 K. For an echo with a path length of 3 cm, the amplitude is a factor of 2 lower than the amplitude in the untransformed crystal. These results show that the ultrasonic attenuation is even more sensitive to the presence of defects than the neutron-scattering techniques are. These ultrasonic results are consistent with neutron-scattering studies in sodium and lithium conducted by Smith and his coworkers. Other ultrasonic studies in Cu-Al-Zn (Ref. 18) and InTl (Ref. 19) systems also show that the transformation affects the

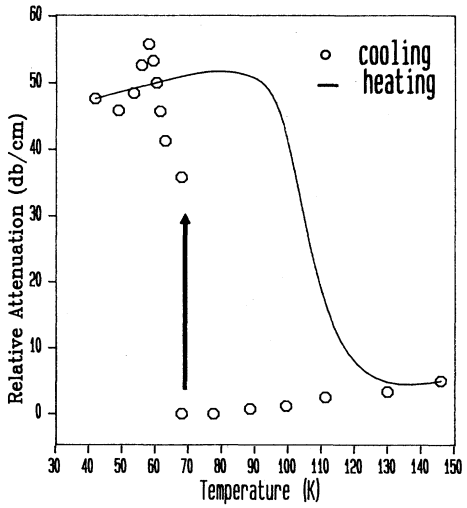

FIG. 1. Temperature dependence of the attenuation of the shear wave corresponding to the elastic constant C' in lithium.

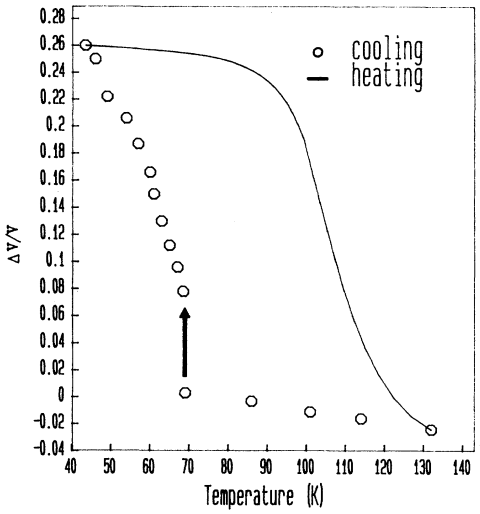

FIG. 2. Temperature dependence of the velocity of the shear wave corresponding to the elastic constant C' in lithium.

elastic properties in a dramatic way, particularly for C' which is more sensitive to the transformation than most other physical properties are. Because of the sensitivity of the ultrasonic method employing electromagnetic transducers and the possibility of the existence of a martensitic transformation or martensitic embryos in potassium, we decided to extend our studies to potassium.

Since the electromagnetic generation takes place in the skin depth, this technique is excellent for studying both bulk and surface properties. Martensitic embryos, if present, are usually associated with defects which occur in a crystal, and the large strains associated with these defects can initiate a transformation. The most likely sites to initiate the transformation in single crystals generally are believed to be at or near the surface. A number of ultrasonic studies have already been done in potassium for temperatures as low as 1.2 K.[20] Most of these studies used longitudinal or fast shear waves to study a variety of magnetoacoustic effects. No evidence of a bulk martensitic effect has been reported in any of these studies. This, of course, does not rule out the presence of martensitic embryos. To look for the lattice instability in K, we decided to study the temperature and magnetic-field dependence of the nonlocal generation of ultrasound associated with the elastic constant C'. In a high-purity crystal at low temperatures elastic waves can be generated even in the absence of an external field if the electron mean free path is larger than the skin depth. The magnetic-field dependence of the nonlocal generation of ultrasound in K at 4.2 K was previously studied in this laboratory.[21] The nonlocal generation of ultrasound is a sensitive probe for studying the presence of a lattice instability. If microstructure develops within the skin depth, the generation efficiency should be reduced. Since premartensitic embryos are most likely to be found in the skin depth, a reduction in the generation efficiency would be observed. Thus, this technique is not only a sensitive probe for observation of microstructural anomalies within the skin depth (1 μm at 10 MHz), but it also allows one to probe

both the surface and the bulk. Our preliminary experiments in NiAl using the electromagnetic-generation technique show that the generation amplitude is affected well above the M_s observed in the bulk, establishing that this technique is extremely sensitive to the formation of defects within the skin depth. The nonlocal generation technique, therefore, is expected to be an even more sensitive probe of microstructure.

The potassium single crystals used in the studies were grown by a modified Bridgman technique. They were optically oriented to determine the nearest [110] direction of the boule axes. The potassium crystals had a residual resistance ratio in excess of 3000 between room temperature and 4.2 K. Because generation in the nonlocal limit requires a mean free path greater than the skin depth, an elaborate lapping technique was used to polish the acoustic specimens to avoid damaging the surfaces. A wheel in a vertical plane was rotated asynchronously with the sample which was mounted in a steel lapping ring held by a magnetic chuck. The sample was positioned so that it did not make contact with the wheel but only with the etchant on the paper spread over the wheel. In this manner highly polished damage-free parallel faces were obtained on the acoustic specimen. The ultrasonic probe had a solenoid transmitter coil which could be rotated, and a fixed pancake receiver coil. By appropriate orientation of both the external magnetic field and the transmitter coil, all three independent elastic constants could be studied for crystals oriented in the [110] direction.

Measurements were made from 77 to 1.5 K for ultrasonic frequencies between 5 and 10 MHz. Although the primary focus was to study nonlocal generation of ultrasound in the absence of an external magnetic field from 9 to 1.5 K, we also studied the temperature dependence of the magnetically generated ultrasound. In the presence of a magnetic field, the generation amplitude showed no anomalous behavior between 77 and 4.2 K. The quality of the echoes for the C' mode was excellent at high fields and three echoes could easily be observed. Near 4.2 K for magnetic fields below the absorption edge, bulk attenuation effects characteristic of electron-phonon interaction at low temperature were clearly evident and estimated to be 30 db/cm at 10 MHz. In addition to the attenuation, the temperature dependence of the velocity was also studied. For all modes studied, the velocity exhibits normal behavior; that is, the velocity increases as the temperature is lowered. This is consistent with our earlier study of the elastic constants of potassium.[22]

Of greater significance is the nonlocal generation of ultrasound. Figure 3 shows the nonlocal generation amplitude as a function of magnetic field at 5 K. It should be emphasized that although the electronic contribution to the attenuation for the C' mode is extremely high, 30 db/cm at 10 MHz, we, nevertheless, can readily detect signals. Again, it is also important to note that, in order to obtain nonlocal generation of ultrasound, the electron mean free path near the surface must be larger than the skin depth. The existence of an ultrasonic signal is obviously clear evidence of a crystal surface of very high quality.

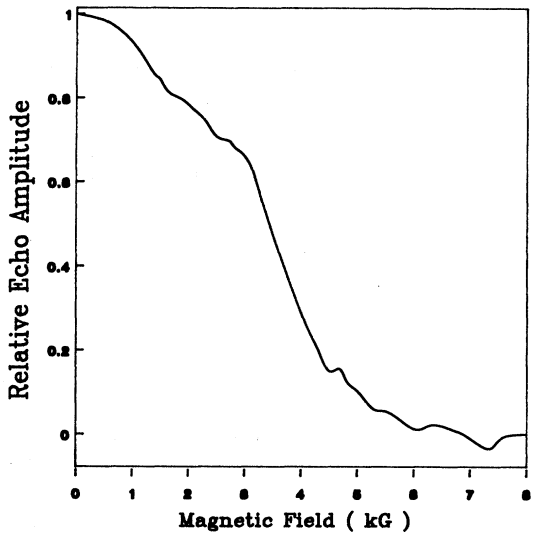

FIG. 3. Detected magnetic-field dependence of the nonlocal amplitude associated with the elastic constant C' in potassium. Corrections for the magnetic-field dependence of the electronic contribution to the attenuation have not been made.

The temperature dependence of the nonlocal generation amplitude was studied between 1.8 and 9 K. Figure 4 shows the detected signal amplitude at $H=0$ as a function of temperature between 9 and 1.5 K. The data were taken by measuring the amplitude at $H=0$ at 5 K as seen in Fig. 3 and then monitoring the amplitude as the temperature was lowered to 1.5 K. In this temperature range the electron mean free path is essentially impurity limited. As a consequence the electronic contribution to the attenuation and the nonlocal generation amplitude are independent of temperature. Clearly no evidence of a transformation or premonitory effects exist in this temperature range. As the temperature is increased above 5 K, the nonlocal generation amplitude decreases and then

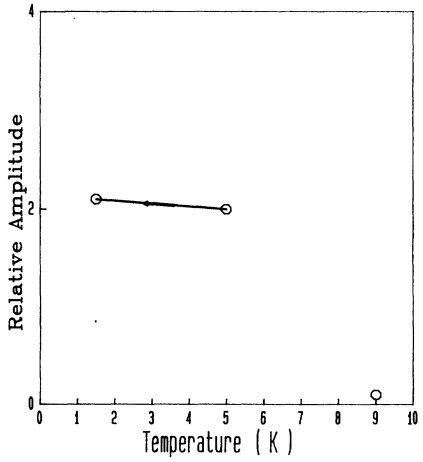

FIG. 4. Temperature dependence of the relative zero-field signal amplitude corresponding to the elastic constant C' in potassium.

disappears near 9 K. This temperature dependence is consistent with the temperature dependence of the electron mean free path which is impurity limited below 5 K and phonon limited above 5 K. Since the electron mean free path decreases significantly near 9 K, the condition for nonlocal generation is no longer satisfied. A growth in the premartensitic embryo density below 9 K would manifest itself both as a decrease in the generation amplitude and as a change in the magnetic-field dependence as the temperature is decreased. These effects are not observed.

Since the work is Ref. 3 showed a spread in the mosaic width of the crystals on cooling, we cycled the sample several times in temperature to check for deterioration in the signals. When the potassium sample was heated to 50 K and then cooled to 5 K, no change of either the ultrasonic attenuation or the generation amplitude in the nonlocal limit was observed. This behavior is consistent with recent neutron-diffraction experiments[23,24] in high-quality potassium single crystals where cycling the sample in temperature had no effect on either the elastic scattering or the mosaic width.

Our nonlocal generation experiments clearly show that the embryo martensites, if present, do not affect the elastic behavior in any detectable way either in the bulk or within the skin depth. Thus, it is unlikely that they manifest themselves in any other bulk physical property. Since our ultrasonic results as well as the neutron-scattering results (Refs. 23 and 24) do not exhibit any changes in mosaic width, we believe the origin of the increase in mosaic width as the sample is cooled as well as the alleged precursor effects that have been reported in K (Ref. 3) is due to the manner in which the samples are clamped. Plastic deformation which results from improperly clamping the soft alkali metals can account for the increase in mosaic width and the so-called precursor effects that have been reported (Ref. 3). The present study, therefore, lends no support to the existence either of a martensitic phase transformation or of an embryo martensitic state in unstrained bulk potassium single crystals or within the skin depth of these crystals.

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