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Absence of precursor effects above the martensitic transformation in a virgin crystal of Li metal

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Measurements of the short-wavelength Σ_4 phonons in a virgin crystal of Li metal at 293, 200, 100, and 80 K show a slight softening of the phonons with a decrease in temperature, as observed in some other alkali metals, contrary to all the other phonon branches measured in high-symmetry directions. Theoretical anharmonicity calculations predict this anomalous behavior even for Rb, which does not undergo a transformation. Diffuse scattering measurements in the vicinity of the (110) and (200) reflections at 200, 100, and 80 K did not reveal any unusual changes. There is an overall increase in the background as the temperature was decreased, which is attributed to the Debye-Waller factor associated with the large spin-incoherent scattering. The widths of the phonon groups also decreased as the temperature was lowered. These and other neutron-scattering measurements, along with ultrasonic attenuation studies fail to give evidence for precursor effects of the $9R$ transformation in virgin crystals of lithium metal.

I. INTRODUCTION

In many materials that undergo first-order martensitic phase transformations there are often precursor effects above the transition.¹ These precursors may manifest themselves in a variety of forms, such as phonon anomalies, diffuse scattering, and/or strong ultrasonic attenuation effects, among others. In our extensive neutron-scattering²⁻⁴ and ultrasonic⁵⁻⁷ studies on the martensitic behavior of metallic lithium, in both single-crystal and polycrystalline samples, at atmospheric and modest pressures, we have looked very carefully for effects that could be considered precursors or premartensitic phenomena—with negative results, contrary to some reports.⁸⁻¹⁰ Clarification of these disagreements may be crucial for distinguishing between different theories¹¹⁻¹⁴ of the mechanism for the transformation.

The main points of contention are: (1) While the short-wavelength low-lying Σ_4 phonons soften somewhat, contrary to quasiharmonic theory, anharmonic phonon calculations¹⁵⁻¹⁷ predict such behavior for this branch in all the alkali metals. Some materials show this behavior and clearly do not transform; Pb, Nb, and TaC are examples. Our initial phonon measurements² found no evi-

dence of even a slight dip in the Σ_4 branch at $(\frac{1}{3}, -\frac{1}{3}, 0)$ as others have claimed.⁸ (2) While we also observed a temperature-dependent diffuse background in the bcc phase, this is attributed¹⁸ in large part to the Debye-Waller factor in the large spin-dependent incoherent neutron scattering in Li, natural or isotopic ⁷Li, and is insufficient evidence for the presence and growth of martensitic embryos. Ultrasonic attenuation measurements provide a very sensitive tool for detecting defects in many systems, but measurements⁷ in Li show no evidence for attenuation until the onset of the transformation. (3) The sudden decrease in the (110) bcc intensity at the transition is corroborated by the sudden appearance of the $9R$ peak without a buildup in diffuse intensity at the appropriate q vector. Recent theoretical studies indicate that for pure materials undergoing first-order transitions, precursors are not required.^{13,14}

Because of the conflicting results and because these results are crucial for distinguishing between different theories, we recently initiated a detailed study of the temperature-dependent behavior of the Σ_4 branch under higher instrumental resolution with a virgin crystal of isotopic ⁷Li. These experiments are discussed below with, for completeness, some previously unpublished results.

II. RELATION OF THE 9R LATTICE TO THE bcc LATTICE

As shown in several studies, bcc Li partially transforms from the open bcc structure to a close-packed Sm-type (9R) structure with numerous stacking faults that broaden and shift some of the Bragg peaks from integer indices. The transition temperature varies from sample to sample and with their thermal history, varying from 60 to over 80 K, and a large fraction of the sample remains bcc (from about $\frac{1}{3}$ to $\frac{2}{3}$). The orientation relation of one variant of the 9R lattice with respect to the bcc lattice is shown in Fig. 2 of Ref. 2. The c and a axes of one 9R variant are oriented about 3° and 5° away from the $[110]$ and $[\bar{1}\bar{1}0]$ bcc directions, respectively. There are four possible variants about each of the six bcc $[110]$ directions. Generally, the variants are not of equal intensity. A neutron-diffraction grid scan in Fig. 1 shows the coexisting (110) bcc and (009) 9R Bragg peaks. In addition to the two (009) peaks shown above the plane at (1.019, 0.924, 0.006) and (0.924, 1.019, 0.006), there are two more below the $(hk0)$ plane.

Since the 9R rhombohedral lattice is indexed on a trigonal lattice, only those indices which satisfy the relation $-H + K + L = 3N$ are allowed. In addition, only those HHL reflections with $L = 9N$ are allowed and they have the maximum possible contribution to the scattered intensity. Also, the latter are the only reflections that are not shifted from integer values. A more detailed description of the 9R lattice and structural parameters has been given previously^{2,3,19,20} and will not be repeated here.

III. EXPERIMENTAL

Our initial published results² on single-crystal lithium were on crystals of natural lithium (crystals *A*, *B*, and *C*), which contain 7.5% of the neutron-absorbing ⁶Li isotope.

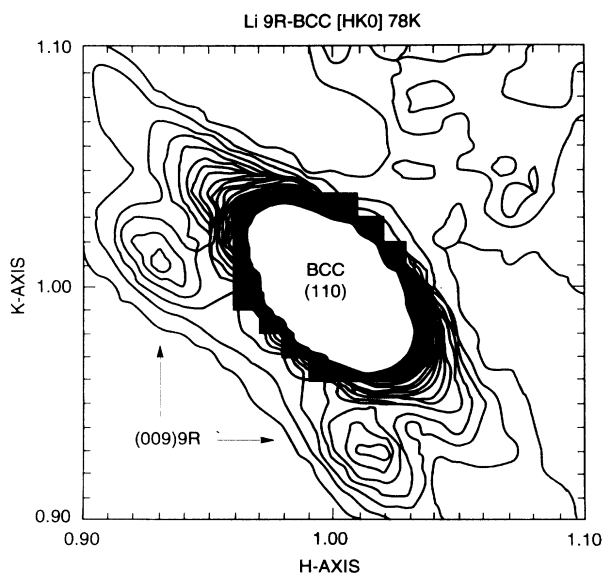


FIG. 1. Coexisting bcc (110) reflection with the (009) 9R reflections from two variants. There are two more (009) 9R peaks below these.

Our most recent neutron-scattering results were obtained with a crystal grown utilizing lithium metal enriched to 99.99% ⁷Li. Although the lower neutron absorption gave stronger Bragg reflections and phonon intensities, the general background was still very high due to the large spin-incoherent-scattering cross section, which is larger than the coherent-scattering cross section.

The data reported herein, new and old, were taken on the HB-3 triple-axis spectrometer at the High Flux Isotope Reactor (HFIR). The crystals were sealed in a vanadium can in a helium atmosphere and mounted in a closed-cycle refrigerator. The temperature was monitored and controlled automatically by the spectrometer computer. To avoid clamping the crystals, and damaging them by introducing plastic deformation, they were lightly packed in quartz wool to keep them from moving during the experiments. The vanadium can was used to avoid the lines and spots from the machined aluminum cans that are often used.

IV. MEASUREMENTS AT 100 AND 80 K

The recent measurements made with the low-absorption ⁷Li crystal were under conditions of good resolution with a Be(002) monochromator plane and either a Be(002) analyzer or a pyrolytic graphite (PG) (002) analyzer with a wavelength of 2.359 Å ($E = 3.555$ THz or 14.70 meV) and collimation of 60° - M - 40° - S - 40° - A - 70° . A PG filter was mounted in the diffracted beam with fixed E_f . (The crystal was in its virgin state, never having been transformed previously). The total width of its rocking curve (which includes the instrumental resolution width), at 200 K was 0.18° with the Be analyzer and 0.35° with the PG analyzer.

The Σ_4 phonons and their widths were carefully measured at 100 K and several quasielastic scans were performed (i.e., centered about $E = 0$) at q values of $(-0.2, 0.2, 0)$ and $(-0.35, 0.35, 0)$. The crystal temperature was slowly lowered to 80 K and the alignment scans made at 100 K were repeated. The rocking-curve width of the (110) reflection was identical to that at 100 K, but the intensity increased slightly due to the decrease in the Debye-Waller factor. On repeating the phonon measurements it was noticed that the intensities were about half their values at 100 K. A remeasurement of the rocking curves revealed a large increase in the mosaic width (0.85° vs 0.35°), indicating the crystal had partially transformed (perhaps 50%). The measurement of the Σ_4 branch was continued, along with the measurement of the peak widths. As shown in Fig. 2(a), the Σ_4 branch shows no dip in either the untransformed crystal at 100 K or the partially transformed crystal at 80 K; nor is there a dip at $(-\frac{1}{3}, \frac{1}{3}, 0)$ in the differences of their frequencies [Fig. 2(b)]. The fluctuations of the differences are of the order of the experimental uncertainties of the measurements. The widths at 80 K are, if anything, slightly lower than at 100 K [Fig. 2(c)], the opposite of what one would expect if the phonons play a role in the transformation. The widths of the quasielastic peaks were also the same, within experimental error. The peak height increased slightly, similar to the Bragg peak and

for the same reason.

In order to detect any defect scattering one must subtract the large temperature-dependent spin-incoherent scattering from the background. This type of scattering in polycrystalline ${}^7\text{Li}$ was extensively studied by McCarthy, Tompson, and Werner,¹⁸ and shown to be large and anharmonic and very temperature dependent. Our results and interpretation are completely consistent with Ref. 18 and also with the very sensitive ultrasonic

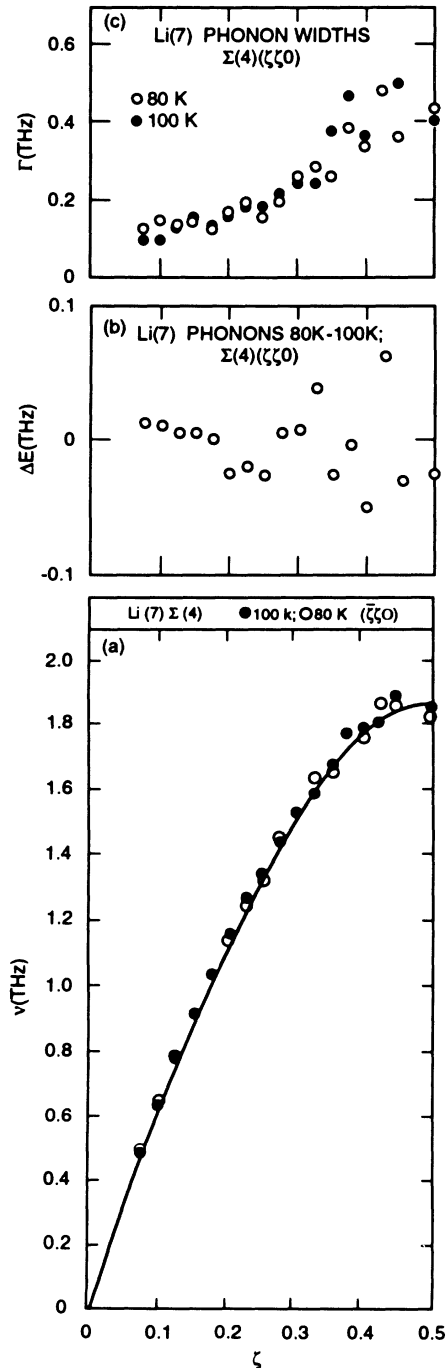


FIG. 2. (a) Dispersion of the Σ_4 branch, $[\bar{1}10]$ direction with $[110]$ polarization, at 100 and 80 K. (b) Difference of the frequencies of the Σ_4 branch between 100 and 80 K. (c) Widths of the Σ_4 phonons at 100 and 80 K.

measurements.^{7,21} Ultrasonic attenuation and velocity measurements show that for all elastic modes the velocities and attenuation change abruptly at M_s , and no precursor effects were observed. Figure 2 of Ref. 21 shows the gradual increase of the velocity associated with the C' elastic constant as the temperature was lowered toward M_s , i.e., there is no precursor softening of C' . The attenuation of the ultrasonic signal for this mode is shown in Fig. 1 of Ref. 21. The latter data are particularly significant in that as M_s is approached the attenuation actually decreases, which is not consistent with the formation of embryonic states prior to the transformation. A partial warming to 118 K and then recooling led to a less sharp transformation near 74 K. However, after the crystal was heating to 180 K and then re-cooled, a sharp transformation was again observed. Evidently, an annealing temperature of 180 K or higher is necessary to remove the defects responsible for the attenuation of the ultrasonic signals. This may be due to the small amount of fcc phase (determined in the neutron studies), that remains on warming to about 180 K. Therefore, both the neutron-scattering and ultrasonic attenuation results strongly suggests that there are no premartensitic embryos in lithium.

V. DISCUSSION

Based on the bcc lattice, the (009) 9R peak occurs at a Q value of (1.019, 0.924, 0.006). A nonvirgin (previously transformed) crystal was set at this position and the intensity of the background was monitored while the temperature was slowly lowered from 78 to 65 K. The background slowly increased, as expected, but there were no indications of a (009) peak until the transformation occurred (monitored in this case at 30-sec intervals); see Fig. 3. The crystal previously had transformed at about

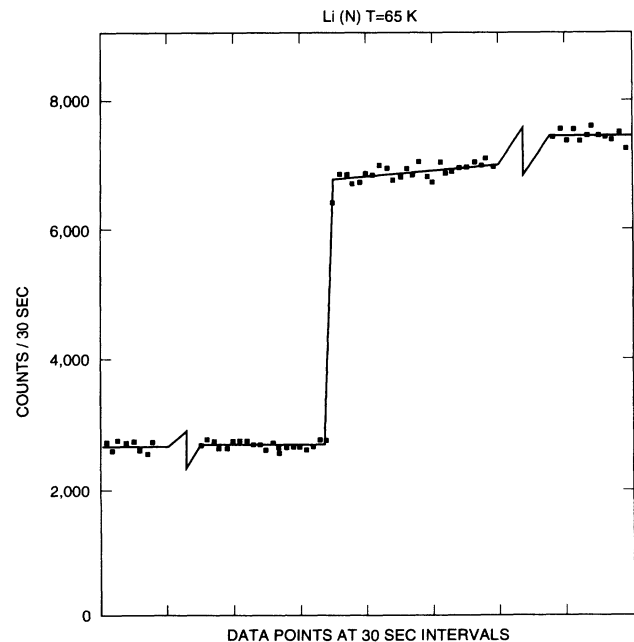


FIG. 3. Onset of the (009) 9R peak, (1.019, 0.924, 0.006) bcc, at 65 K.

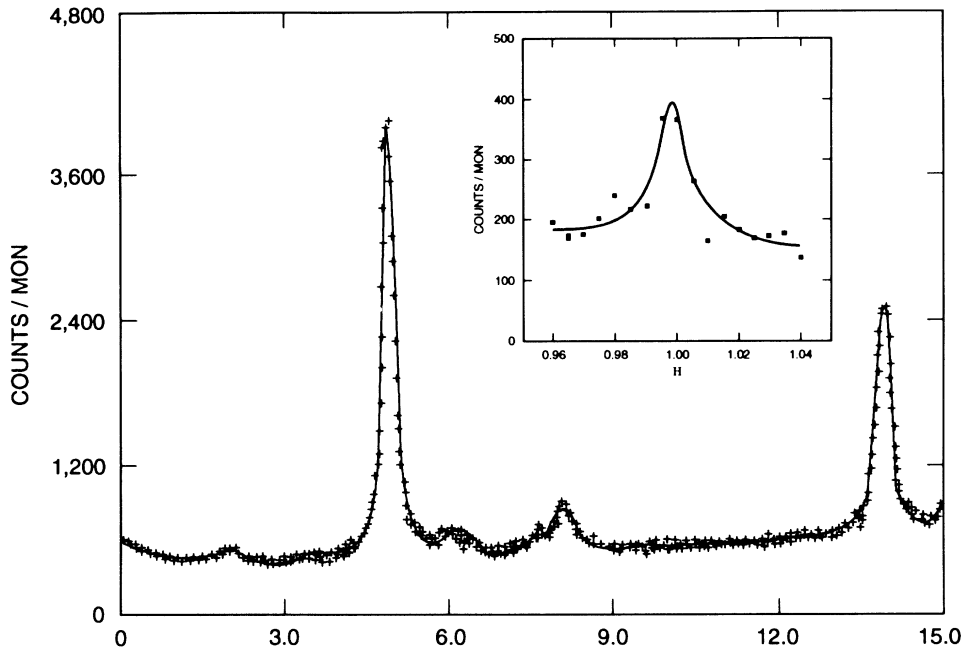


FIG. 4. Partial scan of the $(\bar{1}0L)$ line of the $9R$ reciprocal lattice. The inset shows a scan across the diffuse ridge at $(100.45) 9R$.

74 K and was then warmed and annealed at 200 K, but in this cycle M_s was 65 K, and then only after waiting at this temperature for over an hour.

A typical $(\bar{H}0L)$ scan with the $(\bar{1}02)$, $(\bar{1}05)$, $(\bar{1}08)$, and $(\bar{1}014)$ peaks is shown in Fig. 4. The $(\bar{1}06)$ peak is due to a small amount of the fcc phase and is corroborated by the observed, but weak, (103) and (1012) peaks in the $(H0L)$ scan. The small peaks at $(\bar{1}06.4)$ and $(\bar{1}07.8)$ are unknown, but there are often extraneous peaks in these patterns and one must use caution in interpreting these peaks. Sometimes peaks from other variants can be observed, particularly with coarse collimation. For example, the (1010) peak is usually overwhelmed by the (200) bcc reflection. The increase near $(\bar{1}00)$ can be shown to be associated with the (009) reflection from another variant. The absence of peaks at $(\bar{1}04.5)$, $(\bar{1}09)$, and $(\bar{2}00)$ indicate there is no hcp phase present. (This is in contrast to Na where there is a tendency for hcp-type stacking,²² but no evidence of any fcc phase.) The absence of the $(\bar{1}04)$ peak indicates that there is no submicroscopic twinning such as occurs in samarium metal¹⁹ with the $9R$ structure. The scan centered about $(\bar{1}00.45) 9R$, (Fig. 4 inset), shows the sharpness of the diffuse ridge across the $(\bar{1}0L)$ line in reciprocal space. This diffuse ridge is related to the stacking faults in the transformed crystal; however, there is no evidence for stacking faults in the untransformed portion of the crystal.

Figure 5 illustrates the shifts of the (101) and (104) peaks from integer values. The shifts and widths are indicative of the stacking faults in the system and appear to be sample independent. Model calculations of numerous types of stacking faults by Berliner *et al.*³ show that only

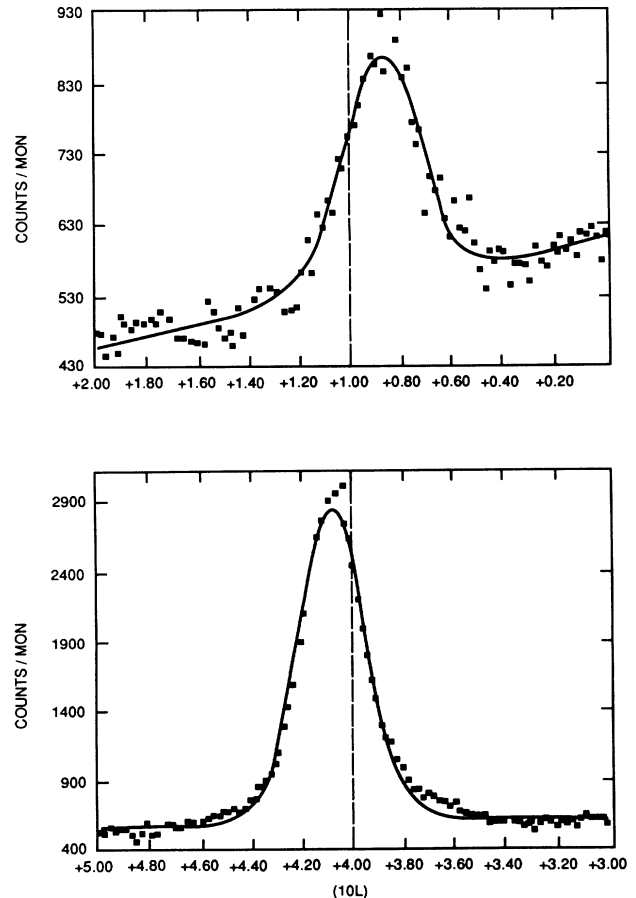


FIG. 5. Shifts and widths of the (101) and (104) $9R$ peaks.

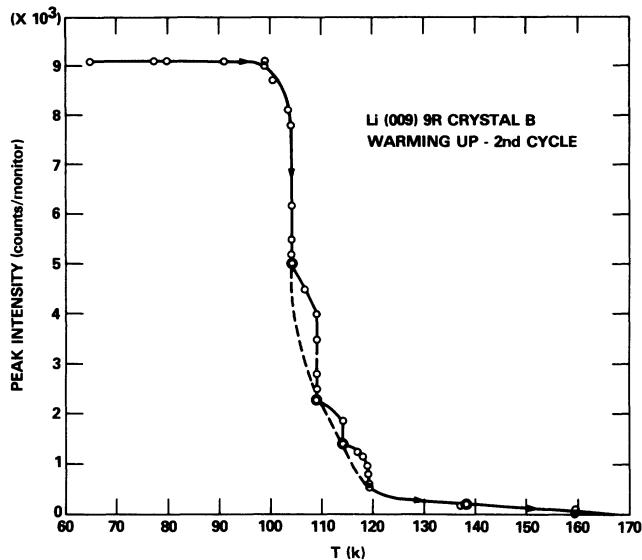


FIG. 6. Peak intensity of the (009) 9R reflection on warming.

one particular fault is consistent with the observed diffraction data.

Finally, Fig. 6 shows the hysteresis of the transformation as the temperature is slowly increased from 65 K. The intensity remains constant until about 100 K and then decreases sharply as the temperature is increased. It was necessary to repeat the intensity measurements several times at each temperature until equilibrium was reached. It is believed that the dashed curve in the figure more nearly represents the true behavior of the reverse transformation of the 9R phase. The slow decrease of the

curve above 120 K is now thought to represent the hysteresis of the fcc phase that had grown at the partial expense of the 9R phase (see Ref. 4).

VI. CONCLUSIONS

The martensitic phase transformation in a virgin crystal of lithium appears to be of first-order character; the onset is abrupt and there is a pronounced hysteresis on warming. There are no observable precursor effects in any way, there are no phonon anomalies in the Σ_4 branch, there is no increase in the bcc phonon linewidths, either before or after the transformation, and there is no change in the rocking curves or Θ - 2Θ scans until the transformation. Furthermore, there was no diffuse scattering observed in the bcc phase that could be attributed to embryonic defect scattering, and this is consistent with the more sensitive ultrasonic attenuation studies. These observations and conclusions appear to be valid for previously transformed crystals as well, if they have been warmed up sufficiently (at least above 180 K), in order to anneal out any 9R and fcc crystallites that may be present. These results are consistent with recent theoretical studies,^{13,14} in which precursors to first-order transitions are not required.

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