

Low-temperature martensitic phase transition of bcc lithium

G. Ernst

Institut für Physik, Forschungszentrum Seibersdorf, A-2444 Seibersdorf, Austria

C. Artner, O. Blaschko, and G. Krexner

Institut für Experimentalphysik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

(Received 25 July 1985)

The low-temperature martensitic phase transition of bcc lithium has been investigated by means of neutron scattering techniques. A softening of the low-lying transverse-acoustic $[110]$ phonon branch polarized along $[1\bar{1}0]$ is found when the transition temperature is approached. Moreover, a diffuse scattering unmodulated in reciprocal space is observed showing a hysteresis in the vicinity of the transition. The low-temperature phase appears at 74 K where an orientation relation $(110)\text{bcc}||(\text{002})\text{hcp}$ is observed. Finally, connected with the appearance of the new phase a streaked intensity extending from the $(110)\text{bcc}$ toward the $(220)\text{bcc}$ reflection is found indicating the presence of stacking faults on $(110)\text{bcc}$ planes. The results corroborate a model for the phase transformation recently put forward for the related transition in Na and describing the basic feature of the transition as a short-wavelength shear instability occurring on $(110)\text{bcc}$ planes.

I. INTRODUCTION

Lithium, while exhibiting a bcc structure at high temperatures, undergoes a martensitic phase transformation near 70 K. The transition was discovered in 1956 by Barrett, who considered the low-temperature phase to be characterized by a faulted hcp structure.¹ Furthermore, he noticed that the transformation shows a hysteresis depending on previous mechanical treatment. Only very recently, in view of neutron scattering results on polycrystalline lithium samples, Overhauser proposed a 9R structure for the low-temperature phase composed of hexagonal planes with an *ABCBCACAB* stacking sequence in contrast to the *ABAB* stacking of the hcp structure.²

In order to elucidate the origin of the structural instability occurring in some bcc alkali metals at low temperatures, recently a neutron scattering investigation on bcc sodium was performed,³ the results of which were essentially based on three findings. First, the low-lying transverse-acoustic phonon branch $\text{TA}_1[110]$ (polarized along $[1\bar{1}0]$) showed a softening of a few percent with decreasing temperature at the zone boundary. Secondly, an elastic diffuse scattering appeared in the vicinity of the transition covering a wide region of reciprocal space and exhibiting a marked hysteresis as a function of temperature while being unmodulated in q space. Thirdly, a measurement of the pressure dependence of the $\text{TA}_1[110]$ phonon frequencies at room temperature yielded a microscopic Grüneisen parameter dispersion curve approaching zero near the zone boundary, contrary to previous theories.⁴

These results have led to the formulation of a phenomenological model describing the onset of the transition as to be induced by a short-wavelength $(110)[1\bar{1}0]$ shear instability. The increase of the microscopic anisotropy of the bcc matrix with decreasing temperature is reflected by the lowering of the $\text{TA}_1[110]$ phonons in the vicinity of the zone boundary. The corresponding enhance-

ment of the instability facilitates the formation of stacking faults on (110) planes which locally implement an hcp stacking sequence and therefore subsequently can act as nuclei for the new phase. As soon as these nuclei have grown sufficiently in size as to make up for the energy due to surface tension and distortions, the transformation will proceed, and after a slight readjustment of the interatomic distances the transition will finally result in a fully developed hcp structure.

A basic physical ingredient of this mechanism is formed by the microscopic shear anisotropy of the bcc matrix in accordance with the seminal work of Zener, who related the phase transitions in several bcc systems to the anisotropy of the macroscopic elastic constants.⁵ In addition, a similar mechanism based on the formation of stacking faults on close-packed (002) planes has been proposed for the pressure-induced phase transition in RbI. This substance likewise exhibits low-lying shear modes decreasing further when approaching the transition pressure.⁶ The applicability of this concept to the transformation in RbI has been corroborated by recent molecular-dynamics calculations.⁷

The transformation mechanism proceeding via the formation of stacking faults as shortly outlined above encompasses the following stages which should be experimentally observable.

- (a) A low-lying transverse-acoustic phonon branch decreasing further near the transition temperature.
- (b) An intermediate defect structure becoming apparent in elastic diffuse scattering.
- (c) The orientation relation $(110)\text{bcc}||(\text{002})\text{hcp}$.

The first two points have been confirmed in the earlier experiment on sodium,³ whereas the validity of the latter could not be examined due to the fact that the development of the new phase remains largely incomplete without the additional application of mechanical deformation. The amount of the sodium sample having actually

transformed to the low-temperature hcp structure was so small that no orientation relation could be established.

The present experiment on lithium was undertaken in order to corroborate the concepts related to the bcc instability in alkali metals. The transformation temperature of lithium is higher (78 K compared to 36 K in sodium), and up to 100% of the crystal volume may form the structure of the low-temperature phase so that the different stages of the transition can be followed in a more complete way. This was done by means of a neutron scattering investigation, the results of which are presented as follows. In Sec. III we describe the behavior of the phonon frequencies of the $TA_1[110]$ branch as a function of decreasing temperature. In Sec. IV we report the results of the search for an orientation relation between the two phases, and Sec. V deals with the investigation of the diffuse scattering. In Sec. VI some further aspects of the phase transition are discussed which arise from a comparison between lithium and sodium.

II. EXPERIMENTAL

The neutron scattering investigation was done on the triple-axis spectrometer VALSE located at the G4.3 neutron guide position of the cold source of the Orphée reactor at Saclay. Pyrolytic graphite (PG) (002) crystals were used both as a monochromator and as an analyzer. A pyrolytic graphite filter was employed in the incoming neutron beam, and correspondingly the energy was set to the filter window wavelength near 14 meV. Collimations of 30' angular divergence were used throughout.

The sample was a cylindrical single crystal of ^7Li with a volume of about 1 cm^3 . The mosaic spread at the beginning of the experiment was approximately 40'. The crystal oriented in [001] direction was mounted in a closed-cycle cryostat.

III. PHONON MEASUREMENTS

The $TA_1[110]$ phonon branch was investigated in the Brillouin zone around the (200) reciprocal-lattice point. Measurements were performed in the temperature interval between 200 and 78 K. The corresponding changes in the phonon frequencies are presented in Fig. 1. The entire branch exhibits a softening of a few percent; this softening becoming even more pronounced with increasing wave vector. This contrasts with the earlier results obtained for sodium where the softening applies only to the phonons near the zone boundary. Between 200 and 80 K the relative frequency shift of the zone boundary phonon in lithium amounts to nearly 10% in comparison with about 3% for sodium. Moreover, the present results show that in lithium the decrease in frequency for the phonon with reduced wave vector $q=0.4$ is even stronger than that for the phonon located exactly at the zone boundary ($q=0.5$).

Earlier measurements of the $TA_1[110]$ phonon dispersion at different temperatures have been performed by Beg and Nielsen⁸ at 293 K and Smith *et al.*⁹ at 98 K. An examination of their respective results already points to a softening of the entire branch in agreement with the present investigation. The frequency shifts obtained from

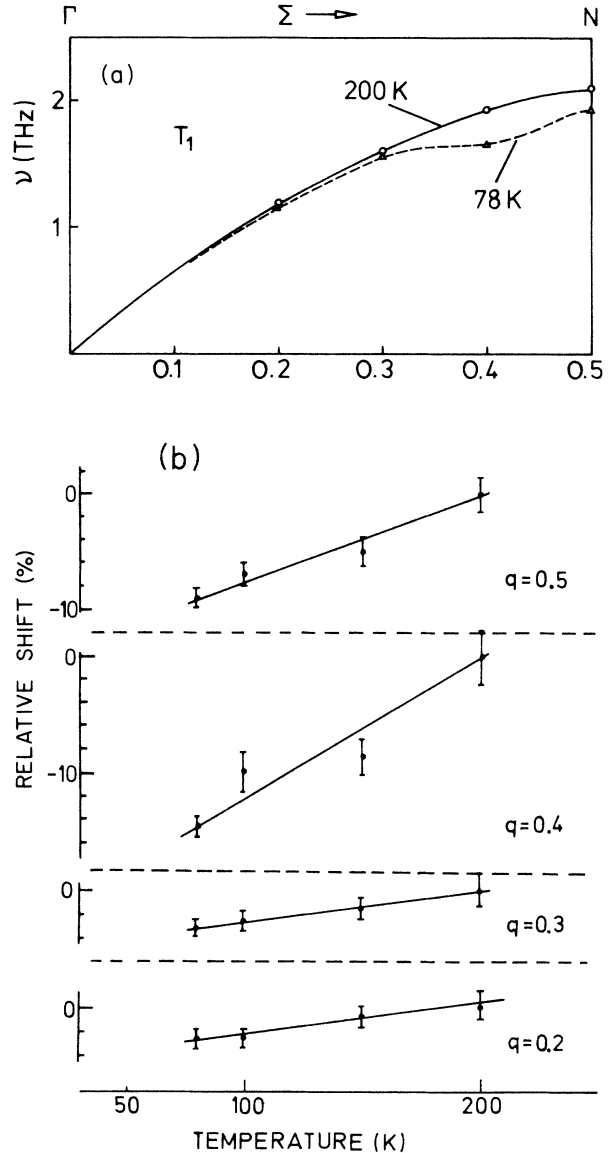


FIG. 1. (a) Phonon dispersion of the $TA_1[110]$ branch at 200 and at 78 K. (b) Relative phonon frequency shifts versus temperature for phonons of the $TA_1[110]$ branch. One scale unit of the ordinate means 2%. In both figures the lines are drawn to guide the eye.

a comparison of their experiments, however, all lie within the combined error bars of their data, and therefore are less conclusive.

IV. THE ORIENTATION RELATION

The low-temperature phase appeared first at 74 K when the intensity of the bcc Bragg reflections decreased by about 20%. A search for Bragg scattering of the low-temperature phase revealed (002)hcp reflections [equivalent to (009) in the 9R structure] in the neighborhood of the (110)bcc reflections as shown in Fig. 2. These

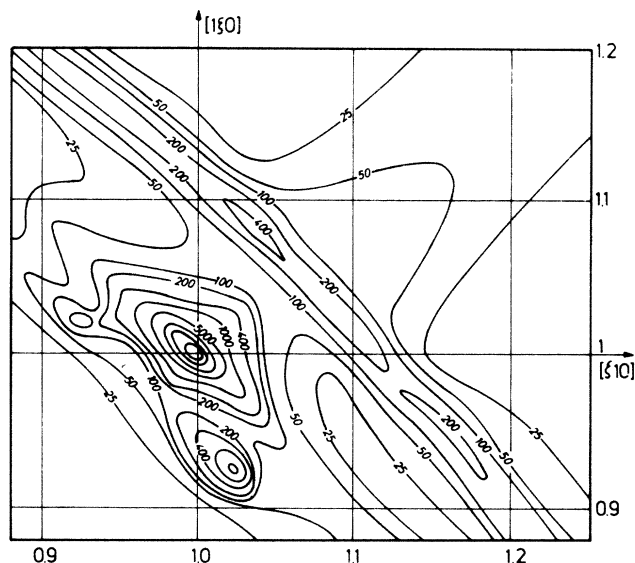


FIG. 2. Isointensity contours of the elastic scattering around the (110)bcc Bragg reflection at 74 K during the first cooling cycle. About 20% of the crystal had transformed. The elongated structure is the (111) Debye-Scherrer circle of the aluminum sample container.

results confirm essentially the expected orientation relation (110)bcc|| (002)hcp or (009) in the 9R structure. However, the (002)hcp reflections appear as twins misaligned by about 4° relative to the [110]bcc direction (see Fig. 2).

After the termination of the above measurements at 74 K the crystal was heated to room temperature. There the hcp reflections, of course, had disappeared, whereas the bcc reflections had regained their original intensity as determined before cooling, indicating the presence of a shape memory effect. However, the mosaic spread of the bcc lithium crystal had increased to 1.4° .

In a second temperature cycle the crystal was cooled again to 74 K where an orientation relation very similar to the one observed in the first cycle was found. Upon further cooling to 60 K the decrease of the intensities of the bcc reflections indicated that nearly 70% of the crystal had transformed. At the same time the intensities of the hcp reflections increased; yet, the splitting and the angle between the two twin reflections as shown in Fig. 2 remained completely unchanged.

No attempt was made in the present experiment to decide whether the correct structure of the low-temperature phase is hcp or 9R as the incident wavelength of our cold neutron spectrometer restricted the Q -range accessible to investigation.

V. DIFFUSE SCATTERING

Measurements of the diffuse scattering intensity were done during all stages of the experiment, covering a wide region of reciprocal space, essentially resulting in two findings. First, similar to the results obtained in the experiment on sodium, a diffuse scattering intensity was

found being unmodulated in reciprocal space, increasing at low temperatures, and exhibiting a hysteresis (Fig. 3) in the vicinity of the transition temperature. Figure 4 shows the temperature dependence of the diffuse scattering intensity upon heating together with that of the (002)hcp Bragg intensities, revealing a somewhat different behavior. The diffuse scattering is still present when the hcp reflections have already disappeared.

Second, the outer intensity contours in Fig. 2, which show the orientation relation between the two phases, form a streaklike structure extending from the (110)bcc to the (220)bcc reflections, suggesting the existence of planar defects on (110) planes.

The diffuse scattering data presented in Figs. 3 and 4 were accumulated during radial scans in [110] direction, which were restricted to the first Brillouin zone, so that no contamination by Bragg peaks of either the high- or the low-temperature phase was to be expected. The time spent at every temperature step varied between 12 hours and several days according to the measurements performed. After a temperature change the intensity of both the Bragg peaks and the diffuse scattering always came up to their final values in less than one hour. Subsequently, no further intensity change could be observed, thus suggesting that equilibrium had been reached. The data presented in Figs. 2, 3, and 4, therefore, reflect a stationary situation and were not influenced by any time development at constant temperature.

In addition, it seems worth mentioning that the diffuse scattering intensity obviously does not depend on the thermal history of the sample. Although Fig. 3 comprises measurements performed during two different temperature cycles, the data points fall on straight lines, and measurements done at the same temperature but during different cooling cycles coincide within experimental errors.

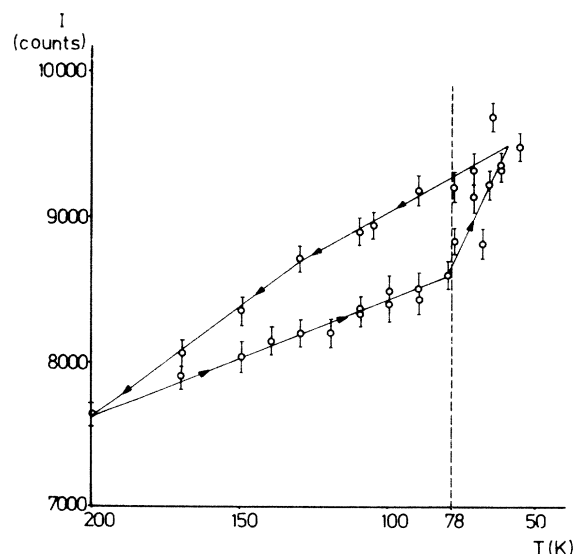


FIG. 3. Temperature dependence of the delocalized diffuse scattering intensity.

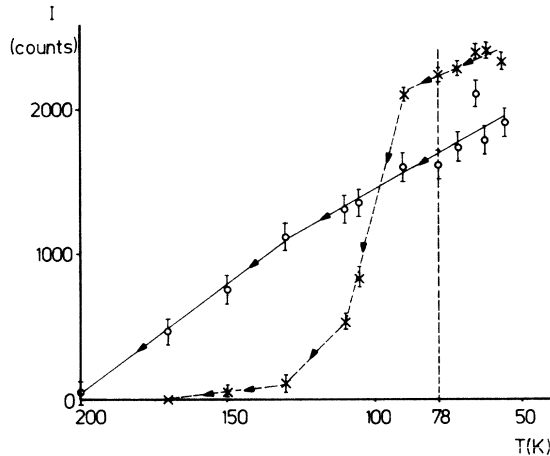


FIG. 4. Decrease of the (002)hcp Bragg intensity (crosses) in comparison to the delocalized diffuse scattering intensity (open circles).

VI. DISCUSSION

The results of the present experiment confirm the essential features of the proposed transformation mechanism outlined in the Introduction. However, based on a comparison of the two investigations on Li and Na, we would like to point out some further peculiarities.

(a) The phonon frequency shifts clearly indicate that there exists a short-wavelength (110)[1 $\bar{1}$ 0] shear instability in the proximity of the zone boundary. Nevertheless, in Li this frequency decrease is most pronounced near $q = 0.4$. This result has to be related to the assumption of the suggested model that the formation of a specific type of stacking fault is facilitated by a softening of a shear mode with appropriate wavelength. As long as only three consecutive planes are considered, the formation of a stacking fault induced by a shear mode with $q = 0.4$ yields the same stacking sequence *ABA* as a shear mode with $q = 0.5$ (cf. Fig. 1 in Ref. 3). However, it can easily be seen that for $q = 0.4$ the hcp stacking sequence *ABAB* can no longer be retained as soon as more complicated stacking faults are taken into account which extend to a larger number of neighboring planes. Consequently, a shear mode with $q = 0.4$ will no longer favor the formation of a perfect *ABAB* stacking sequence, but rather some type of faulted hcp structure.

This structure can, but need not necessarily, be *9R* since several modifications of a faulted hcp structure are possible to develop via a phonon mode with $q = 0.4$. Yet, in any case the *ABAB* stacking sequence of the perfect hcp structure is no longer the most favored. Therefore, from a lattice dynamical point of view one can conclude that the low-temperature phase of Li is more likely to be a faulted hcp structure (which is consistent qualitatively with the *9R* hypothesis of Overhauser). However, in order to gain additional structural information about the low-temperature phase, we plan to do another experiment on a four-circle spectrometer.

It is interesting to note that the occurrence of the maximum softening at $q = 0.4$ possibly has already been observed in Na (cf. Fig. 2 of Ref. 3). However, in sodium the phonon frequency shift between 200 and 80 K was only about 3%, and therefore the difference in the shift between $q = 0.4$ and 0.5 was not significant.

In Na the softening with decreasing temperature occurs for q greater 0.3. In Li the softening as observed by neutron scattering applies to the entire branch. In contrast, this behavior is no longer present in the long-wavelength limit. The elastic constant $c' = (c_{11} - c_{12})/2$ clearly shows a slight increase with decreasing temperature (cf. Ref. 10 and references cited therein). This confirms once again that the lattice instability is basically a short-wavelength phenomenon. Yet, an indication that the elastic constant c' might also be affected to some extent can be derived from the calculations of Vaks *et al.*¹⁰ In their paper pseudopotential calculations of the elastic constants c_{11} , c' , and the bulk modulus B are presented for Li, Na, and K. While the calculations agree very well with the experimental data for c_{11} and B , there is a deviation from the data for c' which is most pronounced in Li. One may conclude that quasiharmonic first-order perturbation theory in this case is no longer adequate to describe properties of the crystal which are closely related to the instability triggering the phase transition.

(b) The diffuse scattering intensity evenly distributed over the entire region of reciprocal space investigated is very similar to the one found in sodium. It provides evidence for the presence of an intermediate defect structure in the transition region. In order to explain the absence of any localization in the scattering pattern, this defect structure has to be considered as consisting mainly of point defects or very small clusters of point defects.

The streaking intensity distribution extending between the (110)bcc and (220)bcc reflections points to the presence of planar defects parallel to (110) planes most likely being stacking faults. Contrary to this, in sodium no streaking has been observed. However, this agrees with the fact that the sodium crystal in the earlier investigation did not transform appreciably to the low-temperature phase, but mainly retained the bcc structure during the entire experiment. In view of the suggested model stacking faults are a necessary prerequisite for the formation of nuclei of the new phase. In sodium, no or only very few stacking faults were present, since no streaking has been observed and therefore the low-temperature structure could not develop.

(c) Finally, we have observed an orientation relation (110)bcc || (002)hcp where the (002) reflections are split and tilted away from the [110]bcc direction by about 4°. A qualitative explanation for this twinning may be given on the basis of the elastic anisotropy of the bcc structure. The distance between neighboring (110)bcc planes is slightly smaller than the distance between the corresponding (002)hcp planes originating from them. Since the hcp nuclei are embedded in a crystal with bcc structure, the expansion necessary for the adjustment of the lattice parameter leads to a distortion of the surrounding bcc matrix. Although this distortion is only small, the amount of energy required for the expansion is rather large as re-

flected by the high frequencies of the LA[110] phonon branch, indicating a strong repulsive potential. On the other hand, a shift parallel to the (110)bcc planes is energetically more favorable because of the inherent anisotropy of the force distribution in the bcc lattice. Thus, in order to minimize the distortion energy resulting from the formation of the hcp nuclei it may be more advantageous to adjust the lattice parameter by tilting the hexagonal

axis of the new phase slightly away from the [110]bcc direction.

ACKNOWLEDGMENTS

This work was partly supported by the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich (Wien, Austria).

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