Observation of static and dynamic pretransitional phenomena near the martensitic bcc-hcp transformation in sodium

O. Blaschko and G. Krexner
Institut für Experimentalphysik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria
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Pretransitional phenomena connected with the bcc-hcp martensitic transformation in Na have been observed by neutron scattering techniques. In the bcc phase a softening of the low-lying transverse-acoustic [110] phonons polarized along [1$\bar{1}$0] is found when the transition temperature is approached. Moreover, a q-independent diffuse scattering showing a marked hysteresis effect is observed. Finally, the microscopic Grüneisen parameters of the transverse-acoustic phonons in the [110] direction polarized along [1$\bar{1}$0] have been determined at room temperature, yielding only small positive values near the zone boundary—in disagreement with present theories.

I. INTRODUCTION

Sodium undergoes a martensitic phase transition from the high-temperature bcc phase to a hcp structure near 36 K originally discovered in polycrystalline material by Barrett.[1] He found the transition to occur only partially, i.e., only an amount of a few percent of the crystal was transformed whereas cold working could increase the proportion of the transformation product. Moreover, the transition is characterized by a hysteresis showing the reverse transformation near 90 K.

Based on geometrical arguments the bcc-hcp transformation has been related phenomenologically to a deformation of the bcc unit cell corresponding to a long-wavelength shear on (112) bcc planes in a [111] direction followed by a short-wavelength (110) [1$\bar{1}$0] shear (Burgers, Ref. 2). First neutron scattering investigations by Dolling *et al.*[3] were undertaken to elucidate the cooperative atomic shear displacements leading to the hcp structure. These investigations were guided by the search for soft-mode-like instabilities but revealed only small temperature effects regarding the phonon frequencies. A similarly negative result concerning phonon frequency anomalies in Na was obtained in a more recent experiment by Stedman[4] who investigated the low-lying branch in the [112] direction and especially the phonons near $\frac{1}{3}k_{[112]}$ polarized along [$\bar{1}\,\bar{1}$1]. There, in fact, the phonon dispersion curve of bcc metals has a minimum which was related within a different context to an instability leading in bcc Zr-based alloys to the martensitic ω phase.[5]

On the other hand, rather early Zener[6] pointed out the small resistance to a (110) [1$\bar{1}$0] shear characteristic of bcc lattices containing ions with closed electronic shells which leads to a strong macroscopic anisotropy. This intrinsic property of especially the alkali metals is also reflected by the phonon dispersion curves, the lowest branch of which is TA_1[110].[7] Furthermore, a rather simple relation between the bcc and hcp structures can be obtained by considering the stacking sequence of "topologically" similar atomic planes in the two structures. The (110) bcc and the (002) hcp plane both show a rectangular atomic configuration with one atom at the center and the atomic distances in these planes differ by only a few percent. Geometrically, a stacking sequence of the hcp type can be achieved by a translation of every second (110) plane by a $\frac{1}{6}k_{[1\bar{1}0]}$ vector (Fig. 1). If in a first step by a local glide of (110) bcc planes in some regions of the bcc matrix a hcp stacking sequence develops, then the formation of a hcp nucleus needs only an accommodation to the hcp structure by an adjustment of the atomic distances by a few percent. Such a relaxation of the local structure characterized by a hcp stacking sequence to the equilibrium hcp lattice of the low-temperature phase should easily occur when the amount of the intermediate structure becomes sufficiently large to overcome energetically the distortion and the surface tension connected with the formation of a hcp nucleus in the bcc matrix.

The proposed mechanism for the bcc-hcp transition in Na describing the nucleation of the hcp structure as a sequence of steps is similar to that generally discussed by Olson and Cohen[8] for martensitic nucleation by faulting on close-packed (002) planes. In addition, a similar mechanism based on the formation of stacking faults on close-packed (002) planes recently could be proposed for the pressure-induced NaCl-CsCl transformation in RbI (Ref. 9) likewise showing low-lying transverse-acoustic phonon branches which exhibit a further softening under pressure. The mechanism in RbI has also been found in a recent molecular-dynamics study.[10]

In the present paper we report neutron scattering measurements on pretransitional phenomena for the bcc-hcp transformation in Na. The experiment was focused in the first place on the temperature behavior of the phonon frequencies in the low-lying TA_1[110] branch when the transition is approached. Neither of the above-mentioned experiments by Dolling *et al.*[3] and Stedman[4] has dealt with this branch except for the TA_1[110] zone boundary phonon at the N point. This phonon actually was already investigated by Dolling *et al.*, yet, due to the restricted accuracy of his experiment guided by the search for a soft-mode behavior, no significant results were obtained.

Furthermore, in the present investigation, pressure-induced phonon frequency shifts were determined at room temperature in order to obtain more insight into a possible

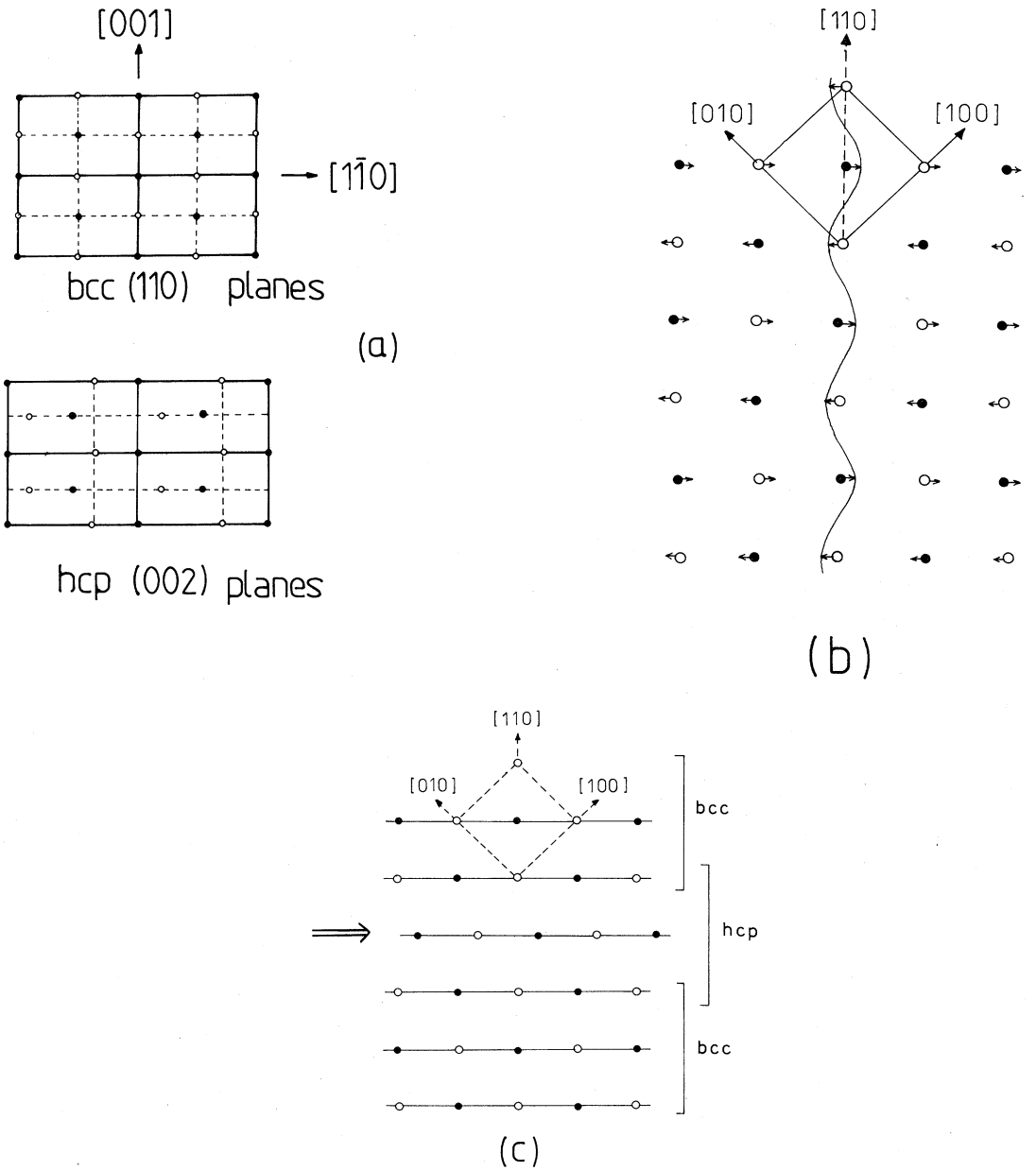

FIG. 1. Schematic illustration of the transformation mechanism. Closed and open circles denote atoms in two consecutive planes. (a) The "topologically" similar (110) bcc and (002) hcp planes exhibiting different stacking sequences in the two structures. (b) The $TA_1[110]$ zone-boundary phonon in a (001) bcc plane. The phonon propagates in the [110] direction and the phase difference between adjacent (110) planes is 180°. (c) A stacking fault with hcp stacking sequence. The solid lines indicate (110) planes.

intrinsic lattice instability connected with the $TA_1[110]$ branch. Finally, the diffuse scattering was investigated with the aim to find some evidence of the occurrence of the expected intermediate defect structure in the vicinity of the transformation.

II. EXPERIMENTAL

The neutron scattering measurements were done on the conventional triple-axis spectrometer Valse located at the 4.3-G cold neutron guide position of the Orphée reactor at Saclay. Pyrolytic graphite was used both as monochromator and as analyzer. The experiment was done at a constant incident neutron wavelength $\lambda=2.45$ Å. A cylindrical Na single crystal (diameter 1 cm, height 1 cm) was mounted in a closed-cycle cryostat after etching the surface with dilute methanol. The mosaic width of the sample was approximately 60′. Bragg peaks, diffuse scattering, and phonon-frequency changes were investigated down to 14 K and several cycles through the transition temperature 36 K were performed. During the whole experiment no measureable changes in the mosaic width and the Bragg intensities were observed when passing through 36 K indicating that only a small amount of the crystal

had transformed ($\lesssim 1\%$).

The pressure-induced phonon-frequency shifts were determined at room temperature using an autofrettaged high-pressure cell described elsewhere.[11] The pressure applied was about 4 kbar. A perfluorated cyclic ether ($C_8F_{16}O$) was used as the pressure transmitting liquid.

III. RESULTS

A. Phonon frequencies versus temperature

The temperature behavior of the entire $TA_1[110]$ branch was investigated from 230 to 14 K (Fig. 2). At small q the phonons show a frequency increase with decreasing temperature as expected, the contribution of anharmonic effects to the phonon frequencies generally being strongly reduced at lower temperatures. However, near the zone boundary the phonons exhibit a softening with decreasing temperature by about 4% between 230 and 40 K [Fig. 2(a)]. For comparison some phonons in other branches were measured characterized by a normal frequency increase at low temperatures [Fig. 2(b)].

B. Mode-Grüneisen parameters

The phonon frequencies of the $TA_1[110]$ branch were measured by constant-$\vec{q}$ scans at 0 and 4 kbar, respectively. The phonon-frequency changes were evaluated essentially along the same lines as described in detail in Ref. 12. They were used to calculate the microscopic Grüneisen parameters

$$\gamma(\vec{q},j) = -\left[\frac{d\ln\omega(\vec{q},j)}{d\ln V}\right]_T ,$$

where V denotes the volume of the sample and ω is the eigenfrequency of a mode with the wave vector $\vec{q}$ and the branch index j. The relative volume change $\Delta V/V$ was obtained from lattice-parameter measurements yielding $\Delta V/V = -6\%$ at 4 kbar in accordance with previously published data. The results are depicted in Fig. 3 and show γ to decrease near the zone boundary.

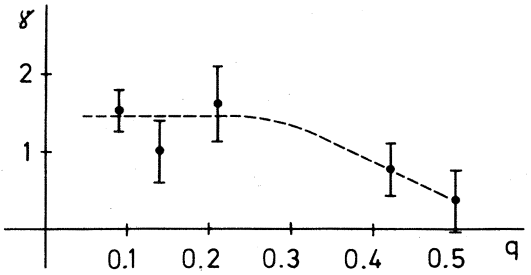

FIG. 3. Mode-Grüneisen parameters of the $TA_1[110]$ phonon branch. The error bars correspond to one standard deviation.

C. Diffuse scattering

The diffuse scattering was investigated in the whole temperature range between 230 and 14 K by scans over a wide region of the reciprocal space. Even after an extensive search no localized diffuse intensity effects could be observed. The bcc Bragg intensities and the scattering in the vicinity of the Bragg reflections did not show any anomalous temperature dependence near 36 K even after several temperature cycles. However, a temperature-dependent diffuse scattering extending over the entire region of reciprocal space investigated was observed. The intensity of this diffuse scattering, resembling the monotonic Laue scattering of binary alloys, increases at low temperatures, this increase steepening markedly near 36 K (Fig. 4).

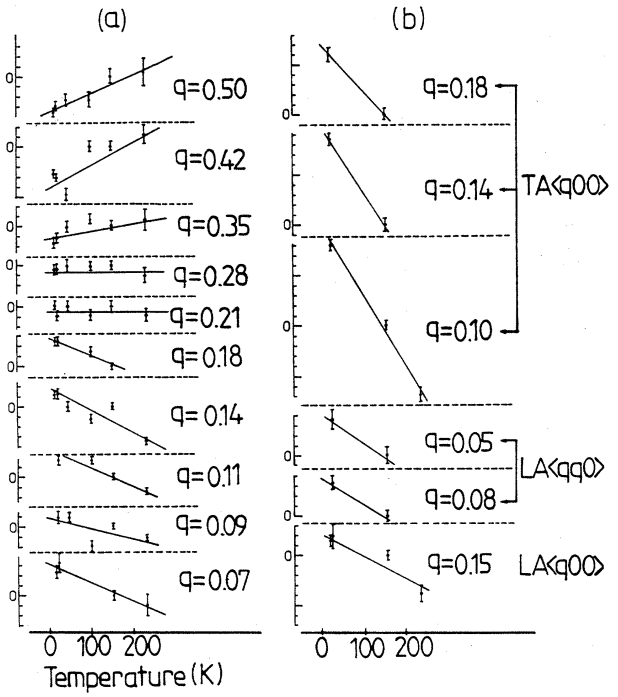

FIG. 2. Relative phonon-frequency shifts $\Delta\omega/\omega$ versus temperature. One scale unit of the ordinate means 1%. As point of reference for the calculation of the phonon-frequency shifts arbitrarily, the phonon frequency at 150 K was chosen corresponding respectively to 0 on the ordinate. The lines have been drawn to guide the eye. (a) shows the frequency change with temperature for the $TA_1[110]$ phonons investigated. For comparison, (b) shows results obtained for some phonons belonging to other branches as indicated in the drawing, respectively.

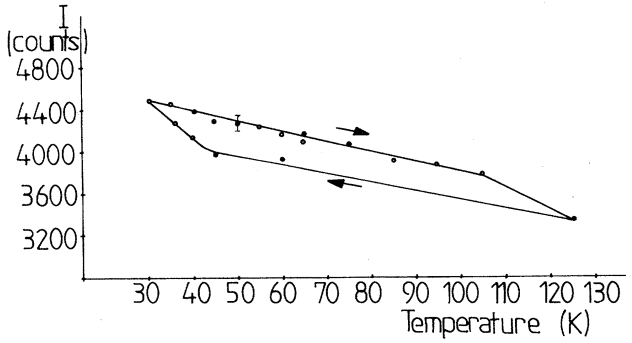

FIG. 4. Temperature dependence of the diffuse scattering observed at low temperatures.

IV. DISCUSSION

The present experiment on pretransitional phenomena related to the bcc-hcp transformation in Na has revealed the following results.

(a) An anomalous softening of the $TA_1[110]$ branch near the zone boundary on cooling indicating a softening of the harmonic potential which favors a shear of two adjacent (110) bcc planes when the temperature is reduced.

(b) The presence of a temperature-dependent diffuse scattering already above the transition temperature exhibiting a steep intensity increase near 36 K and a pronounced hysteresis.

(c) Further, even at room temperature the mode-Grüneisen parameters of the $TA_1[110]$ branch are characterized by rather low positive values near the zone boundary. At small q the measured mode-Grüneisen dispersion agrees well with model calculations performed for a series of alkali metals,[13] but it disagrees with respect to the phonons near the zone boundary where the calculations give $\gamma=1.5$. In addition, the present experiment yielding $\gamma=0.35\pm0.4$ for the $TA_1[110]$ zone-boundary phonon in Na contrasts with the corresponding experimental result for potassium[14] where the comparatively large value $\gamma=1.5$ has been found as expected by theory. It is difficult at present to comment on these discrepancies. Among the few papers dealing with the subject only an empirical model by Barron and Gibbons[15] predicts low microscopic Grüneisen parameters for the $TA_1[110]$ branch in bcc metals. Their result reflects mainly the fact that bcc lattices become inherently unstable if they are treated within the framework of a lattice-dynamical model in which interactions are restricted to central forces between nearest neighbors. This kind of instability is, however, not related to a single wave vector but applies equally to the entire $TA_1[110]$ branch and was already mentioned by Zener[6] (for a detailed discussion cf. Leibfried, Ref. 16).

Yet, the measured small value of the mode-Grüneisen parameter near the zone boundary is qualitatively in agreement with the phonon softening observed at low temperatures, both findings providing evidence of the intrinsic softness of the bcc sodium lattice if it is subjected to a short-wavelength shear of the $TA_1[110]$ type. The proposed transformation mechanism describing the onset of the bcc-hcp transition by a shear of adjacent (110) planes is indeed favored by the zone-boundary phonon behavior observed and may provide a possibility to overcome the energy barrier between the bcc and hcp structures by the formation of a defect structure consisting of stacking faults on (110) bcc planes.

The temperature-dependent diffuse scattering characterized by a strong hysteresis may be ascribed to the formation of the intermediate defect structure. The diffuse intensity evenly distributed over the region of reciprocal space investigated has some similarity with the Laue scattering of uncorrelated atoms in random alloys. In bcc Na this nearly q-independent scattering may arise from point defects, that is, vacancies or interstitials and also small agglomerates of interstitials created at low temperatures especially near 36 K.

In view of the present investigation the bcc-hcp transformation in sodium may be visualized to occur via the following steps. First, the microscopic anisotropy for short-wavelength shear deformations is increased by the softening of the $TA_1[110]$ phonons near the zone boundary, which subsequently facilitates the formation of hcp-type interstitials particularly near preexisting defects of the bcc crystal. If enough interstitials have been formed, the faulted region having acquired a hexagonal stacking sequence finally can transform into an hcp nucleus by the relaxation of the atomic distances toward a fully developed hcp structure.

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[1]C. S. Barrett, Acta Crystallogr. **9**, 671 (1956).
[2]W. G. Burgers, Physica **1**, 561 (1934).
[3]G. Dolling, B. M. Powell, and P. Martel, Can. J. Phys. **46**, 1727 (1968).
[4]R. Stedman, J. Phys. F **6**, 2239 (1976).
[5]S. C. Moss, D. T. Keating and J. D. Axe, Solid State Commun. **13**, 1465 (1973).
[6]C. Zener, Phys. Rev. **71**, 846 (1947).
[7]A. D. B. Woods, B. N. Brochhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. **128**, 1112 (1962).
[8]G. B. Olson and M. Cohen, Metall. Trans. **7A**, 1897 (1976).
[9]O. Blaschko, G. Ernst, G. Quittner, and G. Pépy, Phys. Rev. B **23**, 3017 (1981).
[10]M. Parinello and A. Rahman, J. Phys. C **6**, 511 (1981).
[11]O. Blaschko and G. Ernst, Rev. Sci. Instrum. **45**, 526 (1974).
[12]O. Blaschko, G. Ernst, G. Quittner, W. Kress, and R. E. Lechner, Phys. Rev. B **11**, 3960 (1975).
[13]J. Hafner, Solid State Commun. **21**, 179 (1977); Z. Phys. B **24**, 41 (1976).
[14]J. Meyer, G. Dolling, J. Kalus, C. Vettier, and J. Paureau, J. Phys. F **6**, 1899 (1976).
[15]T. H. K. Barron and T. G. Gibbons, J. Phys. C **7**, 3260 (1974).
[16]G. Leibfried, in *Encyclopedia of Physics,* edited by S. Flügge (Springer, Berlin, 1955), Vol. VII, Part 1, pp. 153ff.