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Diffuse-neutron-scattering investigation of the low-temperature phases of sodium

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The low-temperature phase of sodium is investigated by diffuse-neutron-scattering techniques. In contrast to previous results for lithium no disordered close-packed polytype stacking sequences were observed. The results show the presence of two long-range-ordered, but faulted hcp and 9*R* structures. The temperature behavior indicates a higher stability of cubic stacking faults at lower temperatures.

I. INTRODUCTION

Many bcc metals undergo martensitic phase transformations to close-packed structures at low temperatures (for a review of recent experimental and theoretical investigations see Ref. 1). Martensitic transformations are generally discontinuous and therefore necessitate the nucleation of new phase particles. The formation of martensitic nuclei engenders coherency stresses within the parent matrix. Consequently, the thermodynamics of the system is not only governed by the chemical free energy but also by the elastic strain energy originating from the lattice misfit between the two phases. Generally, the transformation requires a certain amount of undercooling and spreads over a wide temperature range where the two phases coexist. The low-temperature phases observed are often characterized by the frequent occurrence of stacking faults within the sequence of close-packed planes. The formation of these faults is generally attributed to the influence of elastic constraints imposed by the matrix.[2] The faults may be periodic leading to long-period polytype structures or distributed at random giving rise to peak broadening and shifts. Any structural investigation is complicated by these effects so that the actual structures of martensite phases are not always well known. Thus, only recently the low-temperature phase of a NiAl alloy was confirmed to consist of two monoclinic lattices of a seven-layered polytype structure.[3]

The alkali metals Li and Na show a martensitic transformation near 78 and 32 K, respectively. The low-temperature phase of both metals was initially classified by Barrett[4] as a faulted hcp structure coexisting with a considerable amount of the untransformed bcc matrix. Since this assumption did not permit a fit of later neutron powder spectra of Li,[5] Overhauser proposed the 9*R* structure,[6] i.e., a nine-layered hexagonal polytype for the low-temperature phase. Subsequent neutron-diffraction investigations on Li powder[7,8] and single crystals[9] seemed to confirm this hypothesis.

A recent investigation[10] of Li single crystals by diffuse-neutron-scattering techniques, however, revealed a considerable amount of elastic diffuse scattering in addition to sharp 9*R* reflections at temperatures below 80 K as well as a perfect fcc phase at temperatures around 120 K. The diffuse scattering gives evidence of short-range correlated polytype structures indicating a nearly complete degeneracy of the hexagonal (*H*) and the cubic (*K*) ordering tendencies in the stacking sequence of close-packed planes at low temperatures. The formation of the 9*R* structure was explained by competing interactions of the different ordering tendencies in a narrow temperature range.

Although Na is often regarded to be equivalent to Li, recent neutron-diffraction studies of the low-temperature phase indicate a different behavior. So a powder diffraction investigation[8] suggested the presence of a 9*R* structure as majority phase coexisting with a smaller amount of hcp. Both 9*R* and hcp peaks were reported to be broadened and shifted from their ideal positions, indicating a high stacking-fault density. Moreover, a decrease of M_s (i.e., the temperature where the martensitic transformation sets in) was observed for Na upon applying hydrostatic pressure up to several kbar,[11] whereas an increase of M_s was found in Li.[12] In a previous report, precursor phenomena of the phase transformation in sodium were investigated by diffuse-neutron-scattering techniques.[13] In the present communication we present a study of the low-temperature phase undertaken by the same method. In sodium the diffuse scattering experiment reveals essentially long-range-ordered close-packed structures and, in contrast to lithium, no short-range-ordered polytype sequences can be observed. In addition to earlier diffraction works[8] that already described the coexistence of hcp and 9*R* close-packed structures, we present experimental evidence of a change in the stability of the stacking sequences with temperature. At higher temperatures the *H*-type stacking seems to be the more favorable configuration, whereas at lower temperatures the stability and consequently also the density of the *K*-type stacking sequences are increased. The stability regions of the different structural states are deduced from their response to temperature changes.

II. EXPERIMENT

The experiments were performed on the triple-axis spectrometer VALSE located at a cold neutron guide position of the Laboratoire Léon Brillouin in Saclay, France. Pyrolytic graphite crystals were used both as monochromator and analyzer. A graphite filter was put into the incident beam in order to eliminate second-order contaminations. The measurements were done with a neutron wavelength of 2.36 Å using collimations of about 30 min.

Two cylindrical single crystals of Na with the [001] axis parallel to the cylinder axis were investigated. The size of the crystals was a few cubic centimeters, respectively, and the mosaic spread about 20 min. The samples were mounted under argon atmosphere in aluminum containers with a small spring preventing accidental rotations. Since sodium has a larger thermal expansion than aluminum, no additional stress should be produced upon cooling. The container was fixed on the cold finger of a closed-cycle cryostat. Measurements were undertaken in a $(hk0)$ reciprocal lattice plane of the bcc lattice which approximately became a $(h0.l)$ reciprocal lattice plane of the martensite phase (the indices of the martensite phase refer to a hexagonal unit cell of nine atoms with lattice parameters $a=3.73$ Å, $c=27.5$ Å). Upon cooling, parts of the virgin crystals transformed to the low-temperature phase at around 30 K. The transformation was accompanied by a sudden increase of the mosaicity by a factor of about 2 engendering also an increase of the integral intensity of the bcc reflections by the same factor due to reduced secondary extinction. From the relative intensity decrease of small-q phonons it was concluded that about 10–20 % of the original bcc crystals had transformed to the low-temperature phase.

As in Li, four reflections with a q-value corresponding to the spacing between close-packed planes [i.e., $(00.9)-R$] were observed around every (110) bcc Bragg peak.

III. STRUCTURE OF THE LOW-TEMPERATURE PHASE

At 30 K, scans along $[h0.l], h=1,2$ reciprocal lattice lines of one selected variant of the first crystal exhibited the following features: Strong peaks were found in the vicinity of lattice points were 9R reflections are expected, i.e., at $l=3n+1$. Additional weaker peaks were found near $l=\pm 0$, ± 4.5, ± 9.0, etc. corresponding to the (10.0), (10.1), (10.2), and equivalent hcp lattice points (see Fig. 1). The shifts of the 9R peaks from their ideal positions were in qualitative agreement with the powder diffraction data from Berliner.[8] Their half widths (FWHM's) along $[10.l]$ corrected for sample mosaicity and resolution were in most cases only slightly larger than the experimental resolution varying between 0.17 and 0.36 in units of l and comparing well with Ref. 8. Some peaks, however, exhibited a larger broadening: the $(10,\bar{2})$, (10.7), and their second-order reflections, which could not be observed in the quoted powder investigation, had widths of about 0.7 in units of l, the (10.1) and $(20.\bar{1})$ reflections about $0.5l$. The hcp intensities were found to be shifted toward neighboring 9R reflections [see Fig. 2(a)]. Both shifts and widths are larger than those of the average 9R peaks. The intensity profiles of both peak variants show a Lorentzian contribution being comparable to be deconvoluted Gaussian width. Comparing the integrated intensities of peaks belonging to the two structures and taking account of the different structure factors, one can deduce a ratio of 1:3 between the hcp and 9R volume fractions.

In addition to the localized intensities an underlying diffuse intensity ridge was observed. This ridge is well centered on the $[10.l]$ and $[20.l]$ lines and extends out along the whole accessible portion of $[h0.l]$.

With decreasing temperature (10 K) both 9R and hcp intensities grew roughly by a factor of 2 stronger, but no change of the relative volume fractions was noticeable. The experiment on the first crystal shows that the low-temperature structural state can be described by the coexistence of two close-packed polytype structures, namely, hcp and 9R, within a bcc matrix. Since the peak widths of both variants are rather small, the corresponding stacking sequences are long-range correlated extending over about 1000 Å within the crystal.

Upon heating from 10 K the reverse transformation set in at about 30 K, where the 9R intensities started to diminish. During further heating a reduction of the hcp intensities was also noticed, but only above 45 K. At 45 K the 9R peaks had already lost 50% of their original intensities (see Fig. 3). The intensity of the streak decreased in accordance with the temperature behavior of the 9R

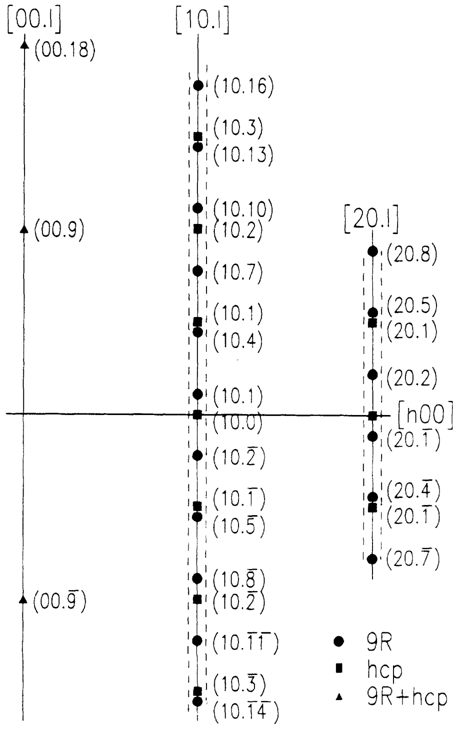

FIG. 1. Schematic representation of peaks found in the 9R reciprocal lattice at 30 K. (●) 9R positions, (■) hcp positions $[(00.9)-9R\equiv(00.2)-\text{hcp}]$. The dashed line indicates the diffuse intensity ridge. There are no traces of 9R twin reflections with one variant.

peaks. At 80 K no traces of reflections of the low-temperature phase were left and the original bcc crystal was recovered, yet with a larger mosaicity of 60°.

During a second cooling cycle the sample was cooled stepwise from 100 to 10 K. In contrast to the first cooling cycle, the intensities of the 9*R* peaks were stronger than those of the hcp peaks by a factor of about 10. This time the 9*R* peaks lay nearly at their ideal positions and had almost resolution limited—although Lorentzian—widths. The intensities of both 9*R* peaks and streak were by a factor of 1.3 smaller with regard to the first transformation. Upon heating the 9*R* peaks moved slightly away in direction to neighboring hcp positions [see Fig. 2(b)]. The hysteresis was much smaller in comparison to the first cooling cycle, the main reflections having nearly vanished at 50 K.

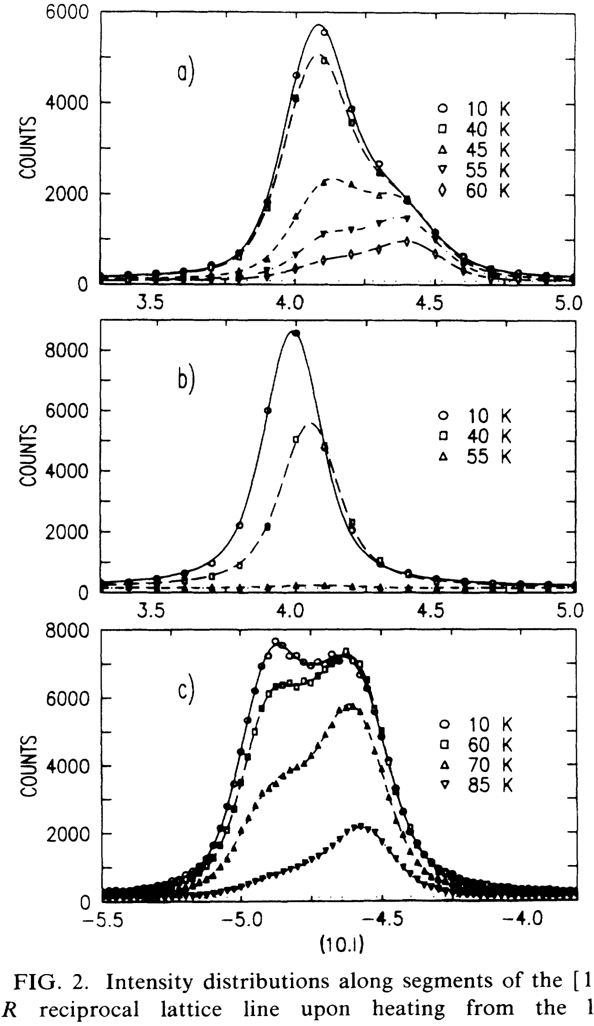

FIG. 2. Intensity distributions along segments of the [10.*l*] 9*R* reciprocal lattice line upon heating from the low-temperature phase. The lines are fits to the data points employing a convolution of Lorentzian and Gaussian line profiles. Two component fits were used for (a) and (c), one component for (b). The dotted lines give the background as obtained at 50 K from regions adjacent to the [10.*l*] ridge. (a) First crystal upon heating from 10 to 60 K. (b) First crystal within a second temperature cycle—the 9*R* intensity is much enhanced, almost no hcp component is discernible. (c) Second crystal—initially nearly equal 9*R* and hcp intensities are observed.

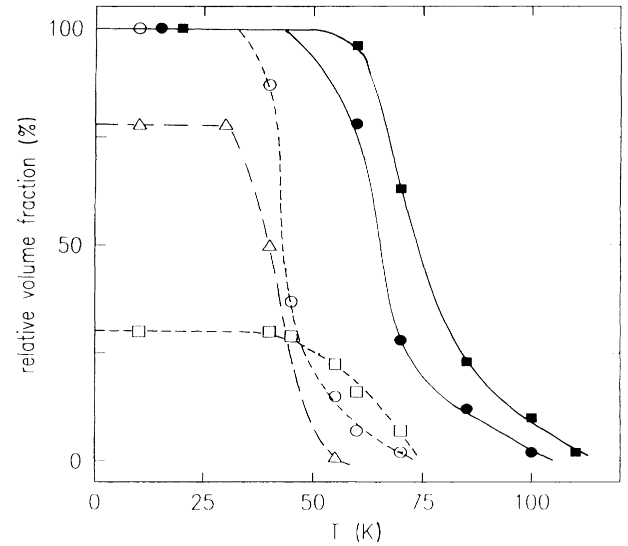

FIG. 3. Temperature dependence of the relative 9*R* and hcp volume fractions. Open symbols, No. 1 crystal: (○) 9*R*, (□) hcp in first cycle; (△) 9*R* in second cycle. Close symbols, No. 2 crystal: (●) 9*R*, (■) hcp. The lines are guides to the eye.

Upon further slow heating, the crystal did not disintegrate into several grains as reported in Ref. 14 and also found in Li,[10] but developed a macroscopic twin twisted by 30° in relation to the original variant. During a third cooling cycle from room temperature at 10 K no transformation at all could be noticed.

The experiment with the second crystal gave slightly different results, when it was directly cooled down to 10 K for a first time [see Fig. 2(c)]. Somewhat sharper 9*R* reflections were accompanied by hcp peaks of nearly equal intensities together with a streak along [10.*l*] (in contrast to the first crystal, where the 9*R* intensities were much stronger).

Upon heating, the crystal showed a larger hysteresis, the decrease of the 9*R* intensities setting in only at 50 K. Upon further heating, the 9*R* intensities decreased more rapidly than the hcp peaks and shifted even farther away from their commensurate *l* values. The hcp peaks, on the other hand, shifted toward their ideal positions and narrowed slightly. At 95 K the hcp intensities were reduced by a factor of 10 with regard to their original intensities, the 9*R* peaks by a factor of 30. Upon a subsequent cooling to 10 K, no substantial changes of the intensity pattern took place, i.e., no further transformation occurred. Also, a further cycling to 110 K and cooling to 10 K did not initiate any further transformation.

It should be emphasized that in the whole temperature range no traces of a fcc structure were found nor were there any indications in the diffuse scattering along the [10.*l*] line of the presence of other polytype structures even as short-range correlated stacking sequences.

Furthermore, it should be noticed that within one orientational variant, i.e., one selected [10.*l*] line, no 9*R* twin reflections could be found. The diffuse intensity ridge along the [10.*l*] line showed no modulation and consequently no extra intensity at the 9*R* twin positions. It follows that within one variant no twins are present neither as long-range-ordered structure nor even as short-range correlated stacking sequences. This complete absence of twinning within one variant was also observed in lithium and therefore seems to be a common feature of the martensitic phase transformation in both Li and Na metals.

IV. DISCUSSION

The present experiment shows that the low-temperature structure of Na consists of both 9*R* and hcp long-range-ordered stacking sequences whose relative volume fractions depend on temperature and specimen characteristics. The presence of a diffuse intensity ridge extending over the whole [10.*l*] axis without any modulation can be attributed to a planar defect structure, i.e., uncorrelated stacking faults statistically introduced into the ordered sequence of close-packed planes. The intensity of the ridge shows a temperature dependence similar to the 9*R* Bragg reflections. It follows that most of the stacking faults are within the 9*R* structure.

The present experiment on Na reveals structural features unlike those previously found in Li. In Li short-range-ordered and even disordered polytype sequences characterize the structural state at low temperatures, indicating the near degeneracy of *H* and *K* stacking sequences. The present investigations in Na, however, show that in all cases essentially long-range-ordered polytype structures are formed. The lack of short-range order indicates that in contrast to Li the ordered stacking sequences associated with hcp and 9*R* (*KHH* in the Jagodzinski notation[15]) are clearly less degenerate in Na.

Furthermore, the shifts and Lorentzian line shapes of Bragg reflections along [10.*l*] give additional evidence of the presence of stacking faults on close-packed planes as discussed in Refs. 7 and 8. The shifts of 9*R* peaks towards neighboring hcp positions indicate the presence of *H* faults, i.e., faults increasing the density of *H*-type planes.[16] This qualitative argument corresponds to the results obtained by Monte Carlo simulations of stacking faults in polycrystalline Na,[8] where the principal fault was concluded to consist of two supplementary *H* planes.

On the other hand, the absence of 9*R* twin intensities indicates that no twin faults are present. It can be concluded that in each 9*R* variant one arrangement of *KHH* planes, e.g., cyclic *ABCBCACAB* sequences, is preponderant[17] and anticyclic *BACACBCBA* sequences do not occur. The absence of twin faults therefore indicates that during the martensitic transformation the symmetry between cyclic and anticyclic stacking sequences is broken.

The reason for this broken symmetry may be found in the martensitic transformation where a long-wavelength $[110][1\bar{1}0]$ shear mode is present since early stages of nucleation. As found in all recent investigations,[18,9,10] the [00.*l*] axis of the close-packed structure is not aligned with the [110] bcc direction but the nuclei of the low-temperature phase are always tilted off the bcc [110] direction by a few degrees. This misalignment is related to the larger interplanar spacing of the close-packed planes with regard to the lattice spacing of (110) bcc planes and is favored by elastic energy considerations, i.e., the lattice strain along the [110] bcc direction necessary for the adjustment of the lattice parameter can be minimized by a tilt of the stacking direction. This tilt corresponds to a long-wavelength $[110][1\bar{1}0]$ shear deformation inherently soft in bcc systems.

The $[110][1\bar{1}0]$ shear induces "in-phase" displacements of adjacent (110)-bcc planes giving way to one type of stacking sequences (e.g., cyclic *ABC*. . .) and consequently to one untwinned 9*R* variant (see Ref. 19), while a twin formation needs either a shear of shorter wavelength or no shear at all. A further indication of an influence of this symmetry breaking $q=0$ shear on the stacking sequence can be found within the faulted hcp phase. The stacking faults within a hcp lattice responsible for peak broadening and shifts are necessarily *K* faults. It is, however, well established[17] that a random distribution of stacking faults within a hcp structure does not lead to peak shifts but only to peak broadening. One therefore has to assume that the two types of *K* faults, i.e., cyclic and anticyclic faults, do not occur at the same rate but that one type of fault has a higher probability. This preference for one stacking cycle of close-packed planes may likewise be attributed to the action of the $q=0$ shear mode during the transformation leading to the same type of *K* stacking faults as those present as *K* planes in the corresponding untwinned 9*R* lattice. The other type of fault would, indeed, induce shifts opposite to those observed in this experiment.

Furthermore, upon cooling from 30 to 10 K the volume fractions of both martensite structures increase by the same amount. At the same time no additional peaks shifts nor any changes in the peak widths can be observed. In contrast, upon heating, the two phases behave differently: In all cases the reverse transformation of 9*R* sets in before that of hcp, thus leading to a hcp majority phase above 50 K. 9*R* and hcp do, however, coex-

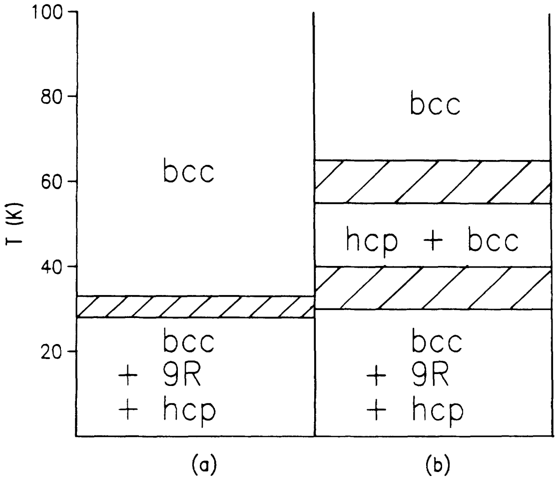

FIG. 4. Schematic representation of phases observed in Na as a function of temperature, (a) during cooling, (b) during heating. The phase boundaries (indicated by hatched areas) are smeared out due to hysteresis effects and depend on the thermal history of the specimens. The quoted phases are the majority phases in the specified temperature region.

ist, until they vanish completely. Although this shows that there is no distinct phase boundary, as is the case between the low-temperature polytype structure and fcc in Li, the hcp structure seems to be more stable at temperatures above 30 K. This is further corroborated by the fact that the hcp peaks shift to their commensurate positions, whereas the 9*R* peaks move even farther away from theirs. It can be concluded that regions of both martensite phases containing *K* stacking faults are the first to revert back to bcc, thus reflecting the higher stability of "pure" hcp in this temperature range.

Besides this an almost perfect 9*R* structure was observed within a second cooling cycle, where nearly no hcp phase was present. This result indicates that at low temperatures hcp can be reduced by an appropriate temperature cycling and hence is metastable with regard to 9*R*. The small hysteresis of this structural state further reflects the reduced 9*R* stability at higher temperatures.

The low-temperature phase diagram therefore looks different from that of Li: in contrast to Li, the *H* stacking sequence seems to be the more stable configuration at higher temperatures, whereas the stability of the *K*-type stacking is increased at lower temperatures (see Fig. 4). The stacking sequences of both hcp and 9*R* are composed mainly of *H*-type planes. In hcp additional *K* stacking faults are *statistically* introduced, whereas 9*R* contains a higher quantity of *periodically* inserted *K* planes.

It follows that at higher temperatures and lower "*K* concentration" these faults are more diluted and hence occur at random within the hcp sequence. At lower temperatures and higher *K*-stacking density an ordered arrangement of *K* faults is favorable, leading to a periodic *H*-*K* sequence and therefore to the 9*R* structure.

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[1] See various contributions in *Proceedings of the Workshop on First Order Displacive Phase Transformations,* edited by L. E. Tanner and M. Wuttig [Mater. Sci. Eng. A **127**, (1990)].

[2] H. Warlimont and L. Delaey, *Martensitic Transformations in Copper- Silver- and Gold-based Alloys,* Progress in Materials Science Vol. 18 (Pergamon, Oxford, 1974).

[3] Y. Noda, S. M. Shapiro, G. Shirane, Y. Yamada, and L. E. Tanner, Phys. Rev. B **42**, 10 397 (1990).

[4] C. S. Barrett, Acta Crystallogr. **9**, 671 (1956).

[5] C. M. McCarthy, C. W. Thompson, and S. A. Werner, Phys. Rev. B **22**, 574 (1980).

[6] A. W. Overhauser, Phys. Rev. Lett. **53**, 64 (1984).

[7] R. Berliner and S. A. Werner, Phys. Rev. B **34**, 3586 (1986).

[8] R. Berliner, O. Fajen, H. G. Smith, and R. L. Hitterman, Phys. Rev. B **40**, 12 086 (1989).

[9] H. G. Smith, Phys. Rev. Lett. **58**, 1228 (1987).

[10] W. Schwarz and O. Blaschko, Phys. Rev. Lett. **65**, 3144 (1990).

[11] H. G. Smith, R. Berliner, J. D. Jorgensen, and J. Trivisonno, Phys. Rev. B **43**, 4524 (1991).

[12] H. G. Smith, R. Berliner, J. D. Jorgensen, M. Nielsen, and J. Trivisonno, Phys. Rev. B **41**, 1231 (1990).

[13] O. Blaschko and G. Krexner, Phys. Rev. B **30**, 1667 (1984).

[14] R. Stedman, J. Phys. F **6**, 2239 (1976).

[15] H. Jagodzinski, Acta Crystallogr. **2**, 201 (1949).

[16] Z. Nishiyama, J. Kakinoki, and S. Kajiwara, J. Phys. Soc. Jpn. **20**, 1192 (1965).

[17] M. T. Sebastian and P. Krishna, Prog. Cryst. Growth Charact. **14**, 103 (1987).

[18] G. Ernst, C. Artner, O. Blaschko, and G. Krexner, Phys. Rev. B **34**, 3586 (1986).

[19] W. Schwarz, O. Blaschko, and I. Gorgas, Phys. Rev. B **44**, 6785 (1991).