In Situ High-temperature Powder Diffraction Study of the Type I ↔ S1 Phase Transition in Decagonal $Al_{71.5}Co_{13.5}Ni_{15}$

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Introduction

The experimental investigation of the type I ↔ S1 phase transition in quasicrystalline $Al_{71.5}Co_{13.5}Ni_{15}$ is aimed at confirming and broadening the results of former dilatometric and electron microscopic investigations. It is part of a systematic study of the phase transitions in the ternary system Al-Co-Ni [1-4].

The presence of a decagonal superstructure in Ni-rich decagonal Al-Co-Ni quasicrystals at low temperatures was first reported by Edagawa et al. [5]. This first investigation was based on selected area electron diffraction patterns of annealed and subsequently quenched $Al_{70}Co_{17}Ni_{13}$. The authors described two distinct sets of superlattice, which are observed in addition to the reflections of the basic decagonal structure. Subsequent studies enabled us to characterize the important structural features of the three different structural states in Ni-rich Al-Co-Ni quasicrystals. It was clarified that the low-temperature phase (“Edagawa” superstructure or type I superstructure) transforms by an order-disorder phase transition into the high-temperature phase (S1 superstructure). It was discovered that the S1 superstructure represents an intermediate state and most likely forms in the solid state via a phase transition from the basic decagonal phase [1, 6], which is considered to be the true high-temperature phase in the Ni-rich part of the decagonal phase region.

However, the experimental data on these high-temperature phases are largely based on investigations of quenched samples and on dilatometric measurements [1, 2, 5]. Only qualitative and little *in situ* information was available about the structural processes at higher temperatures in general [6] and about the two high-temperature phase transitions in Ni-rich Al-Co-Ni quasicrystals in particular. As a consequence, we performed *in situ* powder diffraction measurements on Al-Co-Ni quasicrystals in order to confirm the former dilatometric measurements and to provide quantitative microscopic data, which can help in developing a microscopic model of the structural changes at high temperatures and across the phase transitions.

Methods and Materials

The structural and physical properties of decagonal Al-Co-Ni quasicrystals depend sensitively on the chemical composition. Fine poly-grain samples were therefore produced in selected processing steps that allowed us to control of the chemical composition, chemical homogeneity, and thermodynamic equilibration of the samples. In order to ensure that no significant Al-loss or oxidation processes occurred during our high-temperature measurements, which may have altered the chemical composition and thus the structural properties of the Al-Co-Ni quasicrystals, the powdered samples were flushed with argon and sealed in silica glass capillaries.

Experiments were carried out at APS beamline ID-6 by using 0.031-nm radiation. The chosen furnace for the high-temperature measurements was essentially identical to the furnace described in Margulies et al. [7]. Measurements were carried out at various temperatures up to 925°C. Complete Debye-Scherrer rings were recorded by a Mar3450 image plate system and integrated. The Bragg peak positions were precisely analyzed. On the basis of the positions of nine Bragg peaks on average, the two cell parameters of the quasicrystal were determined. The mean uncertainty of the cell parameter determination was approximately 2×10^{-5} nm.

Results

The cell parameters of $Al_{71.5}Co_{13.5}Ni_{15}$ could be determined very precisely owing to the excellent beam characteristics and the high quality of the recorded Debye-Scherrer rings. The experimental data enabled us to estimate the thermal expansion of both cell parameters at higher temperatures and to characterize the type I ↔ S1 phase transition. In this respect, the thermal expansion data were even more valuable because they could not be inferred from published and unpublished dilatometric data.

The variation of the two decagonal cell parameters across the type I ↔ S1 phase transition proved to be clearly opposite (Figs. 1 and 2). Increased thermal expansion across the phase transition was observed along the periodic c-direction, whereas the expansion of the a-parameter, which characterizes the quasiperiodic layer, is reduced in relation to the thermal expansion at lower temperatures. By contrast, the volume change

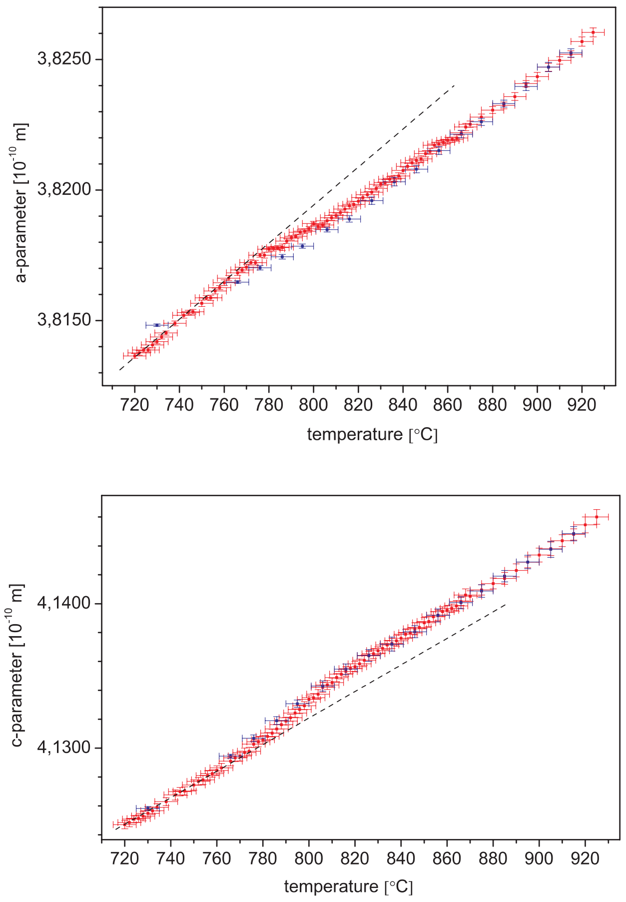

FIG. 1. Temperature dependence of the cell parameters of $Al_{71.5}Co_{13.5}Ni_{15}$ *across the type I ↔ S1 phase transition at increasing (red data points) and decreasing (blue data points) temperatures. The small deviations of the cell parameter variation at decreasing temperatures from the corresponding variation at increasing temperatures are due to delayed relaxation processes owing to the finite cooling rate.*

across the phase transition is only very small.

The observed small volume change in connection with the opposite course of the cell parameters may indicate that the coordination polyhedra in the quasicrystalline structure are distorted systematically during the type I ↔ S1 phase transition, whereas the volume of the coordination polyhedra remains basically constant.

From electron microscopic studies, it was known that the type I superstructure shows only a little interlayer phason disorder, which is principally limited to the skinny and fat hexagons of the quasicrystalline tiling. In contrast, phason disorder is clearly present in the S1 superstructure. Accordingly, the structural changes associated with the type I ↔ S1 phase transition clearly involve the creation of interlayer phason defects. These defects induce larger interlayer distances owing to introduced misfit between the layers, which is consistent with the relatively stronger increase of the c-parameter in comparison with the increase of the a-parameter, as observed during our *in situ* measurements.

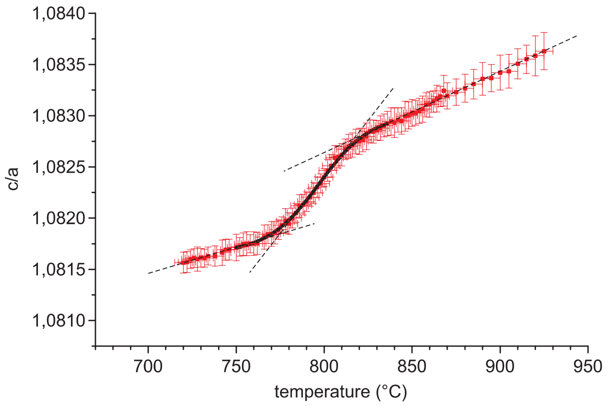

FIG. 2. Thermal evolution of the c/a ratio of $Al_{71.5}Co_{13.5}Ni_{15}$ *in the temperature range 700 to 925°C at increasing temperatures. The principal course of the c/a ratio, as a measure of the structural anisotropy of decagonal quasicrystals, across the type I ↔ S1 phase transition is shown. Three main ranges are indicated by dashed lines that characterize the onset temperature of structural changes in connection with the phase transition and the corresponding transition temperature. The course of the c/a ratio across the phase transition can be approximated well by a logistic (sigmoidal) function (black course).*

This type of phase transition has been predicted theoretically by Jeong and Steinhardt, who described a transition between a so-called locked phase, which corresponds to a Penrose tiling (e.g., the type I superstructure in the Al-Co-Ni system), and a so-called unlocked phase, corresponding to a random tiling (e.g., the S1 superstructure in the Al-Co-Ni system) [8]. Their model is restricted to deviations from the ideal matching on a tiling level, whereas topological constraints and chemical details are not included. Furthermore, it assumes a perfect quasiperiodic tiling, which is not observed experimentally. However, even though their model does not involve the entire complexity of decagonal Al-Co-Ni quasicrystals, it matches fundamental structural features in the temperature range below and across the type I ↔ S1 phase transition [4].

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