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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: Low temperature diffraction experiments on decagonal Al71Co13Ni16	**Experiment number**: HS-2480
Beamline: BM01A	**Date of experiment**: from:16|11|05 to:19|11|05	**Date of report**: 26|06|06
Shifts: 9	**Local contact(s)**: Philip Pattison (pattison@esrf.fr), Dmitry Chernishov (dmitry.chernyshov@esrf.fr)	*Received at ESRF:*

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Report:

1. Single-crystal XRD at room temperature and 100 K

A single crystal with nominal composition $Al_{71.5}Co_{14.5}Ni_{14}$ exhibiting the superstructure of the decagonal Al-Co-Ni quasicrystal [1, 2] was measured at the Swiss Norwegian Beam Lines (SNBL/ESRF). The crystal's dimensions were 0.15x0.15x0.12 mm, the wavelength used 0.7100 Å. A full data set was collected (420 frames @ 0.5° φ per frame) at room temperature and 100 K, using the *mar345* imaging plate system (*marresearch*) and a nitrogen-operated cryojet. Undistorted diffraction patterns were reconstructed with the *Crysalis* software.

Results

The diffraction patterns (figure 1.1+1.2) show the reflections of the type 1 superstructure on a Z-module of rank 5. The reconstruction of the diffuse interlayers exhibit decagonal symmetry like the Bragg-layers. The diffuse interlayers indicate a two-fold superstructure with a large correlation length along the ten-fold axis and a much shorter one within the quasiperiodic layers. The temperature-dependence of the correlation length of this structure was investigated by Steurer et al. [3] between room temperature and 1123 K.

A comparison of the diffraction patterns recorded at room temperature and 100 K (figure 2.3.a) does not reveal any change of the quasicrystal structure at low temperature. Comparable results were obtained from in-house measurements performed on a single crystal having the same structure, like the one measured at SNBL.

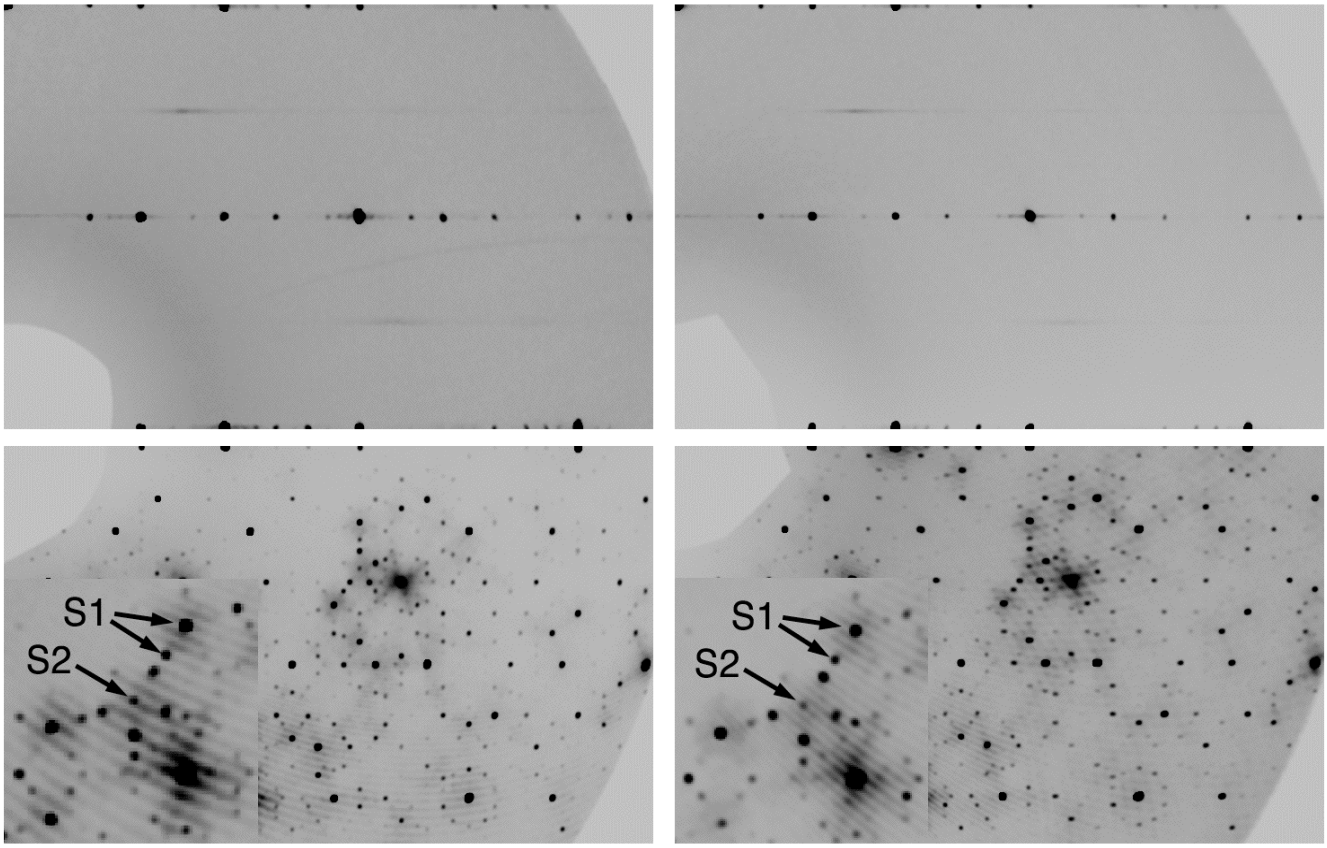

Figure 1.1) Diffraction patterns of d-$Al_{71.5}Co_{14.5}Ni_{14}$, layers ($0h_2h_3h_4h_5$) (left) and ($h_1h_2h_3h_40$) (right) at room temperature (RT, top) and 100 K (bottom); the (10000)-reflection (in *basic* basis), as well as S1 and S2 satellite-reflections are marked

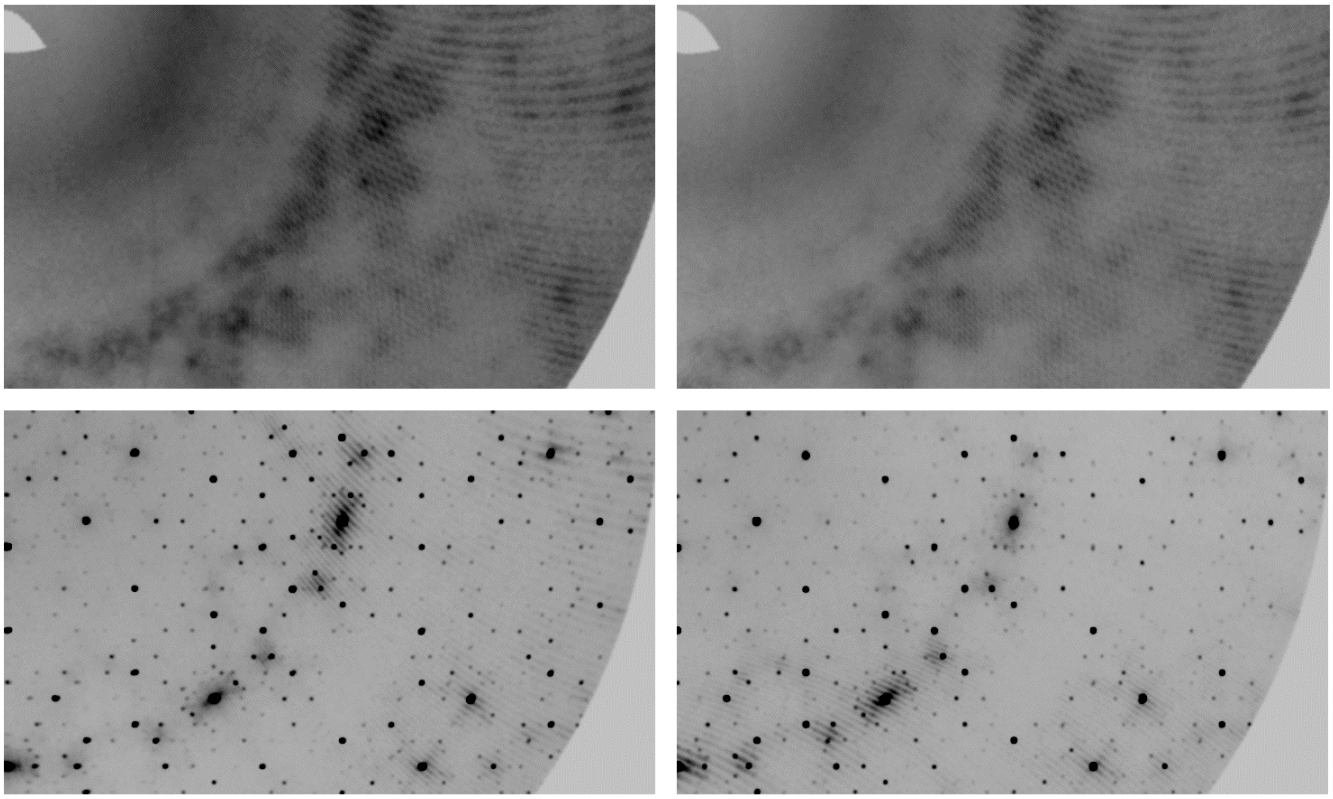

Figure 1.2) Diffraction patterns of d-$Al_{71.5}Co_{14.5}Ni_{14}$, layers ($h_1h_2h_3h_40.5$) (left) and ($h_1h_2h_3h_41$) (right) at room temperature (RT, top) and 100 K (bottom)

2. Single-crystal XRD at room temperature and 15 K; Temperature dependent behavior of the diffuse scattering

The low-temperature diffraction experiments performed in-house and at SNBL do not indicate any structural changes of the decagonal phase under these conditions. A diffusive phase transition to a crystalline phase at lower temperatures cannot be expected due to the sluggish kinetics, because a certain amount of reorganization of the structure would be involved just for topological reasons [4].

However, diffuse scattering phenomena indicate deviations from the strictly ordered quasiperiodic structure. The diffuse scattering is partly due to defects present in the real structure of any crystalline material, like vacancies, impurities and dislocations. Structural disorder, whether displacive, orientational or substitutional, also causes diffuse scattering. The latter also reflects the structural flexibility of a compound. A definition of diffuse scattering in crystalline materials is given in [5], and [6], the latter focusing on diffuse scattering in quasicrystals. Because quasicrystals have additional degrees of freedom, i.e. the perpendicular space, structural disorder can be separated into a contribution of the parallel space and a contribution of the perpendicular space. The resulting diffuse scattering can then be due to thermal diffuse scattering, and/or phasonic diffuse scattering, depending on the source of disorder. Thus, low-temperature measurements at temperatures close to absolute zero can be helpful to investigate the contribution of phason fluctuations on the total diffuse scattering, since the thermal diffuse scattering is very weak under these conditions.

Therefore, an additional measurement was performed at 15 K, using the *mar345* imaging plate system again, equipped with a helium-operated cryojet this time. The X-ray diffraction experiment was carried out with the same single crystal, used for the previous measurement. Because the diffuse scattering is very weak, a high exposure time was used to increase the corresponding signal. However, a higher exposure time causes the saturation of strong Bragg-reflections due to the limited dynamic range of the detector. A new reference data set was collected at room temperature as well. Undistorted images were reconstructed using the software *xcavate* [7]. To guarantee the same scale of intensity, a scaling factor was calculated for each frame based on the average of the background signal.

Results

Looking at the reconstructed diffraction patterns (figure 2.3.b), the position of the reflections has not changed. Thus, no phase transition of the quasicrystal has taken place under these conditions. As before, no peak splitting could be observed in either of the diffraction patterns. There were also no indications for linear phason strain, the precursor of a potential phase transition. The intensity of the Bragg reflections as well as the signal corresponding to the diffuse scattering is stronger at low temperature. This is due to the scaling factor that was applied for the reconstruction of reciprocal space layers. The investigation of the data sets showed that the crystal had moved in the beam during the measurement at low temperature, due to the massive contraction of the goniometer head at 15 K, so the crystal had to be re-centered. Thus, the data sets could only be analyzed qualitatively.

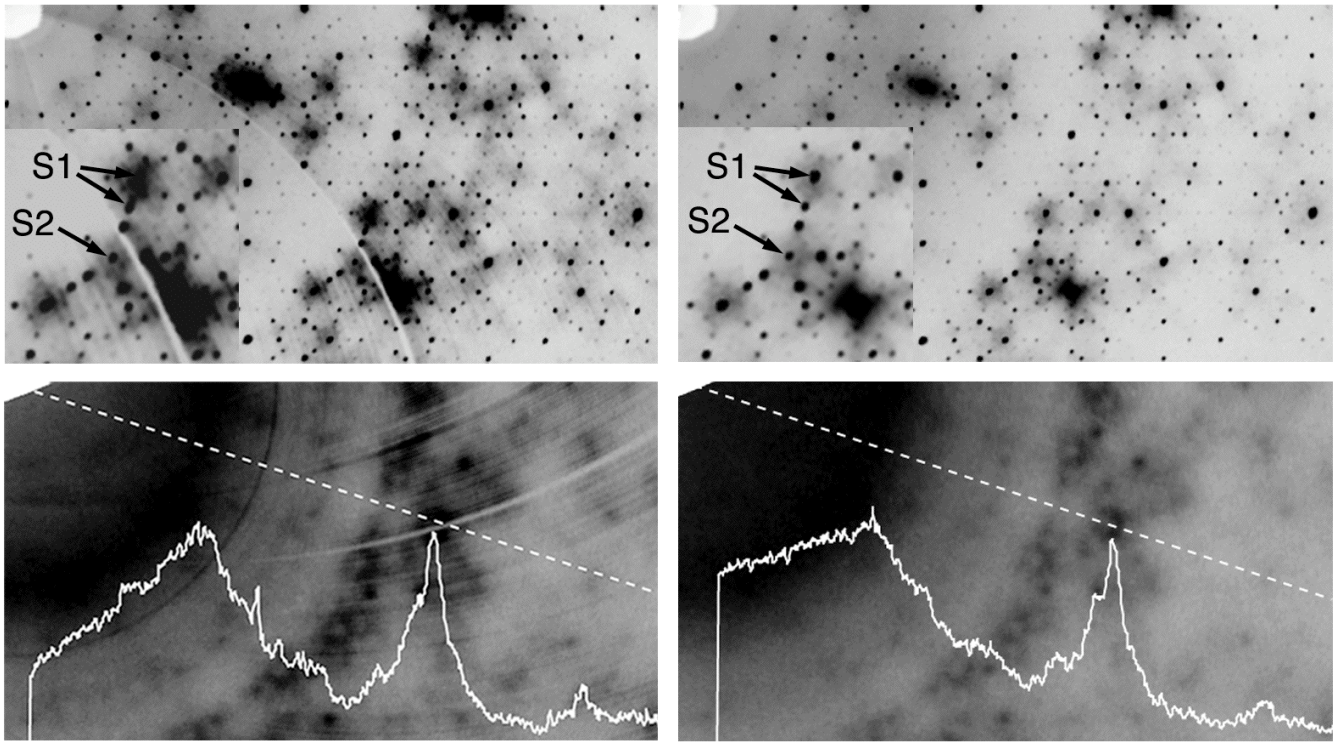

Figure 2.1) diffraction patterns of d-$Al_{71.5}Co_{14.5}Ni_{14}$, layers ($h_1h_2h_3h_40$) (left) and ($h_1h_2h_3h_40.5$) (right) at room temperature (RT, top) and 15 K (bottom); the (10000)-reflection (in *basic* basis), as well as S1 and S2 satellite-reflections are marked; additionally a profile of the diffuse scattering along the dashed line is shown

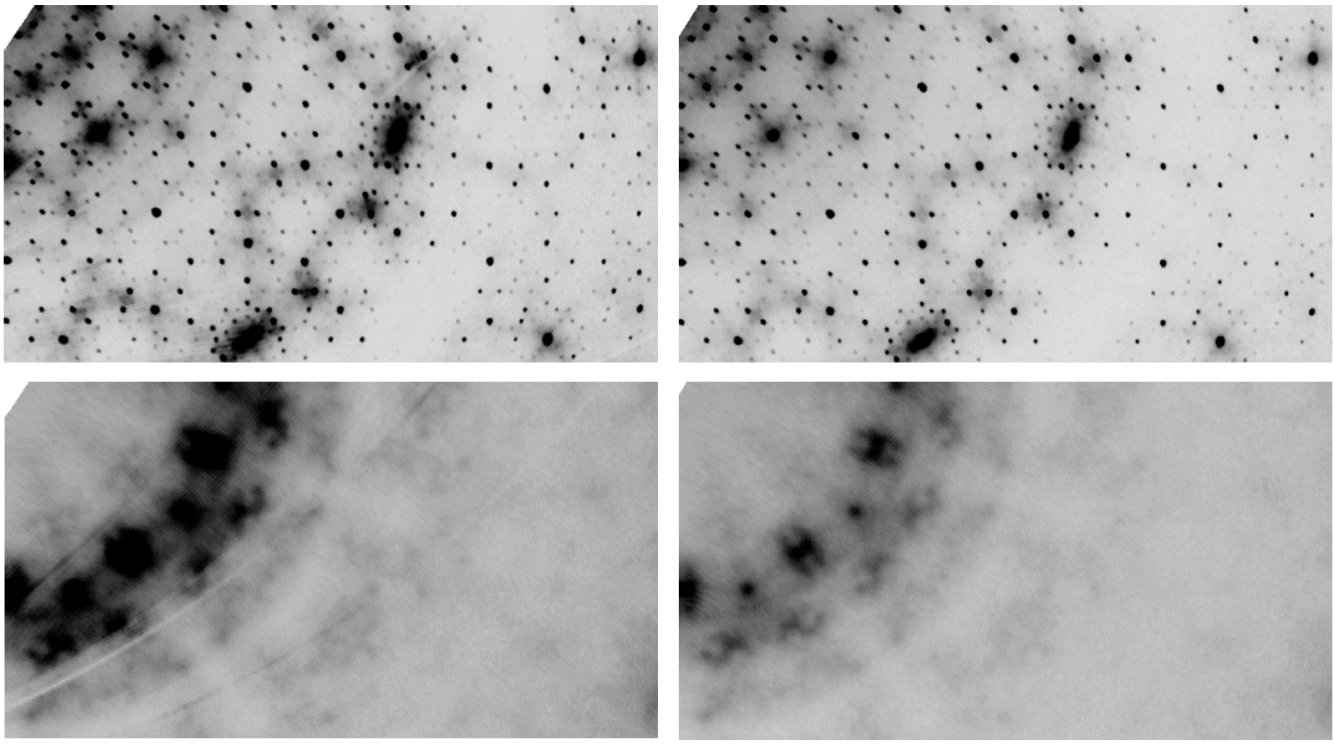

Figure 2.2) diffraction patterns of d-$Al_{71.5}Co_{14.5}Ni_{14}$, layers ($h_1h_2h_3h_41$) (left) and ($h_1h_2h_3h_41.5$) (right) at room temperature (RT, top) and 15 K (bottom)

Discussion

In former high-temperature experiments performed by our group at SNBL/ESRF, a phase transition of the Ni-rich Edagawa-phase of the system Al-Ni-Co was detected by the disappearance of weak superstructure reflections and changes in the structure of the diffuse scattering [3]. In-situ low temperature diffraction experiments on powders of decagonal $Al_{70.7}Co_{13}Ni_{16.3}$ [8] point on a phase transition to a periodic superorder of the quasilattice at 150 K. The low temperature experiments carried out in this study showed that no phase transition of the quasicrystal to a crystalline phase had occurred. Hints for a transformation to another quasicrystal structure could not be found either (i.e. peak splitting or phason strain). No change of the diffuse scattering could be observed in the interlayers. Thus, the results of Kupsch et al. [8] seem to be in contradiction to the results of this study.

The results of this study can be interpreted in terms of thermodynamics. The driving force for the stability of a phase is the minimization of its free energy (under given conditions). At high temperatures, entropy contributes to the minimization of the free energy of any phase. Entropy is a macroscopic measure for the disorder of a system. The third law of thermodynamics states that entropy does not contribute to the free energy of the system at absolute zero. Thus, the disorder of the system will vanish as the temperature approaches zero K. A phase that is essentially entropy-stabilized does only exist at high temperatures, while the phase of lowest internal energy is also stable at absolute zero. Approaching zero K, an entropy-stabilized phase then becomes unfavorable and transforms to the phase of lowest energy if the system is in thermal equilibrium.

The Bragg reflections contain information of the average structure of the decagonal quasicrystal in the system Al–Co–Ni with a 4 Å periodicity. The diffuse scattering contains information of the real superstructure, which shows a 8 Å periodicity that is structurally disordered (as indicated by the diffuse interlayers) throughout the stability area. A quantitative analysis of the diffuse scattering was carried out recently by [Kobas, 2005a,b]. Thus, if decagonal Al–Co–Ni was energetically stable at low temperatures, the diffuse scattering would decrease. The interlayers then should contain sharp Bragg reflections like the Bragg layers. However, no change of the diffuse scattering in the interlayers could be observed. Thus, it can be assumed that thermal equilibrium was not achieved in the single crystal diffraction experiments of this study. The samples were annealed at 900 °C and subsequently quenched to room temperature. At temperatures below approximately 1/2 of the melting temperature of the decagonal phase, which is about 1060 °C depending on its composition, the anticipated kinetics are already too low.

All phase transitions of decagonal Al–Co–Ni using single crystals observed up to now were found at elevated temperatures. Most of them show a disorder-order transformation of the quasicrystal [3, 9, 10]. Thus, the absence of a phase transition is not a proof for the stability of the decagonal quasicrystal under the measurement conditions. The phase transition for milled powders of decagonal $Al_{70.7}Co_{13}Ni_{16.3}$ observed by Kupsch et al. [8] was due to fatigue of the quasicrystal structure induced by the sample pre-treatment, as the authors refer to in a later publication [11]. Thus, other methods have to be applied that allow to equilibrate a system at low temperatures to find the real groundstate of matter.

Literature

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