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Diffuse neutron scattering study of disordered $Al_{72}Co_{16}Ni_{12}$ quasicrystals up to 1000 °C

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Abstract. Disordered decagonal $Al_{72}Co_{16}Ni_{12}$ quasicrystals were investigated by recording diffuse neutron scattering at instruments D10 and IN8/ILL up to 1000 °C. This neutron work supplements X-ray-diffraction investigations, which do not provide a scattering contrast of the transition metals. Moreover, diffuse scattering of inelastic origin could be suppressed, within the resolution limits, by using an analyser. The temperature dependence of the diffuse scattering in the quasiperiodic plane indicates complex re-ordering processes. A one-dimensional superorder along the unique axis, reflected by diffuse layers perpendicular to it, dissolves at 950 °C; short-range-order maxima remain visible at 980 °C.

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Many quasicrystalline structures, and especially the decagonal Al-Ni-Co phases, contain a certain amount of disorder. These phases show different types of structural modifications, ranging from an almost perfectly ordered 2D quasicrystal to a disordered or modulated structure, or 1D quasicrystalline order, depending on composition, temperature and also prior treatment of the sample (see e.g. [1]). The disordering may correspond to thermal equilibrium (high temperature) states of quasicrystals. Metastable intermediate ordered or disordered states may occur.

Generally, an aperiodic structure can be related to a periodic lattice in (hyper-)space with $n > 3$ dimensions. This higher dimensional embedding is useful not only for describing the structure, but also for characterizing various types of disorder specific to quasicrystals. The rationally independent basis vectors $\boldsymbol{a}_i^*$ for integer indexing the diffraction pattern can be thought of as a projection of basis vectors of the $4+1$ dimensional periodic reciprocal "hyper-"lattice. The higher dimensional description entails an additional "phasonic" degree of freedom. Different types of phason disorder are possible, among those linear phason strain and random phason fluctuations. Linear phason strain causes a shear deformation of the lattice. This is accompanied by chemical and displacive disorder, or phason flips in direct space, and, in reciprocal space, shifts or splitting of the Bragg peak positions [4]. The diffraction patterns of the Al-Co-Ni samples investigated, show anisotropically distributed diffuse scattering (diffuse wings, streaks) and more or less diffuse subsidiary reflections ("satellites"), indicating partial periodic order in the qp planes. There is an additional superorder along the unique periodic axis, which gives rise to a particular 1D-columnar cluster ordering, as concluded from the presence of diffuse layers perpendicular to the unique axis. Homogeneous diffuse sheets relate to rod- or column-like, laterally uncorrelated structural units parallel to the c-axis, $n/2$-positions indicate a doubled period $2c$, and the sharpness reflects long-range order along c. From absent meridian reflections with $l = 1/2, 3/2, \ldots$ it may be concluded that the columns are displaced along c relative to one another. Diffuse maxima within these planes relate to short-range ordering between these columnar clusters [2].

1 Experimental

The complementary use of X-ray and neutron methods allows to contrast a dis- or superorder behaviour of the transition metal atoms, if any, because the almost isoelectronic Ni and Co atoms significantly differ in their neutron scattering power. High temperature neutron (instruments D10 and IN8 of the ILL) and synchrotron (instrument D3/DESY) studies were carried out on samples with the nominal composition $Al_{72}Co_{16}Ni_{12}$. Single crystals were grown by the floating zone method. The highest temperatures reached were close to 1000 °C (the melting point is around 1100 °C). For the neutron experiment, the cylindrical sample had a height of 15 mm and a diameter of 7 mm, with a mosaic of roughly 1°. At the D10 experiment ($\lambda = 2.36$ Å, in combination with a $\lambda/2$ filter), we profited from the availability of a microstrip area detector. An analyser was used, set to zero-energy transfer, to

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get rid of possible diffuse scattering of inelastic origin, within the resolution limits of the analyser. The IN8 experiment was carried out with a PG-monochromator and a curved PG analyser in its elastic setting ($k_\mathrm{f} = 2.665\,\text{Å}^{-1}$).

2 Results and discussion

Relatively strong Bragg reflections are accompanied by anisotropic, streak-like diffuse scattering. This type of scattering is very weak at temperatures above 800° in case of the neutron experiments (Fig. 1), the X-ray studies have shown almost no temperature dependence of this phenomenon. The diffuse streaks reappear after cooling and are proven to be of elastic origin indicating the static origin of the underlying disorder phenomenon. A possible explanation might be a "transition" from a low T domain structure, which is governed by a Co-Ni concentration fluctuation (and accompanied by planar defects), to a more homogenous, with respect to the Ni-Co distribution, high T structure. These fluctuations may have been frozen in during a quick cooling of the sample material.

The neutron experiment clearly reveals a remarkable gain in the intensity of (some) subsidiary maxima up to 950 °C (cf. Fig. 1). The synchrotron experiments give conflicting results, some intensities increase, others decrease. Apparently in the high-temperature regime, corresponding to the thermodynamical stability regime of the decagonal Al-Ni-Co phase, there is an onset of re-ordering processes towards an volume increase of domains with periodic order. The subsidiary maxima can described as shifted Bragg peaks, corresponding to a loss of quasiperiodicity in one direction, resulting in a 1d quasicrystal (qc). If the structure becomes periodic in the remaining dimension as well, the structure would be described as an approximant[1]. The reflections of the so-called 4/6 approximant coincide in some areas with those of the 1d qc. The subsidiary reflections gaining in intensity with temperature could be reflections of the 4/6 approximant. The difference in the results of the X-ray and neutron experiments could therefore possibly be caused by a transition of the 1d qc to the 4/6 approximant, which may be a more stable phase at high temperatures than the 1d qc.

The temperature dependence of the diffuse layers and of the modulations within these layers (Fig. 2) was measured up to 980 °C. The experiments revealed a significant difference in the temperature behaviour of the homogenous diffuse background as compared to the superposed diffuse maxima. The diffuse layer was measured in a purely elastic manner at positions not affected by the diffuse scattering concentrated in maxima. This type of scattering decreases continuously with the temperature and has vanished at 950° (Fig. 3). Fitting the cooling curve with a critical power law function gives a value of T_c of 902° ± 1°. The cooling and heating curves do not coincide, this effect is very likely due to the sample not being in thermal equilibrium at temperatures below 800 °C.

Several strong sro maxima were measured within the first and second diffuse layer. They lose much of their intensity up to 880°, but some residual scattering is still visible at 980° (Fig. 4). Fitting the curve shown in Fig. 4 with a critical power law gives a value of $T_\mathrm{c} = 914 \pm 8.2°$. The intensity behaviour up to 900 °C is indicative of a continuous strucural transition.

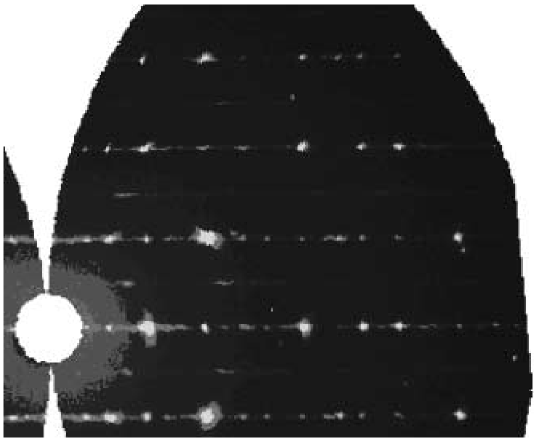

Fig. 2. Diffuse layer line system of decagonal $\mathrm{Al}_{72.5}\mathrm{Co}_{16.5}\mathrm{Ni}_{11}$, X-ray pattern; image plate recording; $\lambda = 0.71$ Å

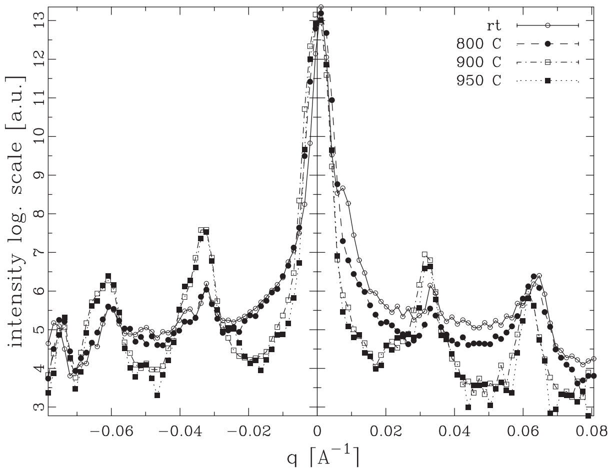

Fig. 1. Measurement along a streak across the $100\bar{1}0$ reflection and "satellites", at different temperatures

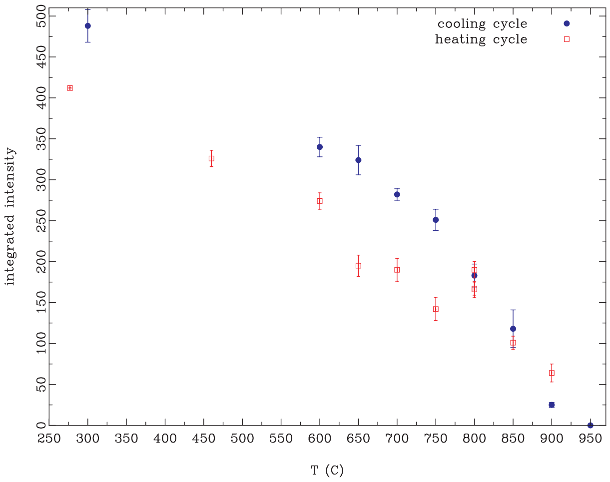

Fig. 3. Temperature dependence of the homogenous part of the diffuse layers, IN8

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[1] An approximant phase denotes a true crystalline structure with often large lattice constants and close local structural similarity

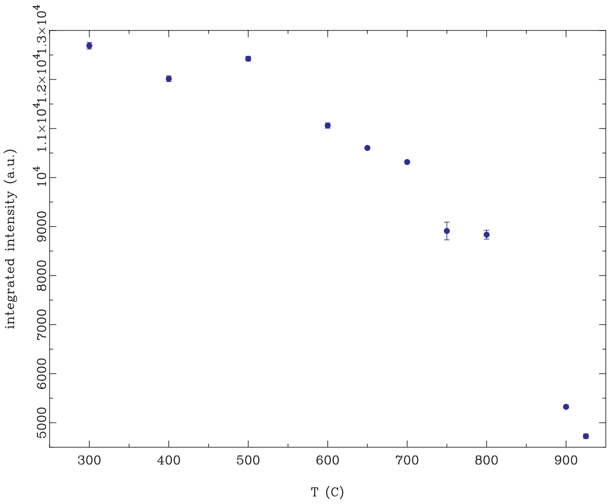

Fig. 4. Temperature dependence of sro maximum 2nd diffuse layer, IN8

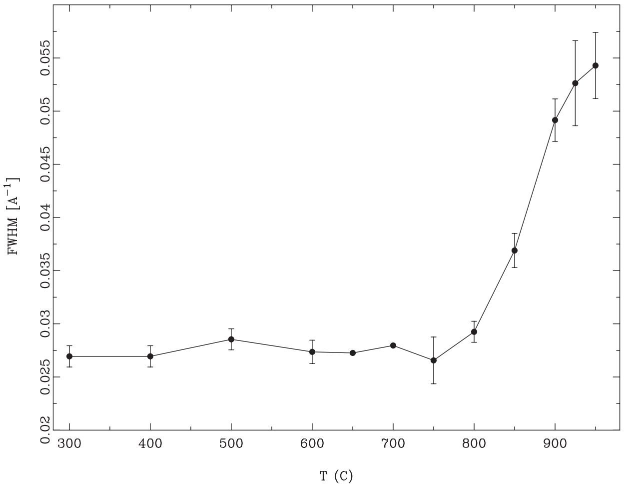

Fig. 5. Temperature dependence of FWHM of sro maximum, IN8

The very weak contribution "surviving" even up to 980° may be related to critical fluctuations of the columnar clusters during the structural re-ordering process.

An ordering scenario is proposed: at very high temperatures the structure has the basic 4 Å period. When cooling below ≈ 915 °C, a short-range ordering process sets in. This ordering may be confined to displacements within the quasiperiodic layers [3]. Figure 5 shows the temperature dependence of the FWHM, and therefore of the correlation length, of this process. At temperatures below 800 °C down to r.t. the correlation corresponds to about 40 Å.

The additional 1D ordering along the unique direction may be a consequence of the ordering causing the sro maxima. At temperatures below 900°, some Al-atoms are pushed off their average positions within the quasiperiodic planes, producing correlated displacements along the unique axis. These displacements are long-range correlated along ***c***, starting from high temperatures, as deduced from the fwhm of the homogenous background, which does not change with temperature.

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