

Temperature dependence of the 8-Å superstructure in decagonal Al–Co–Ni

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Abstract

Diffuse layers corresponding to an 8 Å superperiod along the 'periodic' axis of decagonal Al–Ni–Co phases were investigated by in situ X-ray and neutron diffraction at temperatures up to 980 °C. The diffuse layers consist of an unstructured diffuse background, diffuse bands, and diffuse maxima which (almost) all vanish above 900 °C, but show a different temperature dependence in detail. A tentative scenario of the related structural ordering process during cooling from high temperature is developed. A 1D-columnar cluster model is compared to the experimental results.

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1. Introduction

Various decagonal (Al–Ni–Co, Al–Cu–Co, Al–Ni–Fe) quasicrystals show an 8 Å superperiod along the unique 'periodic' direction, for brevity *c*-direction in the following, as deduced from the observation of modulated diffuse layers in diffraction patterns (Fig. 1). An overview is given in Ref. [1]. In contrast to the work of Yamamoto and Weber [2] who discuss 8-Å-related superstructures in d-phases by an interpretation of 'sharp' satellite reflections, our approach is due to the observation of additional rather broad 8-Å-related diffraction phenomena observed in decagonal quasicrystals with different compositions (and different prior history). It is an open question whether a common explanation for the origin of this kind of superordering can be found irrespective of the individual appearance in various d-phases. Therefore we carried out X-ray and neutron diffraction experiments with different samples at high temperatures. It was intended to follow the

temperature evolution of this superordering outgoing from 'well behaved', i.e. not super- or disordered decagonal structures, which are assumed to exist at least in the thermodynamical stability field close to melting.

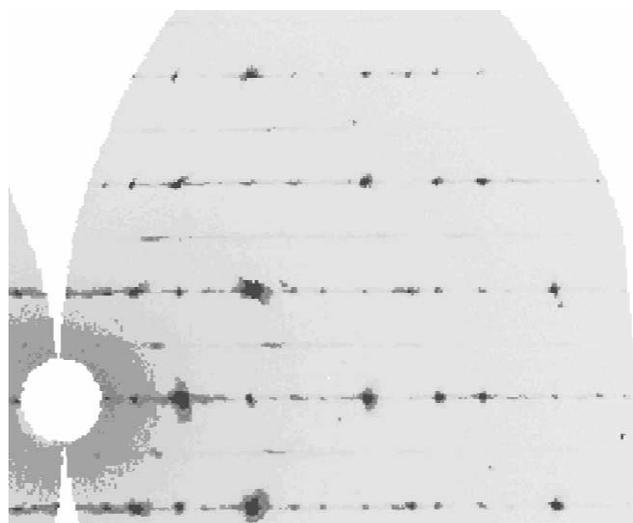
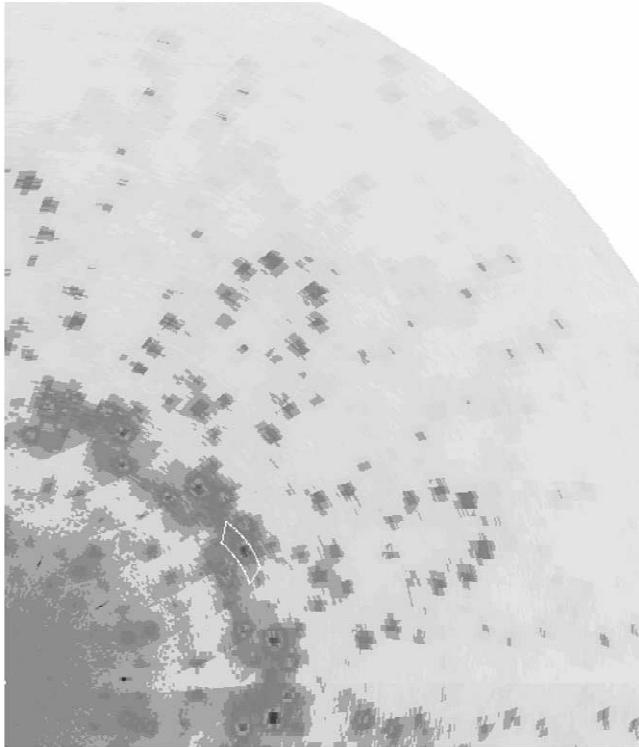


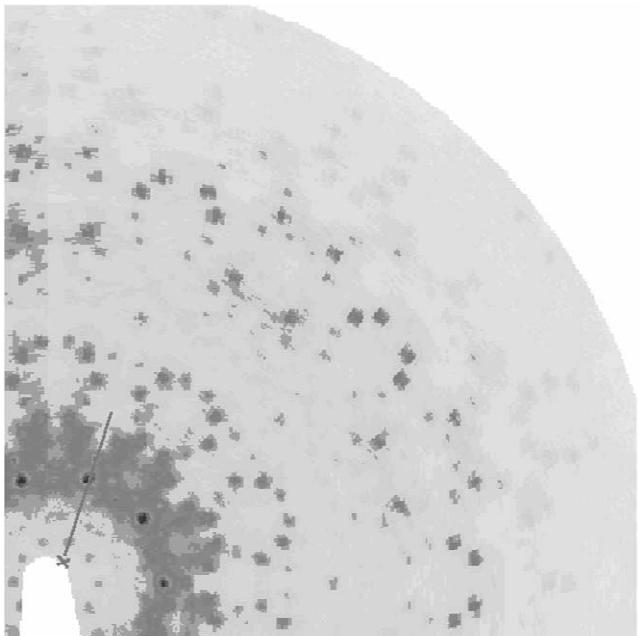
Fig. 1. Diffuse layer line system, *c* axis vertical; sample Z; $\lambda = 0.71$ Å.

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(a)



(b)

Fig. 2. First (a) and second (b) diffuse layers; sample Z; $\lambda=0.71 \text{ \AA}$; in the 1/2-layer the region is marked which was recorded in the neutron D10 experiment (cf. Fig. 7), in the 3/2-layer a solid line marks the scanning (k-) direction in the IN8-experiment (cf. Fig. 8a).

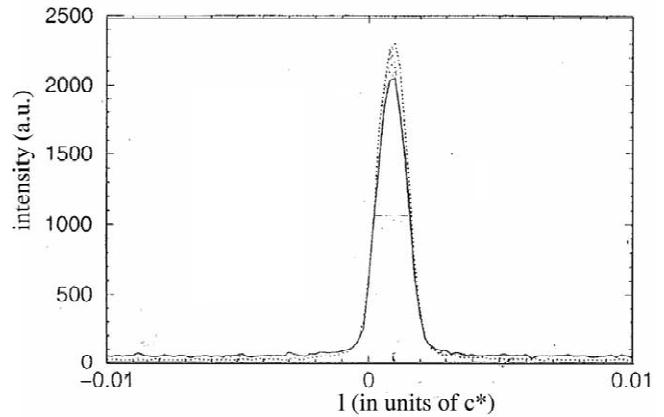


Fig. 3. Scans performed with two ‘near-edge’ wavelengths across the zeroth layer at a position away from any reflection position: the extra-intensity of the 7.4 keV scan is only due to Co.

2. Experimental

High temperature experiments were carried out on d-Al–Ni–Co samples with compositions K, T, Z, where the codes refer to the following compositions (for more details see Ref. [3]): K: $\text{Al}_{70}\text{Ni}_{15}\text{Co}_{15}$; T: $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ and Z: $\text{Al}_{72.5}\text{Ni}_{11}\text{Co}_{16.5}$. X-ray and neutron diffraction was performed to contrast the transition metals (TM) by comparison of X-ray and neutron diffracted intensities and by anomalous X-ray scattering, and to separate ‘normal’ TDS contributions by purely elastic neutron scattering. Synchrotron experiments were performed at the 4-circle diffractometer D3 DESY/Hamburg with a wavelength $\lambda=0.71 \text{ \AA}$. Samples were positioned in a hot-gas-stream furnace which works up to $1000 \text{ }^\circ\text{C}$. In Section 3 we refer also to other synchrotron experiments carried out only at ambient conditions at the beam lines ID01 and D2AM of the ESRF/Grenoble. At the D2AM instrument an anomal-

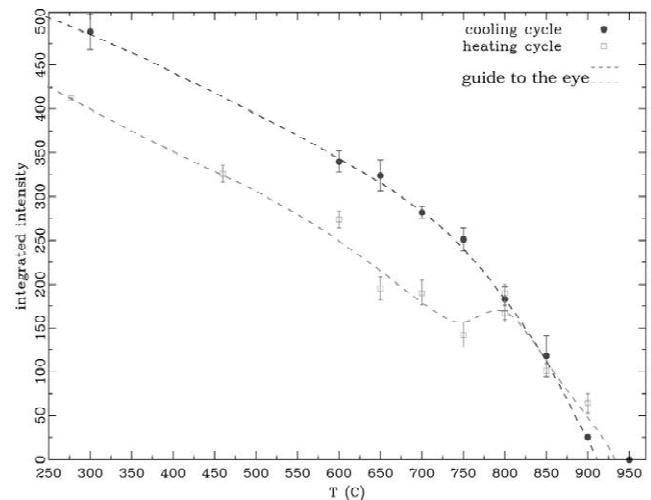


Fig. 4. Temperature dependence of the diffuse background: integrated neutron scans across the layers; instrument IN8, elastic setting.

ous scattering experiment with sample T was performed using a CCD camera. Neutron work with sample T (7 mm diameter \times 15 mm height, mosaic $\sim 1^\circ$) was performed at the triple-axis-spectrometer IN8 of the ILL/Grenoble where the analyser was set to zero energy-transfer, as well as at the diffractometer D10/ILL which is also equipped with an analyzer. Generally neutrons with a wavelength $\lambda = 2.36 \text{ \AA}$ together with a $\lambda/2$ filter were used, thus providing a high Q-resolution. At D10 we took profit from the availability of a microstrip area detector which covered $6.5 \times 6.5^\circ$ (32×32 pixels) [4]. High temperature was

provided by a furnace which operates with direct current heating.

3. Results and discussion

The main observations made at ambient temperature conditions are reported in Ref. [1] and will be summarized here only briefly: There is a homogeneous diffuse ‘background’ in any layer, i.e. also in those belonging to the basic 4 \AA period ($h_5 \equiv 1=0,1,2,\dots$, Bragg layers), including

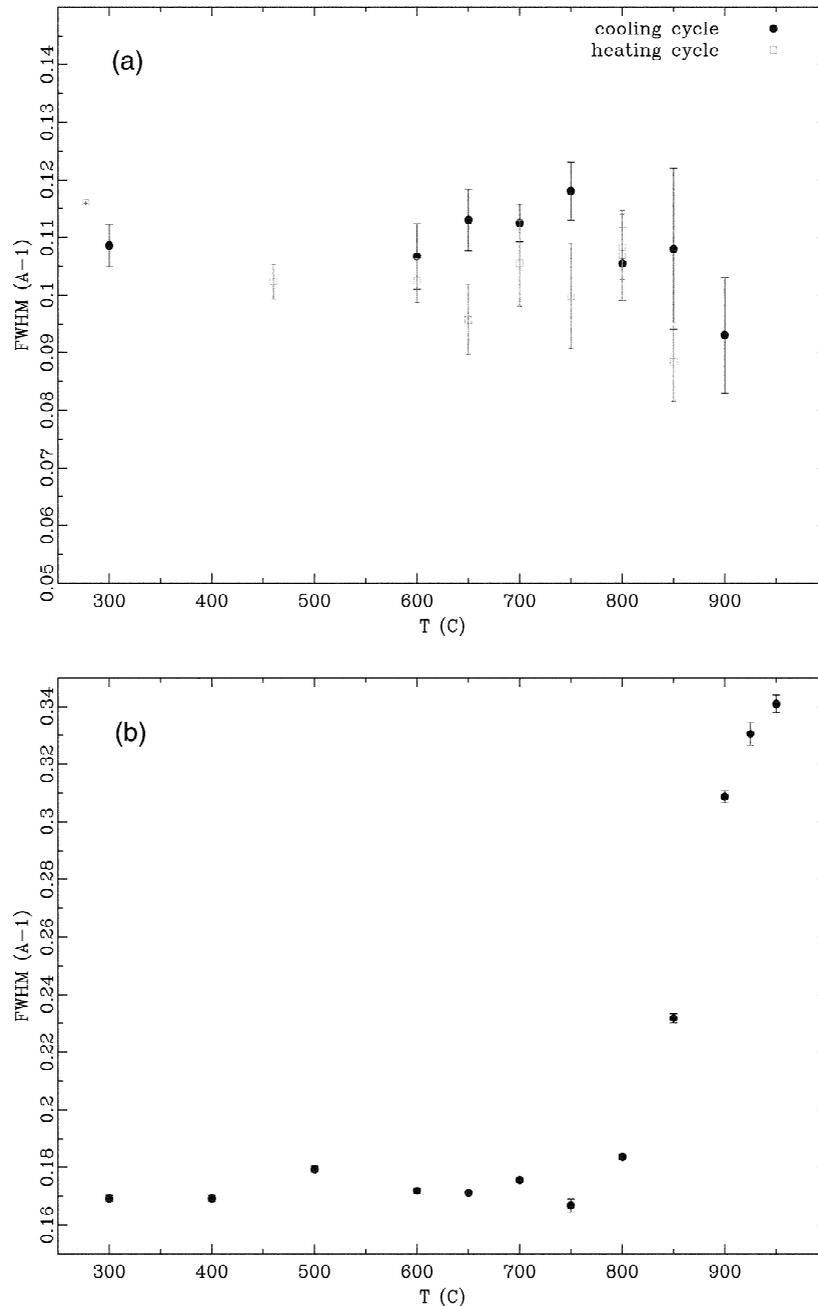


Fig. 5. Width (‘thickness’) of the homogeneous diffuse part (a) and FWHM of a diffuse maximum within the diffuse 3/2-layer (b); instrument IN8, elastic setting.

even the zeroth layer. Therefore, there exists a structural element with 8-Å period, which is strictly one-dimensional, i.e. laterally not long range ordered. There is no Q-dependence of the ‘thickness’ of the layers within the experimental resolution limit. The 1D-superstructure along *c* is periodically long-range ordered. In a high resolution experiment the width of the zeroth layer was measured, a correlation length of at least 3.5×10^3 Å can be estimated (Fig. 3). There are no reflections (000*l*) with *l*=odd (indicating the presence of a 10_5 screw axis) or *l*=integer+1/2 (1/2- layers, no Bragg spots) which may be interpreted in terms of an absent projected structure. The 1/2-layers include modulations, i.e. broad bands and diffuse maxima. Fig. 3 shows patterns of the 1st (*l* = 1/2) and 2nd (*l* = 3/2) diffuse layer of sample Z which obey the same symmetry as the Bragg layers (Fig. 2).

In sample T a major contribution of the transition metals to the diffuse background may be assumed from a rough estimate of the scattering contrast for two different energies, 7.4 and 7.7 keV, i.e. close to the CoK α edge, which is given by $\Delta f'_{\text{Co}} = -3e$. Assuming the 0th diffuse layer being affected either by all atoms or only by the TM atoms gives: $I_{\text{diff}}(7.4 \text{ keV}) \sim (f_{\text{Al}}^2 + f_{\text{Ni}}^2 + f_{\text{Co}}^2) = 0.72 \times 13^2 + 0.12 \times 28^2 + 0.16 \times 27^2 \approx 330$ and 210, respectively. The reduction caused by $\Delta f'_{\text{Co}}$ gives $\Delta I = -24$, i.e. $\Delta I/I \approx -7\%$ and -11.5% , respectively. As shown in Fig. 3 $\Delta I/I_{\text{obs}} \approx (-) 250/2000$ which corresponds roughly to 12.5%.

This is clearly a rough estimate as far as not all of the Al atoms may be ruled out and not all of the TM metals will, most likely, contribute to this particular phenomenon.

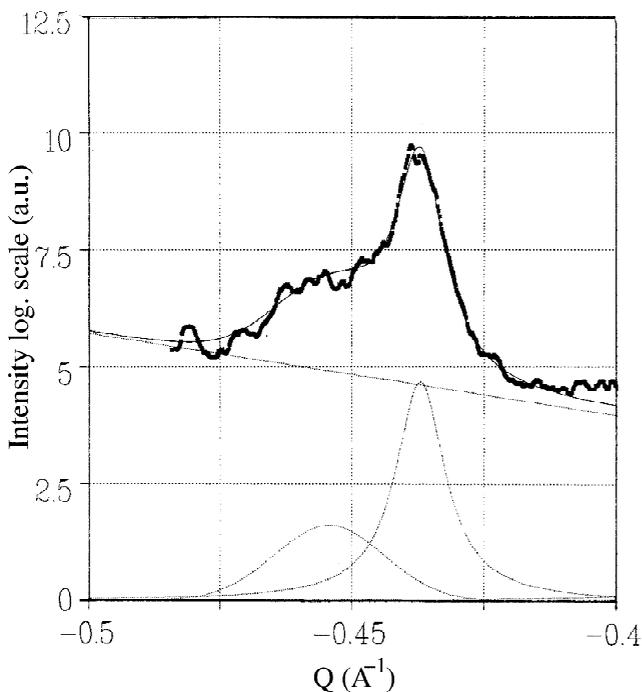


Fig. 6. Tentative separation of the modulations within the diffuse layers into two parts; room temperature neutron measurement.

With increasing temperature we observe the homogeneous diffuse part of the diffuse layers to vanish completely at around 900 °C and reappears during cooling (Fig. 4). However, apparently there are differences in the intensity behavior between heating and cooling of one and the same sample as well as in the onset of the intensity decrease in different samples. Both observations may be related to differing ‘low temperature’ ordering states dependent on the composition and the prior history of a sample. There is no change of the width (‘thickness’) as function of the temperature reflecting an unchanged 1D long-range superorder (Fig. 5a).

The modulations within the diffuse layers are broad features (bands) and diffuse maxima (humps) (Fig. 6) which both decrease also with temperature (Fig. 7). Mainly the diffuse bands vanish at higher temperatures, i.e. between 950 and 980 °C, whereas some of the diffuse humps remain still observable at 980 °C (Fig. 8). Above 800 °C (sample T) these humps broaden considerably (Fig. 5b) which would indicate a rest of short-range ordering even at highest temperatures.

4. Scenario of a structural ordering process exhibiting the 8-Å superperiod

From our experimental findings we propose an ordering scenario in physical space which might be operational during cooling from high temperatures. At very high temperatures close to melting, we assume first the basic 4 Å (two-layer) period. During cooling (from $T \sim 1000$ °C) there is an onset of a displacive and/or migrational chemical short-range ordering process which is basically confined to displacements within the atomic layers. If this lateral ordering is distinct in puckered layers which are 4 Å apart, we have a sequence of structural elements with 8 Å period [1,5]. With further decreasing temperature the lateral correlation length of this process increase and sro-domains grow up which corresponds to a sharpening of the diffuse humps. During growth of the domains a subsequent ‘microstructure’ develops which might correspond to the diffuse bands. Up to this stage the scenario involves the idea of (chemical and/or displacive) reordering within the layers. Support to this idea is given by fitting a critical power law to the experimental data of $I(T)$, i.e. intensity vs. temperature curve of the diffuse hump shown in Fig. 8a: $I(T) \sim (T - T_{c1})^{2\beta}$. As a result we find a critical exponent $\beta \approx 0.11$ and a critical temperature $T_{c1} \approx 910$ °C (Fig. 9a). This trial fit does not include the long intensity tail which extends up to 980 °C: we relate this tail to some kind of ‘critical fluctuations’ accompanying a second order phase transition [6]. The small β value of 0.11 is, however, not far away from the theoretical value of 1/8 to be valid for a 2D-ordering [6]. The term ‘phase transition’ suggests the idea of a transition from a thermally disordered high-*T* phase into a short-range ordered low-*T* ‘phase’ with

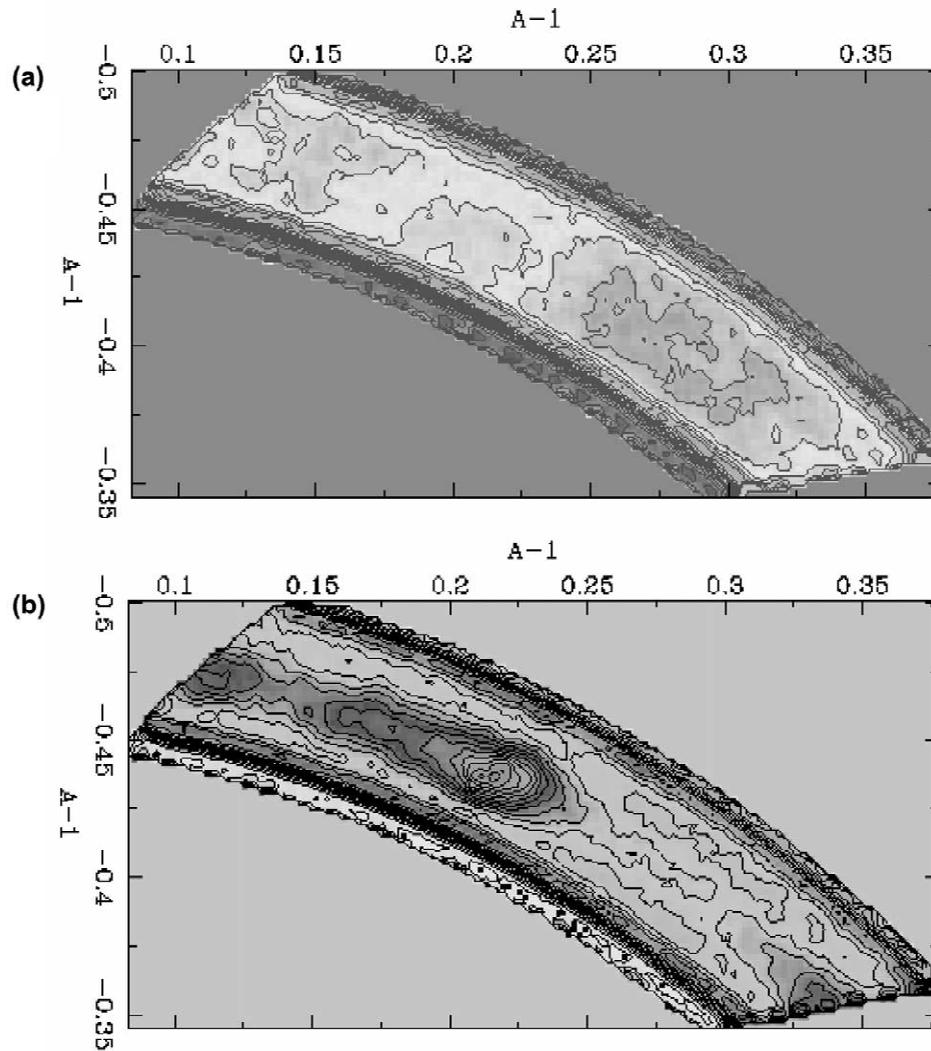


Fig. 7. Section of the first diffuse layer at two different temperatures; instrument D10, area detector (cf. Fig. 2a).

accompanying increase of elastic intensity at the cost of inelastic background scattering. The next step of this scenario involves the additional 1D-ordering along the unique direction which is assumed to be a consequence of the foregoing lateral ordering. Some of the atoms are shifted away from their average positions within the planes, possibly due to atomic size effects accompanied by some freezing of thermal motions along c . Obviously this is a highly cooperative process, producing long-range correlated displacements along one column. From the experimental facts we must conclude that the columns are laterally not correlated, as far as the inter-layer positions of the atoms are concerned. Performing the same analysis $I(T) \sim (T - T_{c2})^{2\beta'}$ now for the (integrated) intensity of the diffuse layer (homogeneous part), one derives values: $\beta' \approx 0.26$ and $T_{c2} \approx 902$ °C (Fig. 9b). These values nicely match the discussed scenario as far as the onset of the longitudinal ($\parallel c$) ordering occurs at or a somewhat lower temperature than T_{c1} . The critical behavior is described by an exponent β' which is closer to the theoretical value for

a 3D ordering process. In other words, the formation of the discussed columns is performed via 3D-interactions. Note that the diffuse layers are treated here as 1D-Bragg peaks, which are the Fourier transform of uncorrelated columns. Clearly this scenario is an oversimplification of a structurally more complicated process which involves the combined intralayer lateral ordering and the interlayer cooperative 1D ordering of particular atoms where the amount of chemical disorder, including vacancies, plays an unknown role.

5. Columnar cluster model

Various models are examined to match the observed diffraction phenomena. For the details of this model and relevant figures we refer to Ref. [1]. Finally we derived a reasonable description by considering prominent structural units in the average structure, i.e. central columns which are surrounded by ten smaller columns [7]. Each of these

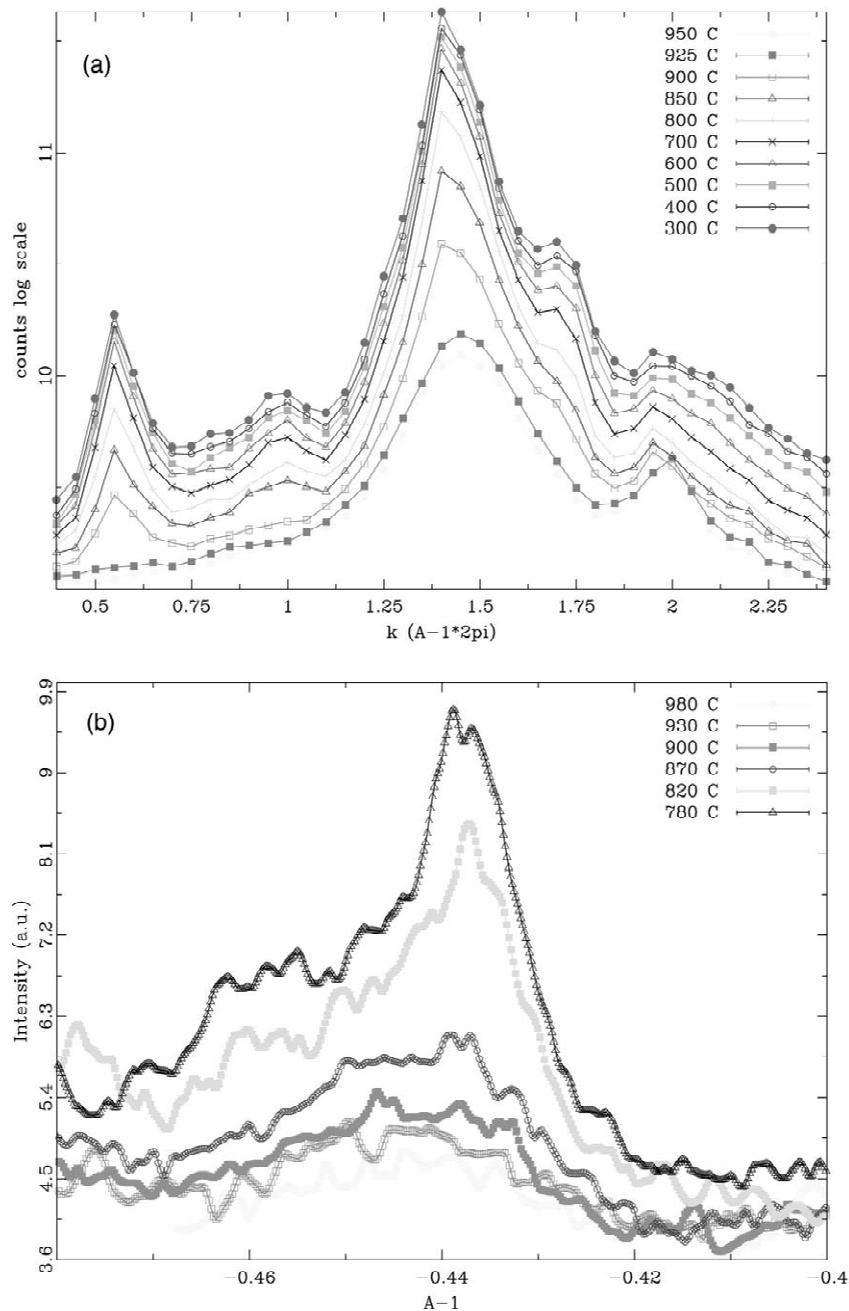


Fig. 8. Temperature dependence of the modulations in the diffuse layers (cf. Fig. 2b): scans within the 3/2-layer; elastic setting (a), and sections through the grid (cf. Fig. 7).

small columns consists of stacks of (twisted) pentagons containing TM atoms and an Al atom in the center. Referring to these small columns, our model combines two processes: (a) some of the Al atoms occupy off-layer positions with variable z coordinates and also lateral displacements from the center positions thus forming 'chains' of Al icosahedra along c . An 8-Å superperiod may be due to unequally puckered layers which are 4 Å apart from one another [5]. These distorted columns are laterally uncorrelated and might be, in addition, 'imperfect' with respect to vacancies and concomitant strain fields; (b) the

second structural ingredient refers to lateral displacements and, possibly, chemical short-range ordering of TM atoms. Thus we have contributions of both TM and Al atoms to the scattering in the diffuse layers. Fourier transforms of this model were calculated for the first and second diffuse layers and compared to the observed patterns (cf. Fig. 9 of Ref. [1]). The general observed features of the 1/2-layer are nicely reproduced. Details cannot be expected to be reproduced properly because the exact chemical composition should play a major role, which is not included in the current stage of modeling. In the light of the new

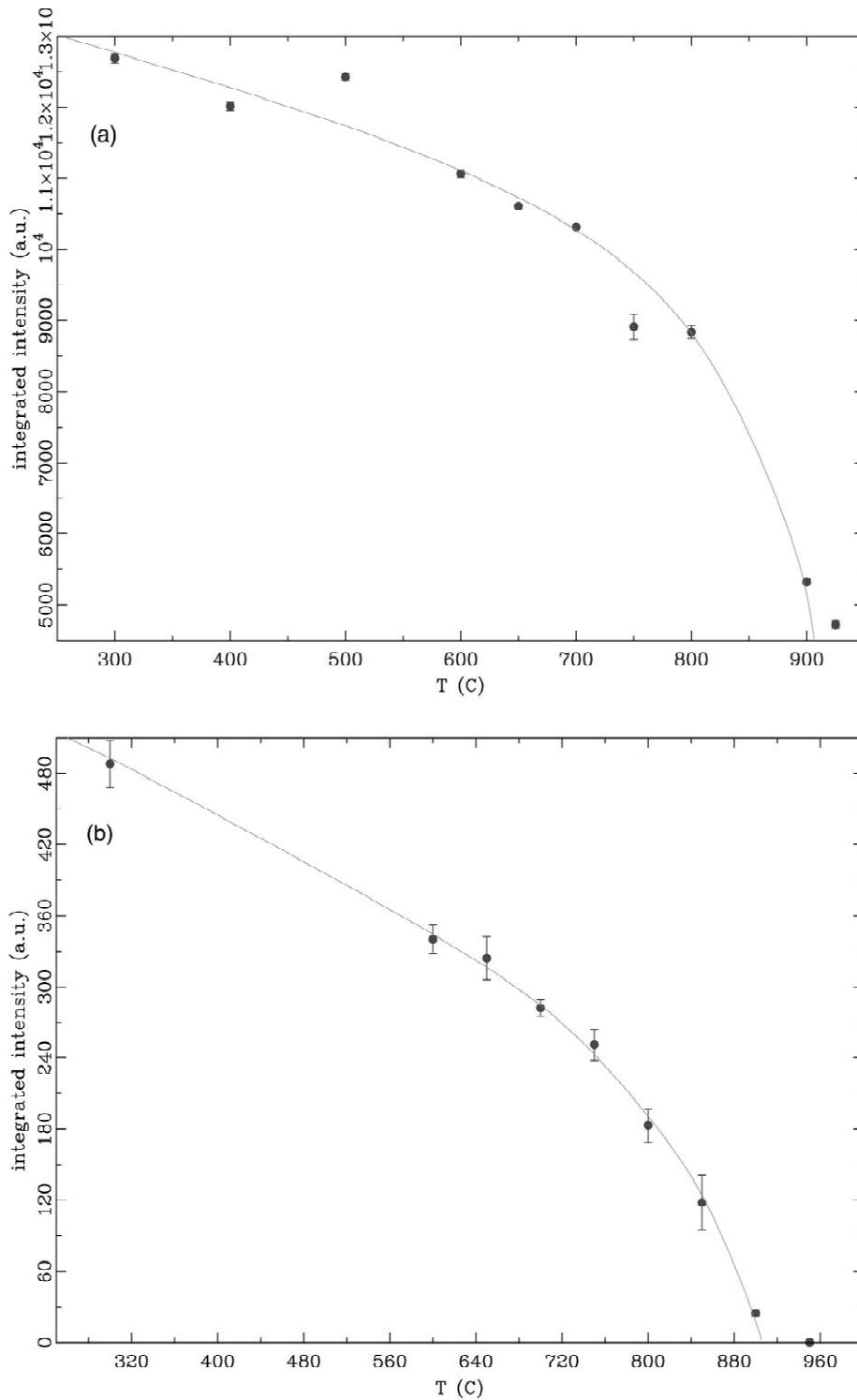


Fig. 9. Fitting of a critical power law to the intensity vs. temperature curves: diffuse maximum within the diffuse layers (a), homogeneous diffuse part-integrated along *c* (b).

scenario outlined above, we tend to modify our discussion given in Ref. [1] in the respect that the lateral displacements of the TM atoms at high *T* are not a consequence, but the cause of the off-Al-positions?

Acknowledgements

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