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Structural Changes in PdD_x in the Temperature Region of the 50 K Anomaly

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Abstract

Diffuse neutron scattering in β-PdD_x (for $x = 0{\cdot}710$, $0{\cdot}742$, $0{\cdot}754$ and $0{\cdot}780$) was observed around the $(1,\frac{1}{2},0)^*$ point in reciprocal space in the temperature range between 50 and 150 K. The detailed shape of the diffuse pattern is dependent on the deuterium concentration for x between $0{\cdot}71$ and $0{\cdot}742$ and nearly independent for higher concentrations. An increase of the diffuse intensities was found when cooling down the samples to 50 K and was associated with the anomaly of the resistivity. During an annealing treatment in $PdD_{0{\cdot}780}$ at 70 and 75 K, superlattice reflections appeared at $(\frac{4}{5},\frac{2}{5},0)^*$ and equivalent positions whose intensity after 53 h was 2% of the intensity of the 200 Bragg reflection of the sublattice.

1. Introduction

Low-temperature ordering in β-$PdD_x(H_x)$, associated with the anomalies in specific heat and resistivity found near 50 K, was recently observed by neutron diffraction. The experiments were done with samples of different deuterium concentration and showed the existence of weak intensities, of the order of 10^{-3} of the intensity of the Bragg reflections of the Pd lattice, at positions in reciprocal space lying along $\langle 210\rangle^*$ directions.

In $PdD_{0{\cdot}63}$, Anderson, Carlile & Ross (1978) found diffuse intensities at the $(1,\frac{1}{2},0)^*$ positions.

In $PdD_{0{\cdot}76}$, Ellis, Satterthwaite, Mueller & Brun (1979) found superstructure reflections at $(\frac{4}{5},\frac{2}{5},0)^*$ and equivalent positions. The ordered state consists of a periodic arrangement of deuterium atoms on the octahedral interstitial sites of the Pd lattice. It was described by the ordered Ni_4Mo structure with a tetragonal unit cell ($a_t = a_c\sqrt{5/2}$ and $c_t = a_c$; a_c is the lattice parameter of the cubic cell). The space group is $I4/m$ (Mueller, Brun, Hiltersman, Knott, Satterthwaite & Ellis, 1979).

In $PdD_{0{\cdot}76}$, Blaschko, Klemencic, Weinzierl, Eder & Just (1980) detected a splitting of the diffuse peaks at $(1,\frac{1}{2},0)^*$ along the $\langle 210\rangle^*$ directions.

The different structural features seem to indicate a change of the ordering process with concentration. In an attempt to explain the different observations it was suggested that the diffuse peak at $(1,\frac{1}{2},0)^*$ belongs to a $(1,\frac{1}{2},0)$ concentration wave corresponding to the first stage of spinodal ordering and that a transition to the equilibrium ordered state containing the reflection at $(\frac{4}{5},\frac{2}{5},0)^*$ takes place (Goldberg & Manchester, 1978). However, in $PdD_{0{\cdot}73}$ no transition from the split peak at $(1,\frac{1}{2},0)^*$ to the reflection at $(\frac{4}{5},\frac{2}{5},0)^*$ was observed even after annealing times of 200 h (Blaschko, Klemencic, Weinzierl & Eder, 1979).

The split peak in $PdD_{0{\cdot}73}$ suggests the existence of long-range forces acting between the interstitial deuterium atoms (Cowley & Wilkins, 1972). A variation of the concentration in the region near $x = 0.73$ may change the forces and therefore new features of the ordering process may be expected. Satterthwaite, Ellis & Miller (1978) found an increase of the temperature of the resistivity anomaly reaching about 80 K at $x = 0{\cdot}78$.

The present investigation of the diffuse neutron scattering in β-PdD_x, for $x = 0{\cdot}71$, $0{\cdot}74$, $0{\cdot}754$ and $0{\cdot}78$, tries to give a contribution to the description of the structural features of the ordering process associated with the anomaly found in this range of concentration.

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2. Experimental

The measurements were carried out at the FR-2 reactor in Karlsruhe on a neutron spectrometer with a multidetector system using a wavelength of 2·44 Å. The neutron beam coming from a double monochromator system was filtered by pyrolytic graphite in order to suppress the second-order contamination. The detector system, consisting of 40 individual ^{3}He detectors, allowed data collection in a wide region of the reciprocal space. The samples were prepared from cylindrical single crystals of Pd (12 mm diameter × 12 mm long) by loading them with deuterium from the gas phase. Pressures up to 200×10^5 Pa were applied at temperatures of 670 K to avoid the two-phase region during loading. The deuterium concentration was determined by weight with a typical accuracy of $\Delta x = \pm 0{\cdot}001$ and, finally, the crystals were sealed by a copper film. The four samples had a concentration ratio D/Pd = 0·710, 0·742, 0·754 and 0·780. The mosaic spread of the loaded crystals, as determined by rocking curves of the 200 and 220 Bragg reflections, was typically 1·4°.

The samples were mounted in a cryostat, cooled down a few degrees below the temperature where for each concentration the maximum of the resistivity anomaly occurs and annealed at this temperature during the measurement. Fig. 1 shows the region of the **a* b*** plane of reciprocal space which was scanned by rotating the sample in steps of 1° with the 40 detectors held fixed. Several measurements were also carried out

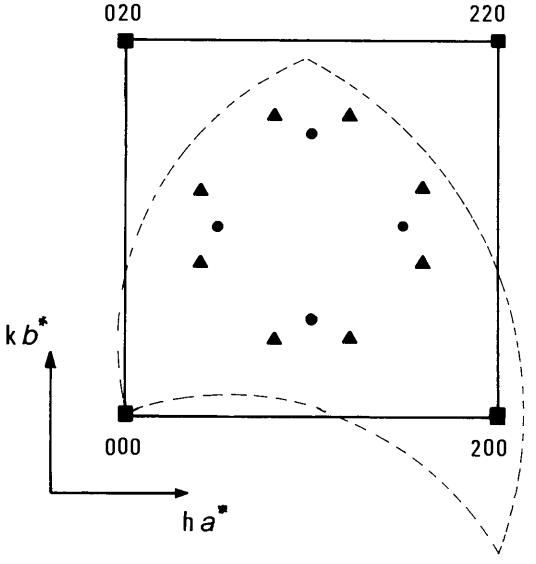

Fig. 1. **a*b*** plane of reciprocal space. The squares indicate the reciprocal-lattice points corresponding to the Bragg reflections of the Pd lattice. The filled circles are located at $(1,\frac{1}{2},0)^*$ and equivalent points and the triangles indicate the $(\frac{4}{5},\frac{2}{5},0)^*$ and equivalent positions. The dotted lines enclose the scanned portion of the **a*b*** plane.

above the anomaly at 110 K and even at 150 K. The data of the neutron diffraction measurements were normalized in units of the background level and plotted as isointensity contours.

3. Results

A diffuse intensity distribution around the $(1,\frac{1}{2},0)^*$ point, due to short-range order, was observed in all four samples cooled down below the anomaly temperature. Fig. 2 shows the isointensity contours for the concentrations x = 0·710, 0·742, 0·754 and 0·780. The peak intensities of the diffuse maxima are generally of the order of 10^{-3} of the intensity of the 200 Bragg reflection of the Pd lattice. The contour maps show a concentration dependence of the diffuse intensity distribution in the concentration range between x = 0·710 and 0·742 – *i.e.* at x = 0·710 one maximum lies near the [210]* direction and at x = 0·742 a second maximum appears near the $(1,\frac{1}{2},0)^*$ point. Only minor changes of the shape are visible between x = 0·742 and 0·780. At all concentrations the outer contours are bent toward the $(\frac{4}{5},\frac{2}{5},0)^*$ and $(\frac{6}{5},\frac{2}{5},0)^*$ points, and the highest intensity of the diffuse distribution appeared for $h > 1{\cdot}0$ (see Fig. 2).

The temperature dependence of the diffuse intensity was studied in detail in $PdD_{0{\cdot}754}$ by heating up the sample from 50 K in steps of 5 K and scanning each time the region around the $(1,\frac{1}{2},0)^*$ point. Fig. 3 shows the temperature dependence of the maximum of the diffuse intensity distribution. At each temperature step up to 150 K the same shape of the intensity distribution was observed together with a decrease of the intensity. The most surprising result is that well above the anomaly temperature weak diffuse intensities are present.

In $PdD_{0{\cdot}710}$, $PdD_{0{\cdot}742}$ and $PdD_{0{\cdot}78}$, measurements carried out at 110 K showed the same behaviour. The characteristic shape found below the anomaly temperature is also visible at 110 K, *e.g.* the essentials of the contours of Fig. 2(*d*) are well reproduced at 110 K, as is shown in Fig. 2(*e*). Therefore, the main effect of cooling down from 110 K to below the anomaly temperature is the increase of the diffuse intensities. The shape of the diffuse intensities remains invariant in this temperature range and no new features appear when cooling through the anomaly.

Somewhat below the anomaly temperature the diffuse intensities reached a value which remained constant when the temperature was further lowered, *i.e.* in $PdD_{0{\cdot}754}$ the intensity was constant below 62 K (as indicated in Fig. 3).

The time dependence of the diffuse intensities was investigated by scanning the region around the $(1,\frac{1}{2},0)^*$ point several times in intervals of a few hours. The first scan was done 30 min after cooling down the samples

to temperatures below the anomaly and showed that the intensity distributions of Fig. 2 are already present. In $PdD_{0.71}$ at 50 K and in $PdD_{0.74}$ at 60 K the intensity increased by only 10% in the next 7 h and reached saturation after another 10 h. Up to 24 h no indication for superstructure reflections was found. The $PdD_{0.754}$ and $PdD_{0.780}$ samples were held at 70 and 75 K respectively, just below the temperatures found by Satterthwaite, Ellis & Miller (1978) for the maximum of the resistivity anomaly, *i.e.* 77 K for D/Pd = 0·754 and 80 K for 0·78. In $PdD_{0.754}$ the initial diffuse intensity did not increase and no indication of superstructure reflections was found within 24 h.

However, in $PdD_{0.78}$ after 14 h at 75 K, when the diffuse intensity was still present, weak superstructure reflections appeared at $(\frac{4}{5},\frac{2}{5},0)^*$ and equivalent positions. (In Fig. 2*d* the small width of the reflections lies within the size of the symbols.) The intensity of these reflections increased in the first 30 h exponentially with a time constant of 4·2 h then showed a linear time dependence and reached saturation after 50 h (Fig. 4). From the beginning, the width of the superstructure reflections was given by the mosaic spread of the sample and the instrumental resolution ($\leq$0·05 in reduced units) and consequently no narrowing with time was observed. Fig. 5 shows rocking curves after 24 and 50 h. The increase of the intensity of the superstructure reflections was accompanied by a decrease of the diffuse intensity distribution which had disappeared when saturation of the superstructure reflections was reached. After 53 h at 75 K the intensity of the superstructure reflection at $(\frac{6}{5},\frac{2}{5},0)^*$ is about 2% of the intensity of the 200 Bragg reflection of the sublattice. The ratio of the intensities of the superstructure reflections found at $(\frac{6}{5},\frac{2}{5},0)^*$ and $(\frac{4}{5},\frac{2}{5},0)^*$ was 2·3 and the ones found at $(\frac{8}{5},\frac{6}{5},0)^*$ and $(\frac{8}{5},\frac{4}{5},0)^*$ was 1·7. When the sample was heated, the superstructure reflections disappeared above 80 K, which is the anomaly temperature.

In a second run, the $PdD_{0.78}$ sample was annealed at 70 K. At this temperature the superstructure reflections appeared later than at 75 K. For instance, after 22 h only one third of the intensity found at 75 K was observed.

At the $(1,1,0)^*$ position in all four samples, no enhancement of the diffuse scattering was observed

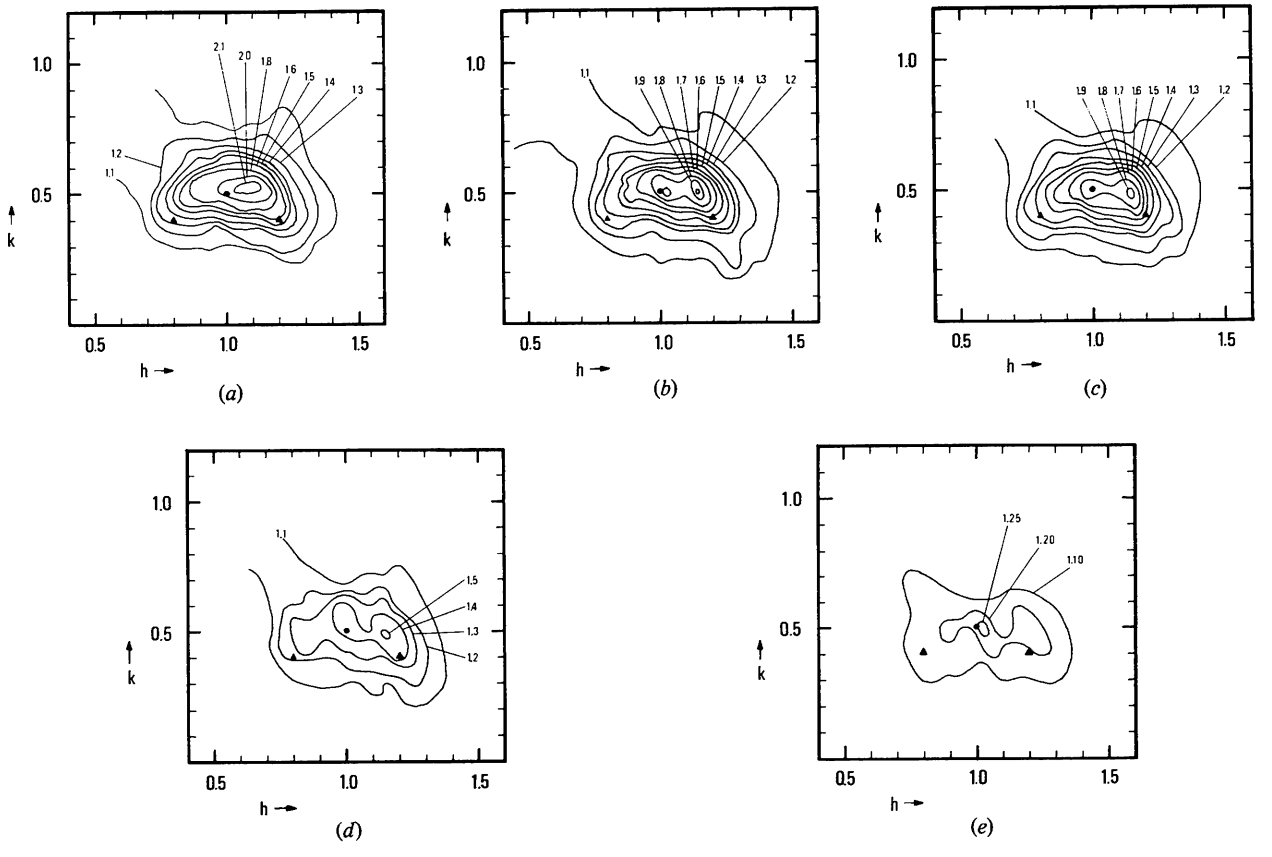

Fig. 2. Isointensity contour maps in the **a*b*** plane of reciprocal space measured by neutron scattering from PdD_x. (*a*) For $x = 0{\cdot}710$ after 7 h at 50 K; (*b*) for $x = 0{\cdot}742$ after 6 h at 60 K; (*c*) for $x = 0{\cdot}754$ after 15 h at 60 K; (*d*) for $x = 0{\cdot}780$ after 14 h at 75 K; (*e*) for $x = 0{\cdot}780$ at 110 K after cooling down from room temperature. The contours are given in multiples of the Laue level. The triangles indicate the positions $(\frac{4}{5},\frac{2}{5},0)^*$ and $(\frac{6}{5},\frac{2}{5},0)^*$ and the circle the $(1,\frac{1}{2},0)^*$ point.

beside weak peaks, of the order of 10^{-4} of the intensity of the 200 Bragg reflection, which could be identified as $\lambda/2$ scattering not completely suppressed by the graphite filter.

4. Discussion

The main results are centred around two points. Firstly, the presence of a strongly temperature-dependent short-range-order intensity around the $(1,\frac{1}{2},0)^*$ position which occurs for all concentrations from $x = 0{\cdot}71$ to $0{\cdot}78$. Secondly, in $PdD_{0.78}$ the additional occurrence of a superstructure which is shown by the observation of Bragg reflections at the $(\frac{4}{5},\frac{2}{5},0)^*$ and $(\frac{6}{5},\frac{2}{5},0)^*$ positions.

(1) *Short-range-order intensity*

The shape of the diffuse intensity distribution is dependent on the concentration of the deuterium atoms. Between $x = 0{\cdot}71$ and $0{\cdot}742$ small changes of the concentration produce different features of the diffuse pattern. This fact is also confirmed by our earlier finding of the split peaks in $PdD_{0.73}$ (Blaschko *et al.*, 1980). A variation of temperature has no influence on the *shape* of these diffuse distributions, but a steep increase of *intensity* was observed when the samples were cooled down through the temperature range of the resistivity anomaly. Below this region the intensity remained constant. We conclude, therefore, that the anomaly in resistivity corresponds to this increase in short-range order. The shape of the intensity distribution is, however, not affected by passing through the anomaly region.

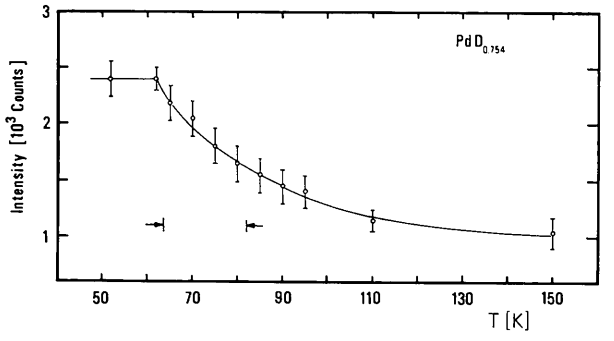

Fig. 3. Variation of the maximum intensity of the diffuse scattering pattern in $PdD_{0.754}$ with temperature. The region of the resistivity anomaly is indicated by arrows.

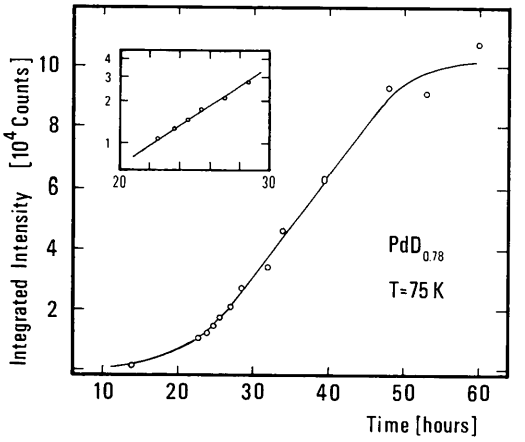

Fig. 4. Variation of the intensity of the superstructure reflection at $(\frac{6}{5},\frac{2}{5},0)^*$ with time in $PdD_{0.78}$ at 75 K.

(2) *The superstructure reflection*

The finding of a superstructure reflection at $(\frac{4}{5},\frac{2}{5},0)^*$ in $PdD_{0.78}$ is consistent with the result of Ellis, Satterthwaite, Mueller & Brun (1979) in $PdD_{0.76}$. However, their peaks are much broader than ours (about 0·10 in reduced units), lower in intensity (only 10^{-3} of the intensity of the 200 Bragg reflection of the sublattice even after 100 h at 70 K) and appeared much later – after 40 h at 70 K. So it seems that our measurements for $PdD_{0.78}$ revealed for the first time a highly ordered state of the interstitial deuterium atoms in PdD_x. The structure factors of this state were

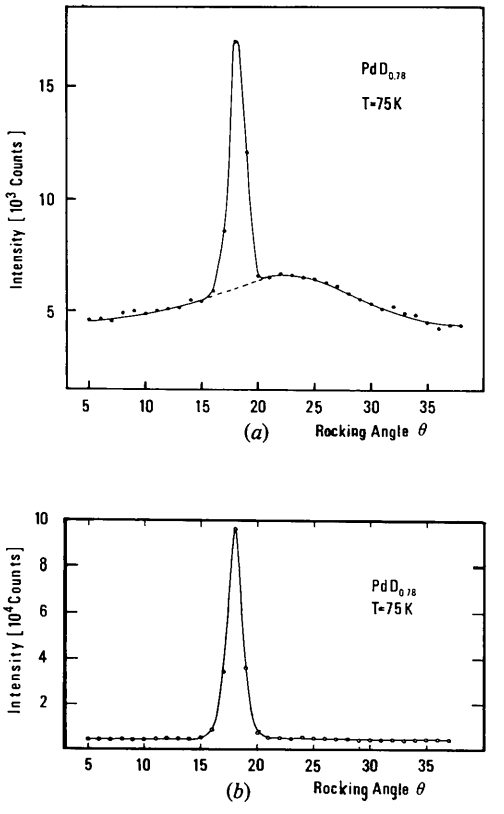

Fig. 5. Scan through the diffuse intensity distribution and the $(\frac{6}{5},\frac{2}{5},0)^*$ point in $PdD_{0.78}$ at 75 K (*a*) after 24 h, (*b*) after 50 h; θ is the angle between the scattering vector **Q** and the [100] direction.

calculated using the tetragonal unit cell and positions of the deuterium atoms as given by the octahedral interstitial sites (Mueller *et al.*, 1979). It turns out that the intensity of the superstructure reflections at $(\frac{4}{5},\frac{2}{5},0)^*$ and $(\frac{6}{5},\frac{2}{5},0)^*$ should be equal if a correction for the Debye–Waller factor is made. However, we found an intensity ratio of 2·3. This large difference may possibly be due to a displacement of the deuterium atoms from their ideal interstitial sites. To elucidate this point, further experimental evidence is necessary.

The shape and the location of diffuse scattering patterns due to short-range order depend, within the framework of the Clapp–Moss theory, on the pair-interaction potential (Clapp & Moss, 1968). The similar diffuse scattering patterns in $PdD_{0.74}$, $PdD_{0.75}$ and $PdD_{0.78}$ may be due to similar interatomic forces. This suggests the possibility that superstructure reflections at the $(\frac{4}{5},\frac{2}{5},0)^*$ points appear in $PdD_{0.74}$ and $PdD_{0.75}$ after longer annealing times than 24 h.

A tentative model

The finding of superlattice reflections at $(\frac{4}{5},\frac{2}{5},0)^*$ and equivalent points indicates a highly ordered interstitial structure where four consecutive (420) planes are filled with D atoms, whereas each fifth is vacant, so that the D arrangement is more compact in the new phase. As was pointed out by Ellis, Satterthwaite, Mueller & Brun (1979), this ordered state could be described as the interstitial analog of the ordered Ni_4Mo structure.

Within the four filled (420) planes all interstitial sites are occupied and one has the PdD structure. This tendency to a more compact D structure below the 50 K anomaly may be due to a strong D–D interaction, known from phonon dispersion curves in PdD_x (Rowe, Rush, Smith, Mostoller & Flotow, 1974). The D–D interaction is also present at higher temperatures where it is responsible for the short-range order found at 110 K. This broad short-range-order intensity around the $(1,\frac{1}{2},0)^*$ point indicates that in microdomains a similar ordering on (420) planes occurs.

Geometrically, there are several ways to achieve in our concentration range a more compact D arrangement, *e.g.* two (420) planes filled and the third vacant correspond to a stoichiometry of 67% D and produce intensity at the $(\frac{4}{3},\frac{2}{3},0)^*$ point; three (420) planes filled and the fourth vacant correspond to 75% D and produce intensity at the $(1,\frac{1}{2},0)^*$ point. The ordered structure produced by this sequence is characterized by the *Strukturbericht* symbol DO_{22}. Finally, four (420) planes filled and the fifth vacant correspond to 80% D and produce intensity at the $(\frac{4}{5},\frac{2}{5},0)^*$ point (Ni_4Mo structure).

In our case, the diffuse intensity is located around the $(1,\frac{1}{2},0)^*$ point with an extension towards the $(\frac{4}{5},\frac{2}{5},0)^*$ points, so that the short-range ordered state found in $PdD_{0.71}$, $PdD_{0.74}$ and $PdD_{0.75}$ and also in $PdD_{0.78}$ before the appearance of the superstructure peaks at $(\frac{4}{5},\frac{2}{5},0)^*$ may be described by an arrangement of mainly DO_{22} and Ni_4Mo microdomains.

The microdomains are partially ordered at 110 K. When cooling down in the anomaly region they increase their order and induce therefore the increase of the diffuse intensity. At lower concentrations the mixed state of differently ordered microdomains may remain stable in the anomaly region, due to a kind of 'frustration' caused by competing ordering tendencies on the (420) planes, *i.e.* mainly the DO_{22} and Ni_4Mo ordering possibilities. At higher concentrations, however, due to the higher deuterium content, the internal energy of the deuterium gas increases and allows the preferred formation of microdomains of the more compact Ni_4Mo structure which produces, therefore, after some annealing, the long-range ordered structure. At present it is difficult to explain the detailed shape of the diffuse intensity; the influence of distortion effects should be taken into account and further investigations are necessary.

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