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► **To cite this version:**

D. Blavette, S. Chambrelaud, A. Loiseau, Jérôme Planès, F. Ducastelle. FIM ATOM PROBE INVESTIGATION OF LONG PERIOD SUPERSTRUCTURES IN $\text{Cu}_3 \pm x\text{Pd}$. Journal de Physique Colloques, 1989, 50 (C8), pp.C8-365-C8-370. 10.1051/jphyscol:1989862 . jpa-00229960

HAL Id: jpa-00229960

<https://hal.science/jpa-00229960>

Submitted on 4 Feb 2008

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FIM ATOM PROBE INVESTIGATION OF LONG PERIOD SUPERSTRUCTURES IN $\text{Cu}_3 \pm x \text{Pd}$

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Abstract : FIM atom-probe techniques have been used in order to investigate concentration modulations related to (001) APB's in $\text{Cu}_3 \pm x \text{Pd}$. Layer by layer analysis of (001) superstructure planes of a long-period single crystal (20.5 % Pd) exhibits LRO modulations with correlation lengths oscillating between 6 and 7 d_{001} . The average wavelength ($6.5 d_{001}$) is in good agreement with the mean size of one-dimensional ordered domains, as measured by HRTEM.

I. INTRODUCTION

Studied for years, the Long Period Structures (LPS) are a very intriguing order phenomenon occurring in numerous and very different alloys. Their structures are based on the $L1_2$ cubic structure and can be described, basically, as one dimensional, commensurate or incommensurate, arrangements of $L1_2$ domains bounded by conservative antiphase boundaries (APB) lying in cubic planes (Fig. 1). From experimental electron microscopy studies, very different topologies emerge depending on the following factors : i) value of the mean size of the domains, M, ii) nature, continuous or discontinuous, of the variation of M with chemical concentration or temperature, and iii) degree of rigidity of the APB's i.e. degree of freedom in the APB positions around their mean position : APB's can be very straight (Pt_3V [1, 2], Cu_3Al [3]) or jogging over one atomic plane ($\text{Ti}_3 + x \text{Al}$ [4]) or wavy and spread over a few atomic planes ($\text{Cu}_3 \pm x \text{Pd}$ [5, 6]). Fig 2 shows a high resolution image obtained by transmission electron microscopy of a structure observed in $\text{Cu} - 20.5 \text{ at\% Pd}$, which is a projection of the structure along a cube direction perpendicular to the modulation axis ; projected atomic columns are monoatomic, either Cu or Pd, Pd columns being seen as white dots except in the planes close to the APB's. There, a grey and diffuse contrast is observed, indicating that the columns are mixed and partially disordered or in other terms that the APB's are rough [4, 5].

It has been shown experimentally that the APB distribution can in all cases be described by a regular hull function in the form of a smoothed square wave function : discontinuities of the function define the mean positions of the APB and the roundings of its corners are related to the diffuseness in the APB positions [7, 8]. A method has been recently developed to determine quantitatively the hull function, consisting in a numerical treatment and a statistical analysis of high resolution images [9].

However, this method does not allow the study of composition modulations of same period which are superimposed on the APB modulation. This affects the composition of the successive (001) planes normal to the modulation axis which are in the perfect case alternatively pure A planes and AB planes (Fig. 1). The existence of this second modulation has been shown from analysis of diffraction patterns. It gives rise to satellite reflections around the fundamental reflections at position $(h k l) \pm n/2M$ (h, k, l of same parity and n integer), whereas satellites due to the antiphase modulation are at positions $(h k l) \pm (2p + 1)/2M$ ($h + k$ odd, p integer). Since a high resolution image is basically a two-dimensional projection, it is not possible to determine the form of the composition modulation using electron microscopy. On the other hand, this is in principle possible from X Ray diffraction experiments if one is able to measure intensity of all the harmonics of the modulation, which is almost impossible in practice.

F.I.M. atom probe techniques are however quite suited to study these concentration modulations on an atomic scale since the composition of the successive (001) atomic planes can be determined from a layer per layer microanalysis of a LP single crystal in (001) orientation, (001) being the modulation axis.

In this paper, we will show the efficiency of this technique to studying the concentration modulation occurring in $\text{Cu}_3 \pm x \text{Pd}$ alloy. LPS are currently extensively studied in this system by electron microscopy [5, 6] and display very interesting features depending on both composition and temperature. At low Pd content (18 - 23 % Pd) the structures are incommensurate with large M values ($15 \rightarrow 6$) and wide APB whereas for higher Pd content (24 - 30 % Pd) the structures are commensurate with smaller M values ($5 \rightarrow 3$) and sharper APB.

II. EXPERIMENTAL

Most of experiments have been performed in Cu - 20.5 at % Pd, annealed at 485°C. This alloy shows a LPS characterized by a M value equal to 6.24. The thickness of APB's, as determined from the statistical analysis of images (figure 2), is around $1.8 d_{001}$.

Large single crystals were elaborated by GODARD (CNRS - ORSAY). Needles for atom probe investigations were cut using a spark machine in such a way to position their axis along the (001) modulation direction. Sharp tips were obtained by standard electropolishing techniques in a solution of 80 % acetic and 20 % nitric acid.

Atom-probe analyses were conducted with a pulse fraction close to 20 %. During experiments, the tip temperature was maintained in the range 60 - 80 K. Although the use of lower temperatures (20 - 40 K) generally minimizes preferential evaporation effects, we chose these experimental conditions in order to reduce the risk of tip failure. All the investigations were conducted with the four-sector detection system we described few years ago [10]. This special detector is quite suited for the analysis of a material on a plane by plane basis. Such investigations are well known to lead to pronounced pile-up effects [11].

The preliminary studies we conducted on (001) superstructure planes, showed that Pd atoms are subjected to preferential retention effects. Pd-rich layers are more stable than Cu rich planes. During field evaporation, Pd atoms of mixed planes (more stable) begin to evaporate upon the completion of the plane desorption and proceed to desorb with the very beginning of the following Cu rich layer. This leads to a constant shift between the observed modulations in the detection flux and the concentration fluctuations due to LRO.

Despite this phenomenon, the careful investigations we made on ordered Cu_3Pd , indicated that a good contrast between Pd-rich and Cu-rich pure planes is preserved in concentration profiles. The measured composition was found in this case, close to that expected.

III. RESULTS

A typical field ion image of a Cu 18.5 at % Pd is given in figure 3. Antiphase boundaries, here parallel to the tip axis (001), lead to well visible discontinuities on the superstructure (001) planes. On the basis of plane by plane analyses we performed, we are convinced that most of bright spots are associated with palladium atoms. Because of the rather low evaporation field of Cu, as compared to Pd, we think that only Pd-rich mixed planes are visible on the (001) pole.

Because of the low Pd content, the width of ordered domains (M) is here larger than that observed in Cu 20.5 at % Pd (figure 2). The average spacing of APB's, as deduced from this FIM image, is close to 38 Å. The corresponding value of M ($M = 38/a$ with $a = 3.7$ Å the lattice parameter) is in good agreement with that expected ($M \approx 10.3$).

The main goal of this work is to analyse (001) planes in a direction perpendicular to APB's. As a result, only orientation domains (variants) for which APB's are normal to the (001) oriented tip axis, are suited. As the three <001> directions of the single crystal are in principle, equivalent, three orientation variants are present in the material. The size of these orientation domains, as measured in high resolution electron microscopy images, is a few hundred Angströms. As conservative APB's do not modify the basic stacking sequence of (001) planes in the direction perpendicular to APB's (see figures 1 and 2), the right variant is well detectable in FIM images. The atom-probe investigations of concentration modulations we present here were performed on (001) poles, for which no discontinuities appear (figure 4).

The concentration profile shown in figure 5 presents a portion of the fluctuations we observed for Pd in the Cu 20.5 at % Pd alloy. The analysis direction is perpendicular to APB's. The fine scale modulations clearly exhibit the expected stacking sequence of superstructure (001) planes for a Ll_2 ordered structure: Pd rich mixed planes alternate with Pd depleted (Cu rich) layers. The most interesting feature of this profile is in fact, the presence of a long range modulation. Despite the unavoidable statistical fluctuations due to the reduced number of collected ions per layer ($N(002) \approx 36$), this analysis shows unambiguously the presence of quasi-periodic extrema for Pd rich layers. This interpretation is reinforced by the distance between concentration maxima which is observed to oscillate between 6 and 7 d_{001} ($d_{001} = a$). The measured width of one-dimensional ordered domain by HRTEM is $M = 6.24$ (figure 2). This latter value is interesting to be compared to the correlation lengths provided by the autocorrelation diagram given figure 6.

In spite of additional beating phenomena sometimes observed in autocorrelograms built from profiles with constant sample size (the number of ions collected per plane varies from one layer to another), the curve shown figure 6 exhibits a modulation wavelength ($\sim 6.5 d_{001}$) close to the expected one. Fourier transform analysis is probably in our opinion, a more reliable tool for the treatment of complex signals which contain various frequencies. The spectral density of a composition signal containing more than 200 planes is presented figure 7. Again, the characteristic wavelength $M \approx 6.5$ appears. However, the Fourier analysis gives rise to under-harmonics of the basic modulation. The higher peak ($\lambda = 34 d_{001}$) observed here was also clearly detected in initial profiles.

As APB's are conservative, it is of course impossible to detect the position of boundaries in figure 5. However, a close examination of concentration profiles indicates that richer mixed planes (marked by 6, 7, 8 in fig. 5) are often associated with pure planes with a very low Pd content. These large amplitude parts of the profile are associated with regions for which the partial long range order is higher (only order fluctuations perpendicular to APB's are detected; the occurrence of an additional disorder inside each analysed plane does not lead to composition variations). Starting from the simple idea that APB's should be located in low order regions, we propose that boundaries are situated in low amplitude regions (marked by 3,4).

IV. CONCLUSION

The investigations we have undertaken on incommensurate LP superstructures in $\text{Cu}_3 \pm x \text{Pd}$ demonstrate again, that atom-probe is a powerful tool for the investigation of fine-scale features in materials. The layer per layer microanalyses we performed have shown that pseudo-periodic APB's are associated with long range order modulations. The statistical tests we performed on concentration histograms (chi-squared tests) confirm this observation. The mean wavelength observed in the related spectral density ($6.5 \pm 0.1 d_{001}$) is close to the average size of ordered domains as measured by HRTEM ($M = 6.24$). A larger number of collected planes would probably provide a value for M, closer to that expected (broadening of Fourier peaks). Fourier transform analyses show that more extended modulations occur ($\lambda = 13$ and 35 \AA for example). Because of the preferential retention effects which were observed, it is difficult to ensure the quantitativity of amplitudes which are measured in concentration profiles. However, these phenomena should not modify to a large extent the form of the observed modulations. Our experiments show qualitatively, that APB's should be associated with low LRO regions for which the concentration difference between mixed and pure planes is rather low. A more refined statistical analysis of concentration profiles could perhaps provide a first analytical description of the form of LRO modulations.

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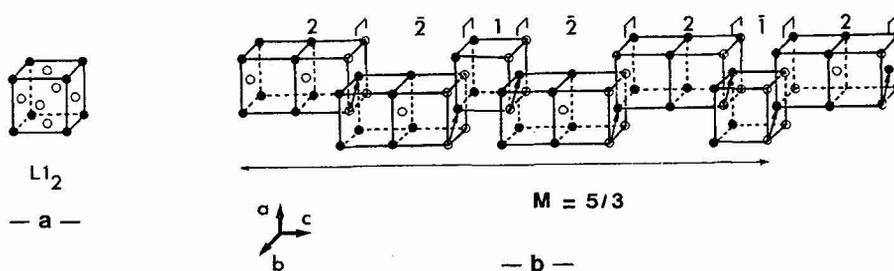


Figure 1 : a) The $L1_2$ structure consists in a stacking of alternate pure A planes and mixed AB planes. b) Long Period Structure such as $M = 5/3$; the APB's are lying in (001) planes, the antiphase vectors indicated by arrows, belong to the plane of antiphase. Only atoms in the mixed planes (001) are shown. The structure is such that three APB are displayed over five $L1_2$ cubes according to the sequence 221.

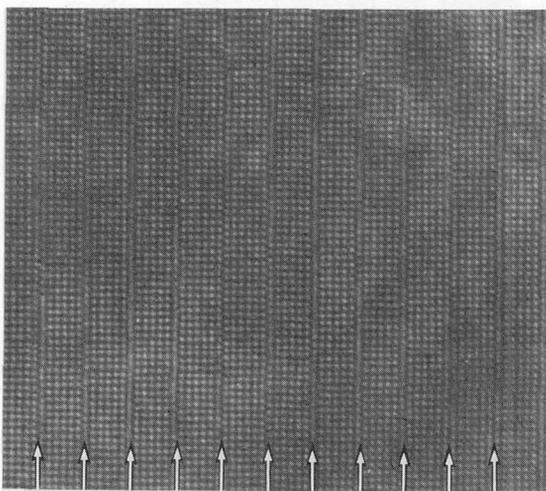


Figure 2 : High resolution image of the LPS $M = 6.24$ observed in Cu - 20.5 Pd at 485°C. White dots represent Pd columns. Arrows indicate the mean positions of the APB's which are spread over two planes.

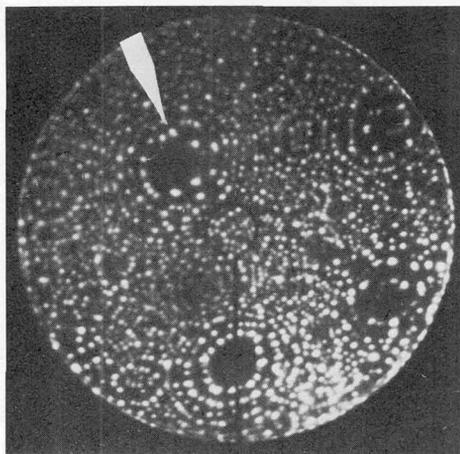


Figure 3 : Field ion image of Cu 18.5 % Pd. The tip radius is close to 400 Å and the average magnification is around $1.6 \cdot 10^6$. The array of parallel APB's leads to well visible discontinuities at the vicinity of the central (001) pole.

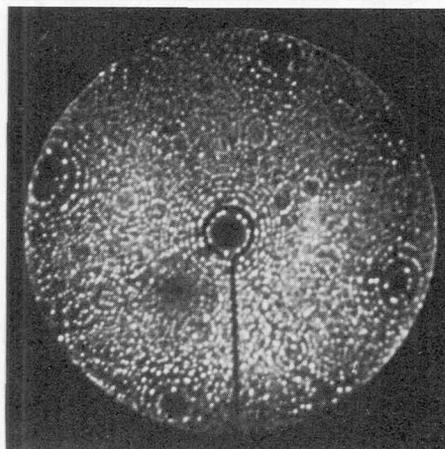


Figure 4 : Field ion image of Cu 18.5%Pd. The absence of discontinuities on the central (001) pole indicates that APB's are perpendicular to the tip axis (analysis direction). The tip radius is here close to 800 Å.

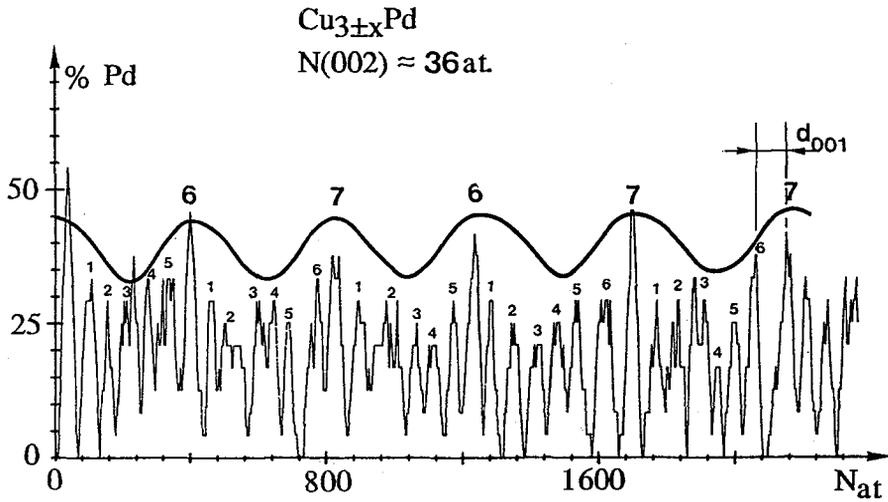


Figure 5 : This concentration profile shows the stacking sequence of (002) planes in Cu 20.5 at % Pd and the long range modulations associated to conservative APB's (\perp (001)).

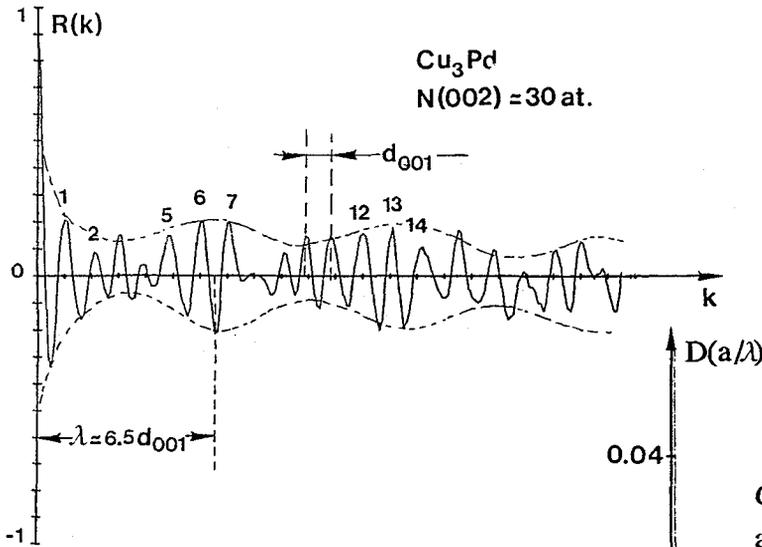


Figure 6 : Autocorrelation diagram related to the concentration profile given figure 5.

Figure 7 : Spectral density showing the Fourier components which occur in observed concentration profiles along (001) direction. The concentration signal has been smoothed over 10 a (a is the lattice parameter) in such a way to enhance low range frequencies ($\lambda = 34 \text{ a}$).

