RIETVELD REFINEMENT OF INCOMMENSURATE MODULATED PHASES

G. BALDINOZZI
LCPS CNRS URA 453, ECP, 92295 Châtenay-Malabry, France

D. GREBILLE
CRISMAT CNRS UMR 6058, ISMRA, 14050 Caen, France

J.-F. BÉRAR
Laboratoire de Cristallographie, CNRS BP166, 38042 Grenoble, France

The program XND has been adapted to refine powder diffraction data of incommensurate phases by the Rietveld method. XND was originally developed for non modulated structures to treat multiple diffraction patterns and to refine simultaneously X-ray and neutron powder diffraction data allowing a complex definition of anisotropic and asymmetrical profiles. It is also possible to refine data collected using variable counting time and variable step scan strategies. All these features constitute a valuable background on which the 4D formalism for mono-incommensurate modulated phases (superspace group symmetry, intensity and positioning of satellite reflections) has been implemented.

1 Introduction

Most of the structural studies of modulated incommensurate phases are developed using single crystal diffraction data. Nevertheless, many compounds are not easily synthesized as single crystals or the interesting phases present complex polydomain structures, so that the study of the structure by single crystal techniques is very complex, or even not possible. Powder refinements are generally less performing than single crystal ones as the three-dimensional information contained in the reciprocal lattice is reduced into a one dimension diffraction pattern. In spite of this basic limit, many structural determinations and refinements have been successfully performed in the last decades. The main advantage of the method consists in fitting the global profile of a powder diffraction pattern with a calculated profile without any prior extraction of structure factors, so that even totally overlapping reflections can be exploited in the refinement. This calculated profile depends simultaneously on the line-shape adjustable parameters and on the usual structural parameters of single crystal refinements.

The satisfactory results obtained on complex structures, have encouraged the extension of the method to the case of mono-incommensurate modulated structures.

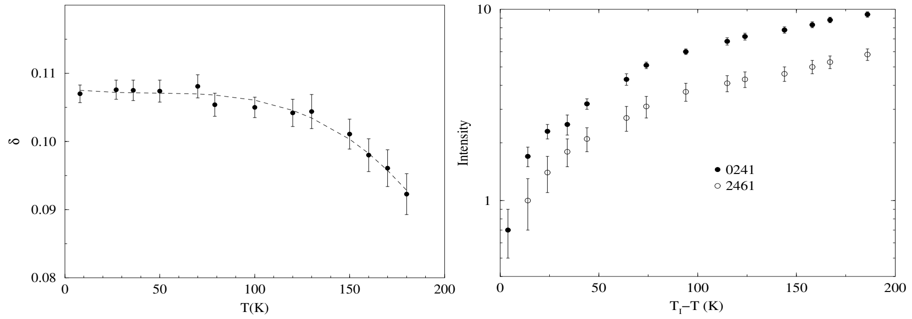


Figure 1: Thermal evolution of the modulation vector and of the intensities of two satellites.

To reduce the number of parameters describing an incommensurate structure, the Rietveld program XND[1] takes full advantage of the four dimensional formalism developed by De Wolff et al.[2]. Satellite reflections of different orders are generated as a function of the given modulation vector and treated as new sets of reflections. Four dimensional symmetry operations can be defined and occupancy or displacive modulation functions can be developed as a Fourier expansion. The incommensurate structure factor is calculated by numerical integration.

2 Phase Transition Analysis

Even without proper structural purposes, one of the advantages of the profile fitting method is to give accurate positions and intensities for very complex peaks. Indexing an incommensurate powder diffraction pattern can be a very difficult task and, in general, some complementary information is necessary (electron microscopy, ...) to reduce the number of possibilities. Nevertheless, when the indexing is successful, the powder pattern can provide a very accurate determination of the metric of the incommensurate phase. In fact, even if the structure is not known, it is possible to define a global profile and determine the position and the intensity of each peak. This feature is quite interesting for the study of the thermal evolution of the metric of incommensurate phases because, even if single crystals are available, the experimental setup is much simpler. To analyse the possibilities of the method and the accuracy on the incommensurate vector and satellite intensities, the modulated phase of Pb_2MgTeO_6 is presented [3]. This compound undergoes a commensurate incommensurate phase transition at about T_I=194 K. The low temperature phase is rhombohedral ($R\overline{3}(\delta\delta\delta)$). The metric (lattice constant, rhombohedral angle and amplitude of the modulation vector) has been refined using four satellites and four main peaks. As it can be seen in Fig. 1, the precision is very good and it has been possible to determine the thermal evolution of the metric and the critical exponent for the satellite intensities.

3 Structure Refinements

In the particular case of modulated phases, when the modulated displacements are quite small, an average structure can be defined. In this case, it is possible to start with a model for the structure, calculate a diffraction pattern and, using the differences between experimental and calculated pattern, determine the parameter shifts for the following refinement cycle.

In all full-pattern refinement, at least two agreement factors should be distinguished: R_{wp} and R_I. The former quantity is calculated from the discrepancies between experimental and calculated intensities while the latter one is something which has been artificially defined in order to provide something close to the single crystal agreement factors.

R_{wp} is strongly dependent on the total number of counts. This means that it is possible to obtain good agreements on diffraction patterns having poor peak to background ratio when the background level is high enough. For this reason the use of a R_{wp} factor defined on intensities where the background level has been substracted should be encouraged, although particular care should be paid to preserve the original statistical weights in this operation.

From a structural point of view, R_I (R_F) is more important than R_{wp}. In incommensurate structure refinements it is necessary to distinguish the different satellite orders so different R_I (R_F) factors have to be defined for each set of reflections. The main problem consists in the fact that the observed intensities of partially or totally overlapping peaks are not available. The estimation of these integrated intensities is performed in different ways. One common procedure, also choosen in the case of XND, is to calculate the observed intensity using the calculated profile and intensity to decompose the experimental pattern.

It is quite apparent that these problems, encountered in standard Rietveld refinements, are strongly enhanced in the case of weak satellite reflections. In general, satellite peaks have low peak to background ratios; as a consequence, the effect of the background noise on the estimated integrated intensity of the satellite is sensible and the R_I factor will be larger for these sets of reflections, even if the structural model is good. A second problem consists in the frequent overlapping of the satellite peaks with intense average structure main peaks; in this case, a small error on main peaks and on the description of their profile will

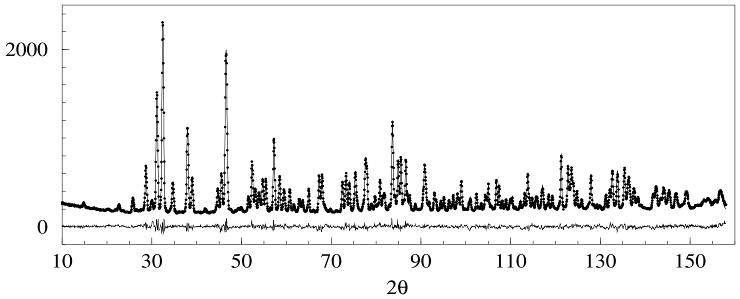


Figure 2: Neutron diffraction pattern of $Ba_{0.85}Ca_{2.15}In_6O_{12}$ at room temperature.

Table 1: Refinement statistics (%) of $Ba_{0.85}Ca_{2.15}In_6O_{12}$.

	X-ray	Neutron		X-ray	Neutron
R_{wp}	8.05	4.82	S	2.13	2.00
R_{F0}	3.30	2.79	R_{Fall}	5.00	4.23
R_{F1}	7.78	5.99	R_{Iall}	4.98	5.42
R_{F2}	9.24	6.09	No. refl.	460-813-485	650-1188-696

strongly affects the estimation of the experimental intensities of satellites. The importance of a very good adequation between experimental and calculated profiles is to be emphasized and in this domain, XND offers a large choice of functions and combinations of functions, with angle dependent parameters to optimize the simulation.

For these reasons, the R_{wp} and the R_I values constitute a good guide during the refinement procedure but they cannot constitute a definitive criterion for the accuracy of the structural model of the modulated crystal. A useful criterion is to compare the determined bond lengths and bonding angles with the values encountered in literature. If these three criteria are simultaneously satisfied, the structural model of the modulated crystal is generally accurate.

In the following, the structure resolution of $Ba_{0.85}Ca_{2.15}In_6O_{12}$, a compound for which single crystals of suitable quality are unavailable, is discussed[4]. In this case, the structure has been determined refining simultaneously X-ray and neutron diffraction data (Fig. 2). In the average structure, the framework of InO_2 double rutile ribbons leaves hexagonal tunnels where Ba atoms are located and prismatical voids where Ca atoms sit. To get an accurate description of the modulated structure, it is necessary to introduce an occupancy modulation for Ba atoms located in the tunnel and displacive modulations for all the atoms. The structure resolution points out that three sites exist

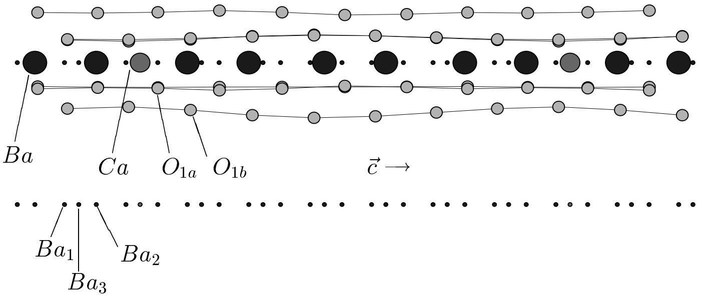


Figure 3: Occupancy and displacive modulation of the tunnels of $Ba_{0.85}Ca_{2.15}In_6O_{12}$.

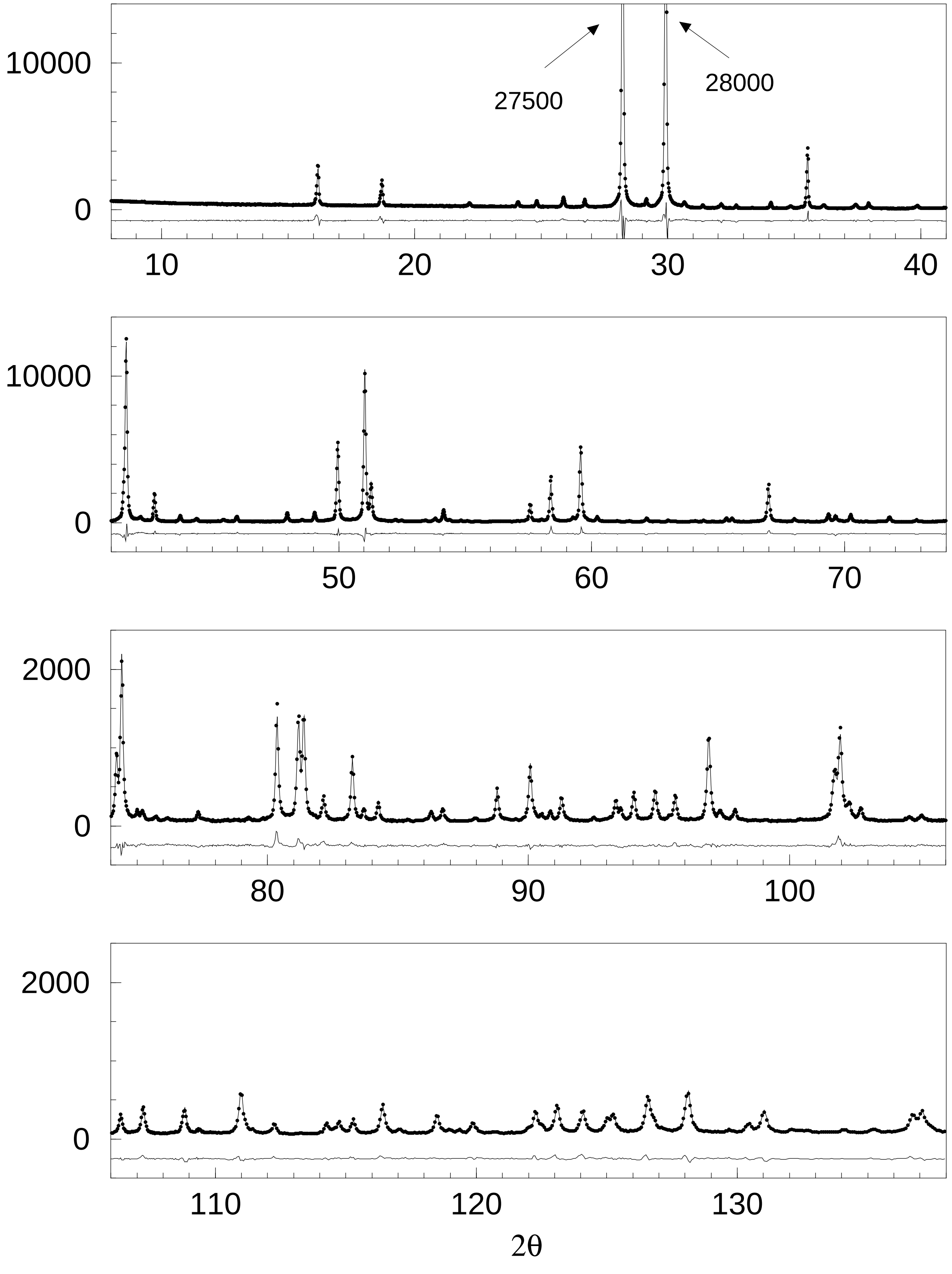
for Ba along the tunnel axis: only one site is occupied in each cell according to the approximate sequence for seven cells: Ba_1, Ba_1, Ba_3, Ba_3, Ba_2, Ba_2 and Ca (or a vacancy) located on Ba_3 site (Fig. 3). The real sequence is a bit more complex because of the defective character of the modulation. This occupancy modulation of the atoms located in the tunnel gives rise to a displacive modulation of the O framework defining the tunnel. This model gives good reliability factors (Table 1) and is consistent with $Ba - O$ bond lengths and $O - O$ distances[4] found in the literature.

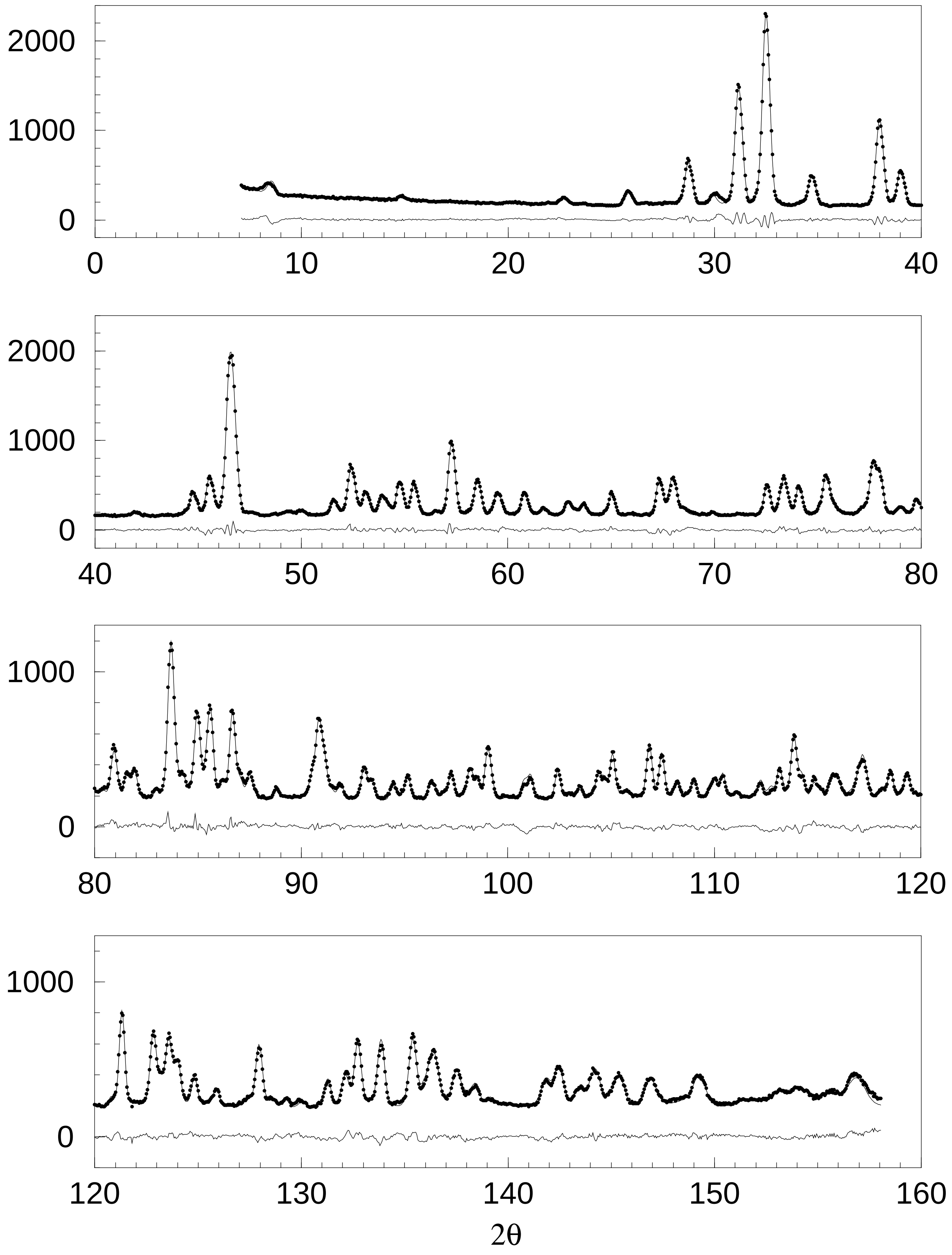
4 Conclusion

The thermal evolution of the metric of incommensurate phases and their structures can be investigated on powder samples using the Rietveld program XND. The lower peak to background ratio available on powder diffraction patterns (especially near the phase transition) can be improved using optimized data collection strategies. One simple way consists in increasing the counting time in the regions where satellites are observed.

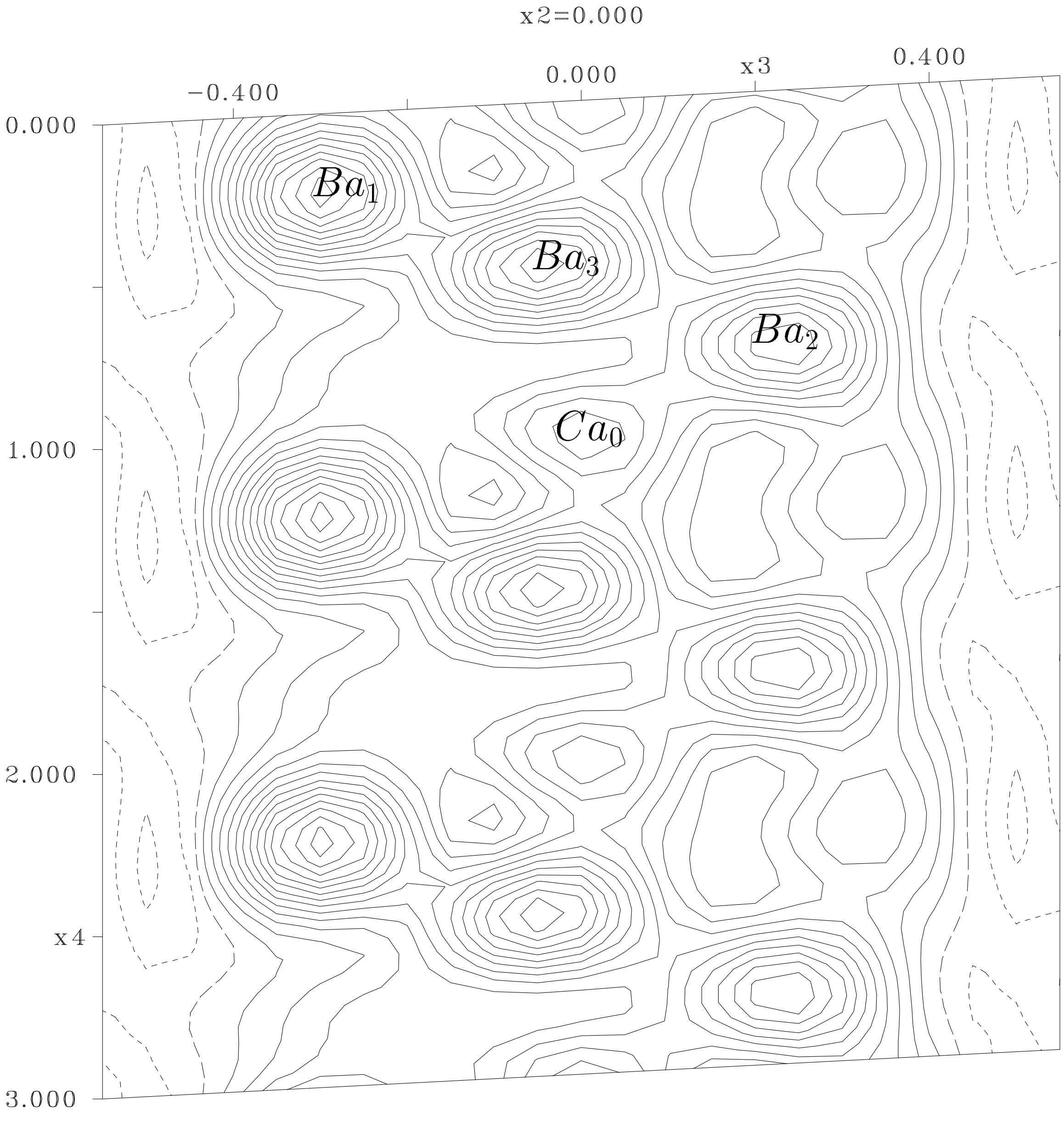
References

1. J.-F. Bérar and P. Garnier *APD 2nd Conference* Gaithersburg, USA: NIST (1992); XND is available on ftp://labs.polycnrs-gre.fr/pub/xnd.
2. P. M. deWolff, T. Janssen and A. Janner *Acta Cryst* A**37** 625 (1981).
3. G. Baldinozzi, Ph. Sciau, J. Moret and P. A. Buffat *Solid St Commun.* **89**-5 441 (1994).
4. G. Baldinozzi, F. Goutenoire, M. Hervieu, E. Suard and D. Grebille *Acta Cryst* B**52** 780 (1996).

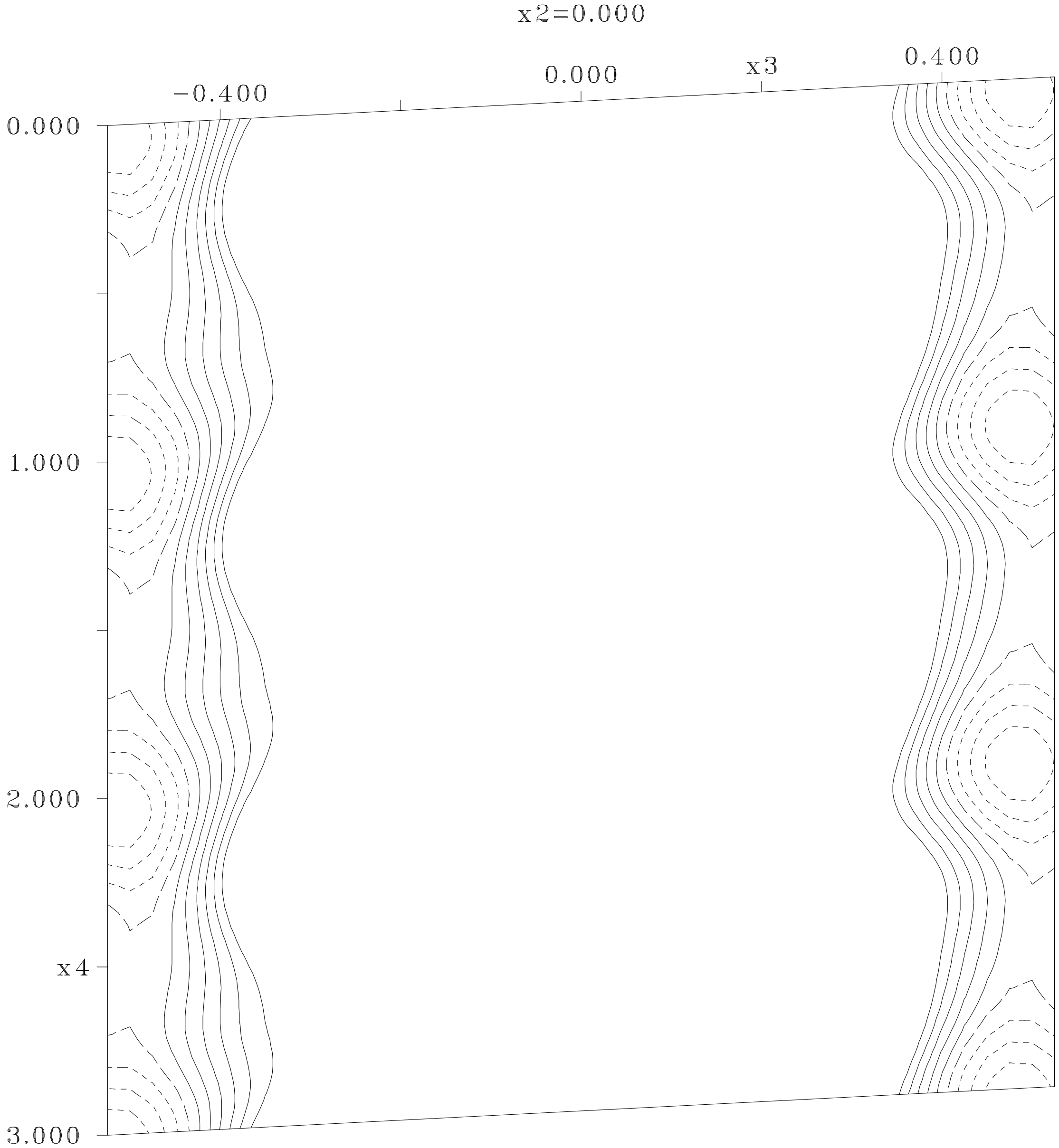

10000
0
27500
28000
10
20
30
40
10000
0
50
60
70
2000
0
80
90
100
2000
0
110
120
130
2θ



2000
1000
0
0
10
20
30
40
2000
1000
0
40
50
60
70
80
1000
0
80
90
100
110
120
1000
0
120
130
140
150
160
2θ



x2=0.000
x3
−0.400
0.000
0.400
0.000
1.000
2.000
x4
3.000
Ba_1
Ba_3
Ba_2
Ca_0


x2=0.000
-0.400
0.000
x3
0.400
0.000
1.000
2.000
x4
3.000