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Structure of synthetic sodium birnessite:

Evidence for a triclinic one-layer unit cell

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ABSTRACT

The structure of a synthetic analogue of sodium birnessite (NaBi) was studied by powder X-ray diffraction (XRD). It is shown that NaBi has a one-layer triclinic structure with sub-cell parameters $a_p = 2.9513(4) \text{ \AA}$, $b_p = 2.9547(4) \text{ \AA}$, $c_p = 7.334(1) \text{ \AA}$, $\alpha_p = 78.72(2)^\circ$, $\beta_p = 101.79(1)^\circ$, $\gamma_p = 122.33(1)^\circ$, and space group P1bar. This sub-cell is equivalent to the base-centered sub-cell with parameters $a = 5.174 \text{ \AA}$, $b = 2.848 \text{ \AA}$, $c = 7.334 \text{ \AA}$, $\alpha = 90.53^\circ$, $\beta = 103.20^\circ$, $\gamma = 90.07^\circ$. A structure model has been refined using the Rietveld technique. NaBi consists of vacancy-free manganese octahedral layers whose negative charge arises mostly from the substitution of Mn^{3+} for Mn^{4+} . The departure from the hexagonal symmetry of layers results from the Jahn-Teller distortion of Mn^{3+} octahedra, which are elongated along the **a** axis, segregated in Mn^{3+} -rich rows parallel to the **b** axis, and separated from each other along the **a** axis by two Mn^{4+} -rows. Structural sites of interlayer Na cations and H_2O have been determined as well as their occupancies. The sub-cells of the two NaBi modifications described by Drits et al. (1997) as type I and II likely contain four sites for interlayer species, two of which are occupied by Na and the other two by H_2O molecules. In the two NaBi varieties, these pairs of sites are split along the **c** axis and related by a center of symmetry. This splitting is consistent with the modulated structure of both NaBi types, which arises from the periodic displacement of interlayer species along the **b** axis with a periodicity $\lambda = 6b$ (Drits et al. 1997).

INTRODUCTION

Birnessite is the most common mineral of the phylломanganate family. It can form under a variety of physico-chemical conditions and is consequently present in different geological environments such as soils (Taylor et al. 1964; Chukhrov and Gorshkov 1981; Cornell and Giovanoli 1988), marine manganese nodules and micro-nodules (Burns and Burns 1976; Glover 1977; Chukhrov et al. 1978, 1985, 1989; Drits et al. 1985), and Mn-rich ore deposits (Usui and Mita 1995). Further, birnessite possesses unique surface charge (Healy et al. 1966; Murray 1974), cation exchange (Balistrieri and Murray 1982; Le Goff et al. 1996), and redox (Stone et al. 1994) properties, which makes it highly reactive with respect to sorption phenomena (Paterson et al. 1994; Tu et al. 1994). It is also easily synthesized under laboratory conditions (Bricker 1965; Stälhi 1968; Giovanoli et al. 1970a, 1970b; Golden et al. 1986; Strobel et al. 1987; Cornell and Giovanoli 1988) and therefore has been often used as a model manganese oxide in environmental chemical studies (Stone and Morgan 1984; Stone 1987; Manceau and Charlet 1992; Xyla et al. 1992; Bidoglio et al. 1993).

Two major synthetic analogues of sodium birnessite (NaBi) have been described in the literature. A three-layer hexagonal modification was synthesized recently under hydrothermal conditions (Chen et al. 1996). However, the most common way to synthesize NaBi is the formation at room temperature and high pH of Na-rich 10Å busserite, which is then partially dehydrated to form NaBi (Giovanoli et al. 1970a; Feng et al. 1997). Post and Veblen (1990) determined for the first time the monoclinic one-layer sub-structure of this phylломanganate using the Rietveld technique, together with transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Drits et al. (1997), and Silvester et al. (1997), using SAED and extended X-ray absorption fine structure (EXAFS) spectroscopy, further studied

the structure and crystal chemistry of synthetic NaBi, concentrating on the nature and origin of its super-cell and modulated structures.

These authors did not perform any additional XRD analysis and assumed that the sub-structure determined by Post and Veblen (1990) was correct. However, the precision of refined structural parameters (atomic positions and occupancies) was not sufficient to allow a complete and unambiguous determination of all details of NaBi sub-structure, even though its main structural and chemical properties were reasonably known. In particular, they were unable to draw definitive conclusions about the respective contributions of layer Mn^{3+} and/or layer vacancies to the layer charge. Accordingly, it was impossible from their results to choose unambiguously between the two structural formulae

$\text{Na}^{+}_{0.29}(\text{Mn}^{4+}_{0.71}\text{Mn}^{3+}_{0.29})\text{O}_2 \cdot 0.75\text{H}_2\text{O}$ and $\text{Na}^{+}_{0.29}(\text{Mn}^{4+}_{0.93}\text{Mn}^{3+}_{0.07})\text{O}_2 \cdot 0.75\text{H}_2\text{O}$. Similarly, the position of the interlayer species could not be determined precisely because the O2 site on the difference-Fourier map was very diffuse, and specific sites for interlayer Na and H_2O could not be determined. This diffuseness was assumed to result from structural disorder (Post and Veblen 1990). Finally, the actual structural features responsible for the pronounced anisotropic peak broadening remained unclear. Anisotropic shapes of the coherent scattering domains (CSDs), and structural disorder along one direction, which was consistent with streaking observed in SAED patterns, were the two hypotheses invoked by Post and Veblen (1990).

In the present article, this anisotropic broadening is interpreted and, as a result, NaBi is shown to have a one layer triclinic sub-cell. By simulating the XRD pattern of NaBi with this sub-cell, new results concerning its sub-structure were obtained. In particular, interlayer sites for Na and H_2O have been re-determined and are now consistent with the modulated structure proposed by Drits et al. (1997) and relating the satellites observed on SAED patterns with a

periodic $\lambda = 6b$ displacement of Na and H₂O along the **b** axis. In addition, simulation of the NaBi XRD pattern provides direct evidence that negative layer charge and departure from the hexagonal layer symmetry originate from the Mn³⁺ for Mn⁴⁺ substitution in octahedral layers.

EXPERIMENTAL

Experimental methods

Sample NaBi1 was prepared following the procedure of Giovanoli et al. (1970a) as described by Drits et al. (1997); its structural formula is Na⁺_{0.31}(Mn⁴⁺_{0.69}Mn³⁺_{0.31})O₂·nH₂O (Silvester et al. 1997). One additional NaBi sample (NaBi2) was synthesized following the procedure of Feng et al. (1997). The initial NaBu suspension was prepared at room temperature using a NaOH/Mn(NO₃)₂ ratio of 3.3, and H₂O₂ as oxidizing agent. This suspension was then hydrothermally treated at 150°C in a 1M NaOH solution for 24 hours to produce a NaBi suspension which was then filtered, washed and dried at room temperature. Powder XRD patterns were obtained using CuK α radiation with a Siemens D5000 powder diffractometer equipped with a Kevex Si(Li) solid detector. Intensities were measured at a 0.04° 2 θ interval with a 30s counting time per step.

The XRD pattern of sample NaBi1 (Fig. 1) is almost identical to that reported by Post and Veblen (1990) but does not contain hausmannite. To a first approximation all major diffraction maxima can be indexed with a one-layer monoclinic sub-cell with $a = 5.169 \text{ \AA}$, $b = 2.848 \text{ \AA}$, $c = 7.321 \text{ \AA}$, $\beta = 103.2^\circ$. As noted by Post and Veblen (1990), there is a strong anisotropic peak broadening, 11ℓ reflections being much broader than 20ℓ reflections for the same ℓ value.

Thermal analysis was carried out with a Netzsch Simultan STA409EP micro-analyzer with a heating rate of 10°C/min up to 1100°C. Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on ~20 mg samples to determine the weight loss due to adsorbed and interlayer water. Figure 2 shows that the heating of NaBi1 sample induces two low-temperature weight losses which are likely related to the release of adsorbed (2.1%) and interlayer (7.1%) H₂O, respectively. To account for the loss of interlayer H₂O determined from TGA, the structural formula proposed by Silvester et al. (1997) for NaBi1 may be refined as Na⁺_{0.31}(Mn⁴⁺_{0.69}Mn³⁺_{0.31})O₂·0.40H₂O.

Simulation of XRD patterns

To build up an initial structure model for NaBi, diffraction effects were calculated for structure models realistic from a crystal chemistry point of view. The agreement between calculated and experimental XRD patterns was first improved using a trial-and-error procedure, as recommended by Drits and Tchoubar (1990) for defective structures. This approach was successfully applied to natural and synthetic one-layer hexagonal birnessites (Chukhrov et al. 1985; Manceau et al. 1997; Lanson et al. 2000), as well as to four-layer monoclinic Ca-exchanged birnessite (Drits et al. 1998). Details on the program used to calculate XRD patterns, as well as on the fitting procedure, are given by Drits et al. (1998). The background was assumed to be constant over the angular range considered (30-65°2θ CuKα, 2.95-1.45 Å). The function used to describe the preferred orientation of particles is given by Drits and Tchoubar (1990).

Sub-cell parameters, atomic coordinates, and occupancies obtained from the trial-and-error approach were used to build up an initial structural model for NaBi. Rietveld refinement of this model was subsequently carried out over a larger angular range using the computer

program XND (Bérar and Baldinozzi 1998). To de-correlate instrumental broadening from defect broadening, PSF parameters and spectral distribution were first refined using a quartz reference, and then set constant during the refinement of the NaBi sub-structure. As in the previous calculations, the background was held constant over the considered angular range ($34-90^\circ 2\theta \text{CuK}\alpha$, 2.95-1.09 Å). During initial cycles of the Rietveld refinement, only the scale factor was refined. In a second step, sub-cell parameters were refined prior to atomic coordinates and site occupancy factors. In the final stages of the refinement, preferred orientation was introduced using orientation dependent profiles, and calculating 00ℓ lines as a separate phase having parameters identical to those used to calculate hkl reflections, but with different orientation-dependent profiles.

RESULTS

Anisotropic broadening

A careful examination of the experimental XRD patterns (Figs. 1, 3a) shows that the broadening of 11ℓ reflections increases with ℓ , whereas 20ℓ reflections are much sharper for the same ℓ value, as described previously by Post and Veblen (1990). However, the intensity of 11ℓ reflections does not decrease strongly as it would if this broadening was related only to structural disorder along the **b** axis. Because of the very similar breadths of 200 and 020 reflections, this broadening is likely not associated with the anisotropic shape of the CSDs as suggested by Post and Veblen (1990). On the other hand, 11ℓ reflections are clearly split for the NaBi₂ sample (Fig. 3b – See especially $11^{\pm 2}\text{bar}$, $11^{\pm 3}\text{bar}$ and $11^{\pm 4}\text{bar}$ reflections) whereas the overall distribution of diffracted intensity is similar for the two samples. This split proves unambiguously the triclinic character of NaBi; and a triclinic sub-cell with parameters $a =$

5.174 Å, $b = 2.848$ Å, $c = 7.334$ Å, $\alpha = 90.5^\circ$, $\beta = 103.2^\circ$, and $\gamma = 90^\circ$ indeed permits to explain the observed selective broadening of 11ℓ reflections. The sub-structure refinement was carried out on sample NaBi1 because sample NaBi2 contains a small manganite impurity, and because a model super-structure was available for this particular sample (Drits et al. 1997; Silvester et al. 1997). As a consequence, it was possible to interpret the structure model refined for NaBi1 in the light of available SAED and chemical data as the same sample was used.

SIMULATION OF THE NABI XRD PATTERN

Trial and error approach

The similarity of the monoclinic (Post and Veblen 1990) and triclinic a , b , c , and α , β , γ sub-cell parameters suggests that the origin of the triclinicity of NaBi is a small layer displacement along the \mathbf{b} axis. This shift lowers the space group $C2/m$ (Post and Veblen 1990) to either $C1\bar{1}$ or $C1$, probably without changing the layer symmetry ($2/m$). The present sub-structure refinement was performed using the centro-symmetric $C1\bar{1}$ space group because no experimental argument in favor of a non-centro-symmetric sub-structure was found. At first, the XRD pattern of NaBi1 was simulated using positions and occupancies of layer and interlayer atomic sites refined by Post and Veblen (1990), taking into account the triclinic character of NaBi. In particular, Post and Veblen (1990) determined the presence of two interlayer sites, host to Na and H_2O , both of which were modeled with the scattering factor for oxygen. The predominant site (0.595, 0, 0.5) and the accessory site (0, 0, 0.5) had occupancy factors of 2.0 and 0.3 oxygen atoms per unit cell, respectively. However, the XRD pattern calculated for this model differs from the experimental one (Fig. 4a).

The trial-and-error approach was subsequently used to improve the initial structural model. Because of the modulated super-structures described by Drits et al. (1997) for sample NaBi1, and because of the diffuseness of the O2 site on the difference Fourier map described by Post and Veblen (1990), splitting of the interlayer site was considered; the agreement between the calculated and experimental XRD patterns was significantly improved (Figs. 3, 4b) by splitting the predominant interlayer position into four sites related by a center of symmetry (0.551, \pm 0.135, 0.500) and (0.449, \pm 0.135, 0.500). Even though at this stage structural sites for Na and H₂O cannot be separated, the trial-and-error analysis clearly demonstrates that the predominant interlayer site is split (Figs. 4b, 4c).

Another conclusion obtained with the trial-and-error method is that NaBi1 contains very few stacking faults or other structural defects which alter its three-dimensional (3D) periodicity. The intensity and profiles of the measured reflections were reproduced assuming that cylinder-like CSDs have a 225 Å radius and contain an average of 20 birnessite layers, the amount of random stacking faults being only 3%. The NaBi sub-structure was further refined using the Rietveld technique.

The Rietveld approach

Atomic coordinates obtained with the trial-and-error approach in space group C1bar were transformed to space group P1bar. The Rietveld refinement of the sub-cell parameters gave values of $a_p = 2.9513(4)$ Å, $b_p = 2.9547(4)$ Å, $c_p = 7.334(1)$ Å, $\alpha_p = 78.72(2)^\circ$, $\beta_p = 101.79(1)^\circ$ and $\gamma_p = 122.33(1)^\circ$. The refined positions and occupancies of structural sites for this sub-cell led to the fit shown in Figure 5. Final R_{wp} and R_B are respectively 10.7 and 6.2%. In spite of these high values, the refinement was stopped because the main discrepancies between experimental and calculated patterns arise from the presence of super-cell reflections in the

XRD pattern of NaBi1. Furthermore, the discrepancy observed for the 200 reflection (Fig. 5) may be explained by the small amount of random stacking faults in this sample. Indeed, calculations performed using the trial-and-error approach show that the intensity calculated for this reflection strongly depends on the amount of such defects, and that the addition of random stacking faults (3-4%) to the refined model significantly improves the agreement between calculated and experimental distributions of intensities. As a consequence no significant modification was expected for the sub-cell parameters. Refined structural parameters and selected inter-atomic distances of NaBi are found in Tables 1 and 2.

Refinement of the layer Mn site occupancy factor for NaBi (range: 1.00 to 1.02) indicated that NaBi layers do not contain vacant octahedral sites. In addition, because the refined position of layer oxygen atoms (O_{layer}) is slightly off the long diagonal of the P sub-cell, the octahedral layer has no mirror plane, and its symmetry is lower than 2/m. Figure 6 shows the positions of four refined interlayer sites and the distances from these sites to the closest O_{layer} atoms. The analysis of these bond lengths allows determination of the nature of the interlayer species in these sites. For example, the two symmetrically related interlayer sites at 2.46 Å from the nearest O_{layer} are likely occupied by Na cations, whereas the other two symmetrically related sites, at ~2.70 Å from the nearest O_{layer} are likely occupied by H₂O (Fig. 6). Using this assumption, refined site occupancy factors for both Na (0.18 ± 0.02) and H₂O (0.27 ± 0.02) are similar to the values derived from the chemical formula (0.145, and 0.20, respectively) and support the hypothesized site allocation.

One may note that the same quality of fit may be obtained for a configuration of interlayer sites which, with respect to the first model, is almost symmetrically reflected by a plane passing through the c^* axis and the long diagonal of the P sub-cell. However, this alternative model was rejected because distances from each of the interlayer sites to the nearest O_{layer}

atoms are significantly shorter than 2.5 Å, which is short for interlayer H₂O - O_{layer} bond lengths.

DISCUSSION

For clarity and to be consistent with previously published data, all structural features of NaBi are hereafter discussed in terms of the base-centered sub-cell with parameters $a = 5.174$ Å, $b = 2.848$ Å, $c = 7.334$ Å, $\alpha = 90.53^\circ$, $\beta = 103.20^\circ$, $\gamma = 90.07^\circ$, which is equivalent to the refined primitive sub-cell with $a_p = 2.951$ Å, $b_p = 2.955$ Å, $c_p = 7.334$ Å, $\alpha_p = 78.72^\circ$, $\beta_p = 101.79^\circ$, $\gamma_p = 122.33^\circ$.

Presence and azimuthal orientation of Mn³⁺ octahedra in the layer

One of the most notable features of the NaBi layer is the strong elongation of individual octahedra along the **a** axis. Within a MnO₆ octahedron, the two Mn-O distances oriented in the **ac**^{*} plane are much longer (2.003 Å) than the other four Mn-O distances (1.945, and 1.925 Å - Table 2). This elongation originates from the displacement along the **a** axis of O_{layer} atoms lowering the ideal symmetry of the octahedron. Additionally, this elongation is responsible for the departure from the hexagonal symmetry of the layer ($a/b = 1.817 = \sqrt{3.30}$). This distortion likely results from the presence of a significant amount of Mn³⁺ cations in NaBi; two Mn³⁺-O distances in Mn³⁺ octahedra are commonly much longer than the other four because of the Jahn-Teller effect. In crednerite for example, Mn³⁺ octahedra contain two 2.260 Å and four 1.929 Å Mn³⁺-O bond lengths, with an average <Mn-O> distance of 2.04 Å (Töpfer et al. 1995). Similar distortions of Mn³⁺ octahedra and <Mn³⁺-O> have been reported

by Shannon et al. (1975) for α -MnOOH (2.041 Å - Glasser and Ingram 1968), γ -MnOOH (2.037 Å - Dachs 1963), and α -Mn₂O₃ (2.039-2.045 Å - Norrestam 1967).

If one assumes that $\langle \text{Mn-O} \rangle$ is a statistically-weighted sum of the mean Mn³⁺-O distance determined for crednerite and for Mn oxy-hydroxides (~ 2.04 Å), and of the Mn⁴⁺-O distance, determined for λ -MnO₂ (1.912 Å - Thackeray et al. 1993), the mean Mn-O distance for the 0.69:0.31 cation composition of NaBi1 should be 1.952 Å. This value is consistent with the observed one (1.958 Å). For the same average layer cation composition (Mn⁴⁺_{0.69}Mn³⁺_{0.31}), the long Mn-O distance calculated as the weighted sum of long Mn-O distances determined for Mn⁴⁺ and Mn³⁺ octahedra for λ -MnO₂ (1.912 Å) and crednerite (2.26 Å), respectively, equals 2.003 Å and coincides with the experimentally determined value (2.002 Å). As a consequence, the origin of the negative layer charge is undoubtedly the presence of Mn³⁺ cations, rather than the existence of vacant layer sites. Furthermore, the distribution of Mn-O distances indicates that all Mn³⁺ octahedra have the same azimuthal orientation with their long Mn-O distance in the **ac*** plane. This unique azimuthal orientation is responsible for the departure from the hexagonal layer symmetry.

Structure of the interlayer region

As compared with the model proposed by Post and Veblen (1990), the main difference in our refined model of the NaBi interlayer region is the determination of specific sites for Na and H₂O. Post and Veblen (1990) did not determine the respective positions of these interlayer species because the maximum observed in their difference Fourier map was very diffuse, and because of the very similar scattering powers of these two species. To account for this diffuseness, these authors invoked positional disorder in the distribution of interlayer species possibly occupying "different sites within a unit-cell and a range of positions in

different unit cells". The results of our refinement support this hypothesis, as within the sub-cell Na and H₂O occupy different sites related by a center of symmetry (Figs. 6, 7 & 8). Such split of Na and H₂O sites is likely responsible for the diffuse character of the electron density described by Post and Veblen (1990).

The existence of two distinct H₂O sites is favored by the equal opportunity for the formation of strong hydrogen bonds between interlayer H₂O and layer oxygen atoms offered by each of these positions (Fig. 7). According to our refinement, the two H₂O sites differ from each other by their z-coordinate; one site is shifted towards the lower octahedral layer ($z = 0.495 - (\text{H}_2\text{O})_1$) whereas the other is shifted towards the upper layer ($z = 0.505 - (\text{H}_2\text{O})_2$). If the nearest oxygen atoms of adjacent lower and upper layers are respectively labeled O₁ and O₂, bond lengths (H₂O)₁-O₁, (H₂O)₂-O₂ (2.69 Å), and (H₂O)₂-O₁ and (H₂O)₁-O₂ (2.71 Å) are typical for the formation of H-bonds (Fig. 8). Furthermore, the 145° angle between O₁, O₂, and H₂O_i (i = 1, 2 - Fig. 7) is also suitable for the formation of strong H-bonds which are responsible for most of the cohesion between layers.

The two Na sites are also shifted along the c^* axis, one towards the lower layer (Na₁) and the other towards the upper layer (Na₂; Fig. 8), leading to typical Na_i-O_i distances (2.46 Å).

Origin of the super-cell and modulated structures

The results of our refinement on NaBi1 confirm unambiguously the assumption of Post and Veblen (1990), Manceau et al. (1992), and Drits et al. (1997) that super-cell reflections and satellites observed in the SAED patterns of NaBi micro-crystals result from a regular distribution of interlayer species rather than vacancies in the octahedral layer.

For NaBi micro-crystals, two types of SAED patterns have been reported (Drits et al. 1997). The distribution of super-cell reflections in NaBi type I corresponds to a base-centered

layer super-cell with $A = 3a = 15.52 \text{ \AA}$, $B = b = 2.848 \text{ \AA}$, and $\gamma = 90^\circ$. To account for these super-cell reflections, Drits et al. (1997) proposed the arrangement of interlayer Na cations shown in Figure 9a. In addition, any sub- and super-cell reflection is surrounded by satellites at $\pm b^*/6$ along the $[01]^*$ direction. According to Drits et al. (1997) these satellites arise from a periodic variation of distances between planes parallel to (010) containing interlayer species (Fig. 10). The distribution of super-cell reflections reported for NaBi type II corresponds to a base-centered super-cell with $A = 3a = 15.52 \text{ \AA}$, $B = 3b = 8.55 \text{ \AA}$, and $\gamma = 90^\circ$. A possible distribution of Na within the interlayer super-cell is shown in Figure 9b. As discussed by Drits et al. (1997), the (0, 0) and the (0.5, 0.5) sites should be fully occupied whereas other sites are occupied by Na with a lower probability to keep its base-centered character to the interlayer Na distribution (Fig. 9b).

In both NaBi varieties, the super-periodicity $A = 3a$ arises from the ordered distribution of Mn^{3+} -rich rows parallel to $[010]$ and separated from each other along $[100]$ by two Mn^{4+} rows (Drits et al. 1997). Along with sub- and super-cell reflections, SAED patterns of NaBi type II contain two types of satellites: 1) the first type are similar to those observed for NaBi type I, and 2) the second type are elongated along $[11]^*$ and $[11\bar{1}]^*$. Satellites elongated along $[11\bar{1}]^*$ are located in the middle of two nearest point reflections located along $[11]^*$. A possible arrangement of interlayer species which accounts for the main diffraction features of NaBi type II is shown in Figure 11. A periodic displacement of Na and H_2O along the \mathbf{b} axis with $B_s = 6b$ accounts for the origin of the satellites of the first type. A periodic modulation along $[13]$ and $[1\bar{1}3]$ of Na and H_2O species located along (110) and (11 $\bar{1}$ 0), respectively, gives rise to the satellites of the second type. As can be seen in Figure 11, waves parallel to (110) located in two neighboring rhomb-shaped unit cells (I and II) do not scatter X-rays

strictly in phase because of opposite displacements of Na and H₂O along the **b** axis. This phase difference is likely responsible for the elongation of the satellites (Drits et al. 1997).

Results from the present refinement may be combined with the above interpretation of SAED patterns to propose consistent 2D distributions of interlayer Na and H₂O responsible for the presence of super-cell reflections and satellites for both NaBi type I and II crystals.

NaBi type II. In agreement with SAED data, Na cations should be distributed with a $3b$ period along the **b** axis to a super-cell with $A = 3a$, $B = 3b$, $\gamma = 90^\circ$ (Fig. 9b). To comply with the two positions determined for Na, these cations are likely shifted along the **b** axis alternately towards the upper and lower layer surfaces to provide homogeneous compensation of the negative layer charge. As a result, Na cations form a $\text{Na}_1\text{-Na}_2\text{-Na}_1\dots$ sequence inducing a $6b$ period along the **b** axis consistent with the satellite periodicity. In addition to O_{layer} atoms, Na cations are likely coordinated by H₂O molecules at 2.60-2.65 Å, and H₂O molecules coordinating Na_{*i*} cations are located in the H₂O_{*i*} sites. The combination of the above conditions leads to the 2D distribution of interlayer Na and H₂O shown in Figure 12.

This distribution presents several remarkable features. First, interlayer cohesion is insured by a set of chains, elongated along the **a** axis, in which Na and H₂O are distributed in a $\text{Na}_i\text{-(H}_2\text{O)}_i\text{-Na}_i\text{-(H}_2\text{O)}_i\dots$ sequence ($i = 1, 2$). As a consequence, each Na is tetrahedrally-coordinated by two O_{layer} atoms at 2.46 and 2.74 Å and two H₂O molecules at 2.61 and 2.64 Å. Similarly, in these chains each H₂O is bound to two O_{layer} atoms (2.69-2.71 Å) and to two Na cations (2.61-2.64 Å). On Figure 12, one may note that successive chains are not linked to each other by inter-chain interlayer species. Second, the distance between successive chains changes periodically along the **b** axis with a $6b$ super-periodicity because the displacements of Na cations along the **b** axis induce the same periodicity in the distribution of

associated H₂O. As shown on Figure 13a, the shift of interlayer Na along the **c** axis and in the **ab** plane likely results from the Mn³⁺-Mn³⁺-Mn³⁺-Mn³⁺-Mn²⁺-Mn⁴⁺... distribution of heterovalent Mn_{layer} in Mn³⁺-rich rows described by Drits et al. (1997), interlayer Na being shifted towards Mn²⁺ cations. To account for the observed $B = 3b$ super-cell periodicity, the respective positions of heterovalent Mn_{layer} sequences in adjacent layers have to be considered. If Mn³⁺-rich rows from adjacent layers are shifted by $-a/3$ with respect to each other, sequences of heterovalent Mn_{layer} cations in these Mn³⁺-rich rows should be shifted along the **b** axis as shown on Figure 13b to induce the observed $B = 3b$ super-cell periodicity. As a result, Na₁ and Na₂ cations are shifted in opposite directions along the **c** axis and in the **ab** plane leading to the modulated distance between successive chains of interlayer species, which in turn is responsible for satellites of the first type observed in SAED patterns of NaBi type II crystals.

The third feature of the interlayer species distribution shown on Figure 12 is the fluctuation, along [13] and [13̄], of interlayer Na and H₂O atomic positions. As an illustration, a rhomb-shaped unit-cell with $2(\mathbf{A} + \mathbf{B})$ and $2(\mathbf{B} - \mathbf{A})$, or $12\mathbf{a}_p$ and $12\mathbf{b}_p$, may be chosen (A , B , a_p , and b_p are parameters of the base-centered super-cell and of the primitive sub-cell, respectively - Fig. 14). One may note that interlayer Na and H₂O (not shown) are distributed periodically as waves parallel to (110), or b_p . The amplitude of these waves varies along [13] with a $8d_{(310)}$ (or $12a_p$) period. Drits and Kashaev (1969) showed that a periodic displacement of atoms along the **a** axis with a $\lambda = nb$ period along the **b** axis induces, in reciprocal space, satellites which are located along the **b**^{*} axis and separated from the main nodes by b^*/n . Similarly, the periodic displacement of interlayer species (Na, and H₂O) along [13] with a $8d_{(310)}$ (or $12a_p$) period along [11] should induce satellites distributed along [11̄]^{*} and separated from super-cell reflections by $a_p^*/12$ (or $B^*/4\sin\gamma$). Similar

displacements of interlayer species along $[13\bar{b}a]$ (not shown) induce additional satellites located along $[11]^*$ at the same distance from super-cell reflections as the previous group of satellites. Such satellite distribution has been described as satellites of the second type in SAED patterns of NaBi crystals type II (Drits et al. 1997).

NaBi type I. As mentioned, this variety has a $A = 3a = 15.52 \text{ \AA}$, $B = b$, $\gamma = 90^\circ$ layer super-cell (Fig. 9a), whereas the presence of satellites indicates the existence of a modulated super-cell with a $6b$ period. As a consequence, the 2D distribution of interlayer Na and H_2O in NaBi type I crystals should satisfy several conditions. First, Na cations should form rows parallel to the **b** axis and separated from each other by $A/2$ along the **a** axis. In addition, successive Na should be separated from each other by distances of $2b$ along the **b** axis to avoid Na-Na pairs. Second, to generate the modulated structure responsible for the satellites, Na cations should be specifically distributed along these rows with a $6b$ period, as in $\text{Na}_1\text{-Na}_1\text{-Na}_2\text{-Na}_1\dots$, and $\text{Na}_2\text{-Na}_2\text{-Na}_1\text{-Na}_2\dots$ sequences. In addition, one may assume that predominant $\text{Na-O}_{\text{layer}}$ distances are $2.61\text{-}2.64 \text{ \AA}$, inducing $\text{Na}_i\text{-O}_i\text{-O}_i\text{-Na}_i\dots$ ($i = 1, 2$) sequences of interlayer species along the **a** axis. Third, to induce an average b period for the base-centered super-cell, the rows separated by A , as well as rows separated by $A/2$, should be shifted at random with respect to each other by $\pm b$.

A 2D distribution of interlayer species in NaBi type I satisfying these conditions is shown in Figure 15. As for NaBi type II, each Na has a tetrahedral coordination with the same bond lengths and each H_2O is bound to the two nearest O_{layer} atoms and to two Na cations. Figure 15a shows that interlayer Na and H_2O form chains elongated along the **a** axis (solid lines). The distance between these chains along the **b** axis changes with a $\lambda = 6b$ period, accounting for the satellites observed in SAED patterns of NaBi type I crystals (Drits et al. 1997). An

alternative origin for these satellites (Drits and Kashaev 1969) is a periodic displacement of interlayer species along the **a** axis with a $6b$ period along the **b** axis (Fig. 15a). In these chains there are two equally probable configuration for H₂O-H₂O pairs. As a consequence, propagation of these chains along the **a** axis may be random (Fig. 15b - dashed lines), inducing the average $B = b$ periodicity.

SUMMARY

A synthetic analogue of sodium birnessite (NaBi) prepared along the protocol of Giovanoli et al. (1970a) has a one-layer triclinic base-centered sub-cell with parameters $a = 5.174 \text{ \AA}$, $b = 2.848 \text{ \AA}$, $c = 7.334 \text{ \AA}$, $\alpha = 90.53^\circ$, $\beta = 103.20^\circ$ and $\gamma = 90.07^\circ$, which is equivalent to the refined primitive sub-cell with $a_p = 2.951 \text{ \AA}$, $b_p = 2.955 \text{ \AA}$, $c_p = 7.334 \text{ \AA}$, $\alpha_p = 78.72^\circ$, $\beta_p = 101.79^\circ$ and $\gamma_p = 122.33^\circ$.

A trial-and-error approach was used to determine an appropriate initial model which was further refined using the Rietveld technique. The NaBi structure consists of vacancy-free layers whose negative charge arises from the substitution of Mn³⁺ for Mn⁴⁺. The Jahn-Teller distortion of Mn³⁺ octahedra, which are systematically elongated along the **a** axis, leads to the departure from the hexagonal symmetry of layers. In the NaBi interlayer two positions were determined for both Na and H₂O. The presence of such split positions, which are related by a center of symmetry, for interlayer Na and H₂O allows to propose 2D distributions of interlayer species responsible for the super-cell and modulated structures observed for NaBi type-I and -II micro-crystals (Drits et al. 1997).

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Figure Captions

Figure 1. Experimental X-ray diffraction pattern of synthetic NaBi1 sample.

Figure 2. Experimental DTA-TG **(a)** and DSC **(b)** profiles obtained for synthetic NaBi1 and NaBi2 samples.

Figure 3. X-ray diffraction patterns of synthetic NaBi1 **(a)** and NaBi2 **(b)** samples. The experimental pattern of NaBi1 sample (crosses), prepared according to the protocol of Giovanoli et al. (1970a), is compared with the optimal one obtained with the trial-and-error approach (solid line – only 20ℓ and $11^{\pm}\ell$ reflections are calculated). R_{wp} was calculated for the $34-62^{\circ}2\theta$ range. $a = 5.174 \text{ \AA}$, $b = 2.848 \text{ \AA}$, $c = 7.334 \text{ \AA}$, $\alpha = 90.8^{\circ}$, $\beta = 103.2^{\circ}$, $\gamma = 90^{\circ}$. Corresponding structural parameters are listed in the text except for the position of layer Mn (origin) and O (0.384, 0, 0.137) atoms and for the occupancy of interlayer sites (0.39 Na or H₂O in each site per unit cell).

Figure 4. Influence of structural parameters on calculated XRD patterns as compared with the experimental NaBi1 pattern (crosses). **(a)** Calculation using the positions, (0.595, 0, 0.5) and (0, 0, 0.5), and the occupancy factors, 2.0 and 0.3, refined by Post and Veblen (1990). Other structural parameters as in the text and the caption of Figure 3. **(b)** Optimum fit obtained by splitting the predominant interlayer position into four sites related by a center of symmetry, (0.551, \pm 0.135, 0.500) and (0.449, \pm 0.135, 0.500), with 0.39 Na or H₂O per site. **(c)** Influence of the predominant interlayer position. Interlayer species are located in a unique non-split interlayer site (0.551(5), 0, 0.5) with 1.56 Na or H₂O per unit cell. All other structural parameters are constant. R_{wp} were calculated for restricted $34-62^{\circ}2\theta$ range as for Figure 3.

Figure 5. Final experimental (crosses), calculated , and difference powder XRD patterns for NaBi1 sample. The calculated background is indicated by the horizontal line.

Figure 6. Schematic location of interlayer Na and H₂O sites with respect to layer O and Mn atoms in projection on the **ab** plane. Inter-atomic distances are given in Å. Positions and distances are listed in Tables 1, 2. Layer O and Mn atoms are shown as large and small circles. Atoms of the lower (subscript 1) and upper (subscript 2) layers are shown as solid and open circles, respectively. Interlayer species closer to the lower and upper layer are labeled with subscripts 1 and 2, respectively. (H₂O)₁ and (H₂O)₂ molecules are shown as solid and open symbols, respectively, whereas the two Na cations are shown as shaded circles. P and B subscripts refer to the primitive and base-centered sub-cell parameters, respectively.

Figure 7. Schematic location of interlayer H₂O sites with respect to layer O atoms in projection along the **a** axis. Inter-atomic distances are given in Å. Positions and distances are listed in Tables 1, 2. Layer O and Mn atoms are shown as large and small circles. Subscripts as for Figure 6. H₂O molecules are shown as shaded circles.

Figure 8. Schematic location of interlayer Na sites with respect to layer O atoms in projection along the **b** axis. Inter-atomic distances are given in Å. Positions and distances are listed in Tables 1, 2. Subscripts as for Figure 6. Layer O and Mn atoms are shown as large and small circles. Na cations are shown as shaded circles. Open circles indicate atoms at $y = 0$, and solid symbols indicate atoms at $y = \pm 1/2$.

Figure 9. Super-cells for NaBi types I and II with $A = 3a$ and $B = b$ (**a**), and $A = 3a$ and $B = 3b$ (**b**). In the two super-cells, solid and open circles correspond to interlayer Na and H₂O positions, respectively. In the first super-cell (**a**) the occupancy factor for Na sites is 0.5, whereas in the second super-cell (**b**), the (0,0) and the (0.5, 0.5) positions (large solid

circles) have a higher occupancy than the other positions (small solid circles – modified from Drits et al. 1997).

Figure 10. Idealized super-structure model for NaBi interlayers of type I. Grey triangles correspond to the upper surface of the lower layer. Solid circles represent Na-rich interlayer sites. The thick vertical lines with variable distances correspond to (010) planes (irregular dashed lines), which contain Na sites (modified from Drits et al. 1997).

Figure 11. Idealized super-structure model for NaBi interlayers of type II. Large and small solid circles represent Na sites with different degrees of occupancy. Small open circles correspond to H₂O sites. Arrows attached to circles indicate the periodic displacement of interlayer species along the **b** axis with a $B_s = 6b$ period. Rhomb-shaped unit cells I and II have the same sizes and shapes but differ slightly in the arrangement of Na and H₂O sites. Variations of $d_{(010)}$ and $d_{(110)}$ are equal to $6b$, and $6a$, respectively (modified from Drits et al. 1997).

Figure 12. Schematic distribution of interlayer species in projection on the **ab** plane for NaBi type II crystals. All symbols as for Figure 6, except for Na₁ and Na₂ cations, which are shown as solid and open large circles, respectively. Na sites with a higher occupancy are shown as enlarged circles. Na_i-(H₂O)_i-Na_i-(H₂O)_i... chains parallel to the **a** axis with $i = 1, 2$ are shown as solid and dashed lines, respectively.

Figure 13. Schematic distribution of interlayer species in projection on the **ab** plane for NaBi type II crystals. All symbols as for Figure 12. Heterovalent Mn layer cations are shown as 2+, 3+, and 4+. **a)** Distribution of heterovalent Mn cations in the lower layer. In Mn³⁺-rich rows, Mn cations are distributed as Mn³⁺-Mn³⁺-Mn³⁺-Mn³⁺-Mn²⁺-Mn⁴⁺... (Drits et al. 1997). The shift of interlayer Na induced by the presence of Mn²⁺ is shown by the arrow. **b)** Distribution of heterovalent Mn cations in the Mn³⁺-rich rows of two adjacent

layers. Mn_{layer} from the upper layer are shifted by $-\mathbf{a}/3$ with respect to those of the lower layer. Shift of interlayer Na towards Mn^{2+} cations is indicated by arrows.

Figure 14. Schematic distribution of interlayer species in projection on the **ab** plane for NaBi type II crystals. All symbols as for Figure 12. Dashed lines outline the periodic displacement of interlayer Na parallel to (110), whose amplitude varies along [13] with a $8d_{(310)}$ (or $12a_p$) period. The thick solid line outlines the rhomb-shaped unit-cell with $2(A + B)$ and $2(B - A)$, or $12 a_p$ and $12 b_p$.

Figure 15. Schematic distribution of interlayer species in projection on the **ab** plane for NaBi type I crystals. All symbols as for Figure 12. One possible 2D distribution of interlayer species is shown in Figure 15a, whereas Figure 15b shows an alternative distribution induced by different geometric configurations of H_2O-H_2O pairs.

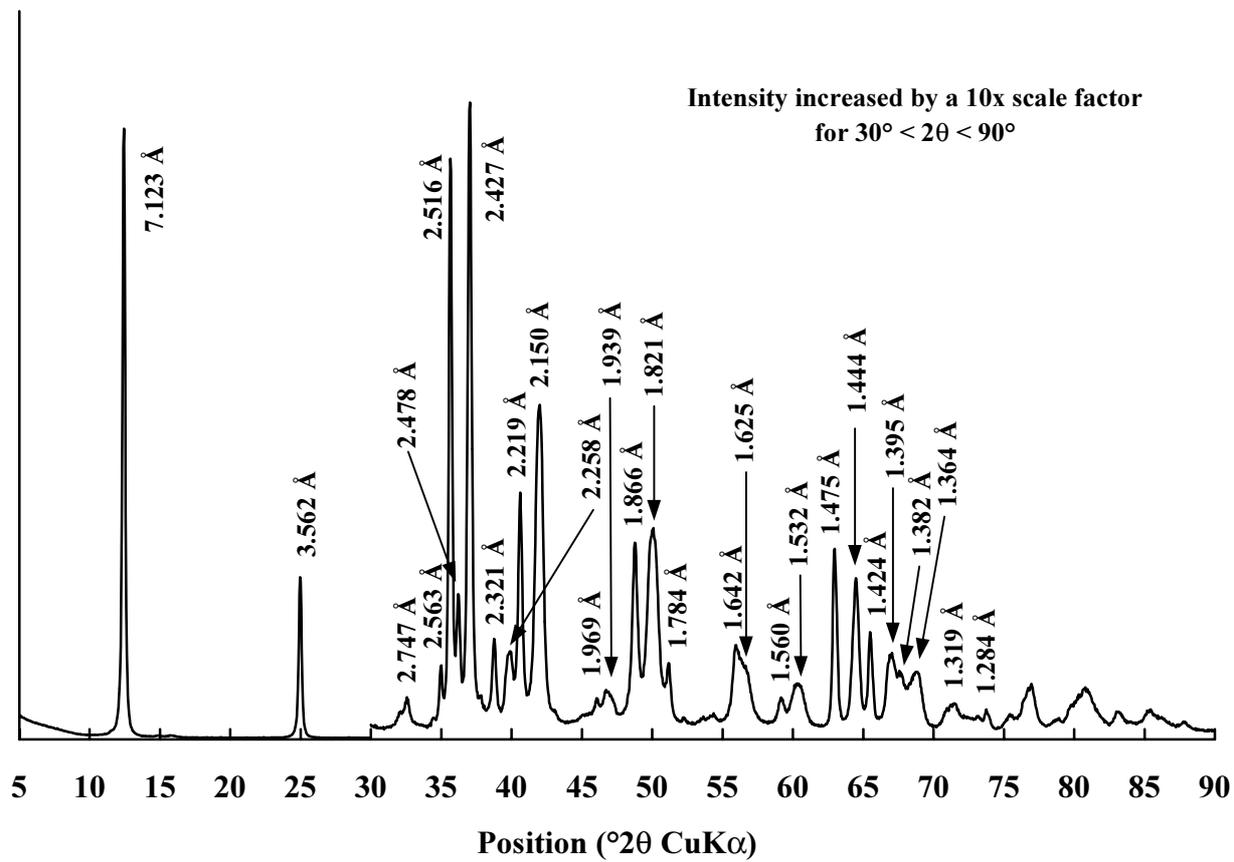
Table 1. Atomic positions, and site occupancy factors determined in the triclinic P sub-cell from the refined model shown in Figure 5.

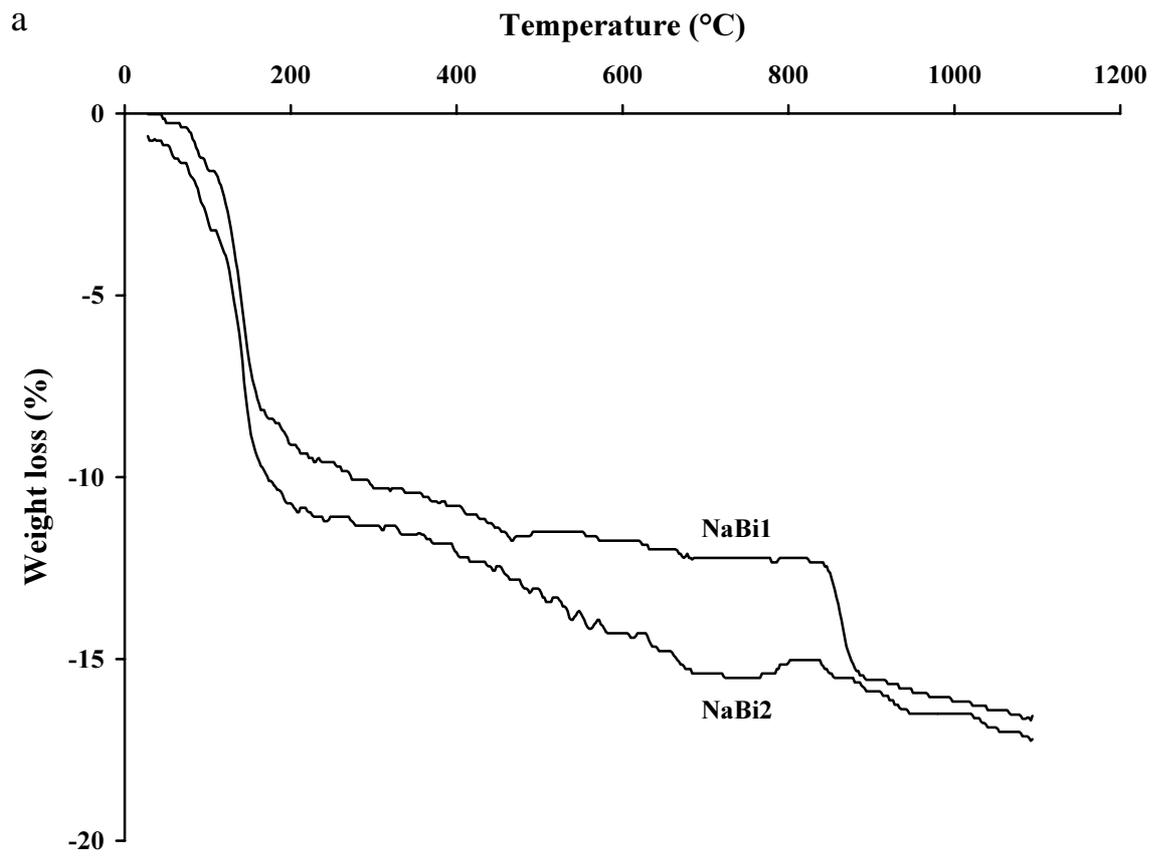
Atom	x	y	Z	Occ.
Mn _{layer}	0	0	0	0.5
O _{layer}	0.3886(26)	-0.3733(26)	0.1396(6)	1
Na _{Int}	0.628(11)	0.476(13)	0.481(3)	0.182(14)
H ₂ O _{Int}	0.290(8)	-0.819(15)	0.496(3)	0.272(16)

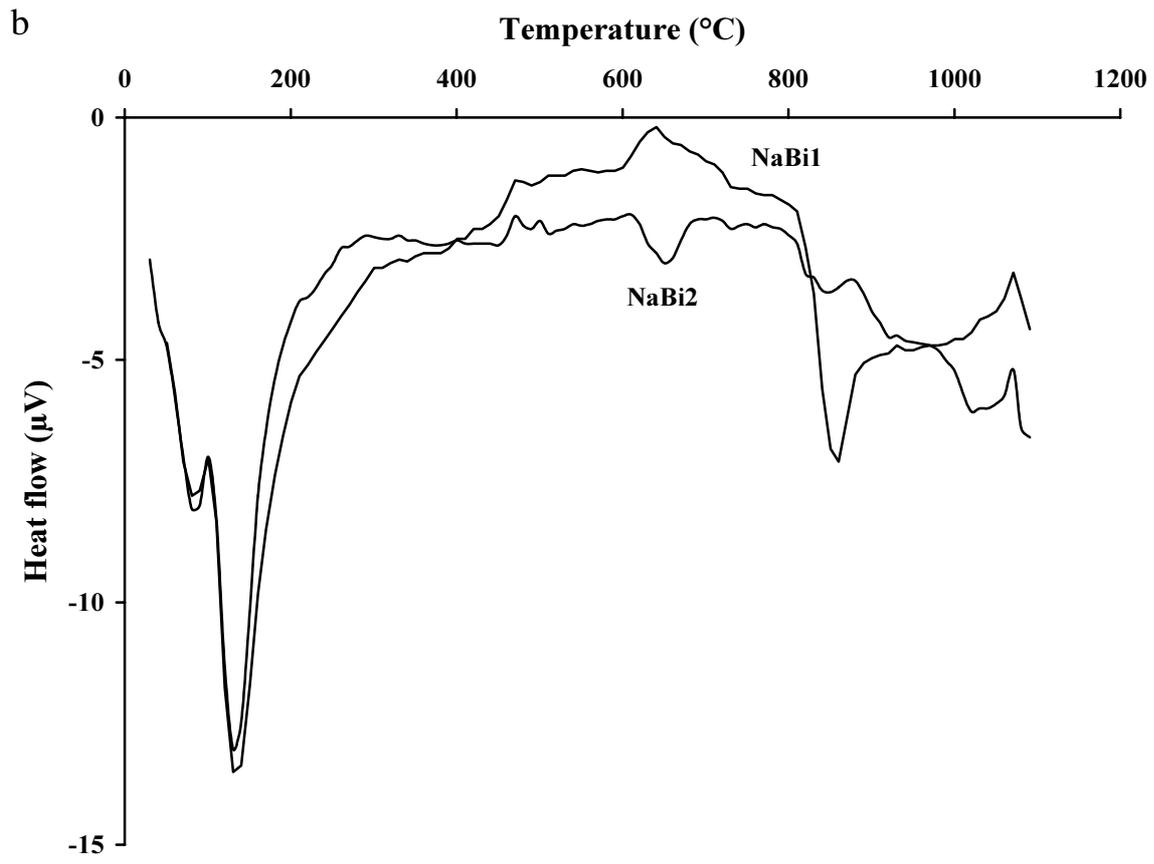
Note: $a_p = 2.9513(4)$ Å, $b_p = 2.9547(4)$ Å, $c_p = 7.334(1)$ Å, $\alpha_p = 78.72(2)^\circ$, $\beta_p = 101.79(1)^\circ$, $\gamma_p = 122.33(1)^\circ$. Positions and site occupancy factors (Occ.) are given for space group P1bar. Un-refined isotropic B factors are 0.5 for Mn, 1 for O, and 2 for interlayer species. Layer and Int subscripts refer to the location of the atoms in the layer and in the interlayer, respectively.

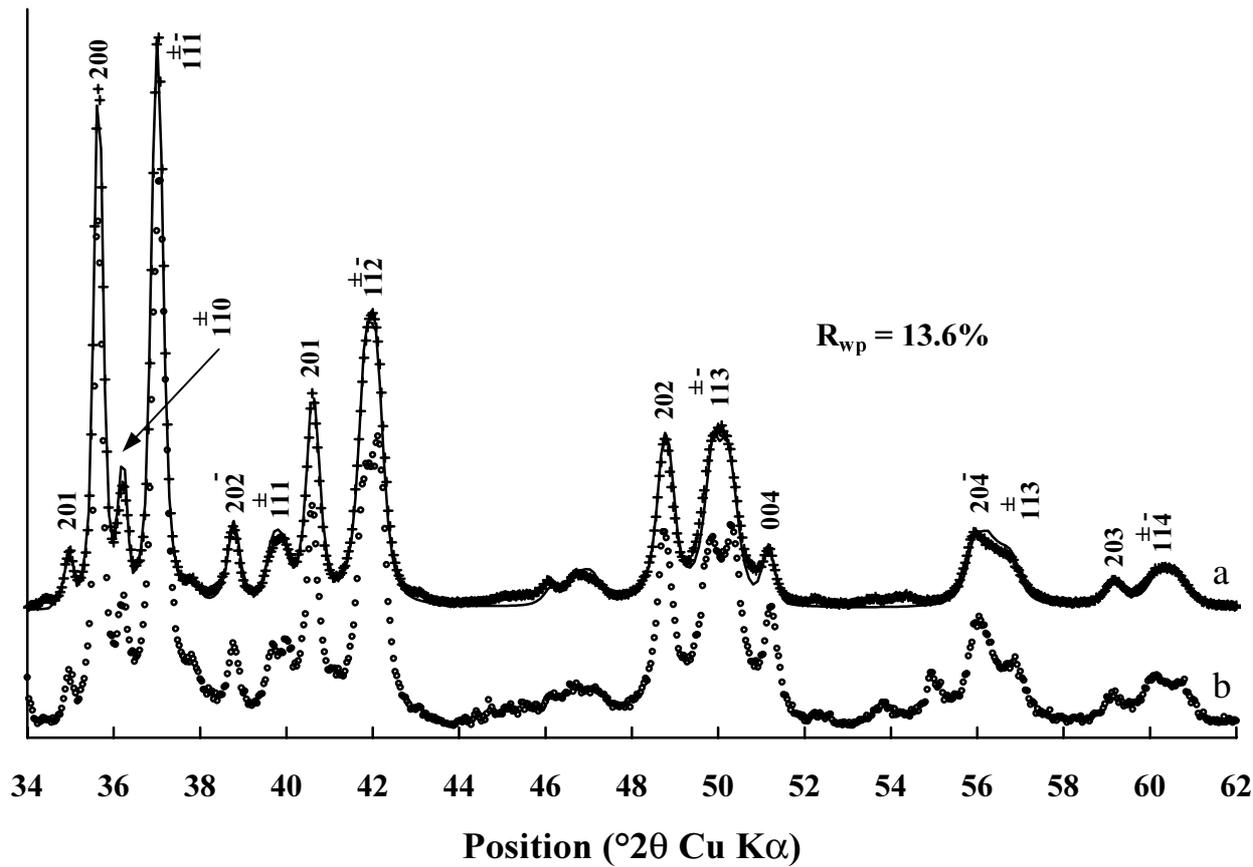
Table 2. Selected bond lengths (Å) determined in the refined NaBi sub-structure.

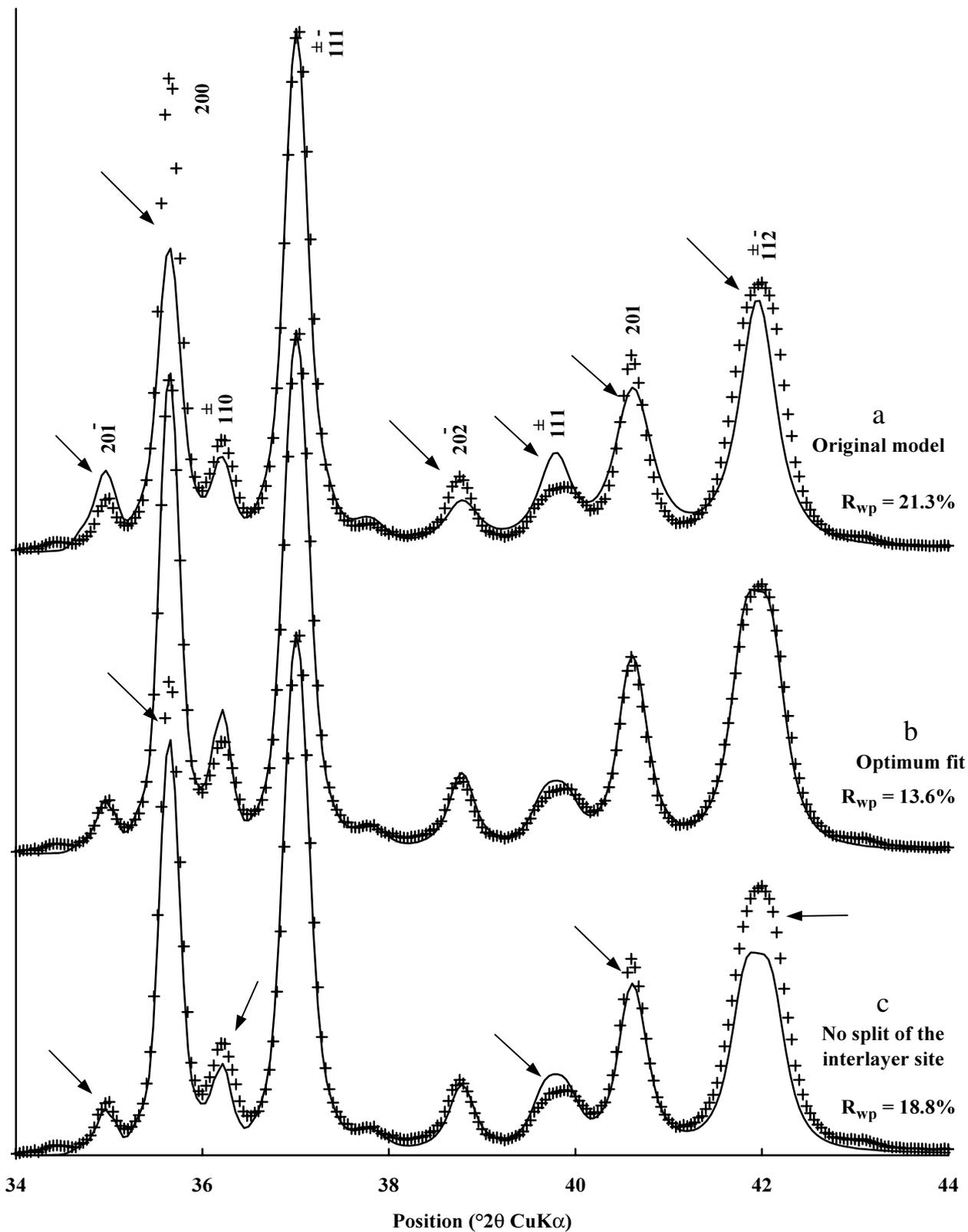
Mn-O ₁	1.925(22) x 2	Mn-O ₁	1.945(27) x 2	Mn-O ₁	2.003(18) x 2
Mn-Mn	2.848 (36) x2	Mn-Mn	2.951(0) x2	Mn-Mn	2.955 (1) x2
O ₁ -O ₁	2.593(41)	O ₁ -O' ₁	2.619(27)	O ₁ -O' ₁	2.848(37) x2
O ₁ -O'' ₁	2.620(18)	O ₁ -O'' ₁	2.951(13) x2	O' ₁ -O'' ₁	2.955(12) x2
Na _i -O _i	2.46(2)	Na _i -O _{i±1}	2.74(2)	Na _i -H ₂ O _i	2.61(6)
Na _i -H ₂ O _{i±1}	2.62(6)	Na _i -H ₂ O _i	2.64(6)	Na _i -H ₂ O _{i±1}	2.64(6)
H ₂ O _i -O _i	2.68(4)	H ₂ O _i -O _{i±1}	2.71(3)		

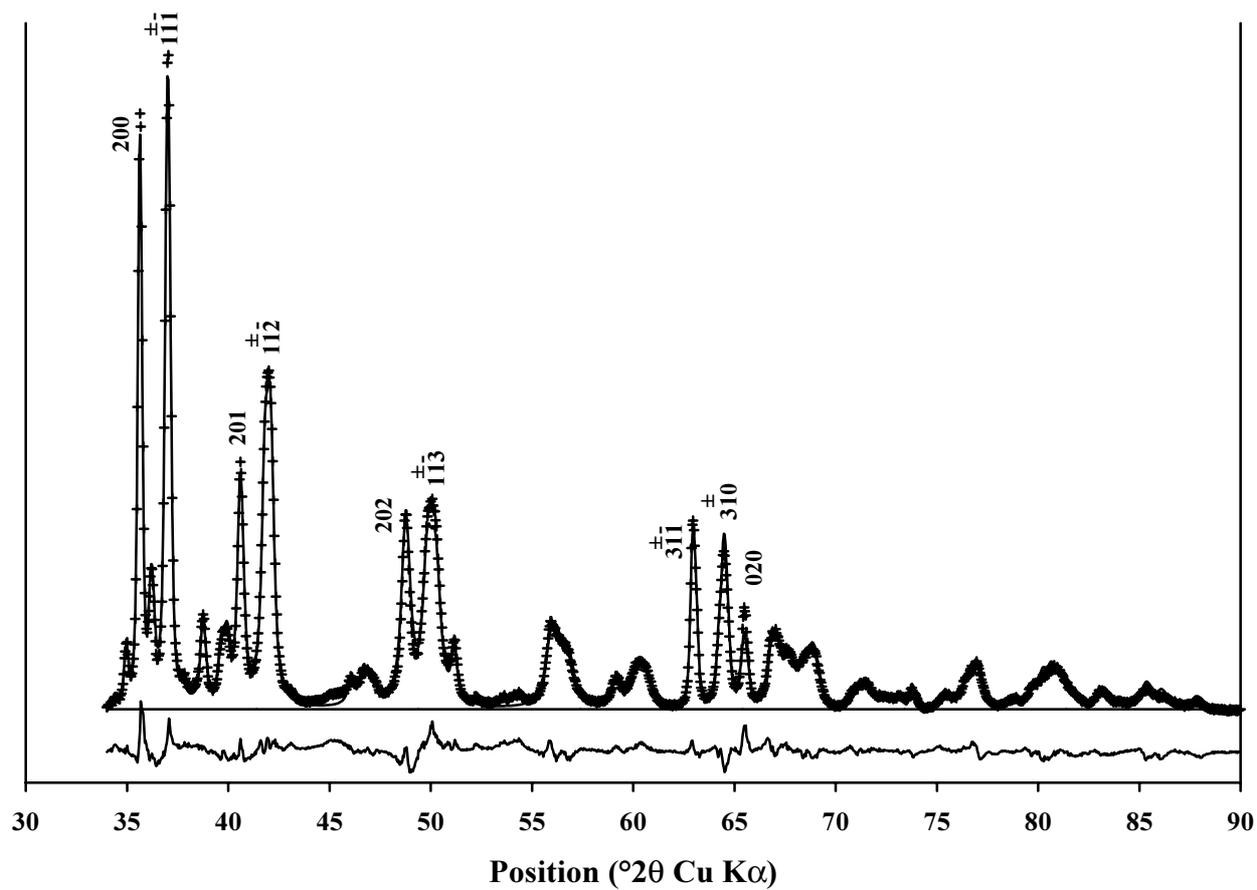


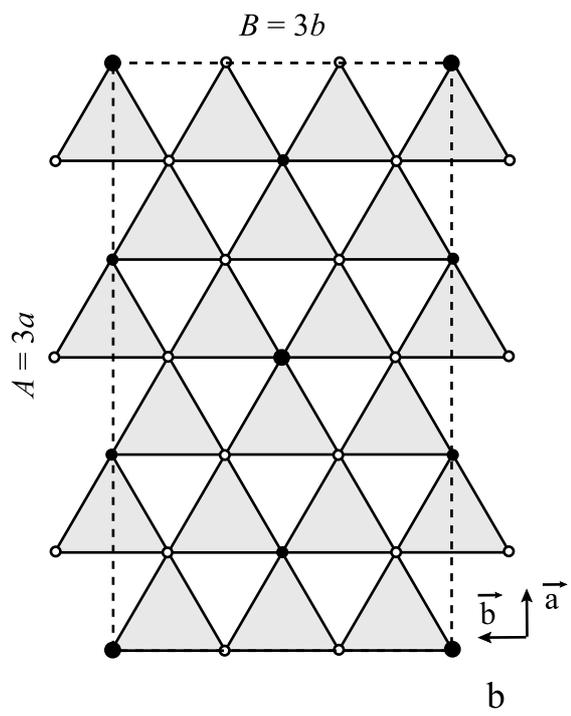
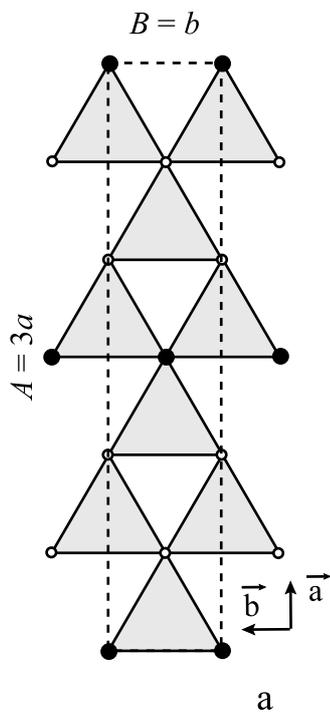


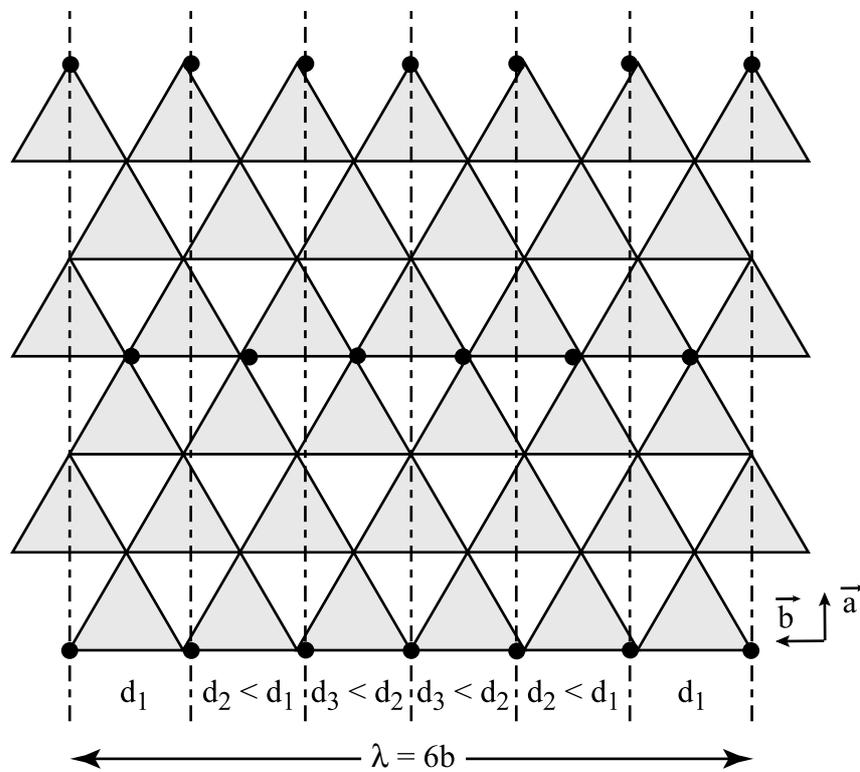


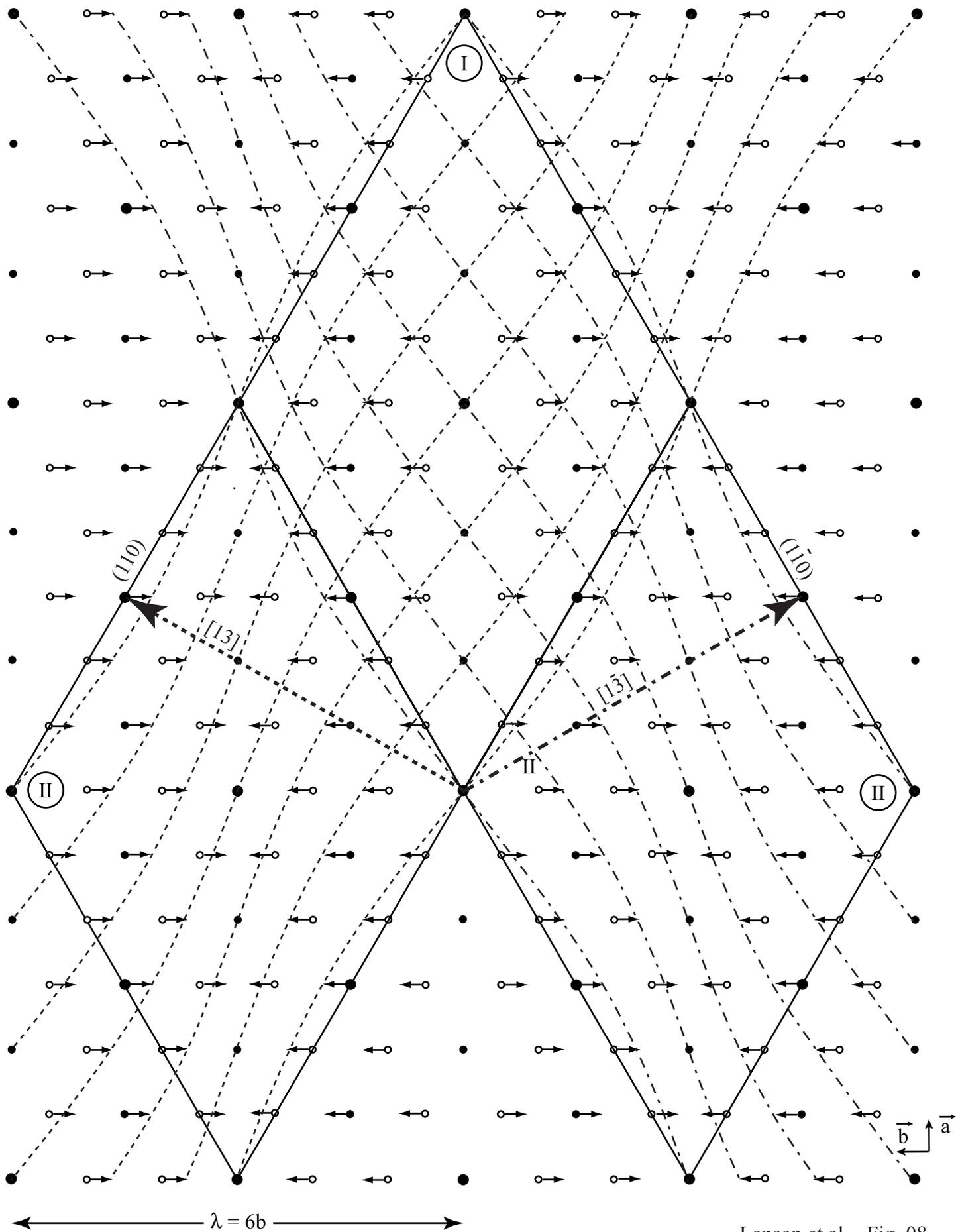












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