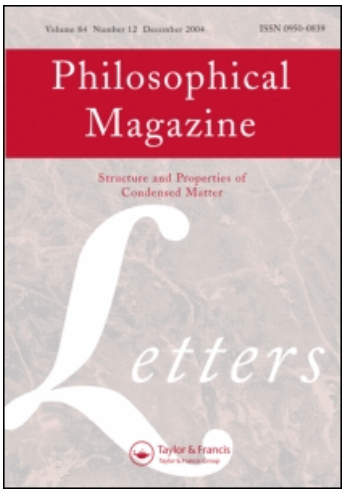

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Validating the model of a (3 + 1)-dimensional incommensurately modulated structure as generator of a family of compounds for the $Eu_2(MoO_4)_3$ scheelite structure

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Validating the model of a (3 + 1)-dimensional incommensurately modulated structure as generator of a family of compounds for the $Eu_2(MoO_4)_3$ scheelite structure

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The previously proposed model postulating that the incommensurately modulated $KNd(MoO_4)_2$ structure can act as a generator of the scheelite family members is validated here by refining the crystal structure of europium molybdate, $Eu_2(MoO_4)_3$. The initial structural model was derived from the superspace characteristics of $KNd(MoO_4)_2$ and the predicted parameters used in the simulation of $Eu_2(WO_4)_3$. The refinement was performed using both superspace and traditional supercell approaches in superspace group $I2/b(\alpha\beta0)00$ and space group $A2/a$, respectively. The results obtained by both approaches are in excellent agreement and coincide with those reported in the literature.

Keywords: scheelite compounds; superspace approach; supercell; crystal structure

1. Introduction

Compounds with the scheelite-like structure have been the focus of recent research owing to their interesting optical properties, which leads to multiple applications in solid-state lasers [1–6]. Such applications depend strongly on the particular structural characteristics of these compounds. For example, the weak coupling among rigid structural groups allows us to obtain intense lines in the Raman scattering spectra, which is consistent with the high-frequency vibration modes of the rigid structural groups [1,2].

In the most general form, the structure of scheelite-like compounds can be interpreted as a set of rigid building units $\{A, [XO_4]\}$ occupying specific positions in the unit cell (Figure 1). The structure can be produced with various chemical compositions defined by $A =$ K, Na, Li, Rb, Ag, La, Ca, Sr, Ba and $X =$ Mo, W, V among others. The A atoms, as well as the $[XO_4]$ groups, can be either identical or not and also partially vacant [7]. The general formula of this family can thus be expressed as

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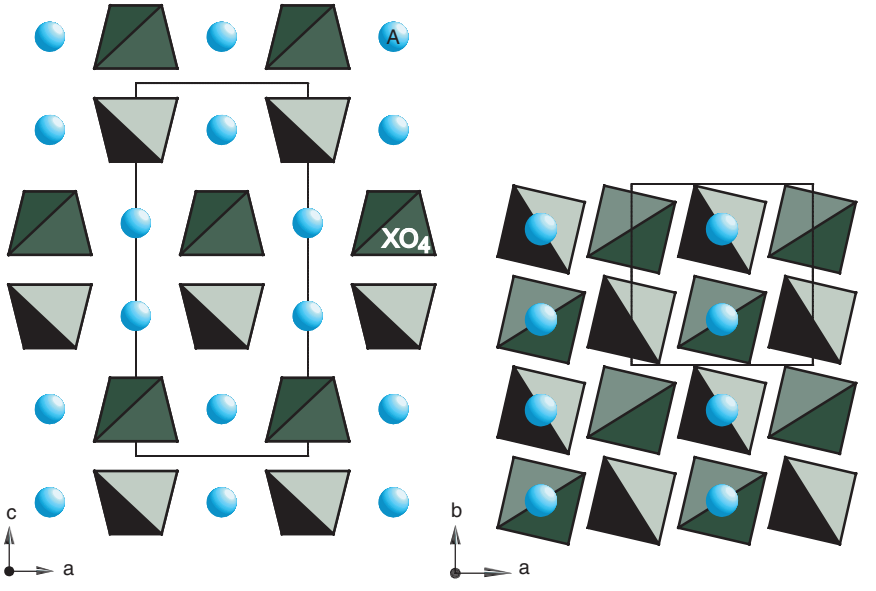

Figure 1. (Colour online). Projections along b and c axes of the basic structure of the scheelite-like compounds.

$(A', A'')_{n-\delta A}$ $[(X', X'')O_4]_{n-\delta X}$, where $A'(A'')$ and $X'(X'')$ denote the atoms occupying A and X positions, respectively, and $\delta A \geq 0$ or $\delta X \geq 0$ define vacancies on the corresponding sites [7]. Different combinations (ordered or not) of the building units lead to different members of the family. Eight known types of ordered distributions have already been described as three-dimensional (3D) periodic compounds [7]. Two incommensurately modulated structures, $KNd(MoO_4)_2$ and $KSm(MoO_4)_2$, also belong to this family [7–9].

In spite of their different structural topology and chemical composition, all these structures have been well described in a unified way by using the superspace concept [10–13]. In this approach, each structure can be interpreted as a 3D section obtained through a rational or irrational cut along the fourth dimension of a $(3+1)$D periodic superspace structure. All members of the family belong to a unique $(3+1)$D superspace group (SSG) accounting for the symmetry of the superspace structure.

Recently, the possibility to use an incommensurately modulated structure belonging to a family of compounds as a superspace model for the description and prediction of the family members [7] has been postulated and discussed. In particular, the incommensurately modulated $KNd(MoO_4)_2$ structure was used as a prototype for the scheelite-like family. Characteristics of $KNd(MoO_4)_2$ attributed to the $(A', A'')_{n-\delta A}$ $[(X', X'')O_4]_{n-\delta X}$ family are:

- Monoclinic SSG $I2/b(\alpha\beta 0)00$ and modulation vector $\boldsymbol{q} = \alpha \boldsymbol{a}^* + \beta \boldsymbol{b}^*$, α and β being variables.
- The basic unit cell is characterised by $a/b \simeq 1$, $c/a \simeq c/b \simeq 2$, $a \simeq 5.5$ Å, $\gamma \simeq \pi/2$.
- The basic structure is composed of four atomic positions: A [4(e): $\frac{1}{2}\frac{1}{4}z_A \simeq 0.88$], X[4(e): $\frac{1}{2}\frac{1}{4}z_X \simeq z_A - 0.5$], O_1[8(f): $x \simeq 0.36, y \simeq 0.02, z \simeq 0.29$], O_2[8(f): $x \simeq 0.77, y \simeq 0.41, z \simeq 0.04$].

- The distribution of $A'(A'')$ and $X'(X'')$ atoms on the A and X positions are described by the respective occupation functions $o(A)$ and $o(X)$.
- The ordering of the building units on the A and X sites is the main factor responsible of the structure modulations. For commensurate cases (i.e. α and β rational numbers), the initial phase of the modulation (t_0-value) also vary for each combination of α and β.

Variations of the components of the modulation vector $\boldsymbol{q}$, site occupation functions $\{o(A), o(X)\}$, and t_0-value (when $\boldsymbol{q}$ is rational), lead to non-equivalent family members differing in their topology, composition and 3D symmetry if $\boldsymbol{q}$ is rational.

It has been shown recently [7] that the structure of $Eu_2\square(WO_4)_3$ ($\square$ stands for a vacancy) can be described as a commensurately modulated member of the scheelite (3 + 1)D structure type with the modulation vector $\boldsymbol{q} = (2/3)\boldsymbol{a}^* + (2/3)\boldsymbol{b}^*$, the initial phase $t_0 = 0$ and the crenel occupation functions $\Delta_{Eu} = 2/3$, $\Delta_{\square} = 1/3$. This $\boldsymbol{q}$-vector and the occupation functions have been used for the simulation of its structure from the $KNd(MoO_4)_2$ prototype. As it was shown (Table 6 in [7]), the simulated structure reproduces the main features of the refined $Eu_2(WO_4)_3$ structure. However, one question has not yet been answered: is it possible to refine this structure (or an isostructural one) as commensurately modulated within the (3 + 1)D SSG *I2/b(αβ0)00*? The aim of this work is to present the proof that this question can be answered in the affirmative.

This article demonstrates that it is possible to refine the structure of $Eu_2(MoO_4)_3$ (isostructural to $Eu_2(WO_4)_3$) by using an initial superspace model derived from the incommensurately modulated $KNd(MoO_4)_2$ structure. Indeed, $Eu_2(MoO_4)_3$ was refined in SSG *I2/b(αβ0)00* with the predicted occupation functions and using the traditional 3D description in space group (SG) *A2/a*. Results obtained by both methods on the basis of synchrotron powder diffraction data are compared with the results reported in the literature.

2. Experimental

2.1. *Sample preparation*

The $Eu_2(MoO_4)_3$ molybdate was synthesised from a (1 : 3) stoichiometric mixture of Eu_2O_3 (99.9 %) and MoO_3 (99.9 %) by the solid state method at $T = 1023$ K for 48 h in air followed by quenching from $T = 1023$ K to room temperature. The intermediate grinding after 24 h was carried out in order to maintain homogeneity.

2.2. *Data collection*

The data were collected at beamline BM01A (Swiss-Norwegian Beamlines) at the ESRF, Grenoble. A wavelength of 0.6942 Å was selected using a Si(111) double crystal monochromator, and the synchrotron beam was focussed on a spot size of 0.3 mm × 0.3 mm using a combination of curved mirrors and sagitally bent second crystal. The sample was filled into a borosilicate capillary of 0.5 mm diameter, and the data were collected at room temperature. A mar345 image plate detector was used to register the powder patterns. The sample-to-detector distance of 250 mm was calibrated using a LaB_6 reference powder. Exposure time was typically 30 s per image,

and the sample was rotated during the data collection at a speed of 1 degree per second. Exposure times were chosen to avoid any pixel saturation. The integration of the 2D powder data was done using the fit2d software package [14].

3. Validating the model

Commensurately modulated structures can be well solved either by the superspace description (basic positions + modulation waves) or by the classical 3D description with an N-fold supercell, $N \leq n_1 \times n_2 \times n_3$, n_1, n_2 and n_3 being denominators of the rational components of the modulation vector $\boldsymbol{q}$. Both approaches are just alternative descriptions of the same structure [15,16].

In order to validate the hypothesis which postulates the $KNd(MoO_4)_2$ compound as a superspace model for the description of the commensurately modulated $Eu_2(MoO_4)_3$ structure, we refined the latter compound from synchrotron powder diffraction data by using both the superspace and traditional 3D descriptions. The *JANA*2006 program package [17] has been used for all calculations.

3.1. *Refinement of commensurately modulated structure model*

In this model, $Eu_2(MoO_4)_3$ is a commensurately modulated structure [7] belonging to the scheelite (3 + 1)D structure type with characteristics given in the introduction. Similar to $Eu_2(WO_4)_3$, this structure is characterised by the modulation vector $\boldsymbol{q} = (2/3)\boldsymbol{a}^* + (2/3)\boldsymbol{b}^*$, $t_0 = 0$ and the crenel occupation function for $A = \text{Eu}$ atomic domain with the length $\Delta_{\text{Eu}} = 2/3$ along the internal space coordinate x_4 and the domain centre $x_4 = 0.5$ [7]. The incommensurately modulated structure $KNd(MoO_4)_2$ [9] has been used as a starting model.

The profile has been successfully refined with scheelite-like lattice parameters of the basic structure (Table 1, left column) and rational values of the components $\alpha = 2/3$, $\beta = 2/3$ of the $\boldsymbol{q}$-vector. Several attempts were addressed to refine these components. However, the results did not depart from the rational values by more than 0.5 standard deviations. This confirms the commensurate modulation of the structure. The atomic positional parameters and amplitudes of positional modulation are shown in Table 2.

The above structural model has been refined using isotropic displacement parameters (IDP) and smoothly converged to a stable solution with reliability factors $R(\text{all}) = 2.44\%$ and $R_w(\text{all}) = 2.92\%$ for 307 observed reflections. Numerical parameters illustrating the quality of the structure refinement are presented in Table 1.

3.2. *Refinement of supercell model*

The lattice parameters of the basic commensurately modulated structure have been transformed to the supercell lattice parameters by the matrix,

$$T_{(b\rightarrow s)} = \begin{bmatrix} -2 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Table 1. Details of the $Eu_2(MoO_4)_3$ structure refinement using both superspace and supercell models.

	Superspace model	Supercell model
Cystal data*		
Chemical formula	$Eu_2(MoO_4)_3$	$Eu_2(MoO_4)_3$
Temperature (K)	293	293
Cell setting	Monoclinic	Monoclinc
(Super) space group	*I2/b(αβ0)00*	*A2/a*
Lattice parameters (Å, °)		
a	5.2328(3)	11.4974(6)
b	5.2214(3)	7.5463(3)
c	11.4529(6)	11.4529(6)
γ	92.414(2)	109.284(4)
Modulation vector	$\boldsymbol{q} = \frac{2}{3}\boldsymbol{a}^* + \frac{2}{3}\boldsymbol{b}^*$	–
Refinement		
Profile functions	Pseudo-Voight	Pseudo-Voight
R(all), R_w(all)	2.44, 2.92	2.44, 2.92
R(all, main), R_w(all, main)	2.33, 3.15	–
R(all, 1st), R_w(all, 1st)	2.54, 2.78	–
R_p, R_{wp}	5.03, 7.49	5.03, 7.49
GOF (χ^2)	3.33	3.33
No. observed reflections	307	307
No. parameters	28	28

Note: *Whole sets of experimental data and characteristics of refinements are available with CSD numbers 420097 (superspace) and 420098 (supercell) in ICSD database: FIZ Karlsruhe (crysdata@fiz-karlsruhe.de).

Table 2. Atomic coordinates, isotropic displacements parameters and Fourier amplitudes obtained from the superspace refinement of $Eu_2(MoO_4)_3$.

Atoms	Harmonics	*x*	*y*	*z*	U_{eq}(Å^2)
Eu		0.5	0.25	0.8772(3)	0.0096(8)
	s,1	−0.0153(7)	−0.0113(8)	0	
	c,1	0	0	0	
Mo		0.5	0.25	0.3820(4)	0.008(1)
	s,1	0.034(1)	0.044(1)	0	
	c,1	0	0	−0.0104(4)	
O_1		0.343(2)	0.011(2)	0.2979(7)	0.0080
	s,1	0.009(3)	−0.011(4)	−0.002(1)	
	c,1	−0.016(3)	−0.047(3)	−0.016(1)	
O_2		0.752(2)	0.409(2)	0.0401(8)	0.0071
	s,1	−0.025(4)	−0.002(4)	0.003(1)	
	c,1	−0.003(3)	0.043(3)	−0.003(1)	

Notes: Harmonics are listed by terms (s for sinus, c for cosinus) and order *n*.

The space group $A2/a$ with the monoclinic axis c is immediately obtained for this supercell. This space group corresponds to $C2/c$ with the monoclinic axis b reported in [18] for $Eu_2(MoO_4)_3$. The refined lattice constants (Table 1, right column) are in good agreement with the published ones [18], $a = 11.5055(5)$, $b = 7.5613(3)$, $c = 11.4685(5)$Å and $\gamma = 109.309(3)^\circ$, transformed by the matrix

$$M = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}. \quad (1)$$

The structure has been refined isotropically in this supercell until convergence with reliability factors similar to those obtained in the superspace description (Table 1). Figure 2b shows the calculated and residual X-ray diffraction patterns. The atomic coordinates and main interatomic distances are listed in Tables 3 and 4 in comparison with those reported in [18].

4. Discussion

The structure of $Eu_2(MoO_4)_3$, has already been determined on the basis of powder diffraction data collected by a conventional diffractometer [18]. The structure was solved in $C2/c$ SG (monoclinic b axis) taking the $Eu_2(WoO_4)_3$ crystallographic data [19] as a starting point. In this section, we will focus on the comparison between the results obtained from our refinement on the basis of synchrotron powder diffraction data and superspace model generated from $KNd(MoO_4)_2$ and those reported in [18].

As can be seen from Table 1, both superspace and supercell descriptions yielded the same refinement results (the same R values). This is an expected result, as the number of refinable parameters, namely 28, was the same in both the refinements (Table 1). It is worth underlining that, in determining the total number of refinable parameters, we took into account that the total number of parameters for an atom in the superspace description must not exceed the number of parameters for the same atom in the supercell. This procedure helped us to avoid extra modulation parameters in the superspace refinement.

The good agreement between both descriptions can be better visualised in Figure 3, where the Mo–O (Figure 3a) and Eu–O (Figure 3b) distances plotted as function of the internal coordinate t are compared with those obtained in the supercell refinement. Distance values obtained in superspace (grey circles) and supercell (red open circles online) refinements, are represented on the intersections with the t-sections where the commensurate structure is physically realised. Such sections correspond to the two inequivalent Mo atoms ($t_0 = 0$, $t_0 = 1/3$ or $2/3$) and to the unique Eu atom, $t_0 = 1/3$. Table 4 reports a comparison among the interatomic distances obtained from the supercell refinement and those reported in [18].

In order to compare the structural solution obtained by our refinement with that reported in the literature, the C-setting (monoclinic c axis) used during the supercell refinement was selected as a common reference frame. We thus transformed the

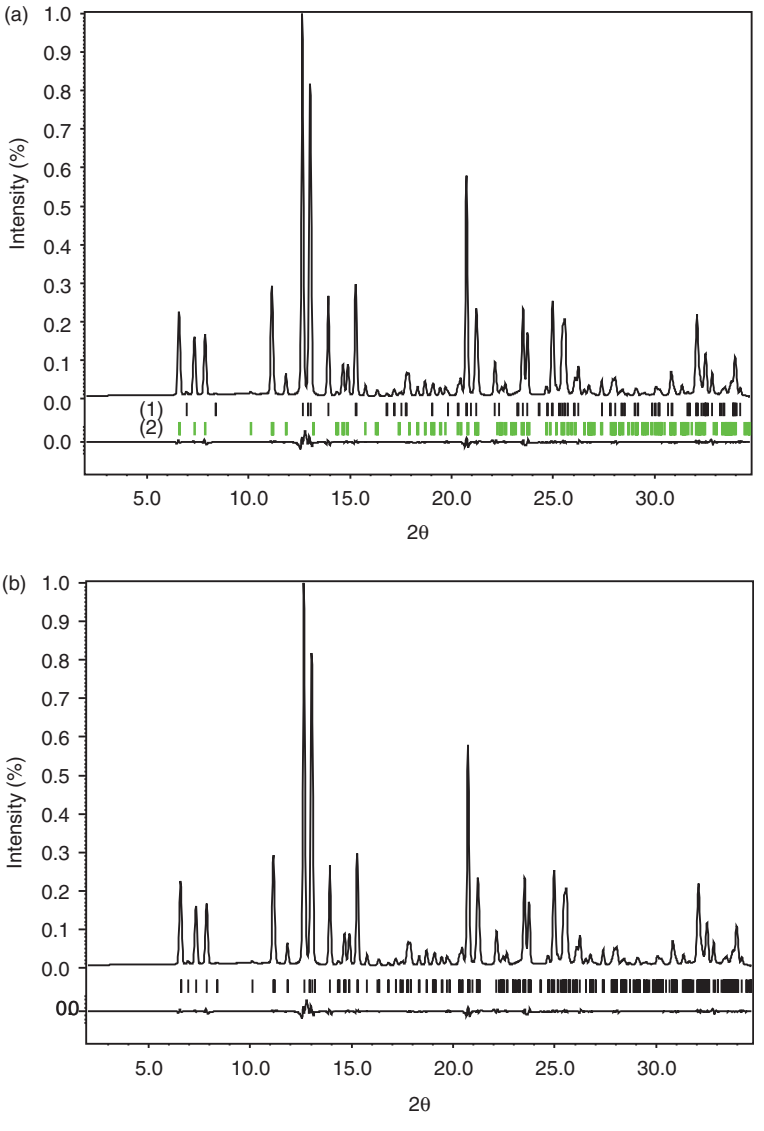

Figure 2. (Colour online). Calculated and residual X-ray diffraction patterns for $Eu_2(MoO_4)_3$. (a) Obtained from superspace model. (b) Obtained from supercell. Main and satellites reflections are identified as (1) (black lines) and (2) (green lines), respectively, in (a).

atomic coordinates reported in [18] for Eu, Mo and O atoms, from the B-setting (monoclinic *b* axis) to the common reference frame, according to

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = M \begin{bmatrix} x_b \\ y_b \\ z_b \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ \frac{1}{2} \end{bmatrix}, \tag{2}$$

M being the matrix defined in Equation (1).

Table 3. Fractional coordinates of the atoms Eu, Mo and O refined from commensurately modulated $Eu_2(MoO_4)_3$ compared with those reported in [18] transformed through Equation (2).

	X		*Y*		*Z*	
Atoms	This work	According to [18]	This work	According to [18]	This work	According to [18]
Eu	0.4089(2)	0.4089(2)	0.3313(7)	0.3325(6)	0.8772(3)	0.8771(7)
Mo1	0.75	0.75	0	0	0.3716(7)	0.3707(5)
Mo2	0.4393(2)	0.4406(2)	0.3488(9)	0.3509(8)	0.3872(4)	0.3885(3)
O1	0.283(2)	0.286(2)	0.337(3)	0.327(3)	0.041(1)	0.046(1)
O2	0.887(2)	0.887(2)	0.123(3)	0.136(3)	0.292(2)	0.289(2)
O3	0.195(1)	0.198(2)	0.746(3)	0.75(3)	0.314(1)	0.313(2)
O4	0.959(2)	0.961(2)	0.645(3)	0.654(3)	0.044(2)	0.039(1)
O5	0.598(2)	0.606(2)	0.951(4)	0.967(3)	0.036(2)	0.025(2)
O6	0.564(2)	0.564(2)	0.452(3)	0.449(3)	0.288(1)	0.292(2)

Table 4. Selected interatomic distances (Å) in $Eu_2(MoO_4)_3$ refined in classical 3D supercell compared with those reported in [18].

	This work	According to [18]		This work	According to [18]
Eu–O1	2.38(2)	2.39(2)	Eu-O6	2.45(2)	2.49(2)
Eu–O2	2.45(2)	2.38(2)	Mo1-O1	1.72(2)	1.78(2)
Eu–O2	2.46(2)	2.49(2)	Mo1-O2	1.79(2)	1.83(2)
Eu–O3	2.44(2)	2.41(2)	Mo2-O3	1.69(2)	1.75(2)
Eu–O4	2.42(2)	2.49(2)	Mo2-O4	1.81(3)	1.79(2)
Eu–O4	2.41(2)	2.37(2)	Mo2-O5	1.91(3)	1.91(2)
Eu–O5	2.33(3)	2.48(3)	Mo2-O6	1.79(2)	1.76(2)

Table 3 reports the fractional coordinates refined in the supercell compared with those transformed through Equation (2). The good agreement achieved can be visualised in Figure 4, where the structure of europium molybdate, $Eu_2(MoO_4)_3$, refined in this work from the superspace model derived from $KNd(MoO_4)_2$ is compared with that obtained from the crystallographic data reported in [18].

5. Conclusions

We have shown that the structural characteristic of the $KNd(MoO_4)_2$ compound can be used as a superspace model for generating and describing all members of the (3 + 1)D scheelite-like family of structures. The model was exploited for the simulation of a large range of compounds differing widely in chemical composition and topology [7]. In addition, this model has also been used as a starting model for the refinement of the partially disordered incommensurately modulated structure of $KSm(MoO_4)_2$ [8].

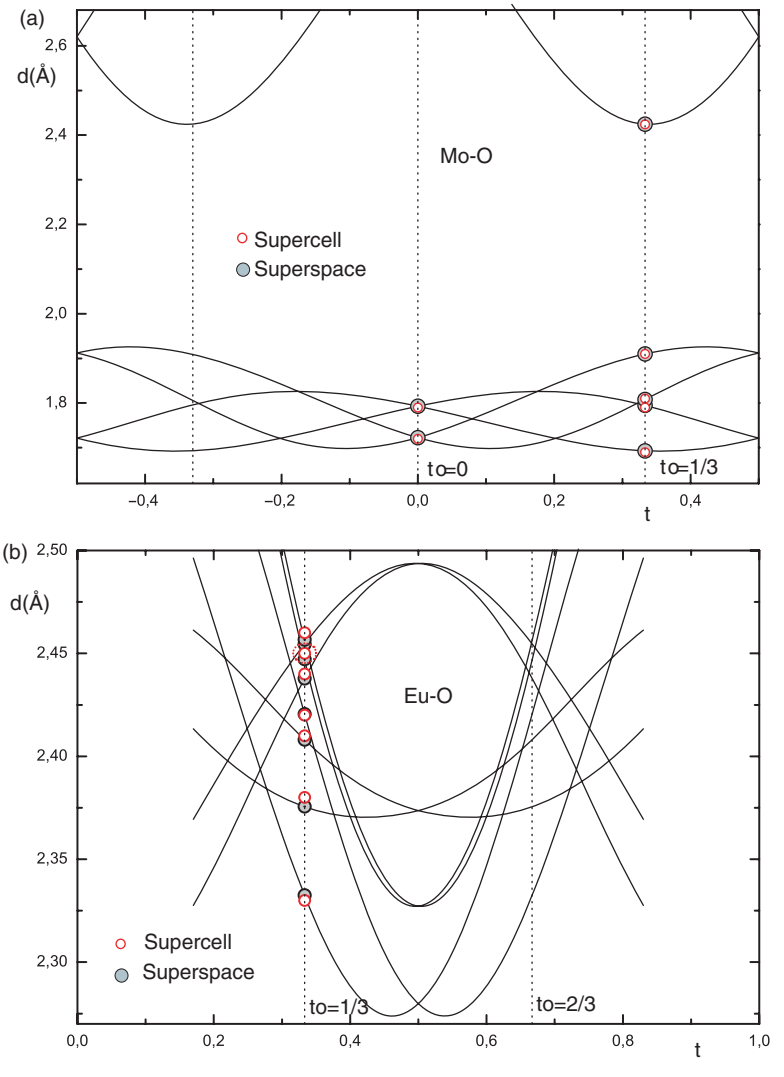

Figure 3. (Colour online). Mo–O (a) and Eu–O (b) distances as a function of the internal coordinate *t*. Lines show distances in the superspace description. Grey circles mark the distances in the commensurate structure for one of the two equivalent *t*-section (dashed lines) representing the real structure. Distances obtained from the supercell refinement are indicated by red open circles. Concentric circles, one of which is dashed as in (b) indicate two superimposed distance values.

In this work, we demonstrate that the superspace model generated from the $KNd(MoO_4)_2$ structure can also be used as a starting model for refining the europium molybdate, $Eu_2(MoO_4)_3$. Starting with the superspace characteristics of $KNd(MoO_4)_2$ and the predicted occupation functions and modulation vector for the simulation of $Eu_2(WO_4)_3$, we refined the structure of $Eu_2(MoO_4)_3$ using both superspace and

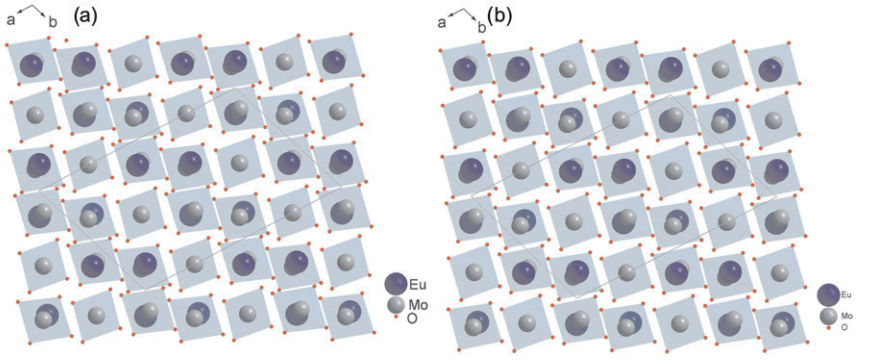

Figure 4. (Colour online). Crystal structure of the commensurate modulated $Eu_2(MoO_4)_3$ compound along the *c* axis. (a) Refined in this work. (b) Generated according to the structural parameters reported in [18] transformed through Equation (2).

supercell descriptions. The results obtained by both approaches are in perfect agreement and coincide with those reported in literature.

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