

Chemical Heterogeneity of a Crystal Built of Nanoscale Coherently Twinned $\text{Yb}_{2-x}(\text{Fe,Ga})_{17+2x}$ Polytypes

Yaroslav E. Filinchuk,^{*,[a]} Henrik Birkedal,^{*,[b, e]} Radovan Černý,^[a] Marc Hostettler,^[c, f] Tamara I. Yanson,^{†[d]} Oksana I. Bodak,^[d] and Klaus Yvon^[a]

Abstract: An X-ray study of single crystals extracted from an arc-melted Yb-Fe-Ga alloy showed that the diffraction pattern can be modeled by an intergrown crystal that has three sorts of domains: one hexagonal (**1**, $\text{LuFe}_{9.5}$ type) and two rhombohedral (**2a** and **2b**, PrFe_7 type), the last two twinned by reticular merohedry. Crystals **1** and **2** are essentially *polytypes* with maximum degree of order (MDO polytypes), built up of nearly identical slabs that are stacked along [001] in ABAB... (**1**) and ABCABC... (**2**) sequences. Structure refinement was per-

formed by a newly developed program that allowed us to refine several structures on a single data set. We found that the hexagonal and rhombohedral domains differ in chemical composition: while **1** shows a higher rate of Yb substitution by Fe_2 dumbbells, **2** shows partial substitution of Fe by Ga. Our observation of the nanoscale phase segregation is supported by latest finding

of nonrandom distribution of stacking faults in a similar 2:17 alloy. An unequal distribution of chemical substitutions in **1** and **2** apparently compensates the inherent mismatch of basal plane dimensions of the individual MDO polytypes and thus constrains their cell parameters within the syntaxy. According to our knowledge this is the first example of two chemically distinct polytypes constituting a single crystal, refined on a single set of diffraction data.

Keywords: alloys • intermetallic phases • polytypes • X-ray diffraction

Introduction

Iron-rich rare-earth transition-metal alloys are of interest as constituents for permanent magnets.^[1] Ytterbium-containing materials have not yet been studied in great detail, because of problems with sample preparation. Recently structural and magnetic properties of aluminum-substituted compounds of composition $\text{Yb}_{2-x}(\text{Fe,Al})_{17+2x}$ have been investigated^[2,3] and structural features of some gallium analogues $\text{Yb}_{2-x}(\text{Fe,Ga})_{17+2x}$ have been reported.^[4] All compounds were found to be ferromagnetic. Depending on the Al(Ga) content they crystallize with either the hexagonal $\text{LuFe}_{9.5}$ type (**1**, $P6_3/mmc$ space group) or the rhombohedral PrFe_7 type structure (**2**, $R\bar{3}m$ space group). Both structures are closely related: they are built up of nearly identical slabs that are stacked along [001]. Each structural slab can be represented by an idealized two-dimensional "layer" (layer group $p6mm$)^[5] as shown in Figure 1. Their hexagonal ABAB... (**1**) and rhombohedral ABCABC... (**2**) stacking leads to layered structures that can be considered as *polytypes* with maximum degree of order (MDO polytypes).^[6] Their cell parameters are related to a common supercell by $a_s = a(\mathbf{1}) = a(\mathbf{2})$ and $c_s = 3c(\mathbf{1}) = 2c(\mathbf{2})$.

Single-crystal laboratory X-ray data have shown that in **1** and **2** the rare-earth atoms are partially substituted by Fe_2

[a] Dr. Y. E. Filinchuk, Dr. R. Černý, Prof. Dr. K. Yvon
Laboratoire de Cristallographie
Université de Genève
quai Ernest-Ansermet 24, 1211 Genève 4 (Switzerland)
Fax: (+41)22-3796108
E-mail: Yaroslav.Filinchuk@cryst.unige.ch

[b] Dr. H. Birkedal
Institut de Cristallographie, Université de Lausanne
BSP, Dorigny, 1015 Lausanne (Switzerland)

[c] Dr. M. Hostettler
Institut de Cristallographie, Université de Lausanne
BSP, Dorigny, 1015 Lausanne (Switzerland)

[d] Dr. T. I. Yanson, Prof. Dr. O. I. Bodak
Department of Chemistry
Ivan Franko National University of Lviv
Kyryla and Mefodia 6, 79005 Lviv (Ukraine)

[e] Dr. H. Birkedal
Present address: Department of Chemistry
University of Aarhus, Langelandsgade 140
8000 Aarhus C (Denmark)
Fax: (+45)8619-6199
E-mail: hbirkedal@chem.au.dk

[f] Dr. M. Hostettler
Present address: Laboratorium für Kristallographie
Universität Bern, Freiestrasse 3, 3012 Bern (Switzerland)

† T. Yanson collaborated in this work until the time of her death.

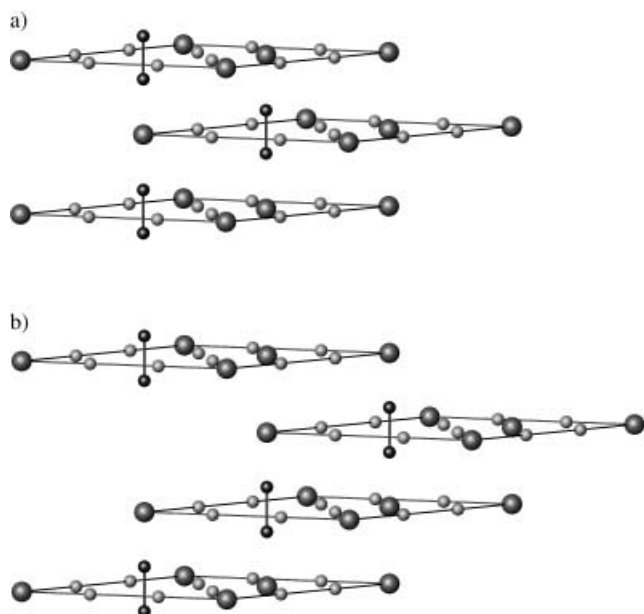


Figure 1. Idealized structural layers stacked in a) AB (**1**) and b) ABC (**2**) sequences. Ytterbium atoms are shown by big spheres, iron atoms by small spheres, and Fe₂ dumbbells by interconnected atom pairs. Iron atoms allocated between the layers (6*g* and 12*k* positions in the hexagonal structure and 9*d* and 18*h* in the rhombohedral one) are omitted for clarity.

dumbbells and vice versa, and that the Fe atoms are partially substituted by Al or Ga atoms.^[2,3,4] The resolution of the data and limitations of the conventional structure determination technique, however, did not allow other structural details to be well characterized, such as stacking faults and possible compositional inhomogeneities along [001]. Consequently, the purpose of the present work was to characterize the structure of gallium crystals by means of a high-resolution synchrotron diffraction measurements with a newly developed computer program that allows several structures to be refined on one single crystal data set.^[7] It will be shown that a crystal of a Yb-Fe-Ga alloy is made up by polytypes **1** and **2**, whose alternation within a crystal is caused by a large concentration of stacking faults. Interestingly, **1** and **2** differ in chemical composition.

Results and Discussion

Our X-ray study of single crystals extracted from an arc-melted Yb-Fe-Ga alloy showed that all the diffraction intensities can be indexed in a common supercell for **1** and **2** with a cell geometry $a_s = a(\mathbf{1}) = a(\mathbf{2})$ and $c_s = 3c(\mathbf{1}) = 2c(\mathbf{2})$. Numerous systematic absences cannot be attributed to any individual space group. The diffraction pattern, which was measured for one of the crystals with an image plate detector and synchrotron radiation, was modeled by superposing **1** and **2** within the approximation of an intergrown crystal that has three sorts of domains (Figure 2): one hexagonal (**1**) and two rhombohedral (**2a** and **2b**), the last two twinned by reticular merohedry. Structure refinement was performed by a newly developed program that allows several structures

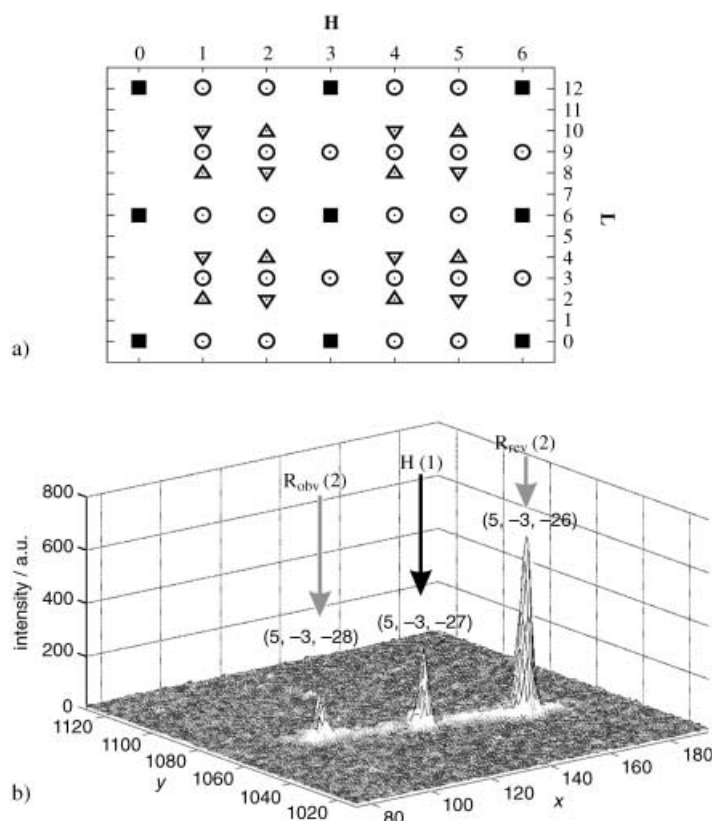


Figure 2. X-ray diffraction pattern of reciprocal space for the crystal extracted from Yb₁₂Fe₆₄Ga₂₄ alloy: a) schematic drawing illustrating an *h0l* section with reflections arising from hexagonal domains **1** (○) and rhombohedral domains **2** in obverse (△) and reverse (▼) settings, overlapped reflections from all three domains are marked by squares; b) the superstructure reflections originating from three types of domains are riding on lines of diffuse scattering, extended along the *c** direction. Indices correspond to the common supercell.

to be refined on a single data set. A good agreement confirms the validity of our approximation with a superposition of independent Bragg scattering crystals. For more details see the Experimental Section. We will not discuss below the crystal chemistry of the phases **1** and **2**, referring to the literature instead,^[2,3,4] but will focus attention on the intergrowth of polytypic structures and on unequal distribution of chemical substitutions in these solid solution phases.

We found that the hexagonal and rhombohedral domains differ not only in their stacking sequences, but also in chemical composition: the Yb-normalized refined chemical composition of the domains is Yb_{1,000(8)}Fe_{9,751(14)} for **1** and Yb_{1,000(6)}Fe_{8,913(7)}Ga_{0,217(6)} for **2**. Thus, there is complete segregation of gallium, which is exclusively present in **2**. Moreover, **1** shows a higher rate of Yb substitution by Fe₂ dumbbells: 21.3% for **1** in comparison with 11.3% for **2**. These preferred substitutions are entirely in accord with observations made for Yb-Fe-Al alloys with hexagonal and rhombohedral structures.^[3] Thus, the present hybrid crystal represents a two-phase region of the ternary phase diagram, with cell parameters of both structures being mutually constrained as a result of nanoscale coherent twinning. We emphasize that no splitting was observed for reflections common to both types of domains.

It is known, that for the individual hexagonal or rhombohedral polytypes of 2:17 alloys, partial substitution of rare-earth atoms by Fe₂ dumbbells, as well as of iron atoms by Al, Si, or Ga, lead to changes of cell dimensions and in particular the c_s/a_s ratio,^[3,8] for example, for Yb-Fe-Al alloys c_s/a_s changes from 2.95–2.96 for hexagonal to 2.90–2.92 for rhombohedral structures.^[2,3] The different degree of chemical substitutions observed in intergrown **1** and **2** of the title alloy may compensate the inherent mismatch of basal plane dimensions of the MDO polytypes. Apparently, cell parameter constraints and chemical substitutions in the Yb-Fe-Ga syntaxy are interdependent.

For inorganic structures, owing to the fact that their structural fragments are often related, coherent twinning and intergrowth are much more frequently observed than incoherently intergrown domains. Nevertheless, for the overwhelming majority of intergrown structures, their cell parameters are not constrained and only a limited number of reflections overlap exactly (see an example in reference [9]). Unfortunately, even in these cases, the results of the single-crystal X-ray structure determination are still of limited quality, because partially overlapping reflections of different domains are typically excluded.^[10] In our case the highest diffraction intensity is observed for “common” reflections, therefore separate refinements on incomplete data sets would not be helpful.

While the single-crystal X-ray diffraction ensures high structural resolution at the atomic level, the main advantage of the high-resolution X-ray powder diffraction is in well-resolved intensity profiles. These are used to extract information about the stacking order in layered structures. X-ray powder diffraction profiles of other examples of 2:17 alloys have been recently analyzed by Estevez-Rams et al., who applied a newly developed formalism based on the correlation distribution function.^[11] The distribution of probabilities of finding two layers a number of layers apart with no lateral displacement between them was extracted. This is, at most, the information on stacking order which can be obtained from a powder diffraction pattern. The results were interpreted in terms of two main types of stacking faults: *growth faults* that change the stacking order and *deformation faults* that are essentially “jumps” in the otherwise perfect stacking sequence. By using this approach, only deformation faults were found in an Y₂Co₁₇ alloy with a 3R host structure,^[12] but for another alloy, Gd₂Co₁₇, the probability distribution could not be described by *random* faults of both types (growth and deformation faults).^[11] We suggest that this distribution (see Figure 11 in reference [11]) is an indication for the occurrence of two clustered MDO polytypes with domain size about 20 interlayer distances, similar to those we have found for the title Yb-Fe-Ga alloy. Indeed, transformations from one small-period polytype into another can be described by nonrandom stacking faults, as was recently simulated using Monte Carlo algorithm for diffraction intensity profiles of close-packed structures.^[13] These recent findings support our observation of the nanoscale phase segregation in 2:17 alloys.

A different strategy was used to describe one-dimensional disorder for layered NbS₂, modeling the variations of the in-

tensity profiles.^[14] A good fit between modeled and experimental powder patterns was obtained assuming 15% uncorrelated stacking fault probability in the 2H host structure. However, this approach is inappropriate for the case of transformation between two ordered stacking sequences. More advanced simulation of powder diffraction patterns using a DIFFaX program can accommodate long-range stacking correlations as well.^[15] For instance, a layered oxide structure was well described by intergrowth of slightly stacking faulted T2 and ordered O2 polytypes.^[16] High-resolution transmission electron microscopy has also been used to find how different polytypes are structured, revealing sometimes sharp transition from one polytype to another, which establishes a lamellar nanostructure.^[17]

Our observation of lines of diffuse scattering for the Yb-Fe-Ga crystal (Figure 2b) shows that the chemical and structural heterogeneities actually occur on a nanometer scale: no diffuse intensity would have been observed along c^* if the domains had been macroscopically large and twin boundaries sparse. We estimate that the average domain size along the stacking direction is at the level of a few tens of unit cell dimensions. The fact that no structured diffuse scattering is observed in the a^*b^* planes indicates that in-layer local ordering is absent, at least at the detection level of our experiment, that is, no clustering of the substituting atoms is observed.

Besides the nanoscale of the coherent twinning, the chemical heterogeneity of the twinned domains is yet more interesting. According to our knowledge, this is the first example of two chemically distinct polytypes, making up a single crystal, that have been refined on a single set of diffraction data. Recently a joint structure refinement of two coherently intergrown stoichiometric phases was reported,^[18] with all diffraction intensities, including those overlapped within instrumental resolution, taken into account. In spite of the formal resemblance to our subject it is essentially an ordinary macroscopic intergrowth of two individual phases, which obviously does not infer a similar mechanism of the phase separation as in a stacking faulted layered crystal. The latter is most properly termed “syntactic coalescence” or “syntaxy”, which is a mutual orientation of two crystals of different species (in general), with three-dimensional lattice control (cell in common), that usually results in their intergrowth.^[19] This term is also used for the case of intergrown polytypic structures.^[20] For the oriented association of two or more polytypes of the *same compound* the term “alloy-twin” was recently introduced.^[21] Some authors prefer the less specific expression “agglutination of crystals”, which does not imply a particular mechanism.^[22]

We believe that the phenomenon discovered for Yb-Fe-Ga is general for similar systems. Coalescence of polytype structures may happen even in a more complex way, along with in-domain stacking disorder and local order of substitution in the plane of layers. This is well illustrated by the reciprocal space sections (Figure 3, reconstructed from our recent X-ray diffraction data collected on Stoe IPDS, Mo_{K α}) of a crystal selected from an aluminum-substituted alloy of nominal composition Yb₁₂Fe₆₅Al₂₃. Similarly to the gallium derivative, the $h0l$ reflections from the rhombohedral do-

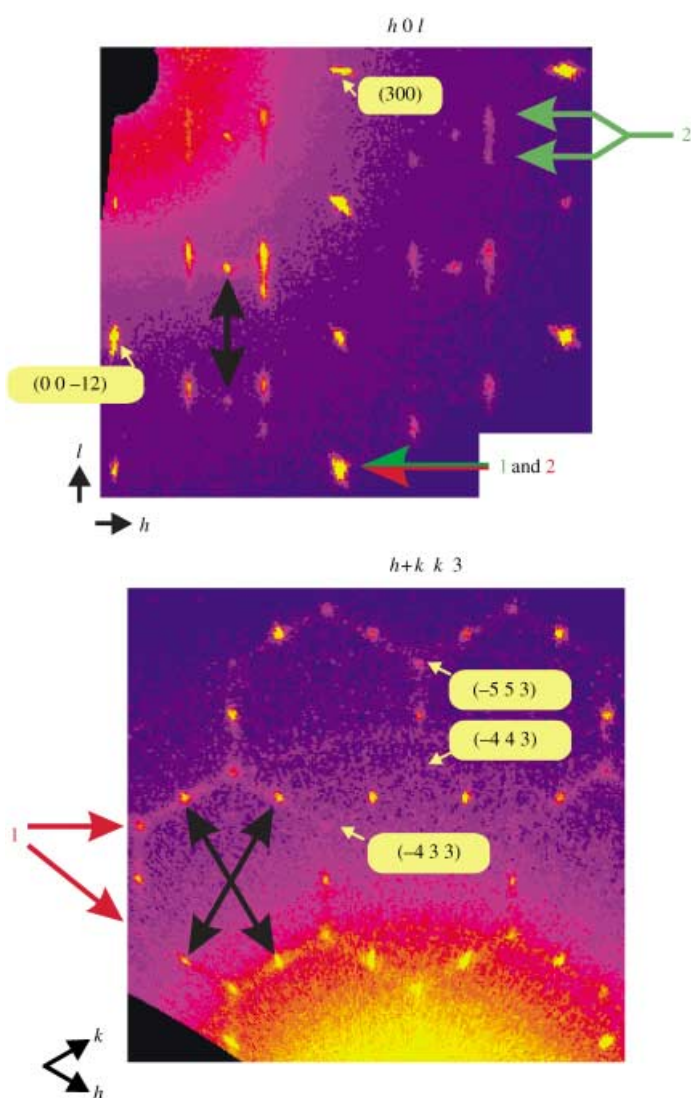


Figure 3. Reciprocal space sections for a crystal extracted from the $\text{Yb}_{12}\text{Fe}_{65}\text{Al}_{23}$ alloy. Red and green arrows indicate reflections from hexagonal and rhombohedral domains, respectively. Black arrows point to the new group of intensities, diffuse in the a^*b^* plane. Indices correspond to the common supercell.

mainly are broadened along c^* , indicating frequent deformation faults.^[14] A second group of diffuse intensities (marked by black arrows on Figure 3) appears along a^*b^* , assuming partial ordering of Yb atom/ Fe_2 dumbbells in the ab plane.

The present study is not the first to establish nanoscale phase coexistence, but it is the first to do so using structure refinement against single-crystal diffraction data.^[23] One interesting example of how complicated the solid state can be is that of the PHTP inclusion compounds, for which it was recently shown that a single-crystalline specimen is chemically inhomogeneous in three dimensions by qualitative analysis of Bragg and diffuse scattering.^[24] Phase separation on both microscopic (0.5–2 nm) and mesoscopic (5–20 nm) scales has been shown to be of great importance in the transition-metal oxides, which encompass high T_c superconductors and colossal magnetoresistance materials (for a recent review see reference [25]). However, these phase-separated

systems do not show syntaxy, and the structures of the individual components have been established by powder diffraction. The importance to understand this phenomenon and general utility of approaches like the one put forth in the present paper is evident.

Experimental Section

The alloy was obtained by arc-melting ingots of the constituting elements of at least 99.9 wt % purity under an argon atmosphere at the nominal composition $\text{Yb}_{12}\text{Fe}_{64}\text{Ga}_{24}$. A preliminary study of three single crystals on a Stoe IPDS diffractometer ($\text{MoK}\alpha$ radiation) showed that they were all equally representative of the bulk alloy they were extracted from, indicating that the phase is macroscopically homogeneous. Synchrotron X-ray diffraction data were measured at the Swiss–Norwegian Beam Line at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The data were collected on the smallest crystal ($\sim 7 \times 72 \times 120 \mu\text{m}^3$) at room temperature by using a MAR345 imaging plate with an effective 240 mm diameter at a crystal-to-detector distance of 130 mm, $\lambda = 0.55091 \text{ \AA}$. A total of 90 images were collected with a 5 s exposure time and a 2° oscillation range per image. The resulting diffraction pattern was indexed^[26] in a hexagonal supercell, $a_s = 8.5965(5)$ and $c_s = 25.1612(15) \text{ \AA}$, based on 3284 reflection positions. Data reduction was performed in the supercell assuming a common subgroup $P\bar{3}$. The reflections were integrated with DENZO and scaled with SCALEPACK to correct for the decay of the incoming synchrotron intensity and absorption anisotropy.^[27] The internal agreement, $R_{\text{int}} = 0.076$, was satisfactory, considering the presence of weak superstructure peaks and diffuse scattering. Considering the small crystal size and short wavelength used no absorption correction was performed. The hexagonal superstructure peaks were nearly five times weaker than the rhombohedral ones.

The diffraction images showed peculiar systematic absences, not attributable to any of the space groups. However, all Bragg peaks could be described by the overlapping of three lattices: one hexagonal, corresponding to **1**, and two rhombohedral lattices, twinned by reticular merohedry, that correspond to **2** (Figure 2a). The superstructure reflections originating from each type of domains ride on lines of diffuse intensity (Figure 2b).

Structure refinement was performed by a newly developed computer program.^[7] We assume that the observed diffraction pattern was the superposition of independent Bragg scattering crystals; interference between the domains was neglected. The background and an example of refinement of a few MDO structures, constituting a hybrid crystal (HgI_2), are described in reference [28]. The rhombohedral twinning was included by an additional scale factor; the structural parameters for obverse and reverse rhombohedral domains were constrained to be equal. In total 43 parameters were refined, 18 structural parameters for **1** and 22 for **2**. Three unconstrained volume fractions of the contributing domains refined to 0.183(2) for **1** and to 0.409(4) for each type of rhombohedral domains. Only Yb sites with complete or dominating Yb occupancy were refined anisotropically; all other atoms were modeled with isotropic displacement parameters. Scattering factors were taken from reference [29], while the anomalous dispersion coefficients were calculated for the wavelength of the experiment using the WWW resource.^[30] R_1 for the individual structures converged to reasonable values of 0.0891 for **1** and of 0.0677 and 0.0670 for the two rhombohedral domains. For all data $R_1 [I \geq 3\sigma(I)] = 0.0799$ (0.0684), wR_2 (all data) = 0.1982 for 1166 reflections, $\text{Goof}(\text{all}) = 1.0793$. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666, e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-412935 and CSD-412936.

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- [1] a) K. Kumar, *J. Appl. Phys.* **1988**, *63*, R13–R57; b) D. Goll, H. Kronmüller, *Naturwissenschaften* **2000**, *87*, 423–438, and references therein.
- [2] O. Bodak, Ya. Tokaychuk, M. Manyako, V. Pacheco, R. Černý, K. Yvon, *J. Alloys Compd.* **2003**, *354*, L10–L15.
- [3] R. Černý, V. Pacheco, T. Yanson, M. Manyako, O. Bodak, *Z. Kristallogr.* **2003**, *218*, 802–810.
- [4] V. Pacheco, Ph.D. Thesis no. 3147, University of Geneva (Switzerland), **2000**.
- [5] *International Tables for Crystallography, Vol. E. Subperiodic groups* (Eds.: V. Kopsky and D. B. Litvin), Kluwer Academic, Dordrecht, **2002**.
- [6] K. Dornberger-Schiff, *Acta Crystallogr. Sect. A* **1982**, *38*, 483–491.
- [7] H. Birkedal, M. Hostettler, W. Paciorek, D. Schwarzenbach, *Bull. Czech Slovak Crystallogr. Assoc.* **1998**, *5*, 200.
- [8] A. Teresiak, M. Kubis, N. Mattern, K.-H. Müller, B. Wolf, *J. Alloys Compd.* **2001**, *319*, 168–173.
- [9] M. Hostettler, D. Schwarzenbach, *Acta Crystallogr. Sect. B* **2002**, *58*, 914–920.
- [10] O. Oeckler, J. Bauer, V. Duppel, H. Mattausch, A. Simon, *Acta Crystallogr. Sect. B* **2002**, *58*, 161–167.
- [11] E. Estevez-Rams, J. Martinez, A. Penton-Madriral, R. Lora-Serrano, *Phys. Rev. B* **2001**, *63*, 54109–54118.
- [12] E. Estevez-Rams, A. Penton-Madriral, R. Lora-Serrano, J. Martinez-Garcia, *J. Appl. Crystallogr.* **2001**, *34*, 730–736.
- [13] J. B. Gosk, *Cryst. Res. Technol.* **2001**, *36*, 197–213.
- [14] H. Katzke, *Z. Kristallogr.* **2002**, *217*, 127–130.
- [15] M. M. J. Treacy, J. M. Newsam, M. W. Deem, *Proc. R. Soc. London Ser. A* **1991**, *433*, 499–520.
- [16] Z. Lu, J. R. Dahn, *Chem. Mater.* **2001**, *13*, 2078–2083.
- [17] a) Y. Lifshitz, X. F. Duan, N. G. Shang, Q. Li, L. Wan, I. Bello, S. T. Lee, *Nature* **2001**, *412*, 404; b) T. L. Daulton, T. J. Bernatowicz, R. S. Lewis, S. Messenger, F. J. Stadermann, S. Amari, *Science* **2002**, *296*, 1852–1855; c) L. Kienle, V. Duppel, A. Simon, M. Schlosser, O. Jarchow, *J. Solid State Chem.* **2004**, *177*, 6–16.
- [18] K. Friese, A. Hönnerscheid, M. Jensen, *Z. Kristallogr.* **2003**, *218*, 536–541.
- [19] S. W. Bailey, V. A. Frank-Kamenetskii, S. Goldsztaub, A. Kato, A. Pabst, H. Schulz, H. F. W. Taylor, M. Fleischer, A. J. C. Wilson, *Can. Mineral.* **1978**, *16*, 113–117.
- [20] C. N. R. Rao, *Acc. Chem. Res.* **1984**, *17*, 83–89.
- [21] M. Nespolo, T. Kogure, G. Ferraris, *Z. Kristallogr.* **1999**, *214*, 1–4.
- [22] F. H. Herbststein, *Acta Crystallogr. Sect. B* **2003**, *59*, 303–304.
- [23] Y. Filinchuk, H. Birkedal, R. Černý, M. Hostettler, O. Bodak, K. Yvon, Proc. XIX IUCr. Congress, Geneva **2002**; [*Acta Crystallogr. Sect. A* **2002**, *58* (Suppl.), C270].
- [24] a) T. Weber, M. A. Esterman, H.-B. Bürgi, *Acta Crystallogr. Sect. B* **2001**, *57*, 579–590; b) T. Weber, H.-B. Bürgi, *Acta Crystallogr. Sect. A* **2002**, *58*, 526–540; c) S. Kluge, F. Budde, I. Dohnke, P. Rechsteiner, J. Hulliger, *Appl. Phys. Lett.* **2002**, *81*, 247–249, and references therein.
- [25] C. N. R. Rao, P. V. Vanitha, A. K. Cheetham, *Chem. Eur. J.* **2003**, *9*, 829–836.
- [26] CrysAlis software, Oxford Diffraction, **2000**.
- [27] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.
- [28] M. Hostettler, H. Birkedal, D. Schwarzenbach, *Acta Crystallogr. Sect. B* **2002**, *58*, 903–913.
- [29] *International Tables of Crystallography, Vol. C*, IUCr & Kluwer, Dordrecht, **1992**.
- [30] http://www-cxro.lbl.gov/optical_constants/pert_form.html, which uses the tables by B. L. Henke, E. M. Gullikson, J. C. Davis, *At. Data Nucl. Data Tables* **1993**, *54*, 181–342.

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