

**STRUCTURAL HETEROGENEITY IN TWINNED Yb<sub>2-x</sub>(Fe,Ga)<sub>17+2x</sub> POLYTYPES**

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Yb<sub>2</sub>Fe<sub>17</sub> substitution derivatives, with Yb and Fe atoms partially substituted by Fe<sub>2</sub> dumbbells and Ga atoms respectively, are ferromagnetic compounds. According to previous work they crystallize with the hexagonal LuFe<sub>9.5</sub> type (I, *P6<sub>3</sub>/mmc*) and/or rhombohedral PrFe<sub>7</sub> type (II, *R-3m*) structure and can be considered as polytypes with maximum degree of order with cell parameter relationships a(I) = a(II) and 3c(I) = 2c(II). In this work we show that both polytypes can occur within the same crystal. The gallium compound was prepared by arc-melting at the nominal composition Yb<sub>12</sub>Fe<sub>64</sub>Ga<sub>24</sub>. Crystals of the cast sample showed non-space group absences and cell metrics a(I) = a(II) = 8.615 Å and 3c(I) = 2c(II) = 25.215 Å. Diffraction patterns were measured (image plate detector, synchrotron radiation) and modelled by superposing I and II within the approximation of a conglomerate-crystal having three sorts of domains: one hexagonal (I) and two rhombohedral (IIa and IIb), twinned by reticular merohedry. Weak diffuse intensity (neglected) indicates a sparsity of stacking faults. Structure refinement was performed by a newly developed program that allows to refine several structures on a single data set. In total 41 parameters were refined to R1 = 0.076 for 1166 unique reflections. The three domains exhibit almost equal volume fractions. I and II display different structure features: I showed a higher rate of Yb substitution by Fe<sub>2</sub> dumbbells, and II showed partial substitution of Fe by Ga. The aluminium compound (Yb<sub>12</sub>Fe<sub>65</sub>Al<sub>23</sub>) revealed the same structural features but showed extra scattering, diffuse in the basal plane and along the c-axis. It suggests short-range order in basal plane and stacking faults, respectively.

**Keywords:** POLYTYPES TWINNING CONGLOMERATE CRYSTAL

**THE OPTIMISATION OF THE GEOMETRY OF THE OCTAEDRAL COMPLEX OF L-ASCORBIC ACID AND METAL IONS(II) USING SEMI-EMPIRICAL CNDO CALCULATION WITH MINIMISATION BASED ON POLAK-RIBIERIA CONJUGATE GRADIENT METHOD**

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Vitamin C is one of the most common natural or artificially enriched ingredients in foods and beverages. E.L. Hirst, P. Karrer, A. Szent-Gyoryi, F. Michel and K. Kraft determined the structure of L-ascorbic acid. The structural formula first reported in 1933 by Hirst was generally accepted. In 1934, T. Reichstein and A. Grussner published a method of synthesis, which is still used, for the technical production of vitamin C. The biological synthesis of L-ascorbic acid 2-phosphate have been described by G. Mouro in 1980 and the structure has been analyzed by X-ray scattering. After its isolation and synthesis, its physical, chemical and biological characteristics were examined by various researches in more detail, when among others, its acidic behavior, reducing character and its role in biological oxidations have been elucidated. In the literature of last 10 years many studies have been published on the toxic effect of bivalent metals on living organisms. In practice, intoxication with some metal ions(II), such as mercury, lead and cadmium is most often encountered. Despite the common use of vitamin C in the detoxification, neither the exact mechanism of its reactions with metal ions(II), nor equilibrium reactions in the Me(II)-Hasc-HO system has not yet been fully explained. Since the question concerning the interaction between these two reactions still remains open. The aim of this presentation is to present the optimization of the geometry of the complex of L-ascorbic acid and metal ion(II). The calculation was made by the Polak-Ribiere`a method. This is a conjugate gradient method using one-dimensional searches. It improves the Fletcher-Reeves method by taking into consideration also the previous conjugate direction.

**Keywords:** VITAMIN C, METALS(II), COMPLEX

**A SINGLE CRYSTAL X-RAY AND HRTEM STUDY OF A NEW SERIES OF INTERMETALLIC COMPOUNDS D<sub>y</sub>Cu<sub>x</sub> (x = 4.5, 4 AND 3.5)**

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A new series of intermetallic compounds having monoclinic symmetry is presented. Their crystal structures can be described by a stacking of structural blocks of composition AB<sub>5</sub> (cubic AuBe<sub>5</sub> type, space group *F-43m*, a around 7 Å) and AB<sub>2</sub> (cubic MgCu<sub>2</sub> type, space group *Fd3m*, a around 7 Å) along various directions. The stacking sequence AB<sub>2</sub> + nAB<sub>5</sub> leads to the compositions A<sub>2</sub>B<sub>7</sub> (n=1) AB<sub>4</sub> (n=2), A<sub>4</sub>B<sub>17</sub> (n=3), A<sub>3</sub>B<sub>22</sub> (n=4), A<sub>6</sub>B<sub>27</sub> (n=5), ... , AB<sub>5</sub> (n=infinite). The monoclinic structure series is reminiscent of the monoclinic/hexagonal/ trigonal/orthorhombic structure series A<sup>n+1</sup>B<sup>n+2</sup> which has been described [1] by a stacking of structural blocks of composition AB<sub>5</sub> (hexagonal CaCu<sub>5</sub> type) and A<sub>2</sub>B<sub>7</sub> (AB<sub>2</sub> + AB<sub>5</sub>) with stacking A<sub>2</sub>B<sub>7</sub> + (n-1)AB<sub>5</sub> along one direction. The superstructure of the present monoclinic series can be derived by introducing planar defects parallel to {hhh} of the cubic subcell, thus leading to nearly orthogonal supercells of multiplicity around (n+2) x (n+2) x (n+2-0.5). The planar defects are of two types: anti-phase boundaries and shear planes. The structures can therefore also be rationalized in terms of an ordered arrangement of twinned micro-domains, the twinning operation being a 2-fold rotation axis about the [110] direction of the cubic subcell. The combination of single crystal X-ray diffraction and high-resolution electron microscopy (HRTEM) was essential to characterize the crystal structures of this series. The first known member was ytterbium based YbCu<sub>4.5</sub> [2] (n=5) and the second one dysprosium based D<sub>y</sub>Cu<sub>3.5</sub> [3] (n=1). Here we report on other members of the dysprosium series, i.e. D<sub>y</sub>Cu<sub>4</sub> (n=2) and D<sub>y</sub>Cu<sub>4.5</sub> (n=5), and on a building principle that allows to predict structural analogues with other rare-earth elements (RE) such as RECu<sub>4.25</sub> (n=3) and RECu<sub>4.4</sub> (n=4), RE=Dy, Yb. Shearing and/or twinning of structural blocks are a quite common building principle in inorganic crystal structures. In the present series, however, it appears for the first time on non co-planar crystallographic planes.

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**Keywords: INTERMETALLIC COMPOUND SHEAR PLANE STRUCTURE SERIE**

Acta Cryst. (2002). A58 (Supplement), C270

**STRUCTURAL STUDIES OF A NOVEL LOW-LIGHT LH2 COMPLEX**

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In photosynthetic bacteria, solar energy is trapped by the bacteriochlorophylls and carotenoids of the light-harvesting system. It is the bacteriochlorophyll Qy transition dipole moments in the NIR that are involved in energy transfer between complexes. LH2 complexes are more numerous and varied in spectral type than LH1 complexes, and in some purple bacteria, different LH2 complexes are expressed under different conditions of light and temperature. A novel low-light LH2 complex has been isolated from *Rps. palustris*. Earlier work had identified a B800-850 complex with a heterogeneous peptide composition and reduced absorption at 850 nm. The work presented shows the B850 nm absorption to be contamination from a high-light B800-850 complex and that the true LL complex is a novel B800 complex composed of eight αβU<sub>4</sub> peptide pairs that exhibit unique absorption and circular dichroism near infrared spectra. Biochemical analysis shows there are 4 bacteriochlorophyll molecules per αβ peptide pair rather than 3. The electron density of the B800 complex at 7.5 Å shows it to be an octamer with 8-fold rotational symmetry. A number of bacteriochlorophyll geometries have been investigated by simulation of the CD and absorption spectra and compared with the electron density. Modeling of the spectra based on the B800-850 structure of *Rps. Acidophila* suggests that the B850 bacteriochlorophylls in LL B800 complex may be arranged radially rather than the more usual tangential arrangement found in B800-850 LH2 complexes. We now wish to confirm the model with a high-resolution structure and perform detailed spectroscopic measurements of this novel complex.

**Keywords:** LIGHT HARVESTING COMPLEX LOW LIGHT B800