

Rare-Earth Metal Chains in the Crystal Structures of Dicarboferrates

Bambar Davaasuren, Horst Borrmann, Enkhtsetseg Dashjav, Guido Kreiner, Walter Schnelle, Frank R. Wagner, and Rüdiger Kniep

The family of ternary carbides can be divided into two groups: carbometalates and metal-rich carbides. Carbometalates contain complex anions $[T_yC_z]^{n-}$ with monoatomic C^{4-} species covalently attached to transition metals. Coordination numbers and oxidation states of the transition metals in carbometalates are low. The compounds are electron precise, i.e., an ionic charge assignment is possible and no perceptible homogeneity ranges are observed. Metal-rich carbides represent alloy type phases, which are best described as interstitial carbides. Due to strong metal-metal interactions, partial structures cannot be clearly distinguished. Recently, we have studied novel rare-earth iron carbides. The crystal structures of $RE_{15}[Fe_6C(C_2)_6(Fe(C_2)_3)_2]$ with $RE = Y, Dy, Ho, Er$ [1] and $RE_{5,64}[FeC(C_2)_2(Fe(C_2)_2)]$ with $RE = Y, Gd, Tb, Dy$ [2] contain complex anions with small coordination numbers and low oxidation states of the iron atoms. The structural motifs resemble those in carbometalates, however the complex anions contain diatomic C_2 units besides monoatomic C species. Therefore, these compounds are not carbometalates in a strict sense (monoatomic ligands). $La_{3,67}[Fe(C_2)_3]$ is an example exclusively containing C_2 units as ligands [3]. An interesting feature of this class of compounds is the presence of noticeable $RE-RE$ interactions leading to the formation of superstructures or incommensurately modulated structures. Here, we report on structural ordering of RE atoms in the crystal structures of $La_{3,67}[Fe(C_2)_3]$ and $RE_{5,64}[FeC(C_2)_2(Fe(C_2)_2)]$. In addition, we discuss the possibility to extend the concept of carbometalates containing monoatomic ligands towards compounds containing C_2 units.

The RE -compounds were synthesized by arc-melting of cold-pressed pellets of mixtures of the elements. Heat treatment of the samples was performed in arc-welded Ta crucibles fused in silica ampoules. For characterization, XRD techniques, metallographic examinations in combination with EDXS, and measurements of the electrical resistivity and magnetic susceptibility were used. The

chemical bonding was analyzed by the COHP method based on LMTO-ASA calculations, and the phase stabilities were investigated by total energy calculations using the PAW method.

Complex Anions in Ternary RE -Iron-Carbides Containing C_2 Units

The crystal structures of $RE_{5,64}[FeC(C_2)_2(Fe(C_2)_2)]$ ($RE = Y, Gd, Tb$ and Dy), $La_{3,67}[Fe(C_2)_3]$ and $RE_{15}[Fe_6C(C_2)_6(Fe(C_2)_3)_2]$ ($RE = Y, Dy, Ho, Er$) contain trigonal planar groups with Fe centers coordinated by three carbon ligands (Fig. 1). A similar structural motif with nitrogen ligands is present in the crystal structure of the nitridoferrate(III), $Ba_3[FeN_3]$ [4]. Trigonal planar units are the only structural entities of the anionic partial structure of $La_{3,67}[Fe(C_2)_3]$, whereas $RE_{5,64}[FeC(C_2)_2(Fe(C_2)_2)]$ in addition contains linear chains of edge-sharing tetrahedra as shown in Figure 1. An analogous polyanion, $[FeN_{4/2}]$, is present in the crystal structure of the nitridoferrate(III), $Li_3[FeN_2]$ [5].

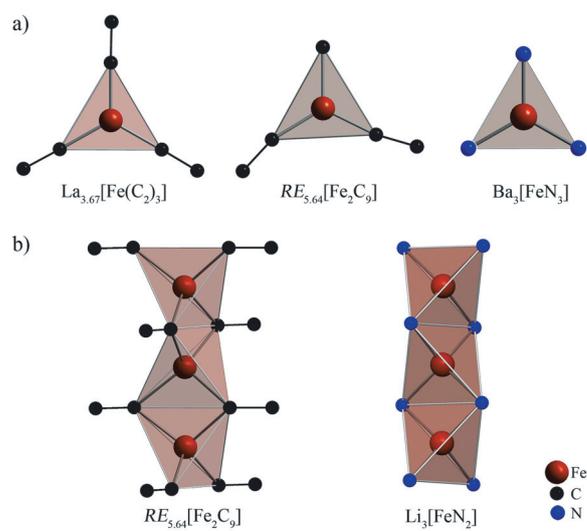


Fig. 1: Complex anions in ternary $RE-Fe-C$ -compounds and nitridometalates.

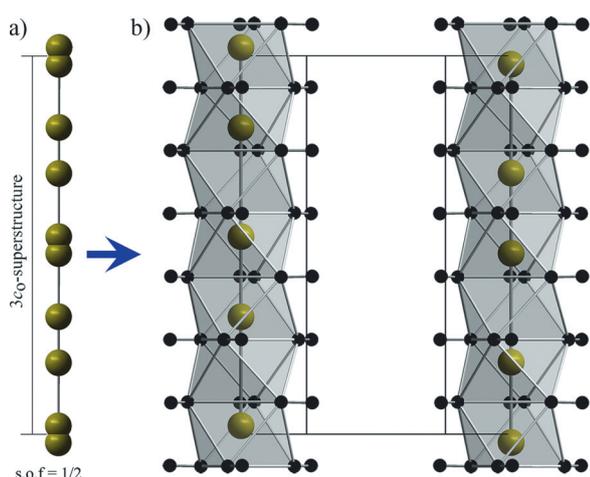


Fig. 2: La chains in the crystal structure of $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$ enclosed within the channels formed by face-sharing $(\text{C}_2)_6$ octahedra. a) Split atom model of La chains within the superstructure; b) shown as ordered chains running antiparallel, within neighbor-channels.

RE-filled Channels of $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$ and $\text{RE}_{5.64}[\text{FeC}(\text{C}_2)_2(\text{Fe}(\text{C}_2)_2)]$

The crystal structures of $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$ and $\text{RE}_{5.64}[\text{FeC}(\text{C}_2)_2(\text{Fe}(\text{C}_2)_2)]$ both contain 1D channels, which are occupied by RE atoms. In case of $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$ the trigonal-planar groups are surrounded by tricapped trigonal prisms of La atoms. These prisms are connected via common triangular faces forming a host framework of the chemical composition $\{\text{La}_x[\text{Fe}(\text{C}_2)_3]\}$, with the channels created via face sharing of octahedra formed by C_2 units as shown in Figure 2. The remaining La

atoms occupy the channels in such a way that a threefold superstructure with respect to the host structure is formed along $[001]$. The total number of guest La atoms per supercell is four. Two different La positions as part of the ordered chains relative to the host structure are possible; both with equal probability, resulting in two partially occupied crystallographic La sites, each of 50% probability. Figure 2 shows the arrangement of La atoms within the channels in more detail. The La atoms forming the chains are characterized by alternating short and long La–La distances. However, due to merely weak interactions between the chains – the interchain distance of 879 pm is quite large – correlations between the chains are lost. The chemical composition $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$ corresponds to the maximum La content of the ternary phase. The phase stability as a function of the La content was studied using first principles total energy calculations, which were performed using the VASP code [6, 7] with generalized gradient approximation for the ordered structural models $\text{La}_{3.33}[\text{Fe}(\text{C}_2)_3]$, $\text{La}_{3.5}[\text{Fe}(\text{C}_2)_3]$, and $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$. The results of the calculations show that the energy differences between the crystal structures with differently ordered chains are less than 20 meV/atom. $\text{La}_{3.5}[\text{Fe}(\text{C}_2)_3]$ and $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$ are both stable at 0 K while $\text{La}_{3.33}[\text{Fe}(\text{C}_2)_3]$ is unstable. This branching up at 0 K supports a small homogeneity range for $\text{La}_x\{\text{La}_3[\text{Fe}(\text{C}_2)_3]\}$ with $0.5 < x < 0.67$ at higher temperatures. Experimental evidence for the homogeneity range is given by the crystal structure determination of $\text{La}_{3.64}[\text{Fe}(\text{C}_2)_3]$ [8].

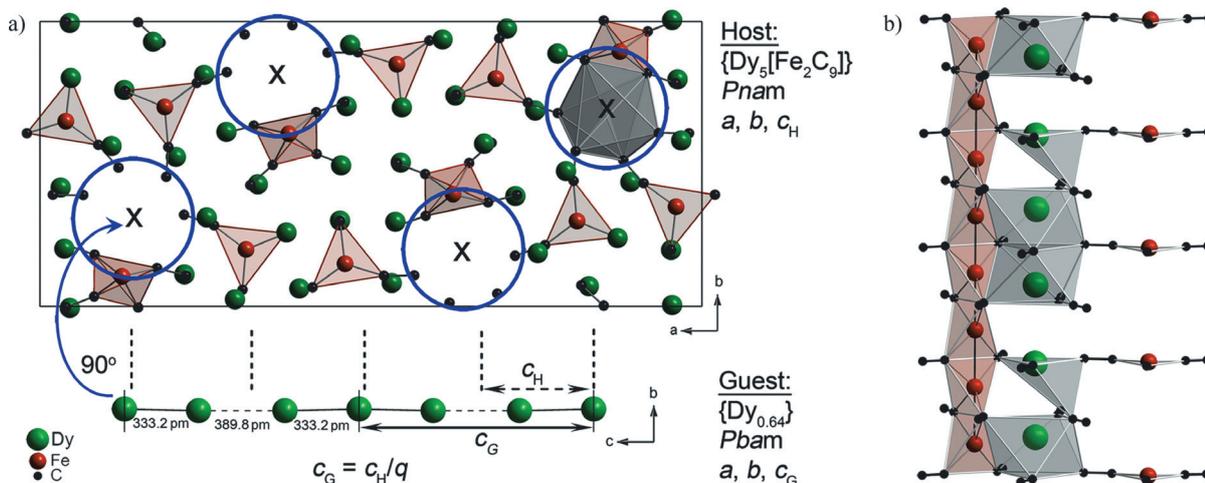


Fig. 3: a) Substructures (host-guest-assembly) in the crystal structure of $\text{Dy}_{5.64}[\text{FeC}(\text{C}_2)_2(\text{Fe}(\text{C}_2)_2)]$. b) Dy-chains of the modulated composite structure located within channels formed by polyanionic tetrahedral strings and trigonal planar groups.

In case of $RE_{5.64}[\text{FeC}(\text{C}_2)_2(\text{Fe}(\text{C}_2)_2)]$, the filling of channels by *RE* guest atoms leads to a modulated structure, which is best described as a composite consisting of two substructures with mismatch of host and guest lattices along [001]. The average crystal structure and the complex anionic parts have already been described in [2]. In the following, we focus on the ordering of *RE* atoms within the channels, which is exemplarily discussed for the Dy compound.

The two substructures are shown in Figure 3a. The first one, $\{\text{Dy}_5[\text{FeC}(\text{C}_2)_2(\text{Fe}(\text{C}_2)_2)]\}$, represents the host structure containing most of the atoms and forming a framework with empty channels running along [001]. The second substructure, $\{\text{Dy}_{0.64}\}$, is the guest structure, which contains chains of Dy atoms with alternating distances short-short-long (333pm–333pm–390pm) within the channels of the host structure. Figure 3b shows a cut-out of the modulated chain of Dy atoms occupying the channels of the host structure together with one adjacent polyanionic tetrahedral string and trigonal planar groups. The guest Dy atoms are located inside the $(\text{C}_2)_6$ octahedra, however, some of them are pushed in direction of the octahedral faces due to limited space, thereby changing their coordination from octahedral to tetrahedral or even to trigonal planar environment. In the composite, both substructures are modulated due to their mutual interactions. All distances exhibit only small variations, except those between the guest Dy atoms.

Extending the Concept of Carbometalates (C-ligands) to Dicarboligands (C_2 -ligands)

The crystal structures of ternary *RE* iron carbides contain complex anions similar to those observed in nitridoferrates. Such an analogy was one of the motivations to develop the concept of carbometalates. Besides the presence of complex anions, the carbometalate concept introduces further criteria that help to assign particular carbides to the class of carbometalates: (i) covalent bonds within the complex anions; (ii) charge-balanced ionic formulae; (iii) absence of significant homogeneity ranges. The key criterion (i) is fulfilled for the examples discussed here: Fe–C distances indicate strong covalent bonds; inspection of the chemical bonding in $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$ shows that Fe–C covalent bondings are indeed dominating and optimized. Criteria

(ii) and (iii) are not strictly valid, although the oxidation states for iron within the trigonal planar and tetrahedral complex anions in the crystal structures of $\text{La}_{3.67}[\text{Fe}(\text{C}_2)_3]$ [3] and $\text{Er}_2[\text{Fe}(\text{C}_2)_2]$ [9] can be clearly assigned as Fe(I) and Fe(II), respectively. The crystal structure of $RE_{5.64}[\text{FeC}(\text{C}_2)_2(\text{Fe}(\text{C}_2)_2)]$ contains both types of environments of Fe atoms by mixed carbon ligands, monoatomic and diatomic. The average C–C distance in the C_2 units amounts to 135 pm indicating the presence of C_2^{4-} species containing double bonds. Thus, taking into account the two different coordinations of iron atoms, we expect oxidation states close to Fe(I) and Fe(II) for the trigonal-planar and the tetrahedrally coordinated Fe atoms, respectively. A nearly charge balanced ionic formula of the composite may be written as $\{(\text{Dy}^{3+})_{0.64}\} \{(\text{Dy}^{3+})_5[\text{Fe}^{2+}(\text{C}_2^{4-})_{4/2}][\text{C}^{4-}\text{Fe}^{1+}(\text{C}_2^{4-})_2]\}$. Nevertheless, the amount of $\{(\text{Dy}^{3+})_{0.64}\}$ within the channels of the crystal structure does not exactly fit to $\{(\text{Dy}^{3+})_{0.67}\}$ which would be needed for perfect charge balancing.

This kind of “electronic flexibility” may be provided by the C_2 units, which allow variations in ionic charges [10].

We thank Dr. M. Mihalkovič (Institute of Physics, Slovak Academy of Sciences, Slovakia) for VASP calculations.

References

- [1] B. Davaasuren, H. Borrmann, E. Dashjav, G. Kreiner, M. Widom, W. Schnelle, F. R. Wagner, R. Kniep, *Angew. Chem.* **49** (2010) 5688.
- [2] B. Davaasuren, L. Akselrud, E. Dashjav, G. Kreiner, W. Schnelle, R. Kniep, *J. Solid State Chem.* (in preparation).
- [3] B. Davaasuren, E. Dashjav, G. Kreiner, H. Borrmann, R. Kniep, *J. Solid State Chem.* **182** (2009), 1331.
- [4] P. Höhn, R. Kniep, A. Rabenau, *Z. Kristallogr.* **196** (1991) 153.
- [5] A. Gudat, R. Kniep, A. Rabenau, W. Bronger, U. Ruschewitz, *J. Less-Common Met.* **161** (1990) 31.
- [6] G. Kresse, J. Hafner, *Phys. Rev.* **B47** (1993) RC558.
- [7] G. Kresse, J. Furthmüller, *Phys. Rev.* **B54** (1996) 11169.
- [8] A. M. Witte, W. Jeitschko, *Z. Naturforsch.* **51b** (1996) 249.
- [9] M. H. Gerss, W. Jeitschko, L. Boonk, J. Nienstedt, J. Grobe, E. Mörsen, A. Leson, *J. Solid State Chem.* **70** (1987) 19.
- [10] F. R. Wagner, E. Dashjav, B. Davaasuren, G. Kreiner, W. Schnelle, R. Kniep, *Scientific Report 2006-2008*, p. 77 (Max Planck Institute for Chemical Physics of Solids, Dresden, Germany, 2009).