Journal of Solid State Chemistry 190 (2012) 73–79

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

$Dy_{0.64}\{Dy_5[Fe_2C_9]\}$: A complex carbide with a composite structure

Bambar Davaasuren [a], Enkhtsetseg Dashjav [a,*], Rüdiger Kniep [a], Guido Kreiner [a,*], Walter Schnelle [a], Lev Akselrud [b], Sander van Smaalen [c], Alexander Wölfel [c]

[a] Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 0118 Dresden, Germany
[b] Ivan Franko National University of Lviv, Kyrylo & Methody Street 6, 79005 Lviv, Ukraine
[c] Laboratory of Crystallography BGI Building, University of Bayreuth, Universitaetsstrasse 30, D-95440 Bayreuth, Germany

ARTICLE INFO

Article history:
Received 20 September 2011
Received in revised form
5 January 2012
Accepted 6 February 2012
Available online 10 February 2012

Keywords:
Ternary carbides
Rare-earth metals
Transition metals
Crystal structure

ABSTRACT

The ternary carbide $Dy_{5.64}[Fe_2C_9]$ has been prepared by high temperature synthesis from the elements. The compound forms as a composite structure with two partial structures, $\{Dy_5[Fe_2C_9]\}$ and $\{Dy_{0.64}\}$ crystallizing in space groups *Pnam* and *Pbam*, respectively. The lattice parameters $a=2934.63(9)$ pm and $b=1263.63(5)$ pm for the two partial structures are identical, whereas the *c* lattice parameters for $\{Dy_5[Fe_2C_9]\}$ ($c_H=504.14(3)$ pm) and $\{Dy_{0.64}\}$ ($c_G=1056.01(5)$ pm) are different. This gives rise to a modulated structure in the (3+1)D superspace group *Pnam*(00*g*) with $q=c_H/c_G=0.4775$. The refinement converged to *R*(*F*) values below 0.055 for each partial structure using harmonic and Crenel functions. The compound is a bad metallic conductor and represents a new structure type composed of Dy^{3+} species embedded in a matrix of discrete planar $FeC(C_2)_2$ units and edge-sharing $Fe(C_2)_4$ tetrahedra forming infinite chains $Fe(C_2)_{4/2}$ running along the *c* axis.

1. Introduction

Carbometalates are ternary and higher carbides containing complex anions ${}^{m}_{\infty}[(T_yC_z)]^{n-}$. They are mainly characterized by covalent bonds between the transition metals *T* and monoatomic carbo ligands C^{4-}. In addition, they contain highly charged cationic components such as rare-earth metals, follow the general formula $RE_x[T_yC_z]$ with an atomic ratio of $(x+y)/z \leq 2$ and do not form perceptible homogeneity ranges [1]. In the ternary systems containing Fe as the transition element, several compounds have already been reported. Their chemical compositions are consistent with the general formula of carbometalates: $La_{3.67}[Fe(C_2)_3]$ [2,3], $Y_2[Fe(C_2)_2]$ [4], $Sc_3[Fe(C_2)_2]$ [5,6], $Sc[FeC_2]$ [7,8], and $RE_{15}[Fe_8C(C_2)_{12}]$ (*RE*=Y, Er, Ho, Dy) [9]. The crystal structures, however, are determined by C_2 units acting as ligands in the complex anions giving rise to problems concerning charge balancing by applying the chemical concept for carbometalates. For the majority of these ferrates the assumption of the presence of C_2^{4-} ligands leads to conclusive results. The observation of a tiny homogeneity range in case of $La_{3.67}[Fe(C_2)_3]$ [2,3] caused by vacancies within the La-chains occupying positions within the channels of the crystal structure can still be explained by the electronic flexibility of the C_2^{n-} ligand. The situation becomes even more complex in crystal structures containing homoatomic *T*–*T* (here: Fe–Fe) interactions, as observed in the isotypic series $RE_{15}[Fe_8C(C_2)_{12}]$ (*RE*=Y, Er, Ho, Dy) [9]. A successful and conclusive extinction of the carbometalate concept on compounds containing C_2 ligands first of all calls for detailed knowledge and specific characterization of the chemical bonding in the diatomic species involved in the formation of complex anions.

Here, we report on a novel dysprosium iron carbide, $Dy_{5.64}[Fe_2C_9]$, containing two different kinds of complex anions with carbo and dicarbo ligands covalently bonded to the Fe atoms. By use of superspace approach [10] the overall crystal structure is best described as a composite consisting of the partial structures $\{Dy_5[Fe_2C_9]\}$ and $\{Dy_{0.64}\}$. $Dy_{5.64}[Fe_2C_9]$, is a bad metallic conductor. Its magnetic properties are governed by the large localized magnetic moments of Dy^{3+} species.

2. Experimental section

2.1. Preparation and phase analysis

The title compound was prepared by arc-melting of cold-pressed pellets of mixtures of the elements Dy (pieces, Ames, 99.99%), Fe (pieces, Alfa Aesar, 99.99%) and graphitic carbon (powder, Chempur, 99.9%) in the molar ratio of Dy:Fe:C=5.7:2:9. The pellets were encapsulated in weld-sealed Ta ampoules, which in turn were jacketed in fused silica tubes and heat treated in a tube furnace at 1373 K for 14 day. The reaction products were

* Corresponding authors. Fax: +49 351 4646 3002.
E-mail addresses: dashjav@cpfs.mpg.de (E. Dashjav), kreiner@cpfs.mpg.de (G. Kreiner).

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2012.02.008

ground and annealed again. After several cycles of grinding and annealing it was possible to obtain a nearly single phase material. However, small amounts of elemental Fe and a hitherto unknown phase causing some very weak Bragg peaks in the powder diffraction patterns were still present. The reaction products (gray with metallic luster) are sensitive to air and moisture. Therefore, all handlings were carried out in a glove box under Ar atmosphere (MBraun, $p(O_2, H_2O) < 1$ ppm).

Powder X-ray diffraction patterns were taken by use of a Huber-Guinier-camera G670 in the range $10^\circ < 2\theta < 85^\circ$, monochromatic Co$K\alpha_1$ radiation ($\lambda = 178.896(1)$ pm) and a step width of 0.005°. No perceptible homogeneity range was observed from powder X-ray diffraction even by varying the carbon content (± 10 at.%) during the synthesis. EDXS (SEM Philips XL30, standardless ZAF) analysis on the single crystal used for the diffraction experiments resulted in the atomic ratio Dy:Fe = 5.7:2.0.

2.2. Crystal structure determination

Prismatic crystals were separated from the surface of the samples in an Ar filled glove box under liquid paraffin. Specimens with average dimensions of about $20 \times 25 \times 40\ \mu m^3$ were selected, mounted on glass fibers and sealed in Lindemann capillaries of 0.2 mm diameter. Intensity data collection was carried out on an imaging plate diffractometer MAR 345dtb with Mo Kα ($\lambda = 71.069$ pm) radiation at room temperature at the Laboratory of Crystallography, University of Bayreuth. For data reduction including Lorentz-polarization factor correction and numerical absorption correction the program EVAL15 [11] was used. The automatic indexing routine applied to the main reflections revealed an orthorhombic unit cell with $a = 2934.63(9)$ pm, $b = 1263.63(5)$ pm and $c = 504.14(3)$ pm. The X-ray diffraction pattern clearly exhibits satellite reflections up to order of two along c^*, indicating a 1D modulation with $q = 0.4775(1)c^*$. In a first step the average structure was solved using the main reflections only, and by direct methods as implemented in the program package SHELXS97 [12]. The structure was refined in the space group *Pnam* with anisotropic displacement parameters for all atoms down to the residuals $R1 = 0.045$ and $wR2 = 0.086$. All crystallographic sites were fully occupied in this model, except for three sites, which were partially occupied by about 30% Dy. The distances between these sites (smaller than 253 pm) were clearly too short for Dy–Dy contacts. Taking into account the satellite reflections several commensurately and incommensurately modulated structures in suitable superspace groups were checked. Finally, the crystal structure of $Dy_{5.64}[Fe_2C_9]$ was successfully refined as a composite structure using the program WinCSD [13]. Composite structures consist of two or more periodic substructures with separate three dimensional symmetry and mismatch in at least one dimension. Such structures cannot be forced into a single unit cell and the misfit of the lattices gives rise to mutual modulations. The data/parameter ratio using this approach usually improves the numerical stability of refinements compared to refinements involving superstructures with large unit cells [14]. In case of the title compound, the structure is composed of two substructures. One partial structure contains most of the atoms while the second substructure fills channels in the larger one. The larger and smaller substructure are called for convenience in the following discussion "host" and "guest", even though there is no host–guest relationship in the strict sense. Both substructures share the *ab* plane, but have different translational periods along [0 0 1]. Two different sets of lattice parameters and a modulation vector for each substructure are needed to describe the crystal structure. Besides *a* and *b*, we have chosen c_H and c_G to describe the unit cells of the two partial structures, respectively. The corresponding modulation vectors are labeled q_H and q_G. Every reflection in the diffraction pattern can in principle be indexed by the (3+1)D host or guest sublattice, and a four-index notation is needed in either case to index all reflections:

$$\mathbf{H}_H = h_H\mathbf{a}^* + k_H\mathbf{b}^* + l_H\mathbf{c}_H^* + m_H\mathbf{q}_H \quad \text{or}$$

$$\mathbf{H}_G = h_G\mathbf{a}^* + k_G\mathbf{b}^* + l_G\mathbf{c}_G^* + m_G\mathbf{q}_G$$

where

$$\mathbf{q}_H = (c_H/c_G)\mathbf{c}_H^* \quad \text{and} \quad \mathbf{q}_G = (c_G/c_H)\mathbf{c}_G^*.$$

The host structure contains the majority of the atoms of the composite structure. Therefore, the host lattice is primarily used to index the reflections, and the indices of the *H* is omitted in the present work. The (*hk*00) plane is common to both substructures, while (*hkl*0) and (*hk*0*m*) reflections are the main reflections of the host and guest substructures, respectively. A general reflection (*hklm*) represents both, the *m*th order satellite reflection of the reflection (*hkl*0) of the host structure and a satellite reflection of the guest structure with indices given by $\mathbf{H}_G = W^{-1}\,\mathbf{H}_H$ (so-called *W* matrix) [15]:

$$W = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

All reflections in the diffraction pattern of $Dy_{5.64}[Fe_2C_9]$ can be indexed with $a = 2934.63(9)$ pm, $b = 1263.63(5)$ pm, $c_H = 504.14(3)$ pm and $c_G = 1056.01(5)$ pm. The modulation vector q_H is given by the ratio $c_H/c_G = 0.4775(1)$. The superspace group symmetry of the composite structure must be compatible with the superspace group symmetries of the pair of substructures. The observed reflection conditions are in accordance with space groups *Pnam* and $Pna2_1$ for the host structure and *Pbam* and *Pba*2 for the guest structure. Refinements for centrosymmetric as well as non-centrosymmetric pairs of space groups were carried out. Finally, the centrosymmetric space groups *Pnam* and *Pbam* were chosen, since they already provide physically meaningful interatomic distances. The combination of this pair of space groups results in the superspace group *Pnam*(00*g*) for the composite structure.

Satellites up to the second order were included in the refinements, which converged to $R(F)$ [*hkl*0] = 0.035/0.036, $R(F)$ [*hk*0*m*] = 0.058/0.062, $R(F)$ [*hkl*1] = 0.134/0.136 and $R(F)$ [*hkl*2] = 0.139/0.142 for (all reflections)/(reflections with $F > 4\sigma(F)$). Further details on data collection and structure refinements are summarized in Table 1. All crystallographic sites are fully occupied except for the Dy_{12} site within the channel. The site occupancy factor of 0.67 is given by a Crenel function, which describes a periodic distribution of vacancies and atoms as a square wave with the center x_4^0 and the width Δ. If $x_4 \in x_4^0 \pm \Delta/2$ an atom is present, otherwise, there is a vacancy. Δ is equal to the average site occupancy factor.

Positional and one occupational modulation of the host and the guest substructures have been described by the modulation functions given in Table 2. Fractional atomic coordinates and anisotropic displacement parameters are listed in Tables 3 and 4. The number of formula units, $Z = 8$ is given with respect to the host unit cell. The host structure comprises 10 Dy sites (4*c*), 3 Fe ($2 \times 4c + 8d$) and 18C (4*c*) in the asymmetric unit cell, while only two Dy sites ($8i + 4g$) are needed to describe the guest structure. The average number of guest atoms in the unit cell of the host structure is obtained as follows: $N_{G\,in\,H} = (8 \times Dy_{11} + 4 \times 0.67\ Dy_{12}) \times 0.4775 = 5.1$; $N_{G\,in\,H}/Z = 5.1/8 = 0.64$.