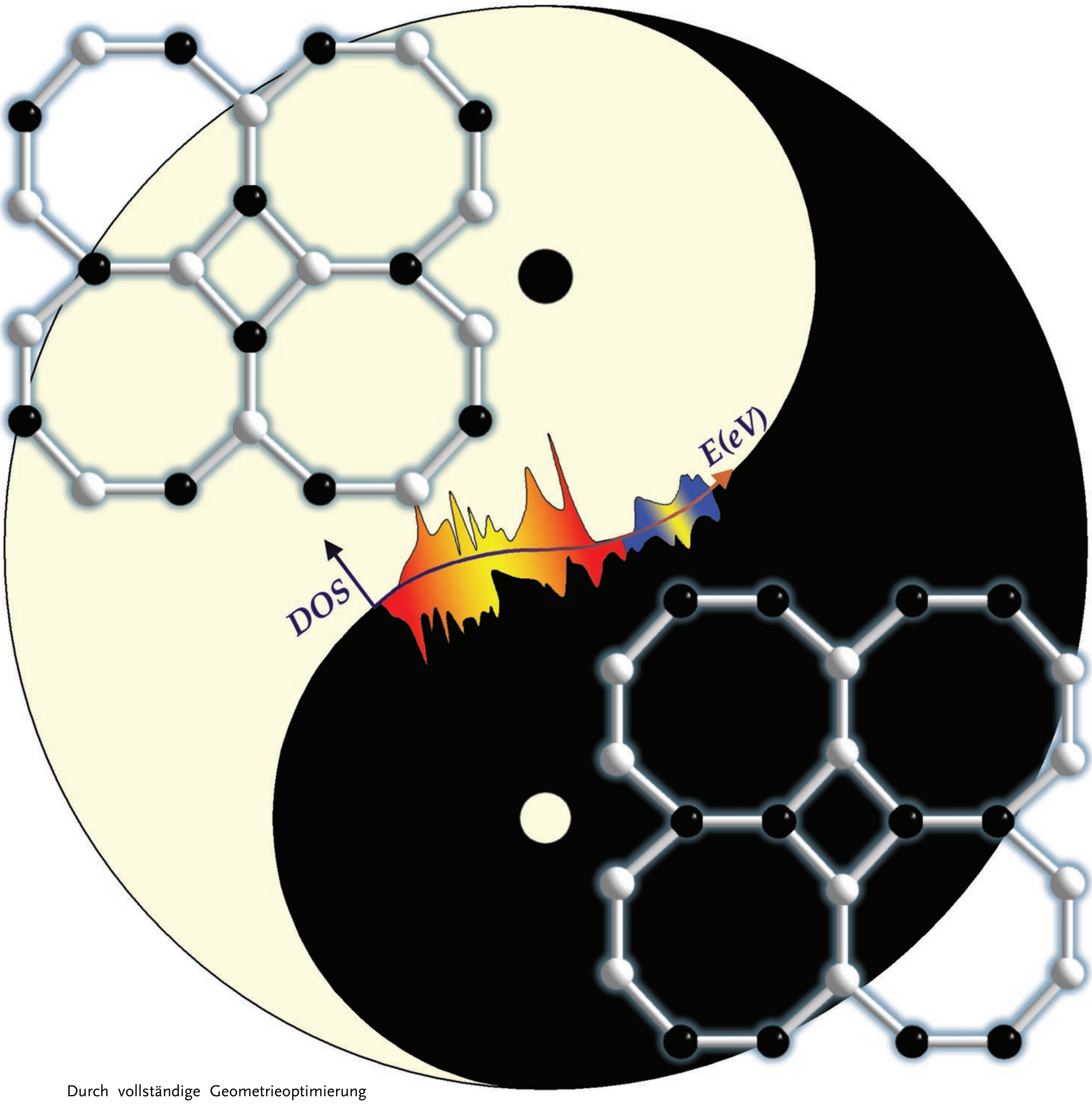
Angewandte
Chemie

Zuschriften

DOI: 10.1002/ange.200503080



Durch vollständige Geometrieoptimierung ließen sich Metallborcarbid(MB_2C_2)-Phasen analysieren. Die Positionen der B- und C-Atome (im Englischen „coloring problem“ genannt) konnten für dreiwertige Metalle mithilfe von DFT-Rechnungen eindeutig bestimmt werden. Einzelheiten dazu finden sich in der Zuschrift von J.-Y. Saillard, J.-F. Halet, X. Rocquefelte et al. auf den folgenden Seiten.

Inclusion Compounds

DOI: 10.1002/ange.200503080

Structural Preference versus Metal within the MB_2C_2 (M = Mg, Sc, Ca, Y, Ln) Phases: The Coloring Problem Revisited by DFT Calculations**

Xavier Rocquefelte, Salah Eddine Boulfelfel,
Mouna Ben Yahia, Josef Bauer, Jean-Yves Saillard,*
and Jean-François Halet**

The chemistry of boron-containing compounds is particularly rich and offers an extremely broad variety of topologies.[1] In the case of the MB_2C_2 phases (M = alkaline-earth or rare-earth metal), for instance, the recent discovery of various potentially interesting properties has revived the interest of the scientific community. For example, CeB_2C_2 is known to exhibit antiferromagnetic ordering at low temperature,[2] and antiferroquadrupolar transitions have been measured for DyB_2C_2[3] and HoB_2C_2.[4] Akimitsu et al. reported that CaB_2C_2 is a high-temperature ferromagnet,[5] although it was shown later by Mori and Otani that this ferromagnetism is due to the presence of an iron impurity.[6,7] Superconductivity at low temperature has also been reported for YB_2C_2, LuB_2C_2, and doped MgB_2C_2.[8] Although the properties of this family of compounds have been widely investigated, some of their structures are still debated, especially with respect to the position of B atoms versus C atoms (the so-called "coloring problem"[9]). Indeed, when the metal is a heavy element, it is not easy to differentiate between these two atoms, either by using X-ray or neutron-diffraction techniques.[10] Indeed, all the known MB_2C_2 structures consist of the stacking of two-dimensional (2D) B/C layers, with metal atoms in between. Four different 2D B/C topologies have been reported so far: fused six-membered rings in the 6^3 net of MgB_2C_2[11] (Figure 1a), fused five- and seven-membered rings in the 57^2 net of ScB_2C_2[12] (Figure 1b) and two different colorings of fused four- and eight-membered rings in the 48^2 net (Figure 1c,d). LaB_2C_2 (Figure 1c) has been proposed by Bauer and Bars[13] to adopt coloring I (BBCC), thus contradicting an earlier study of Smith et al. who suggested coloring II (BCBC; Figure 1d). More recently, neutron-diffraction structures of various lanthanide derivatives were solved assuming the model of Smith et al.[14] On the other hand, Albert et al.[10,15,16] have shown that CaB_2C_2 also adopts coloring II, but with a different stacking of the 2D layers (Figure 1d). Thus, among the 48^2 nets three B/C orderings with two different in-plane colorings have been proposed so far, thereby leading to controversial reports concerning these structures.[17,18]

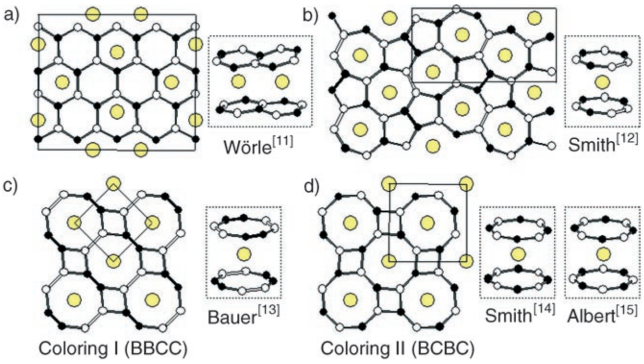


Figure 1. Schematic representation of the MB_2C_2 structure types. a) 6^3 net of MgB_2C_2 (*Cmca*) and b) 57^2 net of ScB_2C_2 (*Pbam*). Three models corresponding to the 48^2 net: c) Bauer model (*P4₂/mmc*) and d) Smith (*P4/mbm*) and Albert (*I4/mcm*) models. The insets show the corresponding stackings.

About 20 years ago, a very elegant theoretical tight-binding investigation of the 2D $B_2C_2^{2-}$ network by Burdett et al.[19] led to the conclusion that coloring II is more stable than coloring I for this formal dianionic charge. Indeed, coloring II allows a band gap at the Fermi level to open, whereas coloring I does not. This prediction was experimentally confirmed later for CaB_2C_2 (formally $[Ca^{2+}, B_2C_2^{2-}]$) by Albert et al.[10,15,16] However, the question of the coloring remains open with one more electron per formula unit (f.u.), that is, when the metal is a trivalent metal. Indeed, the presence of an extra electron occupying antibonding states is expected to destabilize coloring II.

We report herein the first quantitative theoretical analysis of the structural preference of MB_2C_2 (M = Mg, Ca, Sc, Y, La, Ce, and Lu) phases, including the answer to the coloring question for trivalent metals. Full geometric optimizations of the five structure types shown in Figure 1 were carried out for each metal at the DFT level.[20] The cohesive energies estimated from the optimized structures are given in Table 1. The stability of MgB_2C_2 and ScB_2C_2 in their experimentally characterized structures is well reproduced. This result supports our theoretical approach to estimating the relative stability of the models based on the 48^2 nets. Regardless of the metal, coloring II is significantly more stable than coloring I. CaB_2C_2 is found to be more stable in its experimental structure.[15] In the case of the trivalent metals (Y, Ce, and La), coloring II is also found to be the most stable B/C arrangement, with little energy difference between the Albert and Smith models, as observed with Ca. The Smith and

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[*] Dr. X. Rocquefelte, S. E. Boulfelfel,[+] M. Ben Yahia, Dr. J. Bauer, Prof. J.-Y. Saillard, Dr. J.-F. Halet
Laboratoire de Chimie du Solide et Inorganique Moléculaire
UMR 6511 CNRS-Université de Rennes 1
Institut de Chimie de Rennes, 35042 Rennes (France)
Fax: (+33) 2-2323-6840
E-mail: xavier.rocquefelte@cnrs.imn.fr
saillard@univ-rennes1.fr
halet@univ-rennes1.fr

[+] present address:
Max-Planck-Institut Dresden
Nöthnitzer Strasse 40
01187 Dresden (Germany)

[**] The authors thank the CCIPL (Nantes), PCIO (Rennes), and IDRIS (Orsay) computing centers for computational facilities.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Relative cohesive energies for different optimized MB_2C_2 structures (meV f.u.$^{-1}$).

M	Ionic radius [Å][29]	Structure type				
		MgB_2C_2 6^3	ScB_2C_2 57^2	Coloring I 48^2 [a]	Coloring II 48^2 [b]	48^2 [c]
Mg^{2+}	0.78	0	370	1665	732	876
S^+	0.83	133	0	1202	486	399
Lu^{3+}	0.85	281	0	940	263	170
Y^{3+}	1.06	303	94	722	57	0
Ca^{2+}	1.06	169	316	722	0	89
Ce^{3+}	1.07	339	308	577	30	0
La^{3+}	1.22	437	592	625	0	6

[a] Bauer model. [b] Albert model. [c] Smith model.

Albert models differ only by long-distance interactions between the B/C planes and so are expected to be very close in energy. This result suggests the possibility of defaults in the stacking of the 2D B/C nets, which should render the differentiation between B and C by diffraction techniques even more difficult. On the other hand, the ScB_2C_2 structure type is found to be preferred when M = Lu,[25] thus indicating that the B/C topology is related to the ionic size of the metal. Although the structure of LuB_2C_2 in the 48^2 net was recently reported,[18e] it appears from the present calculations that it should also be possible to stabilize this metal in the 57^2 network as well.

The agreement between the most stable computed structure and the corresponding experimentally characterized structure is excellent. Interatomic distances, for example, differ by less than 0.3, 1.3, and 1.5 % in the cases of M = Mg,[11] Ca,[15] and Ce,[18c] respectively. For M = Sc, they differ by less than 1.2 %, except for the B–B distance, which is 5.8 % longer than in the rather inaccurate X-ray structure.[12]

The density of states of CaB_2C_2 is shown in Figure 2 with both coloring I and II (Smith) structure types. As initially qualitatively predicted by Burdett et al.[19] and confirmed recently by Albert et al.,[15] coloring II allows the opening of a energy band gap at the Fermi level. This gap disappears in the case of the less stable coloring I. A rather similar situation occurs for LaB_2C_2, but with one more electron per f.u. In the case of coloring II, this electron occupies the conduction band above the pseudo band gap. Our results (Table 1) show clearly that this extra electron does not destabilize coloring II with respect to coloring I. From this point of view, it is noteworthy that identical B–C distances (short: 1.525 Å; long: 1.603 Å) are computed for CaB_2C_2 and YB_2C_2 in the Smith model despite of their different electron counts.

None of the trivalent metals led to the opening of an energy gap at the Fermi level in any structure type. Band gaps were found only with divalent metals and for the MgB_2C_2 structure type (1.31[26] and 0.41 eV for Mg and Ca, respectively) and the Albert CaB_2C_2 structure type (1.13 and 0.58 eV[26] for Mg and Ca, respectively).

Magishi et al.[28] recently deduced the components of the electric-field gradient (EFG) tensor of CeB_2C_2 from ^{11}B NMR spectroscopic experiments to elucidate its magnetic properties. Such measurements combined with calculated EFG data can also be used to characterize the local environment of the probed atoms. This approach is exemplified by the ^{11}B and ^{139}La EFGs computed for different MB_2C_2 phases using the WIEN2k code[24] (Table 2). A very good agreement between the experimental data of CeB_2C_2 and the calculated data for coloring II is obtained. However, this agreement is not the case for coloring I. Note that, the EFGs are nearly the same in the Albert and Smith models. Such a result is expected because of the similar local environments of the boron atoms in these two models. For the other metals, calculations show that the EFG values, as in the case of Ce, allows differentiation between the two different colorings I and II but not between the Smith and Bauer models.

These calculations provide a clear theoretical answer to the coloring problem in these MB_2C_2 phases. As this problem is experimentally difficult to solve unambiguously by using diffraction techniques (particularly with heavy metals), we suggested EFG measurements from NMR spectroscopy instead. Indeed, our calculations show that EFGs are very sensitive to atomic local environment, and therefore should easily discriminate between colorings I and II.[31]

Received: August 30, 2005

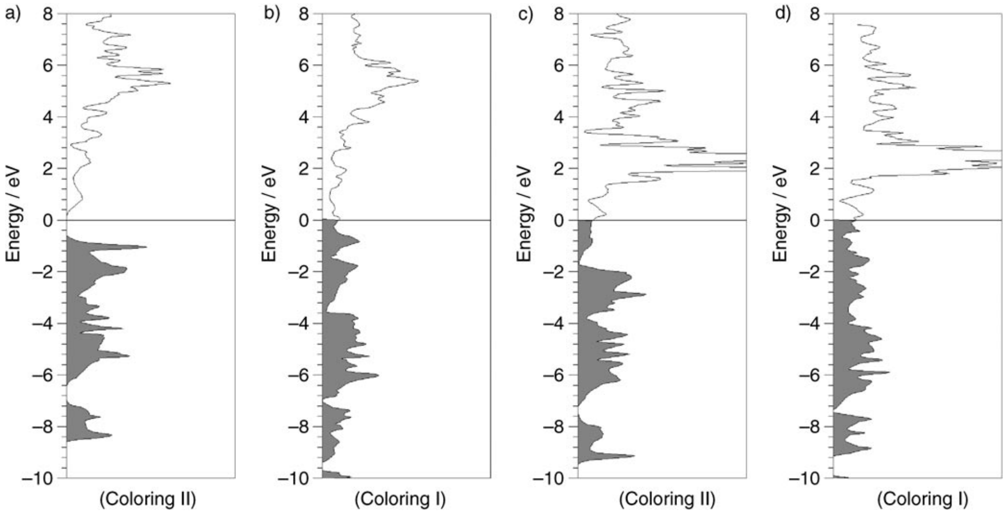

Figure 2. Total densities of states of CaB_2C_2 (a, b) and LaB_2C_2 (c, d). Colorings I and II correspond to the Bauer and Albert models, respectively.

Table 2: Calculated components of the EFG (in MHz using $Q(^{11}B) = 0.04059$ and $Q(^{139}La) = 0.200$)[29] for different optimized MB_2C_2 structures.

	$Lu^{11}B_2C_2$			$Y^{11}B_2C_2$			$Ca^{11}B_2C_2$		
Coloring	I	II		I	II		I	II	
Model	Bauer	Albert	Smith	Bauer	Albert	Smith	Bauer	Albert	Smith
v_{ZZ}	0.59	0.66	0.75	0.61	0.71	0.81	0.79	1.37	1.33
v_{YY}	−0.54	−0.45	−0.48	−0.54	−0.47	−0.50	−0.41	−0.78	−0.78
v_{XX}	−0.04	−0.21	−0.26	−0.07	−0.25	−0.30	−0.38	−0.59	−0.55
η[a]	0.85	0.36	0.29	0.77	0.31	0.25	0.03	0.13	0.17

	$Ce^{11}B_2C_2$				$L^{11}B_2C_2$			$^{139}LaB_2C_2$		
Coloring	I	II			I	II		I	II	
Model	Bauer	Albert	Smith	Exp.[28]	Bauer	Albert	Smith	Bauer	Albert	Smith
v_{ZZ}	0.24	0.78	0.78	0.77	0.64	0.80	0.82	−3.64	−6.95	−6.82
v_{YY}	−0.23	−0.50	−0.50	0.47	−0.51	−0.50	−0.51	1.82	3.47	3.41
v_{XX}	−0.01	−0.29	−0.28	0.30	−0.13	−0.30	−0.31	1.82	3.47	3.41
η[a]	0.89	0.27	0.29	0.22	0.60	0.25	0.24	0.00	0.00	0.00

[a] $\eta = (|v_{XX}| - |v_{YY}|)/|v_{ZZ}|$.

Keywords: boron carbides · density functional calculations · electronic properties · inclusion compounds · structural arrangements

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