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The local environment of Co in B₅CH$_x$

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Cobalt-doped boron carbides produced by simultaneous plasma-enhanced chemical vapor deposition of carborane and cobaltocene are investigated. Cobalt does not dope plasma-enhanced chemical vapor deposition grown boron carbides as a random fragment of the cobaltocene source gas. The Co atoms are fivefold boron coordinated ($R=2.1$ Å) and chemically bonded to the icosahedral cages of B₁₀CH$_x$ or B₉C₂H$_y$. Pairwise Co doping occurs with the cobalt atoms favoring sites about 5.3 Å apart. The cobalt strongly hybridizes with the molecular orbitals of the icosahedral cage, and the states in the region of the band gap probably have a strong cobalt weight. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2836798]

I. INTRODUCTION

The electronic structure and devices fabricated from boron carbides doped with Co (and other transition metals) are of considerable interest in spin electronics and in other areas of nanotechnology.[1] The ability to generate semiconducting grades of boron carbide films by plasma-enhanced chemical vapor phase deposition (PECVD) of carboranes permits the development of corrosion resistant, high temperature devices with many applications including neutron detection.[2–5] These boron carbides have the approximate stoichiometry of B₅CH$_x$ and exhibit a range of *p*- or *n*-type electronic properties, presumably as a result of differing polytypes.[5,6] Because these semiconductor materials have the icosahedra as the basic "building block," the icosahedra have the composition C₂B₁₀H$_x$ ($x \sim 1$), with the 12 main group atoms providing the basic structural framework (of the icosahedra). Successful *n*-type doping of β-rhombohedral boron has been accomplished with transition metal dopants such as iron,[7–11] vanadium,[10,11] chromium,[10,11] nickel,[11] while cobalt,[10,11] and zirconium[10] are more likely *p*-type dopants. For the related B₅CH$_x$ boron carbides, built on the 12 atom icosahedra (C₂B₁₀), *n*-type doping has been seen with nickel[12,13] and cobalt;[1] this is important because the *n*-type doping has been generally seen as the big challenge.

All of the semiconducting boron carbide materials use icosahedral cage molecules as the source molecule for fabrication or preferentially adopt icosahedral cages as the key building block for the bulk inorganic semiconductor. Thus, the icosahedral cage plays an important role in understanding many boron rich semiconductors. Detailed Co *K*-edge x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) measurements of C₂B₁₀H$_x$ have recently been undertaken;[14] providing a starting point for modeling the cobalt doping and cobalt interaction(s). EXAFS experiments indicate that the Co atoms neither cluster nor occupy random sites but form pairs with a Co–Co separation of 5.28 ± 0.02 Å.[1,14] The pairing is reminiscent of the Co clustering in some oxide dielectrics,[15,16] but a coherent embedding in a boron-carbide matrix can be excluded because the absence of EXAFS peaks corresponds to distances larger than 8 Å, and the complex packing of icosahedra indicates the lack of long-range periodicity.

In this paper, we determine the atomic structure, including the XANES, by a muffin-tin method and investigate the role of Co atoms with the help of molecular cluster calculations.

II. ATOMIC STRUCTURE

First-principles Co *K*-edge XANES calculations permit us to investigate the chemical composition and the atomic environment of Co atoms. The doped boron carbide films used for the XANES and EXAFS measurements were produced using PECVD with only metacarborane (an icosahedral carborane molecule), cobaltocene (to introduce the cobalt via a vapor phase organometallic compound), and argon as the plasma reactor gases, as previously described.[1,14] To model the experimental Co *K*-edge XANES spectrum, muffin-tin (MT) potentials were constructed for each specific cluster of atoms assembled as described below. The x-ray absorption cross sections were calculated in the dipole approximation with a basis of *s*, *p*, *d*, and *f* scattering states at each site. Two static limits, namely, fully relaxed $Z+1$ potential and unrelaxed Z potential approximations, were considered.[1,14] The fully relaxed potential brings about a rigid downward energy shift of ~ 1 eV and slightly increases the intensity of the peaks just above the absorption threshold. A modified DLXANES code,[17] carrying out a direct inversion of the scattering matrix, was used.

At small doping concentrations ($x < 0.2$), Co atoms are found to be fivefold boron coordinated, with a distance of 2.10 ± 0.02 Å. They are chemically bonded to the icosahe-

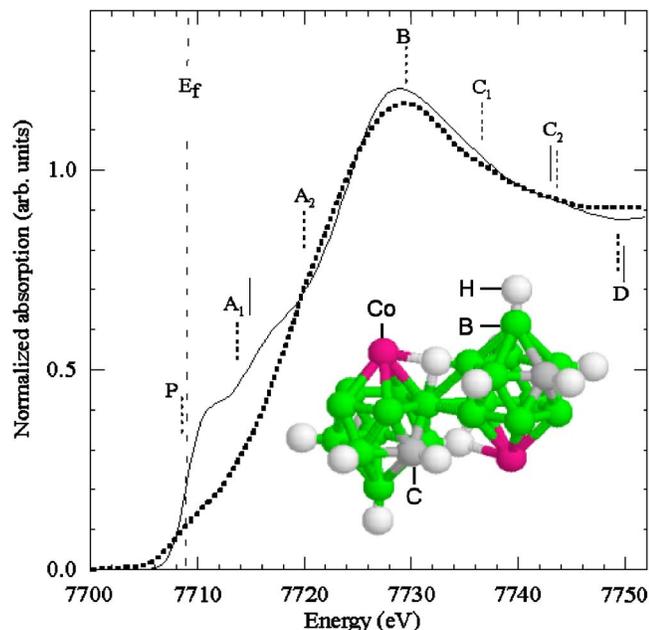a)Electronic mail: rskomski@neb.rr.com.

FIG. 1. (Color online) Comparison of experimental Co *K*-edge XANES of Co-doped boron carbide (dashed line) from Refs. 1 and 6 with a calculated *ab initio* XANES spectrum (solid line) for the cluster shown in the inset.

dral cages of $B_{10}CH_x$ or $B_9C_2H_y$, as shown in Fig. 1. This and the structurally similar types of cobalt pairing sites (with two icosahedral cages involved) are embedded into the boron carbide matrix. Co *K*-edge XANES and EXAFS are not sensitive enough to hydrogen, and hydrogen location and stoichiometry cannot be reliably determined,[14] but Co atoms are 5.28 ± 0.02 Å apart, even in dilute concentrations.[1,14]

Figure 1 compares the experimental and theoretical XANES spectra. The agreement is reasonable; the difference largely reflects the very low concentration of cobalt in a material with only partially known structure and absent long-range order. For example, the shoulder near 7710 eV is explained by the overestimated Co concentration (8% in the calculation, 0.5%–1% in reality). The pairwise cobalt doping may actually promote a polymerization, which goes far beyond the scope of this paper. Part of the disagreement is probably due to the neglect of many-electron effects and to the non-self-consistent field potentials used to save computation time. In any case, the calculation indicates that the icosahedral cage is preserved in the PECVD grown $C_2B_{10}H_x$ semiconducting boron carbides, whereas structures significantly differing from that shown in Fig. 1 yield poor agreement between theory and experiment. In contrast, the Raman spectra of the compounds are compatible with both cage and leaflet structures.[18] The pairing of the cobalt atoms, but not in close proximity, suggests a role for strain and/or extended orbitals.

III. ELECTRONIC STRUCTURE

To model the local electronic structure of boron carbides and the effect of Co introduced into the icosahedral cage building block of this semiconductor (Sec. II), we have performed PM3 molecular-cluster calculations (neglect of differential overlap, parametric method 3).[19,20] The geometric
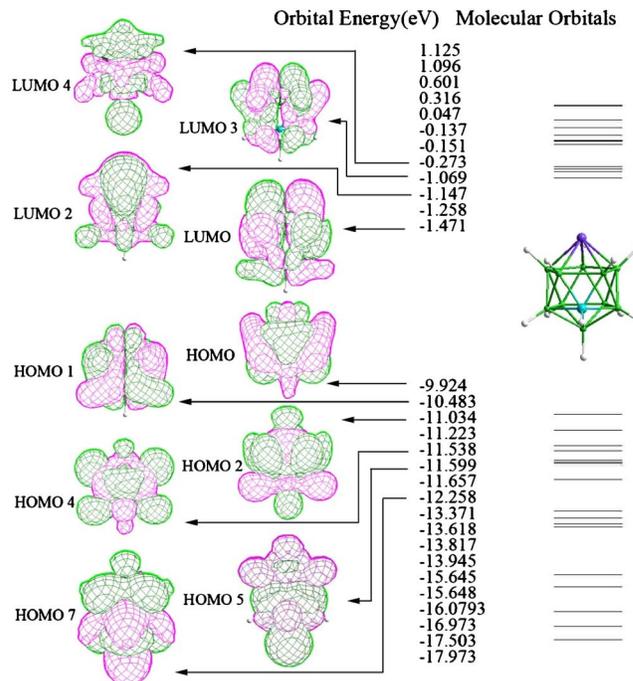

FIG. 2. (Color online) Calculated ground-state molecular orbitals (right) and their respective orbital energies for a *single* icosahedral carborane molecule cage with cobalt in the apical position. Selected schematic representations of the molecular orbitals are also shown (left). The inset contains the schematic structure.

optimization of the system was performed with the starting choices for the model structures (partly illustrated in Figs. 2 and 3 used in these cluster calculations and dictated by the experimentally determined structure in the vicinity of a co-
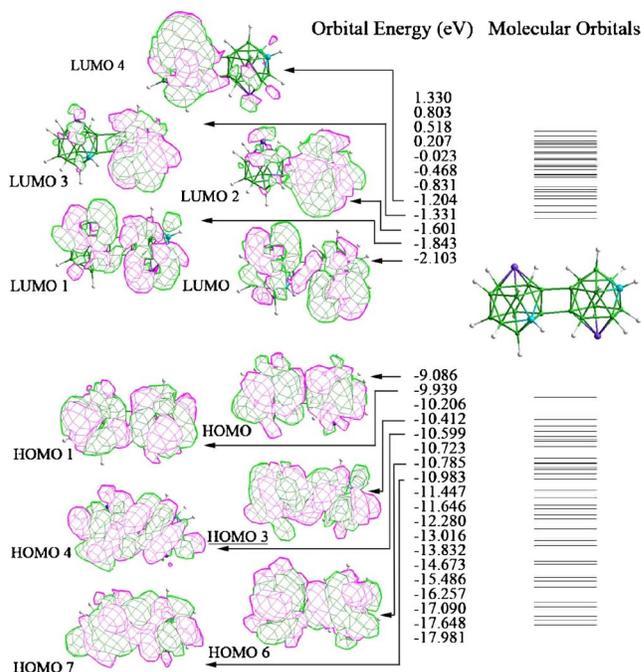

FIG. 3. (Color online) Calculated ground-state molecular orbitals (right) and their respective energies for a *dimeric* icosahedral carborane molecule cage with cobalt in the apical position. Selected schematic representations of the molecular orbitals are also shown (left). The inset displays the structure for a Co-doped carborane in dimeric icosahedral cage structure.

balt doping atom, as discussed above. The geometry optimized clusters were also compared with the results from density functional theory calculations, with little or no difference found. Following geometry optimization, we obtained the lowest unrestricted Hartree–Fock energy states (different orbitals for different spins).

As with all such cluster calculations, the limited number of atoms as well as the hydrogen termination of dangling bonds result in a highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap that is significantly larger that the experimental direct band gap of 1.5 eV of this class of boron carbide semiconductors.[6] Figures 2 and 3 and the underlying calculations show that a single icosahedra having cobalt within the cage does have a larger band gap (8.5 eV) than the dimeric icosahedra cage structure (7 eV). The addition of a boron-carbide matrix about the cluster, with the removal of many of the terminating hydrogen atoms, further reduces the band gap, as confirmed by larger cluster calculations. What is clear from the calculations is that the molecular orbitals in the vicinity of the HOMO-LUMO gap have very pronounced cobalt 3*d* character on the occupied side and cobalt $4p_{x,y}$ character on the unoccupied side.

The molecular orbital diagrams (Figs. 2 and 3) indicate that the molecular orbitals with cobalt character are highly delocalized. This may be one reason for the preference of cobalt atoms to adopt a 5.3 Å pairing in the carbide. It is worthwhile noting that the unpaired spin of a single cobalt atom ($3d^9$) is *paired* in the dimeric icosahedral cluster calculations. Depending on the application, we would expect that iron and nickel should in some ways work as better transition metal dopants. For example, iron dopants are a paired electron system in a singlet state ($3d^8$).

The $\uparrow\downarrow$ paring implies a substantial indirect exchange, involving about a dozen atoms. Interaction distances of 0.5 nm (5 Å) or more are not unusual and may indicate that the band structure is "downfolded" onto states with Co 3*d* character, similar to the orbitals in the CuO_2 plane of high-temperature superconductors.[21]

An intriguing feature of boron-rich solids is that boron and hydrogen are the only elements with nearly zero crystal-field charges.[22,23] While Co may exhibit some magnetic anisotropy, the anisotropy requires some crystal field, and it would be interesting to investigate this aspect of the magnetism of $C_2B_{10}H_x$, as well as some more basic questions, such as magnetic ordering.

IV. SUMMARY

In this paper, we have investigated Co-doped boron carbides with approximate chemical composition $C_2B_{10}H_1Co_{0.1}$. Very likely, Co atoms are chemically bonded within icosahedral boron-carbide cages and give rise to pair interactions in an otherwise amorphous, weakly crystalline, or polymeric arrangement of icosahedral cages. Cobalt atoms are separated by about 5.2 Å, even for dilute Co concentration, and the net moment per pair is zero due to antiferromagnetic indirect exchange. One aspect of this exchange, and of the energetically favorable pair bonding, is that relatively extended 3*d* transition-metal electron hybridize with the valence electrons of the neighboring boron atoms.

[1] L. Carlson, D. Lagraffe, S. Balaz, A. Yu. Ignatov, Y. B. Losovyj, J. Choi, P. A. Dowben, and J. I. Brand, Appl. Phys. A: Mater. Sci. Process. **89**, 195 (2007).

[2] B. W. Robertson, S. Adenwalla, A. Harken, P. Welsch, J. I. Brand, P. A. Dowben, and J. P. Claassen, Appl. Phys. Lett. **80**, 3644 (2002).

[3] K. Osberg, N. Schemm, S. Balkir, J. I. Brand, S. Hallbeck, P. A. Dowben, and M. W. Hoffman, IEEE Sens. J. **6**, 1531 (2006).

[4] A. N. Caruso, P. A. Dowben, S. Balkir, N. Schemm, K. Osberg, R. W. Fairchild, O. B. Flores, S. Balaz, A. D. Harken, B. W. Robertson, and J. I. Brand, Mater. Sci. Eng., B **135**, 129 (2006).

[5] A. N. Caruso, R. B. Billa, S. Balaz, J. I. Brand, and P. A. Dowben, J. Phys.: Condens. Matter **16**, L139 (2004).

[6] P. Lunca-Popa, J. I. Brand, S. Balaz, Luis G. Rosa, N. M. Boag, M. Bai, B. W. Robertson, and P. A. Dowben, J. Phys. D **38**, 1248 (2005).

[7] H. Takizawa, N. Haze, K. Okamoto, K. Uheda, and T. Endo, Mater. Res. Bull. **37**, 113 (2002).

[8] U. Kuhlmann, H. Werheit, J. Pelloth, W. Keune, and T. Lundstrom, Phys. Status Solidi B **187**, 43 (1995).

[9] U. Kuhlmann, H. Werheit, T. Dose, and T. Lundstrom, J. Alloys Compd. **186**, 187 (1992).

[10] T. Nakayama and K. Kimura, J. Jpn. Inst. Met. **63**, 1400 (1999).

[11] H. Werheit, R. Schmechel, V. Kueffel, and T. Lundstrom, J. Alloys Compd. **262**, 372 (1997).

[12] S.-D. Hwang, K. Yang, P. A. Dowben, A. A. Ahmad, N. J. Ianno, J. Z. Li, J. Y. Lin, H. X. Jiang, and D. N. McIlroy, Appl. Phys. Lett. **70**, 1028 (1997).

[13] D. N. McIlroy, S.-D. Hwang, K. Yang, N. Remmes, P. A. Dowben, A. A. Ahmad, N. J. Ianno, J. Z. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. A: Mater. Sci. Process. **67**, 335 (1998).

[14] A. Yu. Ignatov, Ya. B. Losovyj, L. Carlson, D. LaGraffe, J. I. Brand, and P. A. Dowben, J. Appl. Phys. **102**, 083520 (2007).

[15] S. A. Chambers, T. C. Droubay, C. M. Wang, K. M. Rosso, S. M. Heald, D. A. Schwartz, K. R. Kittilstved, and D. R. Gamelin, Mater. Today **9**, 28 (2006).

[16] S. A. Chambers, Surf. Sci. Rep. **61**, 345 (2006).

[17] P. J. Durham, J. B. Pendry, and C. H. Hodges, Comput. Phys. Commun. **25**, 193 (1982).

[18] K. Park, M. R. Pederson, L. L. Boyer, W. N. Mei, R. F. Sabirianov, X. C. Zeng, S. Bulusu, S. Curran, J. Dewald, E. Day, S. Adenwalla, M. Diaz, L. G. Rosa, S. Balaz, and P. A. Dowben, Phys. Rev. B **73**, 035109 (2006).

[19] J. J. P. Stewart, J. Comput. Chem. **10**, 209 (1989).

[20] A. J. Stone, Mol. Phys. **41**, 1339 (1980).

[21] O. K. Andersen and T. Saha-Dasgupta, Phys. Rev. B **62**, R16219 (2000).

[22] D. J. Newman and B. Ng, Rep. Prog. Phys. **52**, 699 (1989).

[23] R. Skomski, Philos. Mag. B **70**, 175 (1994).