Point defects, ferromagnetism and transport in calcium hexaboride

R. Monnier\textsuperscript{1} and B. Delley\textsuperscript{2}
\textsuperscript{1}Laboratorium für Festkörperphysik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland
\textsuperscript{2}Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Abstract

The formation energy and local magnetic moment of a series of point defects in CaB\textsubscript{6} are computed using a supercell approach within the generalized gradient approximation to density functional theory. Based on these results, speculations are made as to the influence of these defects on electrical transport. It is found that the substitution of Ca by La does not lead to the formation of a local moment, while a neutral B\textsubscript{6} vacancy carries a moment of 2.4 Bohr magnetons, mostly distributed over the six nearest-neighbour B atoms. A plausible mechanism for the ferromagnetic ordering of these moments is suggested. Since the same broken B-B bonds appear on the preferred (100) cleavage planes of the CaB\textsubscript{6} structure, it is argued that internal surfaces in polycrystals as well as external surfaces in general will make a large contribution to the observed magnetization.
Recent experiments on alkaline earth hexaborides have revealed an extreme sensitivity of their physical properties to stoichiometry and impurity content. A big surprise has been the observation of high temperature weak ferromagnetism in CaB$_6$, SrB$_6$ and BaB$_6$ lightly doped with lanthanum and thorium, as well as in the isovalent substitutional alloy Ca$_{0.995}$Ba$_{0.005}$B$_6$ [1], soon followed by the discovery of the same phenomenon in nominally pure CaB$_6$ [2], SrB$_6$ [3], and BaB$_6$ [4]. The authors of ref. [2] further found that when CaB$_6$ is grown from a calcium-rich mixture of the elements, it becomes very weakly paramagnetic, while its low temperature ($T<80$ K) resistivity is increased by more than two orders of magnitude. The former observation suggests that the ferromagnetism of the nominally pure systems is related to the presence of vacancies on the metal sublattice and/or to the resulting intrinsic (hole) doping. In an attempt to quantify these apparent correlations, Morikawa et al. [5] have performed a systematic study of the magnetization and electrical resistivity of CaB$_6$ samples synthesized from high purity CaO and B at different temperatures between 1200 °C and 1500 °C maintained between 1 and 24 h. Their results are rather puzzling: samples grown under the same conditions (1500 °C, 6h) show magnetizations differing by a factor of ten, and there is no connection whatsoever between the growth conditions, the resistivity and the magnetization. Our investigations suggest that the observed difference in magnetic moments is due to the fact that their measurements were performed on pressed powder pellets, with empty spaces of varying sizes between the grain boundaries, in contrast to those of refs. [1–4], which were made on single crystals.

Electronic structure calculations in the local density (LDA) or generalized gradient (GGA) approximation yield a semimetallic ground state for all stoichiometric alkaline earth hexaborides, with a small overlap between the valence and the conduction band at the X point of the Brillouin zone [6–8]. Building on this feature, Zhitomirsky et al. [9] and later two other groups [10,11] have put forward a model according to which the above ground state is unstable with respect to the formation of a spin triplet exciton condensate and, upon doping, evolves into a ferromagnetic state with a small spontaneous moment and a high Curie temperature, in line with the experimental observations. A more realistic calculation of the single-particle excitation spectrum of CaB$_6$, based on the so-called GW approximation [12], suggests that this compound is a conventional semiconductor, with a rather large band gap of 0.8 eV [13]. This prediction has very recently been confirmed by bulk-sensitive x-ray absorption and emission experiments at the boron K-edge [14], which definitely rules out the model of refs. [9–11].

In this letter, we investigate the possibility that the observed spontaneous magnetization is localized at imperfections in the CaB$_6$ lattice and qualitatively discuss the effect of these imperfections on the electrical conductivity. Specifically, we perform selfconsistent electronic structure calculations for a number of point defects centered in a 3x3x3 periodically continued supercell, which amounts to a defect concentration of 3.7 %. For each of them we compute the formation energy and the value of the local moment, two quantities for which the GGA used here should give reasonable results, since they are ground state properties [15]. Our results are summarized in Table I. The formation energy is defined as the difference between the binding energy per supercell of the defected crystal and that of pure, stoichiometric CaB$_6$. Geometrical relaxation effects are small, except in the case of the point-symmetry-breaking single boron vacancy, where the distance to the nearest B-octahedron along the broken bond is reduced by 0.1 Å.
We first consider the defects on the metal sublattice. When a neutral Ca atom is removed from the crystal, it takes along two valence electrons, and the vacancy left behind acts as an acceptor. If the stoichiometric compound is a conventional semiconductor [13], holes will be created near the top of the valence band, which belong to orbitals localized on the individual B₆ octahedra [6] and are therefore expected to contribute little to the dc conductivity.

The single crystals studied in refs. [1,2] were grown from mixtures of the pure elements in a liquid aluminium flux, and the question arises, whether Al atoms were incorporated during the growth process. As seen in Table I, it is indeed energetically favourable for an Al atom to fill a Ca vacancy when the crystal is grown from the gas phase. When the “atom reservoir” consists of liquid Al and Ca, as is the case over most of the temperature range of interest here (923 K - 1723 K [16]), the difference between the heat of vaporization of liquid aluminium and that of liquid calcium at the temperature of the reaction has to be added to the formation energy. A lower bound for these two quantities is given by their values at the respective boiling points of the two elements: ∼2.96 eV/atom for Al and ∼1.67 eV/atom for Ca (at one atmosphere) [17]. For the same reason, the heat of vaporization of liquid Ca must be subtracted from the calculated Ca-vacancy formation energy [18]. Once these two corrections have been made, the formation energies for the two defects become ∼5.0 eV.

At constant volume, the equilibrium defect concentration is given by

\[ c = \exp \left( -\frac{E_{\text{Form}} + \Delta F_{\text{vib}}}{k_B T} \right), \]

where \( \Delta F_{\text{vib}} \) is the difference between the vibrational free energy of the crystal with a defect and that of the perfect one. A microscopic calculation of this difference is prohibitive, and the standard treatment [19], based on a description of the solid as a collection of independent Einstein oscillators, predicts that, in the limit of high temperatures, it leads to a T-independent factor in the concentration. For vacancies, this factor is typically of order ten. For a light impurity (Al) substituting a heavier host atom (Ca), it will, in general, be smaller than one. At T=1723 K and from the formation energies alone, we find, for crystals grown in an aluminium flux, equilibrium concentrations of the order of ∼10⁻¹⁴. This is 10 orders of magnitude less than the density of negative charge carriers deduced from transport measurements [21], and we have to conclude that the negative carriers are either due to impurities in the starting materials or to defects in the boron network (see below), if the growth took place under conditions of thermal equilibrium. For the compound synthesized by borothermal reduction of CaO, the same approximation leads to an equally low vacancy concentration of ∼10⁻¹³ [18].

As seen in Table I, the substitution of Ca by La increases the binding energy of the compound [21]. This remains the case even after correcting by the difference in heats of vaporization of La and Ca (∼1.81 eV/atom), and all the lanthanum in the flux should therefore be incorporated. According to our calculation, there is no magnetic moment associated with the La impurity. This is in contrast to the result of Jarlborg [22], who finds a moment of the order of 0.1 \( \mu_B \) in a similar study for La in SrB₆ within the LDA. Our method applied to that system again yields a vanishing moment and we have no explanation for the origin of the difference between the two calculations.

The last impurity we have considered on the metal sublattice is boron, whose presence could explain the metal-deficiency reported by many experimental groups. According to
Table 1, the corresponding formation energy is $\sim 1$ eV higher than for the substitution of Ca by Al, which, combined with the higher cohesive energy of solid boron makes it very unlikely for this defect to form under conditions of thermal equilibrium.

Because of the strong covalent B-B bonds, the vacancy formation energy on the boron sites is expected to be much higher than on the metal sites. This is indeed what we find in our calculations. As seen in Table I the difference between these two energies is considerably reduced when proper account is taken of the growth procedure: under the conditions used in refs. [1,2,5], every B atom lost by the compound condenses into solid boron. The latter has a cohesive energy of $\sim 5.9$ eV/atom [23]. From this, its binding energy at 1723 K is obtained by subtracting the change in vibrational free energy over the corresponding temperature interval, which we approximate by its upper bound $3k_B T = 0.47$ eV/atom. So, at least $\sim 5.4$ eV are gained for every single boron vacancy formed, and therefore the net energy cost per vacancy drops from $\sim 11.0$ eV for the compound grown from the gas phase, to $\sim 5.6$ eV, leading to an equilibrium vacancy (donor) concentration of the order of $10^{-15}$/unit cell at the quoted temperature. This is 11 orders of magnitude lower the measured carrier concentration [20], and it is unlikely that the change in vibrational free energy upon removing a B atom from the crystal can account for such a large difference.

The loss of complete boron octahedra by the structure has been invoked by Noack and Verhoeven [24] in order to explain their gravimetric data on zone refined LaB$_6$. According to our calculations, this process is energetically more favourable than the creation of an equivalent number of well separated, single boron vacancies, but the computed formation energy of 18.3 eV implies that, unless the resulting void is stabilized by another factor, like eg a large impurity cation or a Ca vacancy acting as an acceptor and taking away electrons from interoctahedra bonding orbitals, it will not be formed under thermal equilibrium conditions. What makes it interesting, however, is the large magnetization it carries (see Table I). The moment is mainly localized on the six neighbouring boron octahedra, most of it (6 x 0.24 $\mu_B$) in the dangling bonds from the atoms immediately adjacent to the void; the next shell of boron atoms holds 24 x 0.015 $\mu_B$, while the 6 B atoms furthest away from the defect carry 0.04 $\mu_B$ each; finally, every adjacent Ca has a moment of 0.04 $\mu_B$. A void concentration of the order of $10^{-4}$ would suffice to account for the largest saturation magnetization observed in ref. [1]. A possible explanation for the ordering of these moments can be obtained if one makes the reasonable assumption that, in the presence of compensating cation vacancies and/or impurities, a B$_6$ vacancy can not only be neutral but also positively charged. In this case a “double exchange” [25,26] can take place between magnetic clusters formed by a “void” and its nearest neighbour boron octahedra and Ca ions, provided they are in different charge states. The low concentration of these clusters would require them to form a loosely connected network confined to a limited region of the crystal, for ferromagnetism to occur also at the lowest temperatures. The existence of an inhomogeneous ferromagnetic state in La doped CaB$_6$ has already been proposed by Terashima et al. [27].

A neutral B$_6$ void is the crudest approximation to the crystal surface, which is known to cleave in the [100] plane through the breaking of interoctahedra B-B bonds. Our results immediately lead to the conclusion that the outermost layer of CaB$_6$ will be magnetically ordered, with a sizeable moment per unit cell. This suggests that the very large magnetization observed in polycrystalline samples [3] is located at the surface of the crystallites.

Finally, we have investigated the possibility of antisite defects in which a metal atom
is substituted for the missing boron octahedron. In all cases the formation energy is considerably reduced with respect to that of a $B_6$ vacancy, but still much too high to lead to a measurable concentration in conditions of thermal equilibrium. What is remarkable, however, is that the incorporation of either Al or La completely removes the original, large magnetic moment. This leads us to the following tentative scenario for the evolution of the magnetism in La-doped CaB$_6$: As La is incorporated at the surface of the growing crystal, the resulting local distortion increases the probability of formation of $B_6$ vacancies. If the La concentration in the flux is low, these will remain empty, while the La atoms substitute for Ca. Provided the voids form connected clusters as described above, ferromagnetism can occur, with a moment which increases with the La concentration in the flux. Once the latter exceeds a certain value, some La atoms will start to “see” the $B_6$ vacancies and occupy them, at a considerable energy gain. At still higher La concentration in the flux, every created $B_6$ vacancy is occupied by a La atom, and the magnetization vanishes altogether.

In summary, we have shown that the concentration of point defects in CaB$_6$ grown under conditions of thermal equilibrium is too small to account for the transport properties of this material. Having found that of all intrinsic point defects only the $B_6$ vacancy carries a (large) magnetic moment, we have postulated that, due to kinetic effects, such “holes” are created during the growth of the crystals, especially when the lattice is distorted by large impurities or cation vacancies, and we have presented a plausible scenario for the magnetic behaviour of La-doped CaB$_6$ as function of concentration. The large moment carried by $B_6$ vacancy also leads to a natural explanation for the high saturation magnetization observed in unetched polycrystalline samples as a surface effect.

**ACKNOWLEDGEMENTS**

It is a pleasure to thank A. D. Bianchi for his comments on the manuscript.
REFERENCES

[1] D. P. Young, D. Hall, M. E. Torelli, Z. Fisk, J. D. Thomson, H. R. Ott, S. B. Oseroff, R. G. Goodrich, R. Zysler: Nature 397, 412 (1999).
[2] P. Vonlanthen, E. Felder, L. Degiorgi, H. R. Ott, D. P. Young, A. D. Bianchi, Z. Fisk, Phys.Rev B62, 10076 (2000).
[3] H. R. Ott, J. L. Gavilano, B. Ambrosini, P. Vonlanthen, E. Felder, L. Degiorgi, D. P. Young, Z. Fisk, R. Zysler, Physica B 281 & 282, 423 (2000).
[4] H. R. Ott, private communication
[5] T. Morikawa, T. Nishioka and N. K. Sato, J. Phys. Soc. Japan 70, 341 (2001).
[6] S. Massidda, A. Continenza, T. M. de Pascale, R. Monnier, Z. Phys. B 102, 83 (1997).
[7] C. O. Rodriguez, Ruben Weht, and W. E. Pickett, Phys. Rev. Lett. 84, 3903 (2000).
[8] S. Massidda, R. Monnier, and E. Stoll, Eur. Phys. J. B 17, 645 (2000).
[9] M. E. Zhitomirsky, T. M. Rice, and V. I. Anisimov, Nature 402, 251 (1999), (cond-mat/9904330).
[10] L. Balents and C. M. Varma, Phys. Rev. Lett. 84, 1264 (2000).
[11] V. Barzykin and L. P. Gorkov, Phys. Rev. Lett. 84, 2207 (2000).
[12] L. Hedin, Phys. Rev. 139, A796 (1965); for a recent review, with tabulated band gap values, see L. Hedin, J. Phys.: Condens. Matter 11, R489 (1999).
[13] H. J. Tromp, P. van Gelderen, P. J. Kelly, G. Brocks, and P. A. Bobbert, Phys. Rev. Lett. 87, 016401 (2001).
[14] J. D. Denlinger et al., cond-mat/0107429 (2001)
[15] The calculations are performed at fixed volume, but allowing for geometric relaxation, with the DMOL code, developed by one of us (B.D.), and use the DNP basis set (J. Chem. Phys. 92, 508 (1990); J. Chem. Phys. 113, 7756 (2000)). This basis set includes a numerical atomic response functions of s,p,d (and f for La) character in addition to the exact numerical solutions for the density functional atom, and is expected to give better than 1 m Hartree total accuracy per atom in general. The basis functions have finite tails to help linear scaling methods for all except obtaining the density matrix by diagonalization. Tail lengths is 8. au in these calculations, which is a conservative choice with regards to basis accuracy. k-space integration is done with an unshifted 2 x 2 x 2 mesh for the 3 x 3 x 3 supercells, which amounts to 4 symmetry unique k-points. A thermal broadening of 2 m Hartree is used. The free energy is modified with the entropy term proposed by M. Weinert and J.W. Davenport, Phys. Rev. B. 45, 13709 (1992) to make the energy functional variational.
[16] H. R. Ott, M. Chernikov, L. Degiorgi, E. Felder, Z. Fisk, E. Moshopoulou, Z. Phys. B 102, 337 (1997).
[17] Handbook of Chemistry and Physics, 57th Edition, CRC Press (1976-1977), p. D62.
[18] For the material obtained by boro-thermal reduction of CaO, we assume that the removed calcium atom together with an oxygen atom recombines to calcium oxide. The correction to the value given in Table 5 then consists of three terms: 1) the formation energy of CaO, which varies linearly in T, with an abrupt change in slope at 1490 °C (the boiling point of Ca metal), where it takes a value of ~4.8 eV/formula unit [28]; 2) the dissociation energy of a free BO molecule, ~8.3 eV [29] reduced by k_B T to approximately account for the weakening of the bond at the temperature T; 3) the binding energy of solid boron at 1500 °C , ~5.4 eV/atom (see text). The effective Ca-vacancy
TABLE I. Formation energy (*a* from the gas phase, *b* from the elements dissolved in a liquid aluminium flux, *c* from borothermal reduction of CaO), and local magnetic moment of point defects in CaB₆.

| Defect       | E$_{Form}$ [eV] | Moment [$\mu_B$] |
|--------------|-----------------|-----------------|
| Ca vacancy   | 6.63$^a$, 4.96$^b$, 4.6$^c$ | <0.001          |
| La (Ca)      | -1.94$^a$, -0.14$^b$     | <0.001          |
| Al (Ca)      | 3.73$^a$, 5.0$^b$         | <0.001          |
| B (Ca)       | 4.69$^a$, 8.5$^b$         | <0.001          |
| B vacancy    | 11.05$^a$, 5.6$^b$$^c$    | <0.001          |
| B₆ vacancy   | 50.7$^a$, 18.3$^b$$^c$     | 2.36            |
| Ca (B₆)      | 44.2$^a$, 13.5$^b$        | 1.32            |
| La (B₆)      | 40.6$^a$, 11.7$^b$        | <0.001          |
| Al (B₆)      | 42.5$^a$, 13.1$^b$        | <0.001          |

formation energy is therefore $\sim$4.6 eV. Note that the change in slope mentioned above may account for the widely different properties observed by Morikawa et al. [5] in the two samples grown at 1500 °C for 6 h.

[19] see eg. A. J. Dekker, Solid State Physics, Prentice-Hall, Englewood Cliffs (1957), p. 66, 160.

[20] K. Giannò, A. V. Sologubenko, H. R. Ott, A. D. Bianchi, and Z. Fisk, submitted to Phys. Rev. B [cond-mat/0104511].

[21] As a comparison, the calculated difference between the cohesive energies of the two materials is 4.37 ev/formula unit.

[22] T. Jarlborg, Phys. Rev. Lett. 85, 186 (2000), cond-mat/0103180.

[23] C. W. Bauschlicher Jr., J. M. L. Martin, and P. L. Taylor, J. Phys. Chem. A 103, 7715 (1999).

[24] M. A. Noack and J. D. Verhoeven, J. Crystal Growth 49, 595 (1980).

[25] P. W. Anderson and H. Hasegawa, Phys. Rev. 100, 675 (1955).

[26] P. G. de Gennes, Phys. Rev. 118, 141 (1960).

[27] T. Terashima, C. Terakura, Y. Umeda, N. Kimura, H. Aoki, and S. Kunii, J. Phys. Soc. Japan 69, 2423 (2000).

[28] C. F. Bell and K. A. K. Lott, Modern Approach to Inorganic Chemistry, Butterworths, London (1963), p. 183.

[29] K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Vol IV, Van Nostrand Rheinhold Company, New York (1978), p. 102.