Point Defects, Ferromagnetism, and Transport in Calcium Hexaboride

R. Monnier[1] and B. Delley[2]
[1]*Laboratorium für Festkörperphysik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland*
[2]*Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

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The formation energy and local magnetic moment of a series of point defects in CaB_6 are computed using a supercell approach within the generalized gradient approximation to density functional theory. It is found that the substitution of Ca by La does not lead to the formation of a local moment, while a neutral B_6 vacancy carries a moment of 2.4 Bohr magnetons. 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_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.

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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 2 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 and 1500 °C maintained between 1 and 24 h. Their results are rather puzzling: Samples grown under the same conditions (1500 °C, 6 h) show magnetizations differing by a factor of 10, 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 self-consistent electronic structure calculations for a number of point defects centered in a $3 \times 3 \times 3$ 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 B_6 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 aluminum

TABLE I. Formation energy and local magnetic moment of point defects in CaB_6.

Defect	E_{form} [eV]	Moment [μ_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
B_6 vacancy	50.7,[a] 18.3[b,c]	2.36
Ca (B_6)	44.2,[a] 13.5[b]	1.32
La (B_6)	40.6,[a] 11.7[b]	<0.001
Al (B_6)	42.5,[a] 13.1[b]	<0.001

[a] From the gas phase.
[b] From the elements dissolved in a liquid aluminum flux.
[c] From borothermal reduction of CaO.

flux, and the question arises, whether Al atoms were incorporated during the growth process. As seen in Table I, it is indeed energetically favorable 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 (923–1723 K [16]), the difference between the heat of vaporization of liquid aluminum 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

$$c = \exp\left(-\frac{E_{\text{form}} + \Delta F_{\text{vib}}}{k_B T}\right), \tag{1}$$

where ΔF_{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 10. 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 aluminum flux, equilibrium concentrations of the order of $\sim 10^{-14}$. This is 10 orders of magnitude less than the density of *negative* charge carriers deduced from transport measurements [20], 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 $\sim 10^{-13}$ [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 SrB_6 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 I, the corresponding formation energy is ~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 ~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 $3k_BT = 0.47$ eV/atom. So, at least ~5.4 eV are gained for every single boron vacancy formed, and therefore the net energy cost per vacancy drops from ~11.0 eV for the compound grown from the gas phase, to ~5.6 eV, leading to an equilibrium vacancy (donor) concentration of the order of 10^{-15} per unit cell at the quoted temperature. This is 11 orders of magnitude lower than 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 favorable 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, such as, e.g., 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 neighboring boron octahedra, most of it ($6 \times 0.24\mu_B$) in the dangling bonds from the atoms immediately adjacent to the void; the next shell of boron atoms holds $24 \times 0.015\mu_B$, while the six 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 cannot 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-neighbor 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 sizable moment per unit cell. This suggests that the very large magnetization observed in polycrystalline samples [5] 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 behavior of La-doped CaB_6 as a 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.

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linear scaling methods for all except obtaining the density matrix by diagonalization. Tail lengths are 8 a.u. in these calculations, which is a conservative choice with regards to basis accuracy. k-space integration is done with an unshifted $2 \times 2 \times 2$ mesh for the $3 \times 3 \times 3$ supercells, which amounts to four symmetry unique k points. A thermal broadening of 2 m hartree is used. The free energy is modified with the entropy term proposed by Weinert and Davenport [Phys. Rev. B **45**, 13 709 (1992)] to make the energy functional variational.

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