CaB_6: A New Semiconducting Material for Spin Electronics

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Ferromagnetism was recently observed at unexpectedly high temperatures in La-doped CaB_6. The starting point of all theoretical proposals to explain this observation is a semimetallic electronic structure calculated for CaB_6 within the local density approximation. Here we report the results of parameter-free quasiparticle calculations of the single-particle excitation spectrum which show that CaB_6 is not a semimetal but a semiconductor with a band gap of 0.8 ± 0.1 eV. Magnetism in $La_xCa_{1-x}B_6$ occurs just on the metallic side of a Mott transition in the La-induced impurity band.

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The recent observation of ferromagnetism in La-doped alkaline-earth hexaboride compounds at high temperatures [1] presents three puzzles. First, ferromagnetism is usually associated with elements with a partly filled $3d$, $4f$, or $5f$ shell. Second, ferromagnetic ordering is observed only for a narrow dopant concentration range and for a surprisingly low dopant concentration. The maximum observed moment in $Ca_{1-x}La_xB_6$ is 0.07 Bohr magnetons per La atom for $x = 0.005$. Third, and most surprising of all is the observation of very large Curie temperatures; for $La_{0.01}Ca_{0.99}B_6$ a value close to 900 K has recently been reported [2]. Such a large value virtually excludes the possibility of the observed magnetism being related to magnetic impurities.

In an initial comment on the experimental observations, Ceperley suggested [3] that it might be an example of the long-predicted but never observed ferromagnetic phase of a dilute electron gas; improved calculations increase the estimated density at which this might occur [4]. An alternative explanation proposed by Zhitomirsky *et al.* was that the ferromagnetic hexaborides might be doped excitonic insulators [5]. This explanation requires that the exciton binding energy should be comparable in size to the single-particle band gap. Jarlborg suggested [6] that the magnetism may be conventional itinerant magnetism. Although magnetism in materials which do not have partly filled $3d$, $4f$, or $5f$ shells is rare, it is not unprecedented. A handful of materials does exist, of which $ZrZn_2$ is the best known example, in which the Fermi energy falls at or close to an exceptionally narrow peak in the electronic density of states so that the Stoner criterion for the occurrence of itinerant magnetism is fulfilled. The problem posed by the hexaborides is not so much the occurrence of magnetic ordering but rather the strength of the magnetic coupling as reflected by the very high Curie temperature, and this was not estimated in Ref. [6].

All three suggestions are based on electronic structure calculations which indicate that stoichiometric CaB_6 is a semimetal with a very small overlap between the conduction and valence bands [7–9] or that might have a very small gap [7]. Since the theoretical predictions rely on details of this electronic structure, it is important to examine their validity. Massidda's and Rodriguez' calculations of the electronic structure were performed with the full-potential linearized augmented plane wave method which is probably the most accurate available. They were carried out within the framework of density functional theory (DFT) using the local density approximation (LDA). Such calculations are known to be capable of yielding total energies with a very useful accuracy. However, it is also well known that the eigenvalue spectrum which results from solving the Kohn-Sham equations of DFT cannot be interpreted unreservedly as an excitation spectrum [10,11] and sometimes the results are spectacularly wrong. In particular, the band gaps of semiconductors are typically underestimated by 50% and in extreme cases such as Ge the conduction and valence bands are found to overlap resulting in metallic or semimetallic character.

In order to study single-particle excitations, one should solve Dyson's equation for the single-particle Green's function expressed in terms of the self-energy operator Σ. Σ can be expanded as a perturbation series in the Green's function G and the dynamically screened Coulomb interaction W. The so-called GW approximation introduced by Hedin [12] includes only the first term in this series. In addition, one usually assumes a quasiparticle (QP) expression for the Green's function G. For a large number of semiconductors and insulators such calculations produce band gaps which are in very close quantitative agreement with experimental single-particle band gaps [13]. The main purpose of the present paper is to apply these parameter-free calculations with their proven predictive capability to

CaB_6. From our results we shall conclude that, contrary to what is currently being assumed, the parent material is actually a semiconductor with quite a large band gap. This finding has far-reaching consequences for understanding the basic properties of the doped, ferromagnetic phase and opens up the prospect of a range of novel applications.

The starting point for our *GW* study is an LDA calculation for CaB_6 performed with a plane wave basis and using norm-conserving pseudopotentials to describe the interaction between the valence electrons and the ionic cores [14]. Using the experimentally determined structure, we reproduce essentially perfectly the energy bands calculated by Massidda [8] using an all-electron method. The results are shown in Fig. 1(a). There are ten valence bands (bonding orbitals derived from the boron $2s$ and $2p$ levels) well separated from the conduction bands (antibonding states) with the exception of an overlap of about 0.3 eV in a small region around the X point of the highest occupied and lowest unoccupied bands. The occurrence of such small band overlap (or the presence of a comparably small band gap) is an important criterion for the stability of an excitonic insulator phase [5]. The effective masses in units of the free electron mass for the bands near X, $m_e^{\perp} = 0.215 \pm 0.004$ and $m_e^{\parallel} = 0.50 \pm 0.02$ for the electrons and $m_h^{\perp} = 0.196 \pm 0.003$ and $m_h^{\parallel} = 1.8 \pm 0.2$ for the holes, are close to values reported earlier [5,7,9]. We use the LDA electronic wave functions and eigenvalues as input for the *GW* calculations for which we adopt the space-time approach suggested by Rojas *et al.* [15] in which all operators are represented on grids in real and reciprocal space, in the time and energy domains; details of our implementation have been given by van der Horst *et al.* [16]. By varying the size of these grids we estimate that the calculated QP energies are converged within 0.1 eV. The densest grids we used were a $(12 \times 12 \times 12)$ real-space grid and a $(6 \times 6 \times 6)$ **k**-grid. The Green's function is constructed including the LDA wave functions and energies of the lowest 300 bands.

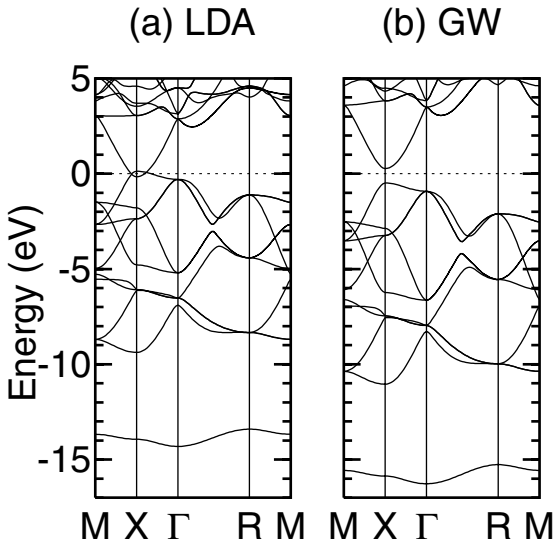

FIG. 1. Energy bands for CaB_6 in (a) the LDA approximation, and (b) the *GW* approximation. The Fermi energy is indicated by the dotted line at 0 eV.

The results of the *GW* calculations are plotted in Fig. 1(b). Throughout the Brillouin zone, the QP corrections to particular LDA bands are rather uniform so that the dispersion of the *GW* bands is very similar to the LDA band dispersion and the effective masses differ only slightly from the values obtained from the LDA calculation. They are reduced on average by less than 10%, to $m_e^{\perp} = 0.196 \pm 0.003$ and $m_e^{\parallel} = 0.48 \pm 0.02$ for the electrons and $m_h^{\perp} = 0.174 \pm 0.003$ and $m_h^{\parallel} = 1.7 \pm 0.2$ for the holes. The sign and size of the corrections to the energy bands depend on their wave function character and vary considerably from band to band. Of particular importance are the relative shifts of the bands at X near the Fermi level. The hole band and electron bands are moved, respectively, downwards and upwards in energy resulting in the opening of a sizable band gap of about 0.8 ± 0.1 eV. The downward and upward shifts can be understood from the bonding and antibonding character of the wave functions in the valence and conduction bands, respectively. This is quite analogous to the situation in silicon [17]. The largest shift in the occupied bands is calculated for the lowest valence band which is lowered in energy by about 1.5 eV. Given the similarity between the LDA band structures of CaB_6 and SrB_6 [8], we expect a *GW* calculation to yield similar results for these two materials.

Our finding that bulk CaB_6 is a semiconductor is consistent with the large value of the low temperature resistivity and with its increase with decreasing temperature recently reported by Ott *et al.* [2] and by Vonlanthen *et al.* [18]. The temperature dependence of the resistivity of the "stoichiometric" sample (labeled $Ca_{1+\delta}B_6$ in Ref. [18]) can be interpreted as that of a doped semiconductor. In the saturation range, around room temperature, all the impurities are ionized, the number of charge carriers in the bands is temperature independent, and the resistivity has a weak temperature dependence. Below $T = 230$ K the impurity charge carriers gradually freeze out and their number decreases exponentially. One might tentatively associate the 84 meV activation energy found for this process by Vonlanthen with an impurity binding energy [19,20]. At temperatures below ~50 K most of the charge carriers are frozen out and the resistivity is determined by hopping between impurity sites. Assuming nearest neighbor hopping, the latter process can be described by an activation energy that is easily an order of magnitude smaller than the impurity binding energy [21,22]. The La-doped samples correspond to a high doping regime, where the impurity concentration is on the metallic side of a Mott transition in an impurity band (see below). For these samples, therefore, a metallic-like resistivity is observed over the whole temperature range. We do not attempt to explain the decrease in resistivity observed below $T = 0.4$ K [2,18].

Our result that CaB_6 is a semiconductor is also consistent with recent angle-resolved photoemission experiments by Denlinger *et al.* on SrB_6 [23], in which a gap of a size similar to what we calculate was found. Using the fact that photoemission experiments are sensitive to the surface electronic structure and assuming that the bulk is a semimetal, the authors interpreted their results in terms of an electron rich surface region (of thickness 6 nm) in which the structure differs from that of the bulk leading to the formation of a large band gap. This surface region has to be large enough to give the bands a bulk-like dispersion. While we cannot exclude the importance of surface states, our results indicate that the photoemission spectrum can be interpreted without invoking such a special surface region. The optical data of Ref. [18] cannot be explained in a simple way, neither on the basis of the (semimetal) LDA nor of the (semiconductor) *GW* band structures. The imaginary part of the calculated dielectric function shows a steep rise only at around 2 and 3 eV, respectively, since transitions between the highest valence and lowest conduction bands are only weakly allowed, whereas the experimental dielectric function shows such a rise below 1 eV.

The result for the stoichiometric phase has important implications for the models proposed to explain the ferromagnetism observed in the doped phase. A low density electron gas is expected to show a ferromagnetic phase; Ceperley [3] and Ortiz *et al.* [4] report critical values for the electron gas parameter of this phase of $r_s = 80$ and $r_s = 20$, respectively. In a solid this electron gas parameter has to be rescaled because the background dielectric constant and the effective masses rescale the potential and kinetic energies of the electron gas and thus change the density at which one expects the ferromagnetic phase to occur [5,9]. Within *GW* one calculates the dielectric response function at the random phase approximation level [12,15–17]. Similar to Ref. [9], using our calculated values for the effective masses and static dielectric constant of 5, we obtain a scaled density parameter r_s of 1.5. This is at least an order of magnitude smaller than the values reported by Ceperley [3] and Ortiz *et al.* [4] which makes the low density electron gas an unlikely candidate for the observed ferromagnetism. Within the effective mass approximation we estimate an exciton binding energy of about 0.07 eV. The excitonic binding energy is an order of magnitude smaller than the calculated QP band gap. The excitonic insulator model requires them to be comparable in size [5], so it is unlikely that this model can be applied to CaB_6.

Instead we note that the ferromagnetism occurs for an impurity concentration which is just on the metallic side of a Mott transition in the impurity band: $n^{1/3}a_H = 0.4$, where n is the dopant concentration 7×10^{19} electrons cm^{-3} and $a_H = 10$ Å is the Bohr radius of an isolated effective mass impurity. Some support for the possible role of an impurity band may be found in the very recent experimental studies on doped hexaborides reported by Terashima *et al.* [24]. He found that some of his La-doped samples were paramagnetic, exhibiting the Curie-Weiss behavior which is to be expected if the dopant concentration were below Mott's critical value. In other samples no indication of saturation of the magnetic moment even in the highest magnetic field reported (10 kOe) was found. Such behavior might be expected for a Stoner model of weak ferromagnetism with partly filled narrow bands on the metallic side of a Mott transition. This model might also be capable of explaining the different values reported for the magnetic moment per dopant atom [1,2,24] if there were a significant deviation from the nominal stoichiometry. Since the effective valence of an impurity atom in a semiconductor is very sensitive to the local environment, it is important to know where the La goes and if all of it actually occupies Ca sites as assumed. In the same context, one should determine the abundance of vacancies on the boron sublattice and whether they have donor or acceptor character. This is particularly relevant in view of the observation of ferromagnetic ordering in an undoped CaB_6 sample with an apparent Ca deficiency [18]. Experimental difficulties in making the samples are apparent from the attribution of de Haas–van Alphen signals in samples on the metallic side of a Mott transition to Al inclusions [24].

Starting from the assumption that the magnetism occurs mainly in the impurity band, we are currently attempting to determine the effective exchange interaction between impurities from total energy calculations, in order to estimate the Curie temperature, and to determine the impurity-state related parameters which govern the physical behavior of the doped system such as the hopping matrix elements between impurity states, the charge and spin fluctuation parameters (Hubbard U and Stoner I, respectively), as well as the impurity binding energy, going beyond the effective mass approximation. The position of the impurity state with respect to the bottom of the conduction band is particularly difficult to estimate reliably because it requires taking into account simultaneously the central cell potential and the long-range Coulomb interaction. One way to assess the importance of dopant atoms experimentally would be to use a field-effect device to inject charge into undoped CaB_6 [25].

Irrespective of the origin of the high Curie temperature in the doped material, the existence of a large gap for the undoped material means a new class of magnetic semiconductors [26] is available. Magnetic semiconductors have attracted a lot of attention recently in the context of spin electronics. The size of the magnetization in doped hexaborides is not high, but it is not obviously inferior to the materials used in Refs. [27,28]. The doped hexaborides possess the unique characteristic of having a Curie temperature sufficiently high to allow room-temperature operation of semiconducting spin devices, something which has only very recently been achieved at low temperatures [27,28]. With the hexaborides it should be possible to inject a spin-polarized current from the doped into the

undoped material in the ballistic regime and study the spin dynamics as a function of temperature, and of current density without the complication of having to apply an external magnetic field [27,28] or without the problems encountered when attempting to inject spins from a low resistivity ferromagnetic metal into a conventional semiconductor in the diffusive regime [29]. It should also be possible to make a field-effect device to modulate a spin-polarized current in the doped hexaboride material and achieve gain. If a p-type hexaboride with some of the Ca replaced by a monovalent ion were also found to be ferromagnetic, it should even be possible to make the spin analogs of bipolar devices.

Both Ca and B are light elements so that the spin-orbit coupling is small. Since the lowest conduction band and highest valence band are both singly degenerate, the intrinsic spin-flip scattering should be weak with spin-flip scattering lengths comparable to what has recently been observed in carbon nanotubes [30]. This should also hold for the impurity states if the latter can be described within an effective mass model. Because of the small size of the spin-orbit coupling, because the magnetic moment is so tiny, and because the hexaborides are cubic, the material should be magnetically extremely soft with a very small intrinsic magnetocrystalline anisotropy. This could be important for sensor applications.

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Note added.—After submission of the manuscript, evidence for the existence of a band of partly localized, partly itinerant defect states and thus implicitly for the existence of a band gap has emerged from NMR spin-lattice relaxation measurements [31] and from thermopower measurements [32].

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