Magnetism in thin films of CaB_6 and SrB_6

L. S. Dorneles, M. Venkatesan, M. Moliner, J. G. Lunney, and J. M. D. Coey[a)]
Physics Department, Trinity College, Dublin 2, Ireland

(Received 12 August 2004; accepted 25 October 2004)

Thin films of disordered hexaborides CaB_6 and SrB_6 deposited by pulsed-laser deposition on MgO (100) or Al_2O_3 (001) substrates are ferromagnetic. A typical room-temperature moment per unit area of substrate is 350 $\mu_B\,nm^{-2}$, with the largest values being found for CaB_6 on Al_2O_3. Lattice defects are the likely origin of the exotic, high-temperature magnetism. The moment, which is present in films as thin as 12 nm, appears to reside in an interface layer whose polarization is approximately 0.4 Tesla. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1840113]

The alkaline–earth hexaborides, AB_6, A=Ca, Sr, Ba crystallize in the cubic CsCl structure where the B_6 molecule forms a large divalent anion (Fig. 1). At first, CaB_6 was thought to be a semimetal, but it was subsequently established that the stoichiometric compound is actually a semiconductor with a gap of about 1 eV.[1–5]

The announcement in 1999 of weak, high-temperature ferromagnetism in $Ca_{1-x}La_xB_6$ with x=0.005 by Young *et al.*[6] was surprising because the compound contains no ions with partially-filled *d* or *f* shells, which are normally a prerequisite for ferromagnetism in ionic solids. The moment was very small, less than 4×10^{-4} μ_B/formula (0.08 μ_B/La), resulting in a magnetization of no more than 45 A m^{-1}. This was originally attributed to the conduction electrons introduced by La doping, a manifestation of the spontaneous ferromagnetism of low-density electron gas first proposed by Bloch in 1929.[7] However, a similar weak ferromagnetism was subsequently found in the undoped hexaborides.[8–10] The moment in CaB_6 was as high as $10^{-2}\mu_B$ per formula, depending on sample stoichiometry. The magnetization, which did not depend on electron doping, was associated with the surface regions of the crystals.[11–13] There were also suggestions by Fisk *et al.*[2] that the magnetism could be associated with a small concentration of intrinsic defects.

Suspicion fell on traces of ferromagnetic contaminants.[10] Prime suspects are αFe(T_C=1044 K), Fe_2B(T_C=1015 K), and FeB(T_C=598 K). Traces of iron and nickel recently identified on the faces of crystals grown from aluminium flux prompted two of the authors of the original report[6] to state that 'the weak ferromagnetism in electron-doped CaB_6 is extrinsic, due to surface contamination by ferromagnetic compounds containing Fe and Ni.'[13] However, retraction of the claim of an exotic origin for ferromagnetism in these hexaborides may have been premature. While no single crystals of CaB_6 made by another group from highly-pure 6N boron exhibited any detectable magnetic signal, some materials made from 3N boron were ferromagnetic with a moment of up to 2×10^{-3} μ_B per formula, depending on stoichiometry and carrier density.[5] Defects or impurities form donor states in the gap, 0.18 eV below the conduction band. Furthermore, experiments where the stoichiometry of ceramic samples was altered by heating in different conditions showed variable magnetic moments of up to about 10^{-2} μ_B per formula, suggesting that the ferromagnetism is defect-related.[14] Defects tend to enhance the magnetization and increase T_C.

Here we try to settle the controversy regarding the origin and significance of the ferromagnetism observed in alkaline–earth hexaborides, by means of thin film samples deposited on different substrates. Thin films have a much greater surface or interface to volume ratio than single crystals or polycrystalline ceramics, so the role of defects may be enhanced.

Targets of CaB_6 and SrB_6 were prepared by sintering 13 mm pressed pellets of commercial hexaboride powders of 99.5% purity in vacuum at 950 °C. Thin films were prepared using a KrF excimer laser operating at 248 nm with an energy density of 1 J cm^{-2} on the target. Substrates were $5\times5\times0.5$ mm^3 slices of MgO (100) or Al_2O_3 (001), maintained at 550 °C in a vacuum of 6×10^{-5} Torr. Film thickness was determined by small-angle x-ray scattering (Fig. 1). No Bragg reflections could be detected for films on MgO substrates, because boride and substrate both have cubic crystal structures, with similar lattice parameters. On Al_2O_3 however, any Bragg peaks were very broad, indicating a disordered lattice. The films appeared smooth in the scanning electron microscope, except for droplets of diameter 1 μm produced by the laser ablation process, which accounted for no more than 5% of the mass of any film. As-deposited films were insulating, but *in situ* postdeposition annealing at 850 °C in the deposition chamber led to film resistivity of order 5 Ω cm for CaB_6, and values an order of magnitude greater for SrB_6. Both showed an upturn in resistance at low temperature corresponding to an activation energy of 1 meV.

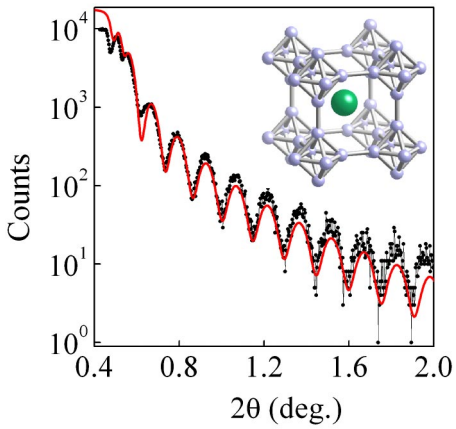

FIG. 1. (Color online) Small-angle x-ray scattering for a thin film of CaB_6 on MgO (100). Inset shows the hexaboride crystal structure.

[a)]Electronic mail: jcoey@tcd.ie

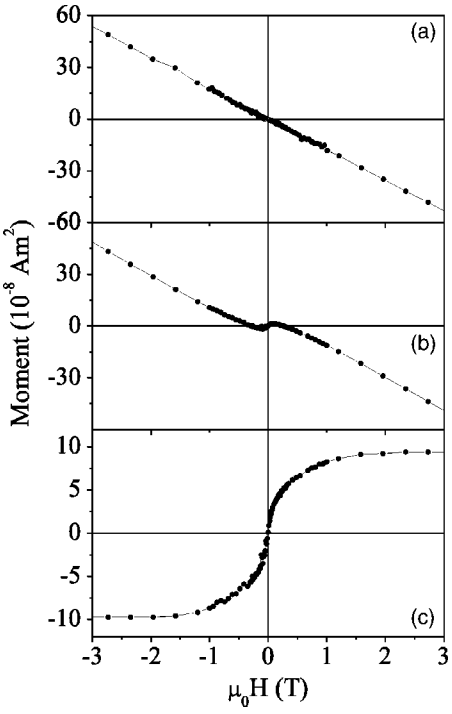

FIG. 2. Room-temperature magnetization curves (a) for a blank Al_2O_3 substrate, (b) for a CaB_6 film on Al_2O_3, and (c) for the film after subtracting the substrate contribution.

No magnetoresistance was observed at room temperature.

Magnetization measurements were made using a 5 Tesla Quantum Design MPMS XL SQUID magnetometer. Samples were mounted in drinking straws after removing the corners of the substrates. Mounting was either horizontal (perpendicular to the applied field) or vertical (parallel to the applied field). All measurements were made at the maximum gradient point of the second derivative curve, with no autotracking. The SQUID is calibrated for a sample occupying a volume of diameter 3 mm and height 3 mm at the center of the pickup coils; since the substrates exceed this volume, the sensitivity of the instrument depends on sample orientation. It was calibrated by measuring a film of magnetite in both orientations.

The first curve in Fig. 2 shows the diamagnetism of a blank Al_2O_3 substrate subjected to the same thermal cycle in the deposition chamber as one with a thin film deposited on it. The susceptibility, -4.8×10^{-9} m^3 kg^{-1}, is in agreement with the handbook value for Al_2O_3, -4.6×10^{-9} m^3 kg^{-1}. It is practically independent of temperature; the amount of paramagnetic 3*d* ions present is less than 2 ppm, judging from the weakness of the Curie-law upturn in susceptibility at low temperature, and assuming $S=5/2$. Neutron activation analyses of the substrates indicated that Fe and Ni were below the detection limit of 1 ppm; Mn and Co were 2–3 ppm. For some of the MgO substrates, however, there was a clear Curie–Weiss upturn of the susceptibility below 50 K. Attributing this to Fe^{2+} impurities, their concentration in the substrate is estimated as 100 ppm. The room-temperature magnetization curve of the thin film shown in Fig. 2(c) was obtained after subtracting off the diamagnetic background due to the substrate. This measurement was made with the field applied perpendicular to the substrate plane. Moments are quite variable, depending on the film–substrate pair as shown in Table I; SrB_6 has roughly the same moment on both substrates, 6×10^{-8} A m^2. CaB_6 on MgO has the smallest moment 3.6×10^{-8} A m^2, whereas the greatest moment of 15×10^{-8} A m^2 is obtained for CaB_6 on Al_2O_3. Averaged over the film thickness, the latter corresponds to a moment of 0.5 μ_B per formula unit or a film magnetization of 65 kA m^{-1}. However, the moment does not vary in any systematic way with film thickness. For example, the moment of a 12 nm film of CaB_6 on Al_2O_3 exceeds that of a 150 nm film. This is why moments are expressed in Bohr magnetons per unit area of substrate in Table I.

TABLE I. Magnetic moments and anisotropy fields of the thin films.

Film	Substrate	σ (μ_B nm^{-2})	Anisotropy field (kA m^{-1})
CaB_6	MgO	170	150
CaB_6	Al_2O_3	689	370
SrB_6	MgO	252	330
SrB_6	Al_2O_3	321	180

Figure 3 shows the anisotropy of the magnetization of a film of SrB_6 on MgO. Little hysteresis is observed in the room-temperature magnetization curves. A demagnetizing effect is evident in the perpendicular direction, which is consistent with the magnetization of a nonuniform thin film, but not, for example, with spherical clusters. Judging from the initial slope of the perpendicular curve, the demagnetizing field is at least 0.4 T. Assuming a demagnetizing factor of 1, the magnetic moment is located in a thin layer of thickness of 10 nm. In view of the dependence of magnetic moment on the substrate, this layer should be at the substrate/hexaboride interface rather than at the free surface. The location of the magnetization in a thin layer is borne out by the absence of any systematic variation with film thickness.

The observed moments per formula unit of CaB_6 or SrB_6 in the thinnest films are between two and four orders of magnitude greater than anything previously seen in single crystals or polycrystalline hexaboride ceramics. The hypothesis that extraneous ferromagnetic phases are the source of the ferromagnetism can be excluded on the basis of the data at hand: (i) iron is the most likely ferromagnetic contaminant,[11,13] but an Fe/Ca atomic ratio exceeding 100% would be needed to explain the magnetization of the thinnest CaB_6 films on Al_2O_3, for example. No such impurities were detected by EDAX analysis which showed an Fe/Ca ratio of

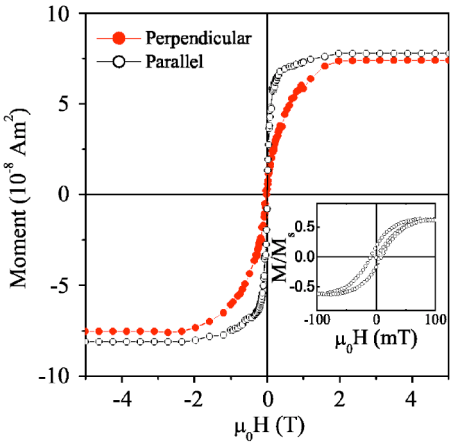

FIG. 3. Magnetization curves for SrB_6 on MgO, with the field applied perpendicular or parallel to the substrate.

less than 3%; (ii) much smaller moments are observed for CaB_6 films on MgO which proves that no extraneous ferromagnetism arises from the substrate or deposition process; and (iii) an anisotropy of the ferromagnetism found in some of the films is quite unlike that of any known ferromagnetic phase, although it is similar to that discovered in thin films of HfO_2 (Ref. 15) and also in films of ZnO (Ref. 16) or SnO_2 (Ref. 17) with various dopants.

What then is the origin of this remarkable ferromagnetism? The data suggest that the effect is governed by the material/substrate combination. It is known that certain atomic defects in ionic crystals with two trapped electrons or holes may have a low-lying triplet state.[18] We suggest that these states overlap to form an impurity band, which somehow mediates a long-range ferromagnetic interaction between the magnetic moments associated with molecular orbitals in the vicinity of the defects. The appearance of magnetic moments on anion defects was proposed by Monnier and Delley,[19] who ascribed the ferromagnetism in CaB_6 to anion vacancies (F^0 centers), although the exchange mechanism was not explained. A neutral B_6 vacancy was found to create a moment of $2.4\mu_B$ distributed over the six neighbouring boron octahedra.

Models of spin triplet states associated with degenerate molecular orbitals predict a spin moment of $2\ \mu_B$ per defect. Large defect concentrations in the interface region ($10^{28}\ m^{-3}$) are therefore needed to explain the magnetization of the disordered hexaboride films. The anisotropy of the magnetization of some films suggests that the moment may also have significant orbital character. How this arises is not clear. According to Hund's rules, a single boron $2p$ electron occupies a nonmagnetic $j=0$ state. But the electrons associated with point defects are expected to occupy extended orbitals whose spatial distribution will be influenced by the proximity of the film interface or surface. Because of their spatial extent, the orbital moment may be unquenched.

In conclusion, our results on disordered hexaboride thin films establish that the high-temperature ferromagnetism is a novel physical phenomenon, which demands an original explanation, although not the one originally advanced. Retraction of the claim of an exotic origin was premature. Much work needs to be done to characterize the defect and interface states in hexaboride and other thin films that exhibit d^0 ferromagnetism. Thin film devices, if they are to be made, will need to use layers about 10 nm thick. Theory will have to address the issue of the anisotropy of the saturation magnetization and the nature of the strong ferromagnetic coupling.

This work was supported by Science Foundation Ireland. We are grateful to Stefano Sanvito, Charles Patterson, and Claudia Felser for helpful discussions, and to Yang Zhou for the AGFM measurement.

[1] J. D. Denlinger, J. A. Clack, J. W. Allen, G. H. Gweon, D. M. Poirier, C. G. Olsen, J. L. Sarrao, A. D. Bianci, and Z. Fisk, Phys. Rev. Lett. **89**, 157601 (2002).
[2] Z. Fisk, H. R. Ott, V. Barzykin, and L. P. Gor'kov, Physica B **312**, 808 (2002).
[3] S. Souma, H. Komatsu, T. Takahashi, R. Kaji, T. Sasaki, Y. Yokoo, and J. Akimitsu, Phys. Rev. Lett. **90**, 027202 (2003).
[4] Z. Wu, D. J. Singh, and R. E. Cohen, Phys. Rev. B **69**, 193105 (2004).
[5] B. K. Cho, J. S. Rhyee, B. H. Oh, M. H. Jung, H. C. Kim, Y. K. Yoon, J. H. Kim, and T. Ekiino, Phys. Rev. B **69**, 113202 (2004); cond-mat/0310068.
[6] D. P. Young, D. Hall, M. E. Torelli, Z. Fisk, J. L. Sarrao, J. D. Thompson, H. R. Ott, S. B. Oseroff, R. G. Goodrich, and R. Zysler, Nature (London) **397**, 412 (1999).
[7] F. Bloch, Z. Phys. **57**, 545 (1929).
[8] P. Vonlanthen, E. Felder, L. Degiorgi, H. R. Ott, D. P. Youmg, A. P. Bianchi, and Z. Fisk, Phys. Rev. B **62**, 10076 (2000).
[9] T. Moriwaka, T. B. Nishioka, and N. K. Sato, J. Phys. Soc. Jpn. **70**, 341 (2001).
[10] H. R. Ott, J. L. Gavilano, B. Ambrosini, P. Vonlathen, E. Felder, L. Digiorgi, D. P. Young, Z. Fisk, and R. Zysler, Physica B **281–282**, 423 (2000).
[11] K. Matsubayashi, M. Maki, T. Tsuzuki, T. Nishioka, and N. K. Sato, Nature (London) **420**, 143 (2002).
[12] C. Meegoda, M. Trenary, T. Mori, and S. Otani, Phys. Rev. B **67**, 172410 (2003).
[13] M. C. Bennett, J. van Lierop, E. M. Berkeley, J. F. Mansfield, C. Henderson, M. C. Aronson, D. P. Young, A. Bianchi, Z. Fisk, F. Balakirev, and A. Lacerda, Phys. Rev. B **69**, 132407 (2004).
[14] S. E. Lofland, B. Seaman, K. V. Ramanujachary, N. Hur, and S. W. Cheong, Phys. Rev. B **67**, 020410(R) (2003).
[15] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature (London) **430**, 630 (2004).
[16] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. **93**, 177206 (2004).
[17] C. B. Fitzgerald, M. Venkatesan, and J. M. D. Coey (unpublished).
[18] A. M. Stoneham, *Theory of Defects in Solids* (Clarendon, Oxford, 1975), Chap. 16.
[19] R. Monnier and B. Delley, Phys. Rev. Lett. **87**, 157204 (2001).