The Origin of Weak Ferromagnetism in CaB_6

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Abstract

We have combined the results of magnetization and Hall effect measurements to conclude that the ferromagnetic moments of lightly doped CaB_6 samples display no systematic variation with electron doping level. Removal of the surface with acid etching substantially reduces the measured moment, although the Hall constant and resistivity are unaffected, indicating that the ferromagnetism largely resides on and near the sample surface. Electron microprobe experiments reveal that Fe and Ni are found at the edges of facets and growth steps, and on other surface features introduced during growth. Our results indicate that the weak ferromagnetism previously reported in undoped CaB_6 is at least partly extrinsic.

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The discovery of ferromagnetism in La doped CaB_6 [1] was both remarkable and unexpected. Angle resolved photoemission (ARPES) measurements [2] find that undoped CaB_6 is a direct gap semiconductor, in agreement with pseudopotential calculations of the electronic structure using the GW approximation [3]. Electrons may be introduced by replacing divalent Ca ions with trivalent La ions, leading to the formation of a Fermi surface, confirmed by both de Haas - van Alphen [4] and ARPES [5] measurements on $Ca_{1-x}La_xB_6$ ($0.1 \leq x \leq 0.2$). Despite the apparently nonmagnetic and semiconducting character of the system, ferromagnetism was observed in $Ca_{1-x}La_xB_6$ for ($0.001 \leq x \leq 0.05$) [1], with a maximum saturation moment $M_S = 0.07$ μ_B per electron for $x = x_c = 0.005$. Since these moments would on average be separated by ~ 25 $\mathring{A}$ at optimal doping x_c, it was remarkable that Curie temperatures as large as 900 K were observed [6].

These observations have been discussed in several different theoretical frameworks. In the first, ferromagnetism is considered to be an instability of the low density electron gas which is introduced by doping, analagous to Wigner crystallization [7, 8]. While the systematics of how moments and Curie temperatures depend on electron concentration remain lacking, the electron concentrations in the La doped samples are seemingly too large for the high temperature ferromagnetism to be explained by this scenario [9]. Subsequently, attention has shifted to the defect states themselves as the origin of the moments [10, 11], which are envisaged to play a role similar to that of the localized dopant moments in dilute magnetic semiconductors. However, the central challenge to both these theoretical scenarios lies with reproducing a Curie temperature which approaches the Fermi temperature, in a system with weak and dilute moments.

The possibility that the weak ferromagnetism in CaB_6 might be of extrinsic origin has been considered since its discovery. Young et al [1] pointed out that the largest moments were found for the same critical concentration x_c in trivalent La, Ce, and Sm doped CaB_6 and SrB_6, where each dopant ion introduces a single electron, and that this concentration is exactly double that found in tetravalent Th doped CaB_6, where each Th ion introduces two electrons. These results argue against accidental contamination of the samples with a ferromagnetic substance. Subsequently, acid etching experiments [12, 13, 14] found that the magnetization can sometimes, but not always, be reduced by removing the surface of the sample. While these experiments would not necessarily rule out surface contamination, they may also argue that the ferromagnetism is a feature of the intrinsic surface electronic struc-

ture of CaB_6, and not of the bulk. However, recent mass spectrometry measurements [15] have shown that Fe is present in several ferromagnetic samples, in rough proportion to the measured saturation moment. Still, the role of these Fe contaminants in the high T_C ferromagnetism is ambiguous, as they may simply introduce a nucleation center in the bulk for an extended magnetic state, involving both electrons from the Fe and from the intentional dopants, much as is found in dilute magnetic semiconductors [11, 16]. Explicating the role of these Fe contaminants is crucial for distinguishing between an essentially intrinsic source for the high T_C ferromagnetism in electron doped CaB_6, or a wholly extrinsic mechanism.

The goal of the experiments presented here is to determine whether an intrinsic factor, electron concentration, or extrinsic factors, such as ferromagnetic contamination, control the magnitude of the measured saturation moment in electron doped CaB_6. We have performed magnetization and Hall effect measurements on 16 different undoped CaB_6 single crystals, taken from several different batches. All samples were single crystals of CaB_6 prepared using an Al flux technique. None of these crystals were intentionally doped, and variation in the Ca:B stoichiometry is presumed to be responsible for the different carrier densities observed [11]. Hall effect measurements were carried out for temperatures from 0.3 K - 100 K using a 9 Tesla superconducting magnet and also the 50 Tesla medium pulse length magnet at the National High Magnetic Field Laboratory in Los Alamos. In every sample and at every temperature, the Hall voltage was entirely linear in field, with a slope which indicates that electrons are the dominant carriers. The electron concentration n is almost temperature independent, although there is some indication of magnetic freezeout in the most lightly doped samples at the lowest temperatures. Magnetization measurements were carried out using a Quantum Design MPMS magnetometer.

All of the samples we investigated were ferromagnetic, with highly nonlinear magnetization curves and coercive fields which vary from $\sim$ 40 - 200 Oe, consistent with previous results on La-doped CaB_6 [1]. A Langevin function was fit to each M(H) curve, and the resulting saturation moment M_S at 250 K is plotted in Fig. 1a for each sample as a function of its electron density n, measured at 0.3 K. There is no apparent trend in M_S with n, although we note that the moments found in our samples are in some cases substantially larger than those reported in $Ca_{1-x}La_xB_6$ [1]. The corresponding moment per electron M_S/n is plotted in Fig. 1b. The moment per electron reaches unphysically large values in the most lightly doped samples, approaching 35 μ_B per electron. Consequently, we conclude that the

variations in the ferromagnetic moments of our samples are not likely to be controlled by the measured variations in electron concentration.

Etching experiments indicate that the saturation moment can be significantly reduced by removing the crystal surface. A 50% solution of aqua regia was used to etch the samples, and using an edge profiler we determined that the etch rate for flat surfaces was 300 ± 100 $\mathring{A}$ per second, approximately linear in time. The effect of etching on the magnetization of a sample with an electron concentration of 1.2×10^{19} cm^{-3} is depicted in Fig. 2a. The first etch removed approximately 6000 $\mathring{A}$ of the surface, and resulted in a 47% reduction in M$_S$. A repeat of the etch did not result in any further decrease of M$_S$, although it was confirmed that the etch removed an additional 6000 $\mathring{A}$ of the sample surface. The temperature dependence of the resistivity of this sample is plotted before and after the etch in Fig. 2b. The resistivity is unchanged by the etch, suggesting that it is representative of the bulk resistivity. The Hall effect was similarly found to be unaffected by etching. These etching experiments suggest that at least part of the ferromagnetic moment is associated with the crystal surface, although they do not rule out an additional bulk contribution.

Direct observation of the crystal surfaces by electron microscopy reveals the identity of this inferred surface magnetic phase. We have performed electron backscattering and microprobe experiments on the as-grown crystals using a Cameca Microprobe Analyzer with five wavelength dispersive spectrometers at the University of Michigan Electron Beam Microanalysis Laboratory. We have examined a total of 10 different crystals, which overall display two qualitatively different surface morphologies. A number of our samples grow with extremely flat and smooth crystal facets, often with distinct macroscopic terracing. An example of this type of crystal surface is shown in the electron backscattering image of Fig. 3a. It is evident from this image that the sample composition is quite homogeneous, but that the edges of the growth steps are decorated with a substance with a large atomic number. Microprobe experiments found that the only atomic species present above background in this field of view were Ca, B, O, Fe, and Ni. Microprobe maps for Ca, Fe, and Ni (K-α transitions) are presented in Fig. 3 b-d. The Ca map(Fig. 3b) indicates that the surface is clean and unobstructed, except perhaps in the deepest recesses of the terraces, and that the overall Ca composition is spatially uniform. Strikingly, Fig. 3c shows that Fe is only found on the edges of the terrace steps, and on the natural facets of the crystal. Fig. 3d shows that a small amount of Ni also is found on these edges, although not everywhere that the

Fe is observed. These decorative phases are likely to be close in composition to pure Fe and Ni, since we observe no significant enhancement of other elements in these regions. Some as-grown single crystals have rough surfaces, although the degree of roughness is highly variable among samples. Fig 4a is a backscattering image of one such crystal, showing that the contaminants are trapped in some of these surface features. The Fe and Ni microprobe maps(Figs 4b,4c) show that here Fe and Ni are present in roughly equal amounts, but again are preferentially found in different areas.

Acid etching is generally less effective at removing Fe and Ni found at crystal facets and growth steps than the Fe and Ni found trapped in surface features. The Fe microprobe map of Fig. 4d shows that the surface of this crystal is partially covered by an Fe film. The Fe film is almost completely removed by a 30 second acid etch (Fig. 4e), although new areas of Fe decoration are subsequently revealed at the edges of the crystal facets. We think it is unlikely that this Fe is actually introduced by the acid etch. Instead, we suggest that the Fe decoration found at the facets in this sample extends into the crystal, and that new decorated facet edges are exposed by etching. A subsequent 60 second etch (Fig. 4f) removed most of the Fe exposed at the facet, as well as the last remnants of the original film. While the amount of Fe decorating the facets of the sample in Fig. 4f is reduced by almost a factor of five by the first 30 second etch (Fig. 4g), virtually all of the remaining Fe was removed by the second 60 second etch. A similar examination of the crystal used in the magnetization study, shown in the inset of Fig. 2a, revealed that the Fe remaining after the final etch was similarly confined to the crystal facets. In every crystal which we examined, the electron backscattering image performed after etching reveals that while the Fe and Ni decoration of the step edge was removed - or at least greatly reduced - the underlying steps and facet edges remain and are undecorated.

To summarize, we have found Fe and Ni contaminants preferentially decorating the edges of facets and step defects in single crystals of undoped CaB_6, although in some samples they were also randomly dispersed over rough surfaces. The contaminants are generally found within $\sim$ 10,000 - 20,000 $\mathring{A}$ of the sample surface, and can be removed with the surface by acid etching. We demonstrate that the saturation moment of the sample is simultaneously reduced by the etching process, although the etch is more effective at removing Fe and Ni contaminants on the surface than from the step and facet edges. This observation suggests that variations in surface morphology from sample to sample may explain the rather different

etching results which have been reported [12, 13, 14]. Finally, we note that all the as-grown samples we investigated were to some degree ferromagnetic, independent of the amount of self-doping introduced by variations in the stoichiometry of the crystals.

The observation of Fe and Ni at the edges of step defects and facets introduced during crystal growth indicates that these contaminants were present in the melt. Step decoration has been extensively documented as a feature of epitaxial crystal growth [19, 20]. The preferential segregation of contaminants to the step edges requires that the Fe and Ni ions have high mobility on the crystal layers as they form, so that they diffuse to the edges of the layers without trapping. This is presumably only possible in CaB_6 because of the very high degree of crystalline perfection found in the alkali earth hexaborides [21]. It is unusual, but not unprecedented, that the minimum energy configuration for the Fe and Ni contaminants is at the step edge, and not the more highly coordinated environment found at the bottom of the step. We suggest that there is considerable lattice strain associated with replacing a Ca ion with the much larger Fe and Ni ions, and the step edge is preferred as a nucleation site for groups of defect ions because the strain can be relaxed here [22]. We speculate that the polar character of the B_6 octahedra may also assist this process by introducing uncompensated negative charge at the step edge, enabling bonding with the Fe and Ni ions which would be impossible along a flat surface of B_6 octahedra. Thus, the Fe and Ni migrate with the step edge, which moves vertically as the crystal grows layer by layer. In this way, the Fe and Ni contaminants end up at or near the surface of the crystal, as we observe.

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FIG. 2: (a): The measured magnetization M(H), for an as-grown crystal($\bullet$), and after 6000 $\mathring{A}$ ($\bigcirc$) and 12,000 $\mathring{A}$ ($\triangle$) of the surface have been removed by an acid etch. Inset: the Fe microprobe map obtained after the second etch clearly shows residual Fe caught in deep surface recesses. (b): The temperature dependence of the electrical resistivity ρ of the as-grown crystal ($\square$) and after 6000 $\mathring{A}$ of the surface($\bullet$) have been removed.

FIG. 3: (a): Electron backscattering image of an unetched single crystal, demonstrating contaminant decoration of the crystal facets. (b)-(d): Electron microprobe maps of the same region for Ca (b), Fe (c), and Ni(d).

FIG. 4: (a): Electron back-scattering image of an unetched single crystal. Electron microprobe maps of the same region for Fe (b) and Ni (c) demonstrate that the contaminants are caught in surface features. Fe microprobe maps of two different unetched samples (d,g) and after a 30 second acid etch (e,h), and after a subsequent 60 second etch (f,i).

FIG. 1: (a): The saturation moment M_S at 250 K as a function of the electron concentration n. Filled circles are from a previous La doping study [1], and for these four samples n is deduced from the nominal composition. (b): The same data, plotted as the moment per electron M_S/n. The overall slope results from the normalization to electron concentration n.

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