

due to a magnetic phase that exists in both CaB_6 and LaB_6 .

We found that there was a strong correlation between ΔM and m_{Fe} , where ΔM is the difference in magnetization at around 90 K (measured before and after acid treatment) and m_{Fe} is the mass of iron dissolved in the acid. There is also a correlation between $\Delta M/m_s$ and m_{Fe}/m_s , where m_s is the sample mass (Fig. 1c). The data correspond well to the saturation magnetization, straight-line curves for the ferromagnets FeB and Fe_2B that have critical temperatures at around 598 K and 1,015 K, respectively³. We conclude that the high-

temperature ferromagnetism observed by Young *et al.*¹ should be ascribed to these Fe–B phases.

The magnetization of CaB_6 also depends on the type of crucible used for synthesis: M measured at about 5 kOe at room temperature is roughly 0–2, 5–15 or 30 electromagnetic units (e.m.u.) per mol for samples synthesized using the BN, ZrO_2 or MgO crucibles, respectively. Inductively coupled plasma analysis of the used crucibles gave iron weight-concentrations, C_{Fe} , of 2–4, 17–46 and 160 parts per million for the BN, ZrO_2 and MgO crucibles, respectively. We find a correlation between M and C_{Fe} , indicating that the iron atoms moved from the crucible to the sample during synthesis.

Non-doped CaB_6 has also been claimed to exhibit ferromagnetism^{2,4}. It has been suggested³ that, as magnetic moments are confined within the sample surface of single-crystalline materials⁶, there can be no intrinsic ferromagnetic moments inside the sample. It is therefore likely that the origin of the ferromagnetism in $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ is the same as in CaB_6 . A sintered material is useful for revealing the origin of the ferromagnetism, as it has a large surface/volume ratio compared with a single crystal. We contend that ours is a reasonable explanation for why almost all samples should exhibit the same Curie temperature, despite their experimental differences.

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Young *et al.* reply — The results of Matsubayashi *et al.* on nominally stoichiometric, CaB_6 sintered powders arrive at a conclusion concerning our study¹ on ferromagnetism in this and related materials that differs in several ways from the conclusions of ongoing studies of aluminium-flux-grown single crystals (Z.F., S. Nakatsuji, F. Drymiotis, M. Bizimis, S. Yeo, J.D.T., A. Bianchi and H.R.O., unpublished results).

At issue is whether alien Fe–B phases are responsible for all of the observed ferromagnetism. Our conclusion is partly contained in ref. 2, in which it is stated that strongly interacting defects in off-stoichiometric CaB_6 (that is, comprising a few-tenths of a per cent) that carry magnetic

moments are responsible for the observed ferromagnetic properties. These defects may be iron atoms scavenged during the growth of CaB_6 crystals from boron-rich flux growths. We outline experimentally based arguments (Z.F. *et al.*, unpublished results) against the suggestion of Matsubayashi *et al.* that extrinsic Fe–B phases are the source of the ferromagnetism here. Almost all studies show the surface moments to be removed in acid solution, and these will not be discussed further.

In single crystals of CaB_6 grown from molten aluminium flux (starting composition for Ca:B, 1:1–1:9) with added iron (Ca:Fe, 1:0.01–1:1), high-temperature ferromagnetism is generally observed in crystals with Ca:B ratios greater than 1:6; the magnitude of the ordered moment is 3–5 e.m.u. per mol CaB_6 for all iron concentrations in the flux (Z.F. *et al.*, unpublished results). This lack of dependence of the measured ordered moment on the iron concentration in the flux suggests that alien Fe–B phases are not the source of ferromagnetism. Also, ferromagnetic CaB_6 crystals have a metallic electrical-resistivity characteristic ($dp/dT > 0$; ref. 2) that is consistent with the introduction of defects into the material.

If cobalt or nickel is added to the flux in concentrations equal to those of added iron, the crystals of CaB_6 show small-moment ferromagnetism only below about 10 K (Z.F. *et al.*, unpublished results), indicating that cobalt or nickel enters CaB_6 as low-concentration defects in preference to iron, and that cobalt and nickel do not magnetically interact as strongly as iron defects.

A picture emerges in which iron is involved in the weak high-temperature ferromagnetism of CaB_6 and in which off-stoichiometric growth of CaB_6 from excess boron melting results in the scavenging of iron from the flux, giving rise to crystals of CaB_6 containing about 0.1 atomic per cent Fe. Theoretical³ and experimental^{4,5} studies of CaB_6 indicate that the stoichiometric material is a semiconductor. This suggests that the physics here shares many similarities with that of manganese-doped GaAs. It will be interesting to determine the chemistry of the iron defects, as well as how they interact so strongly and conspire to magnetic order at higher temperatures.

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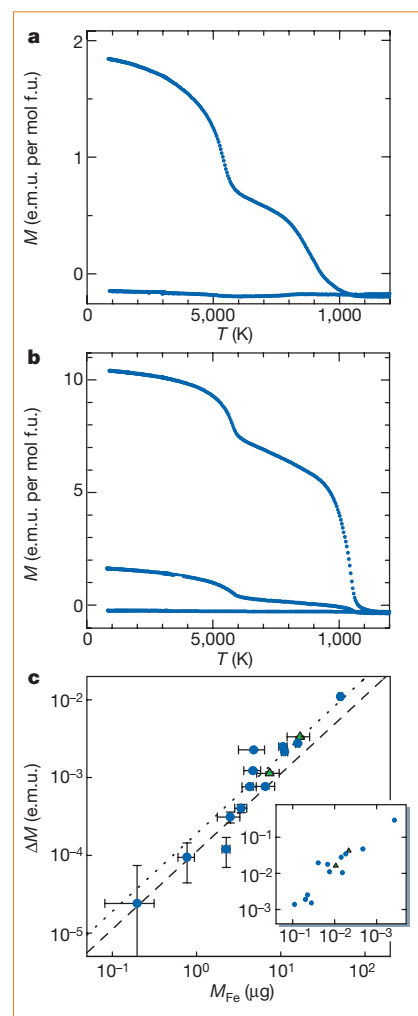


Figure 1 Magnetization of CaB_6 and LaB_6 . **a**, Temperature (T) dependence of magnetization (M , in e.m.u. per mol formula unit) of CaB_6 , measured at 5.1 kOe with decreasing temperature. Top and bottom curves, before and after acid treatment, respectively. **b**, Temperature dependence of magnetization of LaB_6 . Top and middle curves represent the sample synthesized using ZrO_2 before and after acid treatment, respectively; bottom curve represents the sample synthesized using BN. **c**, Correlation between magnetization reduction, ΔM , and iron mass, m_{Fe} . The data are consistent with the curves indicating the saturation magnetization of FeB (dashed line) and Fe_2B (dotted line). Inset, plot of $\Delta M/m_s$ in e.m.u. per gram (m_s , sample mass) against m_{Fe}/m_s in $\mu\text{g g}^{-1}$. Circles, CaB_6 ; triangles, LaB_6 .