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Defect driven magnetism in calcium hexaboride

S. E. Lofland, B. Seaman, and K. V. Ramanujachary
Department of Chemistry and Physics, Rowan University, Glassboro, New Jersey 08028-1701

Nanjing Hur and S. W. Cheong
Department of Physics, Rutgers University, Piscataway, New Jersey 08854-8019
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We have completed a systematic investigation of the structural and magnetic properties of CaB_6 over a wide range of temperatures. Unlike conventional magnetic systems, the mechanism for magnetism in this compound appears to be intimately connected to defects. We present direct evidence that introducing defects not only enhances the magnetization but also increases the ordering temperature.

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It has recently been noted that La-doped alkaline-earth hexaboride compounds such as $Ca_{1-x}La_xB_6$ have several puzzling properties. None of the elements individually is magnetic, but the compounds are ferromagnetic and have extremely high Curie temperatures T_C (~600 K).[1] This interest has greatly increased due to recent band-structure calculations that CaB_6 is a semiconductor,[2] making it a potential candidate for spintronics. It has been suggested that it is a ferromagnetic phase of a dilute electron gas,[3] the result of Ca vacancies in the hexaboride structure[4] or an excitonic ferromagnet.[5–7] In any case, the mechanism for ferromagnetism remains controversial. We have completed a systematic study of the interplay of structure and magnetism and demonstrate that defects mediate the magnetic interaction.

We have investigated two different samples of CaB_6, one purchased from Alpha Aesar and the other synthesized by solid-state reaction. The results are nearly identical for the two samples. The magnetization M was measured for fields H up to 12 kOe, in an atmosphere of either air or argon with a PAR455 vibrating sample magnetometer as the temperature T was varied between room temperature and 1100 K. X-ray-diffraction spectra were taken for T from 300 to 1100 K with a Scintag X-2 diffractometer in an atmosphere of either air or helium with Cu $K\alpha$ radiation. The scan rate was 2°/min. No background subtraction was used and Cu $K\alpha_2$ stripping was applied. A Pt standard was used in air, while a W standard was employed in He.

When the temperature dependence of the magnetization is first measured (''virgin curve'') in air at $H=10$ kOe (Fig. 1), it is nonmonotonic. The magnetization shows a small increase just above room temperature before decreasing, and it then increases at ~725 K and disappears at about 1025 K. Subsequent cooling and reheating curves do not repeat the virgin curve; however, they do retrace each other with a significant increase in the room-temperature magnetization as compared to that of the virgin curve. It appears that an irreversible process took place around 750 K. On the other hand, the high-temperature magnetization taken in argon (Fig. 2) is rather different: it is always less than that of sample in air, monotonic, reversible, and it shows a T_C for this material of ~900 K.

This difference between the samples measured in air and in an inert gas is elucidated in the temperature-dependent x-ray-diffraction patterns. The patterns taken in air (Fig. 3) clearly show new peaks belonging to CaB_4O_7 appearing at

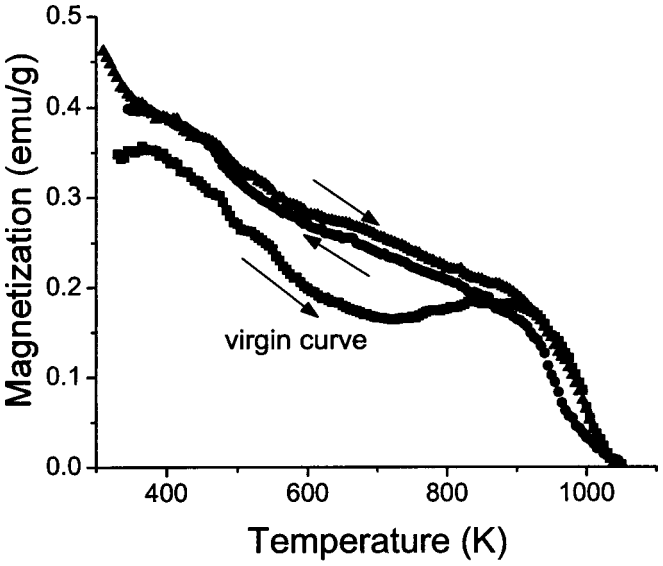

FIG. 1. The magnetization curve of CaB_6 in air. The ''virgin'' curve shows an unexpected increase in magnetization near 750 K.

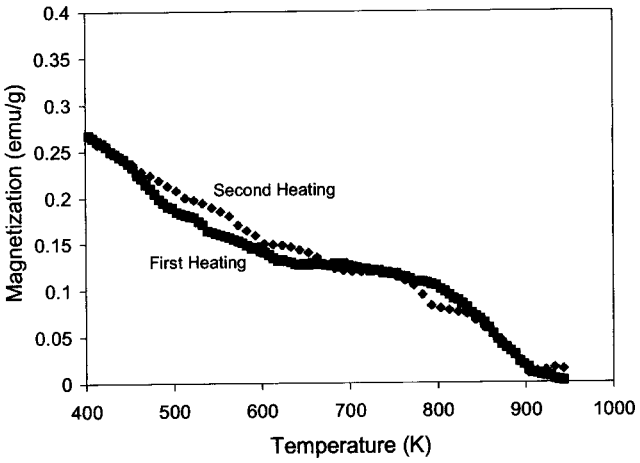

FIG. 2. The magnetization curve of CaB_6 in argon. The temperature dependence of the magnetization is repeatable.

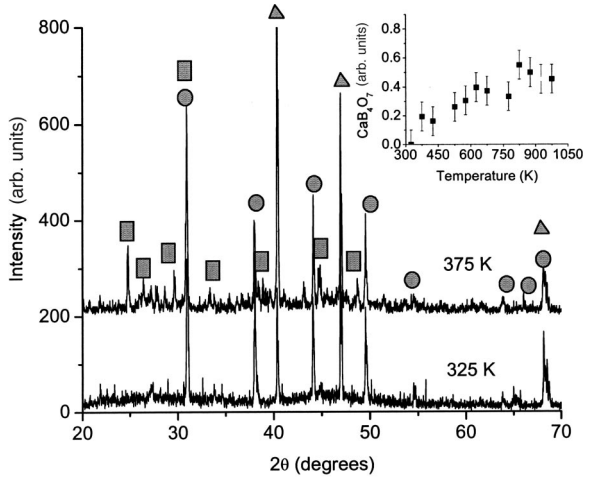

FIG. 3. X-ray-diffraction patterns for calcium hexaboride in air at 325 and 375 K. The circles correspond to diffraction peaks for CaB_6 (JCPDF 74-117) squares to CaB_4O_7 (JCPDF 31-0253) and triangles to Pt. The inset displays the intensity of the CaB_4O_7 diffraction peaks as a function of temperature. After the initial formation of the borate, the amount remains constant to about 800 K, where it again increases.

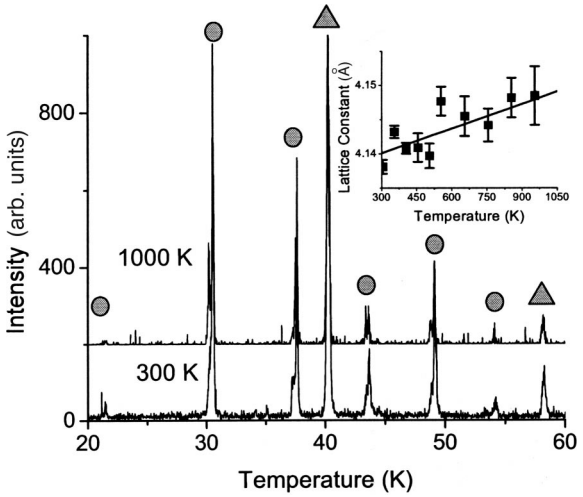

FIG. 4. X-ray-diffraction patterns for calcium hexaboride in helium at 300 and 1000 K. The circles correspond to diffraction peaks for CaB_6 and triangles to W. Unlike the sample done in air, the patterns remain unchanged. The inset shows the lattice constant as a function of temperature, yielding a coefficient of thermal expansion of 3×10^{-6} K.

375 K. The intensity of those peaks remains more or less constant to about 800 K (Fig. 3, inset), where they again increase. On the other hand, patterns taken in helium (Fig. 4) show single-phase material. All the peaks were indexed to a cubic structure and the lattice constant was determined with a least-squares-fitting program.[8] The extracted coefficient of thermal expansion $\alpha=3\times10^{-6}$ K^{-1} (Fig. 4, inset), in agreement with previous low-temperature measurements.[9]

There are clear correlations between the structural and magnetic data. The magnetization of the sample in air clearly begins increasing just above room temperature when the borate begins to form (Fig. 3, inset). The amount of borate remains more or less constant to about 800 K, where it increases again. This temperature coincides with the large increase in magnetization as well as the enhancement of T_C. The creation of the borates obviously introduces defects into the system, and it appears that these defects not only enhance the local moment but also the interaction.

These results appear to contradict some of the excitonic models of ferromagnetism[6] which seem to suggest that when T_C is high, an increase in T_C generally leads to decreased magnetization. These data also contradict the model proposed by Murakami *et al.*,[10] which indicates that T_c should be invariant and that significant introduction of defects would destroy magnetism, contrary to the observations here. These results can be interpreted in terms of either the impurity-induced ferromagnetism suggested by Ichinomiya[11] or vacancies of B_6 clusters as suggested by Monnier and Delley.[12] A similar conclusion was made by Fisk *et al.*[13]

While it has been suggested that the magnetism in CaB_6 can be attributed to Fe impurities,[14] our results indicate otherwise since there is the enhancement of both the ordering temperature and magnetization in air. If anything, air would cause the formation of Fe oxides, particularly for the small Fe particles. All iron oxides have a both lower T_C and a smaller magnetization than that of pure Fe, in contrast to the results presented here.

In conclusion, we have investigated the structural and magnetic properties of CaB_6 at high temperature. The pure sample has a T_C of about 900 K and a moment of about $0.01\mu_B$/f.u. However, by heating the sample in air to introduce defects, the moment can be increased by 20% even while the amount of CaB_6 is reduced and T_C can be raised to over 1000 K. We have presented the *in situ* observation of defect enhancement of the magnetic properties of this compound.

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