PERGAMON

Solid State Communications 123 (2002) 287–290

solid state communications

www.elsevier.com/locate/ssc

Ferromagnetism in lanthanum doped CaB_6: is it intrinsic?

Takao Mori[a,b,*], Shigeki Otani[a]

[a]Advanced Materials Laboratory, National Institute for Materials Science, Namiki 1-1, Tsukuba 305-0044, Japan
[b]PRESTO, Japan Science and Technology Agency (JST), Japan

Received 8 June 2002; accepted 24 June 2002 by H. Akai

Abstract

Magnetism of flux grown single crystals of undoped and lanthanum doped $Ca_{1-x}La_xB_6$ was systematically investigated, taking especial care in the preparation and quality control of crystals. $Ca_{1-x}La_xB_6$ ($x = 0.0029$, 0.0051, 0.015) crystals showed ferromagnetism at 300 K, which could be removed by treatment with hydrochloric HCl acid, indicating that the phenomena is due to iron impurities rather than being intrinsic. Chemical analysis which has been lacking in previous reports, was performed on HCl treated and untreated $Ca_{1-x}La_xB_6$ crystals and showed that the magnitude of observed ferromagnetism can be explained by the iron content. Crystals grown using HCl treated aluminum flux revealed that undoped CaB_6, which has a higher resistivity, accumulates less iron on the surface compared to $Ca_{1-x}La_xB_6$ and is diamagnetic, agreeing with our previous idea that iron is electrochemically plated onto the crystal surface during the flux removal procedure. The temperature dependence of the spurious magnetism of $Ca_{0.985}La_{0.015}B_6$ crystals was measured at high temperatures and exhibited anomalies around 780 K but also at 640 K. Previously, differences of the transition temperature with bulk iron metal were given as one of the reasons to support the ferromagnetism of $Ca_{1-x}La_xB_6$ to be an intrinsic effect, but this result indicates that this shift can be attributed to the environment of iron impurities on the crystal surface. These results strongly indicate that the ferromagnetism in lanthanum doped CaB_6 is not an intrinsic phenomenon.

PACS: 75.50.Cc; 81.05.Je

Keywords: A. Magnetically ordered materials; B. Crystal growth; D. Phase transitions

1. Introduction

The reported magnetism in lanthanum doped CaB_6 [1] has attracted great interest, since apparent ferromagnetism was induced in a compound composed of non-magnetic elements. However, there have been some conflicting data on the reproducibility of this phenomenon, with some doped samples not exhibiting ferromagnetism [2] and an apparent non-correlation between the magnetism and doping as monitored by resistivity [3]. Furthermore, we have previously observed that small amounts of iron can sometimes be found in even apparently high quality boride and borocarbide compounds and pointed out that explicit evaluation of iron impurities should be carried out when considering the weak magnetism of such compounds [4]. The lack of such chemical analysis must be noted in the previous work on the small moment ferromagnetism in boron compounds [1,5]. These sticking points motivated us to attempt to systematically investigate this phenomenon.

In a previous report we have demonstrated that ferromagnetism in $Ca_{0.9949}La_{0.0051}B_6$ and CaB_6 samples is indicated to arise from iron impurities on the surface of the crystals which could be removed by washing in hydrochloric acid [6]. It was also demonstrated that an iron impurity free synthesized sample of CaB_2C_2, which has similarities in the band structure to $Ca_{1-x}La_xB_6$ and was reported to be ferromagnetic [5], is actually diamagnetic with a magnetic susceptibility of -2.6×10^{-7} emu/g (-2.2×10^{-5} emu/f.u.) at 300 K [7]. In this work, we report on quality control and magnetism of $Ca_{1-x}La_xB_6$ crystals, since our previous report was not complete in that the undoped CaB_6 sample also showed ferromagnetism and corresponding iron content [6]. We find that in the case of crystals grown with the same HCl treated aluminum flux,

* Corresponding author. Tel.: +81-298-51-3354x530; fax: +81-298-52-7449.

E-mail address: mori.takao@nims.go.jp (T. Mori).

0038-1098/02/$ - see front matter
PII: S0038-1098(02)00308-3

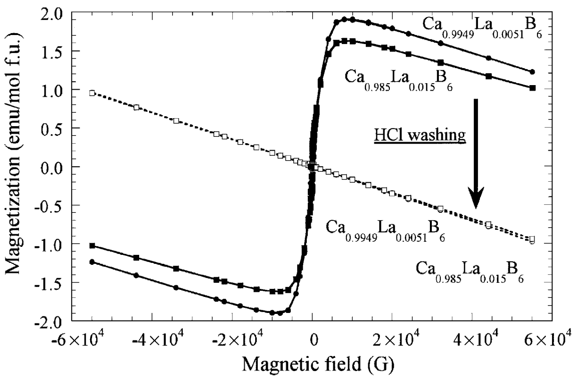

Fig. 1. Magnetic field dependence of the magnetization of $Ca_{0.9949}La_{0.0051}B_6$ (closed circles) and $Ca_{0.985}La_{0.015}B_6$ (closed squares) at 300 K, and the magnetization of HCl washed $Ca_{0.9949}La_{0.0051}B_6$ (open circles) and $Ca_{0.985}La_{0.015}B_6$ (open squares). The data for $Ca_{0.9949}La_{0.0051}B_6$ is the same as that given in Ref. [6].

undoped CaB_6 which has a higher resistivity accumulates less iron impurities than $Ca_{1-x}La_xB_6$ ($x = 0.0029$, 0.0051, 0.015). This suggests a simple non-intrinsic explanation to the reported different behavior of the magnetism for undoped and doped CaB_6 [1]. Furthermore, we have measured the high temperature susceptibility of the spurious iron-derived-ferromagnetism and found an anomaly at 640 K, which indicates that the iron on the surface of $Ca_{1-x}La_xB_6$ crystals is not in the bulk state and at least partially explains previous high temperature measurements by other researchers [1].

2. Experimental

Undoped and lanthanum doped CaB_6 were grown by the flux method using aluminum flux. The CaB_6 starting material was synthesized by reaction of $Ca(OH)_2$ and boron. CaB_6 and aluminum flux were put into an AlN crucible together with excess Ca in the form of $Ca(OH)_2$ in order to suppress the formation of AlB_2 crystals and calcium vacancies. Lanthanum was doped by adding commercial LaB_6 powder. The samples were reacted at 1450 °C in a flow of argon gas for 24 h, slowly cooled to 800 °C by 15 °C/h and then quenched. The aluminum flux was removed by NaOH solution, which is the typical method employed, see for example Ref. [8]. The $Ca_{0.9949}La_{0.0051}B_6$ and CaB_6 crystals reported in our previous work [6] were not quality controlled in the sense that different aluminum flux was used for the two samples. In this work, all the samples were prepared using HCl treated aluminum flux in order to lower the iron level and make a comparison for the doped and undoped samples.

Samples were characterized by crushing part of the crystals and using a high resolution powder X-ray diffractometer (Rigaku Co.; RINT2000) with Cu Kα radiation. Chemical analyses of all the samples were done with inductively coupled plasma (ICP) atomic emission spectroscopy after the samples were dissolved in nitric acid for 16 h at 110 °C.

Magnetization was measured by using a SQUID magnetometer at temperatures up to 800 K. Care was taken to construct a sample holder in which background effects were minimized.

3. Results and discussion

The room temperature resistivity of undoped CaB_6 was 21 mΩ cm. Upon doping 0.51% lanthanum, the resistivity of $Ca_{0.9949}La_{0.0051}B_6$ took a value sizably lower, 0.8 mΩ cm, indicating that the doping has intrinsically succeeded. The resistivity of $Ca_{0.985}La_{0.015}B_6$ was 1.1 mΩ cm, which is higher than the less doped $Ca_{0.9949}La_{0.0051}B_6$ and could possibly be due to effects of disorder, although a systematic investigation of the resistivity is beyond the scope of this work. Chemical analysis of the single crystals further supported the success of doping by yielding values of lanthanum content, which are used in the notations.

The magnetization curves of lanthanum doped calcium hexaboride $Ca_{1-x}La_xB_6$ ($x = 0.0051$, 0.015) at 300 K are shown in Fig. 1. Both of the samples exhibit ferromagnetism with hysteresis. The general magnitude of ferromagnetism (~2 emu/mol f.u.) is comparable to what was reported previously [1]. $Ca_{0.9971}La_{0.0029}B_6$ also shows a similar magnitude of ferromagnetism.

However, as reported earlier for $Ca_{0.9949}La_{0.0051}B_6$ [6], we find that by washing these samples in hydrochloric acid, the ferromagnetism disappears and the magnetism becomes diamagnetic (Fig. 1). Chemical analysis of the samples reveals an iron concentration of 0.012, 0.010, and 0.009 wt% for untreated $Ca_{0.9971}La_{0.0029}B_6$, $Ca_{0.9949}La_{0.0051}B_6$, and $Ca_{0.985}La_{0.015}B_6$, respectively. The magnitude of the ferromagnetic component of the untreated samples can sufficiently be explained by such an amount of iron impurities as are detected here. The iron concentration after washing in HCl of all three doped crystals is 0.001 wt% or less, which is the detection level of our analysis. The lanthanum concentration does not change on treatment with HCl. Therefore, it is further strongly indicated that the ferromagnetism observed originates from the iron impurities rather than being an intrinsic effect of the lanthanum doping of CaB_6.

The magnetization curve of undoped CaB_6 is plotted in Fig. 2. Whereas previously we observed ferromagnetism for the undoped sample also [6] due to a significant content of iron, we found that for undoped crystals grown with HCl treated aluminum flux, the iron content is low (0.001 wt%) and correspondingly the magnetism is diamagnetic -2.2×10^{-7} emu/g (-2.3×10^{-5} emu/f.u.). Since the

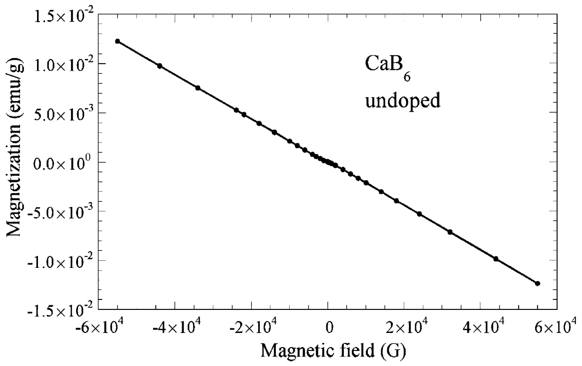

Fig. 2. Magnetic field dependence of the magnetization of undoped CaB_6 at 300 K.

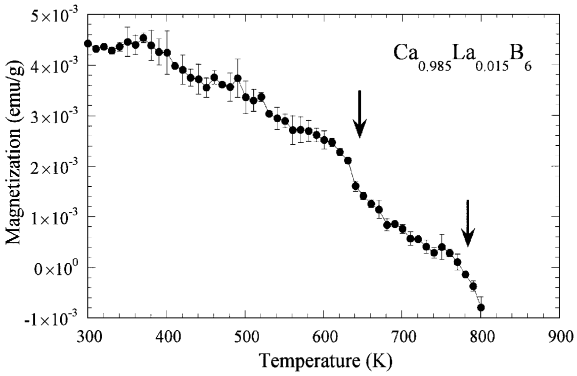

Fig. 3. Temperature dependence of the magnetization of $Ca_{0.985}La_{0.015}B_6$ measured with a field of 1 kG. The arrows indicate the anomalies observed at 640 and 780 K.

same HCl treated flux was used to grow the undoped and doped CaB_6 crystals in this work, we can conclude that the undoped CaB_6 accumulates less iron. Undoped CaB_6 has a higher resistivity than the $Ca_{1-x}La_xB_6$, and therefore, this supports our idea of a small amount of iron impurities being electrochemically plated onto the surface of the crystals during flux removal. This also explains why researchers studying this phenomenon have had a tendency to observe ferromagnetism only in the doped samples. And it should be stressed that this is an explanation, which points to the phenomena being non-intrinsic.

The high temperature magnetic susceptibility of $Ca_{0.985}La_{0.015}B_6$ is plotted in Fig. 3. Anomalies indicated by the arrows in the figure are observed at around 640 and 780 K. We have already demonstrated that the ferromagnetism in $Ca_{0.985}La_{0.015}B_6$ is indicated to be non-intrinsic and can be removed by washing the crystals in HCl acid. Although not sharply defined, the data indicate the ferromagnetism to have at least two components with transition temperatures of around 640 and 780 K. The ferromagnetism in $Ca_{1-x}La_xB_6$ first reported by Young et al. was observed to have a transition temperature at around 600 K and this was one of the reasons put forward that the phenomena was intrinsic since T_C is different from bulk iron ($T_C = 770$ K) [1]. Our results show that non-intrinsic iron impurities on the surface of $Ca_{1-x}La_xB_6$ crystals also can display similar transition temperatures. A possible explanation is that the iron impurities plated onto the surface of the $Ca_{1-x}La_xB_6$ crystals have a different environment than the bulk metal, although the exact state of impurities is not clear. A component with T_C similar to the bulk metal is also observed in our sample.

4. Conclusions

The magnetism of flux grown single crystals of undoped and lanthanum doped $Ca_{1-x}La_xB_6$ ($x = 0.0029$, 0.0051, 0.015) was systematically investigated, taking especial care in the preparation and quality control of crystals. All the lanthanum doped samples exhibited ferromagnetism at 300 K, which could be removed by treatment with HCl acid, and the iron content was revealed to be sufficient to explain the magnitude of the ferromagnetism. It was found that undoped CaB_6 accumulates less iron impurities than lanthanum doped samples, with the magnetism being diamagnetic for crystals grown with HCl treated aluminum flux. This further supports our previous conclusion that iron impurities were electrochemically plated onto the surface of $Ca_{1-x}La_xB_6$ crystals, since undoped CaB_6 has a higher resistivity than doped CaB_6. It also possibly explains the trend for researchers to observe ferromagnetism in the doped CaB_6 versus the undoped CaB_6.

Furthermore, we have measured the high temperature susceptibility of the spurious iron-derived ferromagnetism and found an anomaly at around 640 K, which indicates that the iron on the surface of $Ca_{1-x}La_xB_6$ crystals is not in the bulk state. This effectively refutes claims that the ferromagnetism observed in $Ca_{1-x}La_xB_6$ is intrinsic solely because T_C is different from that of bulk iron. Together with the previous report, the results obtained in this work strongly indicate that the ferromagnetism in lanthanum doped CaB_6 is not an intrinsic phenomenon.

Acknowledgments

The authors are greatly indebted to Dr E. Takayama-Muromachi for helping us with measurements. We also wish to acknowledge Mr Y. Yajima for performing chemical analyses on our samples. This work was partially supported by Special Coordination Funds.

References

[1] 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, R. Zysler, Nature 397 (1999) 412.

[2] T. Terashima, C. Terakura, Y. Umeda, N. Kimura, H. Aoki, S. Kunii, J. Phys. Soc. Jpn 69 (2000) 2423.
[3] T. Moriwaki, T. Nishioka, N.K. Sato, J. Phys. Soc. Jpn 70 (2001) 341.
[4] T. Mori, J. Phys. Soc. Jpn 71 (2002) Suppl. 323.
[5] J. Akimitsu, K. Takenawa, K. Suzuki, H. Harima, Y. Kuramoto, Science 293 (2001) 1125.
[6] S. Otani, T. Mori, J. Phys. Soc. Jpn 71 (2002) 1791.
[7] T. Mori, S. Otani, J. Phys. Soc. Jpn 71 (2002) 1789.
[8] S. Kunii, J. Phys. Soc. Jpn 68 (1999) 3189.