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Crystal Growth by the Floating Zone Method of Ce-Substituted Crystals of the Topological Kondo Insulator SmB$_6$

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Abstract: SmB$_6$ is a mixed valence topological Kondo insulator. To investigate the effect of substituting Sm with magnetic Ce ions on the physical properties of samarium hexaboride, Ce-substituted SmB$_6$ crystals were grown by the floating zone method for the first time as large, good quality single crystal boules. The crystal growth conditions are reported. Structural, magnetic and transport properties of single crystals of Sm$_{1-x}$Ce$_x$B$_6$ ($x = 0.05, 0.10$ and $0.20$) were investigated using X-ray diffraction techniques, electrical resistivity and magnetisation measurements. Phase composition analysis of the powder X-ray diffraction data collected on the as-grown boules revealed that the main phase was that of the parent compound, SmB$_6$. Substitution of Sm ions with magnetic Ce ions does not lead to long-range magnetic ordering in the Sm$_{1-x}$Ce$_x$B$_6$ crystals. The substitution with 5% Ce and above suppresses the cross-over from bulk conductivity at high temperatures to surface-only conductivity at low temperatures.

Keywords: crystal growth; optical floating zone method; SmB$_6$; Sm$_{1-x}$Ce$_x$B$_6$; topological insulator; kondo insulator

1. Introduction

Extensive investigations of the physical properties and excitations in the rare earth (RE) hexaboride compounds, REB$_6$, have been carried out over the past decades. These strongly correlated electron systems display an array of interesting magnetic and electrical properties, such as superconductivity (YB$_6$ [1–3]), intricate antiferromagnetic ordered phases owing to the displacement of rare earth ions within the rigid framework formed by the boron ions (GdB$_6$ [4–6]), complex antiferromagnetic phases with Kondo-like characteristics (CeB$_6$ [7–10]), semimetallic behaviour correlated with the transition to an unusual ferromagnetic state (EuB$_6$ [11–13]), typical metallic behaviour (LaB$_6$ [14–16]) or an exotic Kondo-like topological insulating state (SmB$_6$ [17–19]). Amongst the rare earth hexaboride compounds, cerium and samarium hexaborides have puzzled experimentalists and theoreticians alike, for a long time, in view of their intriguing physical properties. SmB$_6$ and CeB$_6$ are isostructural, crystallising in the same cubic CsCl-type structure ($Pm\bar{3}m$ space group) [20–22]. Sm and Ce ions replace the Cs ion, whilst the B$_6$ cubo-octahedral clusters take the place of the Cl ions at the corners of the cube. Nevertheless, the similarities between samarium and cerium hexaborides stop at the structural level, as they display very unusual, but different physical properties.

SmB$_6$ has long been known to be a Kondo insulator [23,24]; in recent times, new theoretical and experimental studies demonstrated that samarium hexaboride is a topological Kondo insulator (TKI) exhibiting topological surface properties [18,25–31], although this remains open to further
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investigation [32]. SmB6 is one of the most investigated Kondo insulators, mainly due to its exciting low temperature transport behaviour. As the temperatures decreases, an energy gap arises due to the interaction of the strongly correlated f-electrons and the conducting d-electrons, leading to an exponential increase in the electrical resistance of SmB6 [33–35]. Unexpectedly, upon further cooling, the resistance of SmB6 does not continue rising, as would be the case for a conventional insulator, but instead the resistance saturates at a finite value, below 5 K. This plateau in the resistivity has been attributed to a transition from a bulk conductivity characteristic of the high temperature region to a surface-dominated conductivity with bulk insulation at low temperature [36]. SmB6 is a mixed valence system that does not order magnetically, despite exhibiting antiferromagnetic correlations [33,37–40]. The Sm3+:Sm2+ ratio was determined to be independent of the temperature, and equal to approximately 0.6~0.7:0.4~0.3 [37,41]. Nevertheless, recent studies have shown that, upon the application of an external pressure, the Sm3+ configuration can be stabilised for sufficient time to allow long-range magnetic ordering of the samarium ions [42,43].

CeB6 is known to have a typical dense Kondo compound behaviour and a complex magnetic phase diagram [44–47]. Cerium hexaboride exhibits Kondo-like behaviour and has a Kondo temperature of $T_K = 19$ K. Upon cooling, CeB6 undergoes two magnetic ordering transitions: the first to a state in which antiferroquadrupolar and field-induced octupolar order coexist, below $T_Q = 3.2$ K, and then to an antiferromagnetic ordering of the Ce dipoles, below $T_N = 2.3$ K. Moreover, a subsequent study reported a new transition, of unknown origin, at $T_2 = 1.6$ K [45].

Recent progress, e.g., the discovery of the coexistence of an unusual metallic surface state and an insulating bulk state in SmB6 [19,48] and the observation of the long-range-ordered multipolar phases in CeB6 [47], has generated new interest in these materials. One route towards the investigation of the exotic metallic surface state arising in SmB6 and understanding of its topological nature, is through chemical substitution in this TKI with other rare earth ions. Recently, studies have been carried out on Eu, Gd, La, Y and Yb-substituted SmB6 [18,21,49–54]. High levels of substitution of non-magnetic ions (above 30%), and substitutions with small amounts of magnetic ions, were found to destroy the saturation seen in the low temperature resistivity of pure SmB6. It would therefore be interesting to investigate the effect that the substitution with a magnetic rare earth, such as Ce, in samarium hexaboride has on the robustness of the topological surface state of this TKI. Such an investigation is of course best carried out on high quality single crystals. In the present work, we investigated single crystals of Sm$_{1-x}$Ce$_x$B$_6$, with a focus on studying the effects that the substitution of the magnetic Ce ion have on the structural and physical properties of SmB6. The physical properties of Ce-substituted SmB6 samples have previously been investigated; however, this has only been done on polycrystalline samples and flux grown crystals [21,49,54]. Crystals of pure cerium and samarium hexaboride have previously been grown using the floating zone (FZ) technique [55–57]; however, Ce-substituted SmB6 compounds have only been grown in crystal form using the flux method [54]. SmB6 crystals grown using Al flux could suffer from contamination by the flux affecting some of the physical properties of the crystals, thereby making it difficult to study the intrinsic properties of pure samarium hexaboride [58]. We have successfully grown, for the first time, crystal boules of Sm$_{1-x}$Ce$_x$B$_6$ by the FZ method, which yields large, good quality crystals, free from flux or crucible contamination. The crystals obtained are especially suitable for the investigation of how the substitution with magnetic ions affects the surface and bulk behaviour of this interesting TKI.

2. Materials and Methods

Crystal boules of Sm$_{1-x}$Ce$_x$B$_6$ (x = 0.05, 0.10 and 0.20) were grown by the floating zone technique [57] using a CSI FZ-T-12000-X_VI-VP four-mirror xenon arc lamp (3 kW) optical image furnace (Crystal Systems Incorporated, Yamanashi, Japan). The crystal quality was checked using a backscattering X-ray Photonic-Science Laue camera system (Photonic-Science, St Leonards-on-Sea, UK). Single crystal samples were aligned for selected experiments, and rectangular prism-shaped
samples with [001], [1-10] and [110] directions perpendicular to the faces of the prism were cut from the Sm\(_{1-x}\)Ce\(_x\)B\(_6\) crystal boules.

Phase composition analysis was carried out using a Panalytical X-Pert Pro MPD diffractometer (Malvern Panalytical Ltd, Malvern, UK) with Cu Ka\(_1\) radiation (\(\lambda_{\text{Ka1}} = 1.5406\) Å). The diffraction patterns were collected at room temperature over an angular range of 10 to 110\(^\circ\) in 2\(\theta\) with a step size in the scattering angle 2\(\theta\) of 0.013\(^\circ\) and at various scanning times. The analysis of the X-ray patterns was performed using the Fullprof software suite [59].

Chemical composition of the crystal boules was investigated by energy dispersive X-ray spectroscopy (EDX) using a Zeiss SUPRA 55-VP scanning electron microscope (Carl Zeiss GmbH, Jena, Germany). LaB\(_6\) was used as a standard for the EDX measurements. X-ray photoelectron spectroscopy (XPS) analysis was also carried out in order to determine the elemental composition and the valence of the Sm ions. The samples were attached to electrically-conductive carbon tape, mounted on to a sample bar and loaded into a Kratos Axis Ultra DLD (Kratos Analytical Ltd, Manchester, UK) spectrometer (base vacuum of \(\sim 2 \times 10^{-10}\) mbar). The measurements were performed using a monochromated Al Ka X-ray source, at room temperature and at a take-off angle of 90\(^\circ\) with respect to the surface parallel. The data were analysed in the CasaXPS package (Casa Software Ltd, Teignmouth, UK), using Shirley backgrounds and mixed Gaussian-Lorentzian (Voigt) line-shapes and asymmetry parameters, where appropriate.

Magnetic susceptibility measurements were performed with a Quantum Design Magnetic Property Measurement System (Quantum Design Incorporated, San Diego, USA) on rectangular-prism-shaped Sm\(_{1-x}\)Ce\(_x\)B\(_6\) samples with an applied field parallel to the [100] (tetragonal), [110] (rhombic) and [111] (trigonal) crystallographic directions. The samples were cooled to 1.8 K in zero field and then the susceptibility as a function of temperature up to 300 K was measured on warming and then cooling with an applied field of \(H = 500\) Oe.

Alternating current (ac) resistivity measurements were performed using a Quantum Design Physical Property Measurement System on bar shaped samples of the Sm\(_{1-x}\)Ce\(_x\)B\(_6\) single crystals using the standard four-probe technique. Silver wire contacts were attached with silver paint, in a linear configuration, to the surfaces of the samples. The resistivity measurements were made from 2 to 300 K on both cooling and warming in zero applied field with an ac current of 1 mA at a frequency of 113 Hz.

3. Results and Discussion

3.1. Crystal Growth

Stoichiometric ratios of high purity SmB\(_6\) (99.9%, American Elements UK, Manchester, UK) and CeB\(_6\) (99.5%, Cerac Incorporated, Milwaukee, USA) powders were mixed together by ball milling for over 15 h, to prepare 5%, 10% and 20% Ce-substituted SmB\(_6\) polycrystalline samples. The resulting materials were then isostatically pressed into rods (typically 5–7 mm diameter and 40–50 mm long) and sintered in an alumina boat, at 1450 °C in a flow of argon gas for 12 h. Before the sintering process, the furnace was evacuated to give a vacuum of \(\sim 10^{-5}\) mbar. The resulting polycrystalline feed rods were used for the crystal growth. A binder (polyvinyl alcohol or polyvinyl butyral) was mixed with the powders in some cases to facilitate the formation of the rods.

Crystals of Sm\(_{1-x}\)Ce\(_x\)B\(_6\) (\(x = 0.05, 0.10\) and 0.20) were successfully grown by the floating zone method. The growths were carried out in an argon atmosphere at a pressure of \(\sim 3\) bar, using a growth rate of 18 mm/h. The feed and the seed rods were counter-rotated at \(\sim 15–25\) rpm. Initially, a crystal boule of SmB\(_6\) was used as a seed. Once good quality crystals were obtained, Sm\(_{1-x}\)Ce\(_x\)B\(_6\) crystal seeds were used for subsequent growths. A dark grey coloured deposition on the quartz tube surrounding the feed and seed rods was observed for all the growths, indicating the evaporation of boron during the growth process.
The Sm$_{1-x}$Ce$_x$B$_6$ boules were typically 4–5 mm in diameter and measured approximately 45–50 mm in length. All the crystals obtained developed facets as they grew and two very strong facets were present on almost the entire lengths of most of the grown crystals. Figures 1a–c show photographs of Sm$_{1-x}$Ce$_x$B$_6$ crystals grown in argon atmosphere at a growth speed of 18 mm/h. The quality of the grown boules was investigated by X-ray Laue diffraction, and Laue photographs were taken along the length of the boule, on the faceted sides (see Figure 1). The Laue patterns were identical along the whole length of the crystal boules.

![Figure 1](image)

**Figure 1.** Crystal boules of (a) Sm$_{0.95}$Ce$_{0.05}$B$_6$, (b) Sm$_{0.90}$Ce$_{0.10}$B$_6$, and (c) Sm$_{0.80}$Ce$_{0.20}$B$_6$, prepared by the floating-zone method in argon atmosphere at a growth rate of 18 mm/h. X-ray Laue back reflection photographs show the [001] orientation of aligned Sm$_{1-x}$Ce$_x$B$_6$ samples used for the physical properties measurements.

### 3.2. Structural and Composition Analysis

Structural and phase purity analysis was carried out using powder X-ray diffraction measurements on small pieces of the Sm$_{1-x}$Ce$_x$B$_6$ crystals selected from close to the end of each crystal boule. Figures 2a–c show the patterns for $x = 0.05$, 0.10 and 0.20, and profile matching (goodness of fit, GOF = 1.35, 1.51 and 1.92, respectively) to the cubic $Pm\bar{3}m$ space group [20] indicates that in each case the main phase is Sm$_{1-x}$Ce$_x$B$_6$, with no significant impurity phases present. One peak that does not belong to the $Pm\bar{3}m$ cubic structure can be observed at $\sim 26.6^\circ$ in the powder X-ray profiles of each of the Sm$_{1-x}$Ce$_x$B$_6$ crystals grown. The impurity was identified to be a hexagonal ($P6_3/mmc$) SmBO$_3$ phase [60]. Lattice parameters calculated from the profile matching were determined to be 4.1351(2) Å, 4.1384(2) Å and 4.1393(2) Å, respectively, for Sm$_{0.95}$Ce$_{0.05}$B$_6$, Sm$_{0.90}$Ce$_{0.10}$B$_6$ and Sm$_{0.80}$Ce$_{0.20}$B$_6$ (see Table 1). The values are in agreement with those reported in previous studies on Sm$_{1-x}$Ce$_x$B$_6$ polycrystalline samples [21].
with cerium is followed by a subtle lattice contraction, which is attributed to the replacement of the ionic radius of Sm$^{3+}$ (1.01 Å) is larger than the ionic radius of Sm$^{2+}$ ions (0.958 Å); thus, the substitution of samarium with cerium ions results initially in a lattice expansion (up to $x \sim 0.6$). Further substitution of samarium with cerium is followed by a subtle lattice contraction, which is attributed to the replacement of the larger Sm$^{2+}$ ions (1.15 Å) with Ce$^{3+}$. A similar effect on the lattice constant has been observed in the case of Gd and La-substituted SmB$_6$ [38,50,65].
Table 1. Lattice parameters calculated from profile matching the powder X-ray diffraction patterns of the $\text{Sm}_{1−x}\text{Ce}_x\text{B}_6$ ($x = 0.05, 0.10$ and $0.20$) crystals to the $\text{Pm}$ cubic structure. The previously reported structural parameters quoted for other members of the $\text{Sm}_{1−x}\text{Ce}_x\text{B}_{6−y}$ series [21] are included for completeness.

| $\text{Sm}_{1−x}\text{Ce}_x\text{B}_{6−y}$ | Chemical Composition | $a$ (Å) | Study |
|--------------------------------------|----------------------|---------|-------|
| $\text{SmB}_6$                      | $x = 0, y = 0$       | 4.1340(2) | Present work |
| $\text{Sm}_{0.05}\text{Ce}_{0.05}\text{B}_6$ | $x = 0.05, y = 0$ | 4.1351(2) | Present work |
| $\text{Sm}_{0.10}\text{Ce}_{0.10}\text{B}_6$ | $x = 0.10, y = 0$ | 4.1384(2) | Present work |
| $\text{Sm}_{0.11}\text{Ce}_{0.11}\text{B}_{6.9}$ | $x = 0.11, y = 0.1$ | 4.1358 | Ref. [21] |
| $\text{Sm}_{0.20}\text{Ce}_{0.20}\text{B}_6$ | $x = 0.20, y = 0$ | 4.1393(2) | Present work |
| $\text{Sm}_{0.22}\text{Ce}_{0.22}\text{B}_{5.7}$ | $x = 0.22, y = 0.3$ | 4.1378 | Ref. [21] |
| $\text{Sm}_{0.34}\text{Ce}_{0.34}\text{B}_{5.9}$ | $x = 0.34, y = 0.1$ | 4.1399 | Ref. [21] |
| $\text{Sm}_{0.38}\text{Ce}_{0.38}\text{B}_{5.7}$ | $x = 0.38, y = 0.3$ | 4.1403 | Ref. [21] |
| $\text{Sm}_{0.50}\text{Ce}_{0.50}\text{B}_6$ | $x = 0.50, y = 0$ | 4.1418 | Ref. [21] |
| $\text{Sm}_{0.65}\text{Ce}_{0.65}\text{B}_{5.7}$ | $x = 0.65, y = 0.3$ | 4.1421 | Ref. [21] |
| $\text{Sm}_{0.75}\text{Ce}_{0.75}\text{B}_{5.9}$ | $x = 0.75, y = 0.1$ | 4.1424 | Ref. [21] |
| $\text{Sm}_{0.82}\text{Ce}_{0.82}\text{B}_6$ | $x = 0.82, y = 0$ | 4.1418 | Ref. [21] |
| $\text{Sm}_{0.92}\text{Ce}_{0.92}\text{B}_6$ | $x = 0.92, y = 0$ | 4.1412 | Ref. [21] |
| $\text{CeB}_6$                      | $x = 1.00, y = 0$   | 4.1407(1) | Present work |

Composition analysis of the crystals of $\text{Sm}_{1−x}\text{Ce}_x\text{B}_6$ was carried out by EDX to determine the concentrations of Ce in each crystal. The results, given in Table 2, show that the ratios for Sm:Ce are similar to the expected chemical compositions for the crystals, relative to the starting compositions of the polycrystalline materials (5%, 10% and 20% Ce-substituted $\text{SmB}_6$ samples).

Table 2. Chemical composition and valence of the Sm ions determined by EDX and XPS for the $\text{Sm}_{1−x}\text{Ce}_x\text{B}_6$ crystal boules grown. The data collected on a pure $\text{SmB}_6$ crystal are included for completeness. The XPS measurements were carried out on a piece of an as-grown $\text{SmB}_6$ crystal boule and on a sample cleaved (in-situ) from the as-grown $\text{SmB}_6$ crystal fragment.

| Chemical Composition | Sm:B Ratio (EDX) | Sm:B Ratio (XPS) | Sm Valence (XPS) | Study |
|----------------------|------------------|-----------------|-----------------|-------|
| $\text{SmB}_6$       | 1.00(2):5.50(2) | 1.00(3):6.40(3) | +2.80(2)        | Present Work (Refs. [37,41]) |
| $\text{SmB}_6$ cleaved | -               | 1.00(3):7.30(3) | +2.72(2)        | ~2.6–2.7 |

Core level XPS spectra were recorded using a pass energy of 20 eV (resolution ~0.4 eV) on an area of 300 µm × 700 µm of the $\text{Sm}_{1−x}\text{Ce}_x\text{B}_6$ crystals and used to study the electronic states of Sm 4$d$, Ce 3$d_{3/2}$ and Ce 3$d_{5/2}$ levels, shown in Figure 3. The Sm 4$d$ XPS spectrum (see Figure 3a) is composed of one singlet, at 123.5 eV, and one multiplet, at 134.1 eV, separated by approximately 10.6 eV. The Sm$^{2+}$ ($4f^6$ ground-state) feature appears near 129 eV (Sm 4$d$ photoelectron line position), which is in agreement with previously published XPS studies on pure SmB$_6$ [66,67]. The Sm$^{3+}$ ($4f^5$) multiplet appears at a higher binding energy, well separated from the 2+ peak. The contributions of the two features to the XPS spectra were used to determine the valence of the Sm ions. The results, given in Table 2, reveal that $\text{Sm}_{1−x}\text{Ce}_x\text{B}_6$ are mixed valence systems, similar to the parent compound $\text{SmB}_6$ [37,38]. The average Sm valence values of the $\text{Sm}_{1−x}\text{Ce}_x\text{B}_6$ boules are slightly larger than the values determined previously for pure SmB$_6$ [67–70], due to surface oxidation effects (an increased
concentration of Sm$^{3+}$ to the detriment of the Sm$^{2+}$ ions). Previous XPS results reported an increased average Sm valence and a B/Sm ratio lower than the nominal stoichiometric value of 6:1 when the SmB$_6$ crystals were exposed to ambient conditions [67]. To confirm this hypothesis, XPS spectra were collected on two SmB$_6$ crystal samples, an as-grown and a cleaved crystal fragment. The average samarium valence is $\sim$2.8 for the as-grown crystal fragment of SmB$_6$. In the case of SmB$_6$ cleaved in-situ from the as-grown crystal, the Sm valence is 2.7, corresponding to a Sm$^{3+}$:Sm$^{2+}$ ratio of approximately $\sim$0.7:$\sim$0.3, which is in agreement with previous results [37,41].

![Figure 3. (a) Sm 4$d$ XPS spectrum and (b) Ce 3$d_{3/2,5/2}$ XPS spectra collected for the Sm$_{1-x}$Ce$_x$B$_6$ $(x = 0.05, 0.10, \text{and} 0.20)$ crystal boules.](image)

The Ce 3$d$ spectrum, shown in Figure 3b, is comprised of two multiplets, at 885.8 eV and 904.8 eV, corresponding to the spin-orbit split 3$d_{5/2}$ and 3$d_{3/2}$ core levels. The spin-orbit splitting is approximately 19 eV, with the complex electronic structure of different Ce oxidation states yielding useful spectral features which can be used to distinguish Ce$^{3+}$ and Ce$^{4+}$. In our data, each component of the Ce 3$d$ XPS spectrum is dominated by two features. The absence of a third component at 916 eV, characteristic of the Ce$^{4+}$ (4$f^0$) [71,72], indicates that the Ce ion is in the 3+ state in the Sm$_{1-x}$Ce$_x$B$_6$ samples. The analysis of the XPS results, given in Table 2, allowed us to estimate the amount of Ce-substituent in the Sm$_{1-x}$Ce$_x$B$_6$ crystal boules. A comparison of the Ce concentrations determined from the XPS spectra and those estimated from the EDX compositional analysis is provided in Table 2.

3.3. Magnetisation

Zero-field-cooled warming (ZFCW) and field-cooled cooling (FCC) magnetisation versus temperature curves were collected on pieces of the Sm$_{1-x}$Ce$_x$B$_6$ $(x = 0.05, 0.10 \text{and} 0.20)$ single crystals with an applied field of 500 Oe along three different crystallographic directions ([001], [110] and [111]). The temperature dependence of the dc magnetic susceptibility, $\chi(T)$, is shown in Figure 4a. The magnetic susceptibility measured along the different crystallographic directions for all three Sm$_{1-x}$Ce$_x$B$_6$ crystals decreased on warming from 1.8 K to room temperature. In addition, for each Sm$_{1-x}$Ce$_x$B$_6$ composition, the magnetic susceptibilities collected with field applied along the three different high-symmetry directions all overlap to within experimental error across the whole temperature range.

The temperature dependent magnetic susceptibility of the Sm$_{1-x}$Ce$_x$B$_6$ crystals was compared with data collected on a pure SmB$_6$ crystal grown by the floating zone method [57]. In the temperature range 300 to 60 K, the magnetic susceptibility of Ce-substituted and pure SmB$_6$ crystals show a similar behaviour, i.e., a gradual increase of $\chi(T)$ with decreasing temperature. Below 60 K, the Sm$_{1-x}$Ce$_x$B$_6$ crystals exhibit a more rapid increase in susceptibility, down to 1.8 K. In contrast, the susceptibility data of pure SmB$_6$ crystals contain a broad maximum centred around 50–60 K, characteristic of a
Kondo insulator, before a more gradual upturn at lower temperatures. Moreover, in the temperature range 1.8–60 K, the magnetic susceptibility of Sm$_{1-x}$Ce$_x$B$_6$ crystals increases sharply with increasing Ce content. The change in the magnetic response of both Ce-substituted and pure SmB$_6$ crystals below 60 K coincides with the increase observed in the resistivity (see Figure 5).

![Graph](image1)

**Figure 4.** (a) Temperature dependence of the dc magnetic susceptibility, $\chi$ versus $T$, in the temperature range 1.8–100 K for the Sm$_{1-x}$Ce$_x$B$_6$ ($x = 0, 0.05, 0.10$ and $0.20$) crystals, with a magnetic field applied along the [001] (black), [110] (red) and [111] (orange) crystallographic directions. The previously reported susceptibility data for a SmB$_6$ crystal [57] are given for comparison. The inset shows $\chi$ versus $T$, on a logarithmic scale, in the temperature range 1.8–300 K. (b) Temperature dependence of the reciprocal of the dc susceptibility, $\chi^{-1}$ versus $T$, of Sm$_{1-x}$Ce$_x$B$_6$ for a field applied along the [001] direction. The inset shows the normalised magnetic susceptibilities of Sm$_{1-x}$Ce$_x$B$_6$ samples, with a magnetic field applied along the [001] direction. The $\chi/\chi$ (10 K) versus $T$ data increase rapidly at low temperatures, but with no signature of long-range magnetic order, for all Ce concentrations.

![Graph](image2)

**Figure 5.** Temperature dependence of the bulk ac resistivity, $\rho$ versus $T$, in the temperature range 1.8–300 K for the Sm$_{1-x}$Ce$_x$B$_6$ ($x = 0, 0.05, 0.10$ and $0.20$) crystals. The previously reported resistivity data for a SmB$_6$ crystal [57] are given for comparison.
Attempts to fit the temperature-dependent reciprocal magnetic susceptibilities, $\chi^{-1} (T)$ (see Figure 4b), in the temperature range 100–300 K reveal that pure SmB$_6$ and the Sm$_{1-x}$Ce$_x$B$_6$ materials all appear to follow a Curie-Weiss law. The effective moment, $\mu_{\text{eff}}$, per formula unit at 300 K varies from 2.4(1)$\mu_B$ for $x = 0.00$ to 2.5(1)$\mu_B$ for $x = 0.20$. The form of $\chi (T)$ for the Sm$_{1-x}$Ce$_x$B$_6$ crystals is qualitatively similar to data reported for aluminium flux grown Ce-substituted SmB$_6$ single crystals, although the effective moments in our samples are substantially lower, especially for lower Ce concentrations [54]. The $\chi (T)$ data are consistent with magnetic response expected for a mixture of $4f^1$ Ce$^{3+}$ ions $\left(2.54\mu_B/\text{Ce}^{3+}\right)$ and divalent and trivalent Sm ions in a variety of magnetic and nonmagnetic electronic configurations, $\left(4f^6\right)$, $\left(4f^5d^1\right)$, and $\left(4f^5\right)$ [68,73,74].

A previous study reported that substituting Sm with another magnetic rare earth ion, such as Gd$^{3+}$, in large concentrations (≥40%), leads to antiferromagnetic ordering at low temperature due to coupling between the Gd sites [18]. This is predicted by the existence of a saturation plateau in the normalised magnetic susceptibility data of 40% Gd-substituted SmB$_6$. In contrast, the magnetisation curves for our Sm$_{1-x}$Ce$_x$B$_6$ crystals exhibit a rapid increase at low temperatures, but with no evidence for the onset of long-range magnetic order down to 2 K, as shown in the inset of Figure 4b. For the Ce$^{3+}$ concentrations used in our work, the magnetic data suggest that the Ce ions are distributed randomly in the lattice.

3.4. Resistivity

Alternating current resistivity versus temperature, $\rho (T)$, measurements were made on bar shaped samples cut from the Sm$_{1-x}$Ce$_x$B$_6$ ($x = 0.05, 0.10$ and $0.20$) single crystals. The $ac$ resistivity data are shown in Figure 5 for temperatures between 1.8 and 300 K. These resistivity data are compared with data for a pure SmB$_6$ crystal grown by the FZ method and reported in our previous work [57]. At 300 K, the Sm$_{1-x}$Ce$_x$B$_6$ samples all have resistivity values similar to SmB$_6$ and $\rho (300 \text{ K})$ increases with $x$. Below 300 K, SmB$_6$ exhibits a continuous increase in the bulk electrical resistivity. In contrast, the $\rho (T)$ data for the Ce-substituted samples exhibit a broad maximum centred around 150 K, followed by an increasingly prominent minimum at ~50 K. On further cooling below 50 K, the resistivity of SmB$_6$ increases by four orders of magnitude, whereas the resistivity of the Ce-substituted samples increases by only a single order of magnitude or less. Nevertheless, the Sm$_{1-x}$Ce$_x$B$_6$ samples still have resistivities larger than pure CeB$_6$, over the entire temperature range studied. The resistivity of CeB$_6$ is approximately $10^{-5} \Omega$-cm from 2 to 300 K [75], whereas for the Sm$_{1-x}$Ce$_x$B$_6$ samples it is $10^{-3} \Omega$-cm or higher over the same temperature range, for the $x = 0.20$ sample.

In contrast to the saturation plateau seen in the resistivity of SmB$_6$ at lowest temperatures, $\rho (T)$ for the Sm$_{1-x}$Ce$_x$B$_6$ samples increases monotonically with decreasing temperature below 10 K. These results are in agreement with the transport measurements performed on aluminium flux grown Ce-substituted SmB$_6$ single crystals [54]. There is an evolution from the TKI behaviour of pure SmB$_6$ to a dense Kondo system with low temperature spin ordering of CeB$_6$ [7,8,75]. The data suggest that it is bulk conductivity, modified by crystalline electric field and Kondo effects alongside phonon scattering, that determines the form of the $\rho (T)$ curves for these Sm$_{1-x}$Ce$_x$B$_6$ samples over the entire temperature range studied. A more quantitative description of the transport properties of the Sm$_{1-x}$Ce$_x$B$_6$ crystals, including extensive measurements in a magnetic field, will be presented elsewhere [76].

4. Conclusions

Crystal boules of Sm$_{1-x}$Ce$_x$B$_6$ ($x = 0.05, 0.10$, and $0.20$) compounds were grown, for the first time, by the FZ technique. Investigation of the crystals using X-ray diffraction techniques revealed that the Ce-substituent is successfully incorporated in the SmB$_6$ structure and that the structural distortions due to the substitution of Sm with Ce follow a similar trend to the one reported for polycrystalline samples of Ce-substituted SmB$_6$. EDX and XPS results confirm that the Ce concentration is close to the nominal stoichiometric values of $x = 0.05, 0.10$ and $0.20$. Analysis of the average Sm valence data determined by XPS on Sm$_{1-x}$Ce$_x$B$_6$ and pure SmB$_6$ samples showed that the results are extremely
dependent on the quality of the surface studied; i.e., an increase in the Sm valence is observed when the surface is exposed to ambient conditions. Magnetic property measurements show that our Sm$_{1-x}$Ce$_x$B$_6$ crystals exhibit no sign of long-range magnetic ordering, at substitution concentrations below 20%. Temperature dependent resistivity measurements revealed that a 5% (and above) substitution with Ce suppresses the crossover from bulk to surface conductivity seen in pure SmB$_6$ as the temperature is reduced. Detailed low temperature magneto-transport measurements are now being carried out to investigate the bulk and surface properties of the Sm$_{1-x}$Ce$_x$B$_6$ crystals.

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**Abbreviations**

The following abbreviations are used in this manuscript:

- **RE** Rare earth
- **TKI** Topological Kondo insulator
- **FZ** Floating zone
- **EDX** Energy dispersive X-ray spectroscopy
- **XPS** X-ray photoelectron spectroscopy
- **ac** Alternating current
- **ZFCW** Zero-field-cooled warming
- **FCC** Field-cooled cooling

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