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Abstract. We report low temperature magnetization measurements on several samples of CeCoSi$_3$ synthesized by induction melting and the Czochralski method. We aim to investigate whether the noncentrosymmetric material CeCoSi$_3$ is a superconductor as there are conflicting reports in the literature. Induction melted samples were generally found to display superconducting signals with up to a 12% superconducting volume fraction. However most samples grown by the Czochralski method produced no superconducting signal although the boules were generally inhomogeneous. Superconducting impurity phases could not be identified from powder x-ray diffraction studies. Further work is necessary to determine whether CeCoSi$_3$ may be classified as another noncentrosymmetric superconductor in the same series as CeRhSi$_3$, CeIrSi$_3$ and CeCoGe$_3$ and the first at ambient pressure.

1. Introduction

There has been recent interest in noncentrosymmetric superconductors. These are good candidates for unconventional gap symmetries since the lack of an inversion centre in the crystal structure may lead to the mixing of singlet and triplet pairing states. In particular CeRhSi$_3$, CeCoGe$_3$ and CeIrSi$_3$ become heavy fermion (HF) superconductors under pressure whilst displaying antiferromagnetism (AFM) in ambient conditions [1,2,3]. The requirement of pressure for the emergence of superconductivity in the rest of the series limits experimental investigations, whilst the existence of AFM order further complicates the analysis of data.

CeCoSi$_3$ crystallizes in the same noncentrosymmetric BaNiSn$_3$ structure as the aforementioned HF superconductors. There are conflicting reports about whether CeCoSi$_3$ becomes superconducting at ambient pressure. Superconductivity was first reported in CeCoSi$_3$ in ac magnetic susceptibility and resistivity measurements in polycrystalline samples with a T_c of 1.2 - 1.4 K [4]. A subsequent NMR study confirmed superconductivity in the material and further ac susceptibility measurements indicated a T_c of 1.1 - 1.2 K in as cast samples and 0.7 - 0.8 K in annealed ones [5]. However, other more recent studies do not report superconducting transitions in the resistivity down to 0.5 K in both polycrystalline [6,7] and single crystal samples [8]. The confirmation of superconductivity at ambient pressure in this system would provide a ready means of studying the nature of the superconducting states in the CeTX$_3$ (T = Rh, Co, Ir, X = Si, Ge) series. Due to the conflicting reports in the literature, the emphasis of this study is on producing a larger number of samples and checking the reproducibility of results.

2. Experimental

Polycrystalline samples of CeCoSi$_3$ were made using stoichiometric quantities of elemental Ce, Co and Si. These were melted together using rf induction heating under an argon atmosphere. Attempts at growing single crystals were made by the Czochralski method using a Cyberstar tetra-arc furnace. Prior to these growths, the constituent materials were melted in an rf induction furnace. For the majority of growths a stoichiometric Ce : Co : Si ratio of 1 : 1 : 3 was used. Following recent reports [9] some growths were made using a ratio of 1 : 1 : 3.5. However, we were unable to isolate large enough single crystals for measurements with either of these starting ratios. Samples were wrapped in Ta foil, sealed under vacuum in a quartz tube and annealed at 900°C for between five days and two weeks. High resolution powder x-ray diffraction (XRD) measurements were made using CuKα radiation on a Panalytical X-Pert Pro MPD. AC resistivity measurements were collected down to 1.8 K using a Quantum Design Physical Property Measurement System (PPMS) using the 4 probe technique. Magnetization measurements were made down to 1.8 K using a Quantum Design SQUID magnetometer. Magnetization measurements down to 0.48 K were made using an iQuantum ^{3}He insert.

3. Results and Discussion

A number of samples were synthesized by the methods described. We have chosen to present the results for two of the samples made by induction melting and these will be referred to as RF-A and RF-B. X-ray diffraction measurements made on the sample RF-A showed that, as well as peaks corresponding to the main phase, a small number of low intensity impurity peaks are present which we were unable to match to any known superconducting phases. The resistivity measurements on the samples indicate a residual resistivity ratio (RRR) of 29 for RF-A and 31 for RF-B after annealing for 170 hours at 900°C.

The magnetization (*M*) against applied field (*H*) is shown for two induction melted samples in figure 1. The negative gradient at low fields indicates approximately a 12% superconducting fraction for RF-A and a 2% fraction for RF-B. These values were calculated assuming the superconducting fraction had the same density as the reported values for CeCoSi$_3$. Figure 2 shows *M* vs *H* for an arc melted ingot from which a growth by the Czochralski method was made. This sample has approximately a 35% superconducting volume fraction.
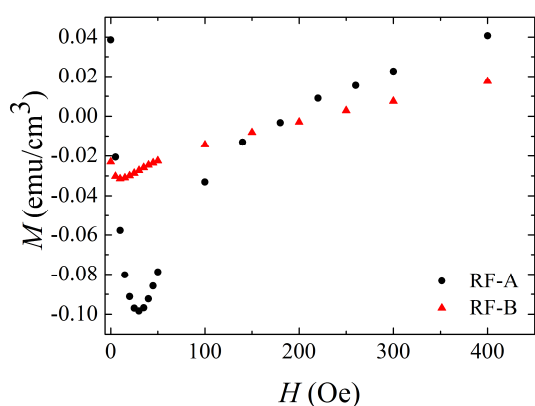

Figure 1. *M* vs *H* of CeCoSi$_3$ at *T* = 0.5 K for two samples made by induction melting.
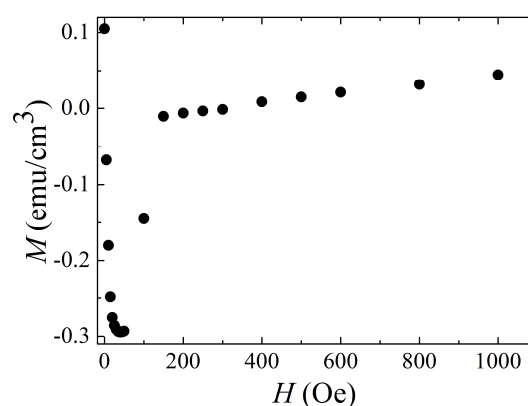
Figure 2. *M* vs *H* of CeCoSi$_3$ at *T* = 0.48 K for an arc melted ingot from which a crystal growth was attempted.

As sizeable crystals could not be isolated from the samples pulled by the Czochralski method, small sections of the grown boule were used for magnetization measurements. Figure 3 shows *M* vs *H* for samples grown by the Czochralski method with a stoichiometric starting composition. All samples,

apart from sample C display no evidence of superconductivity at $T = 0.48$ K. Sample C displays superconductivity with approximately a 3% volume fraction at 0.48 K. No superconductivity is measured in sample B despite being cut from the same growth as sample C, around 1 cm further down the boule. This boule was pulled from the arc melted ingot for which M vs H data are shown in figure 2 with a superconducting volume fraction of around 35%. Figure 4 shows M vs H for a growth with a starting composition Ce : Co : Si of 1 : 1 : 3.5. No superconducting signal is observed in either the as cast or annealed samples. The data in the figures have not been offset and are shown as measured. Further measurements are required to establish the origin of the finite magnetization in zero applied field.
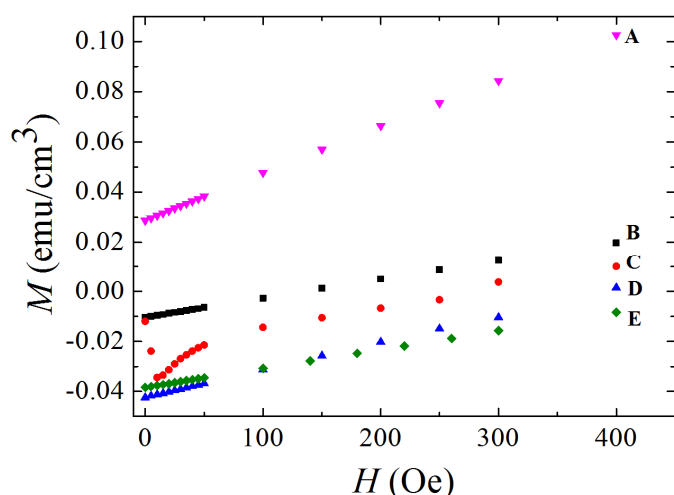

Figure 3. M vs H of CeCoSi$_3$ at $T = 0.48$ K for various samples grown by the Czochralski method with a stoichiometric starting composition. Sample A was annealed for two weeks, E for one week whilst D is as cast. Samples B and C are from the same growth, annealed for five days.
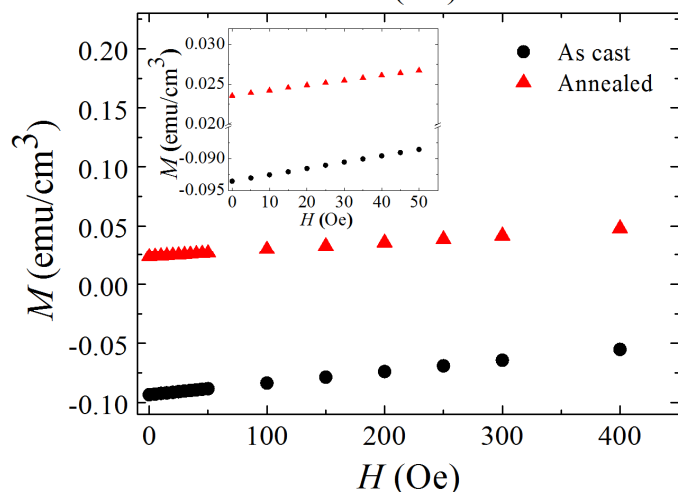

Figure 4. M vs H of CeCoSi$_3$ at $T = 0.48$ K for a growth with an off stoichiometric starting composition (Ce:Co:Si ratio of 1 : 1 : 3.5). The sample was annealed for five days at 900°C.

It can be seen that the induction melted samples generally had an observable superconducting fraction of varying magnitude, whilst most of the samples pulled using the Czochralski method were entirely paramagnetic. However the one growth where a small superconducting fraction was observed also had sections further along the boule where superconductivity was not detectable. It is therefore possible that samples which showed no superconductivity when tested may contain superconducting regions which were not measured. Annealing did not appear to have an effect on the occurrence of superconductivity, in line with previous measurements [9]. The maximum superconducting volume fraction that we have measured amongst the induction melted samples was 12% for Sample RF-A. If the superconductivity in this sample was due to the presence of an impurity phase, this could in principle be detected by high resolution powder x-ray diffraction. As stated earlier, we were unable to categorically assign any of the observed low intensity extraneous peaks to any superconductor.

4. Conclusion

Several samples of $CeCoSi_3$ were synthesized by rf induction melting and the Czochralski method. Superconducting fractions of approximately 12% and 2% were detected in induction melted samples, but were not detectable in those made by the Czochralski method. However, a superconducting fraction of around 35% was measured in an arc melted ingot used for one of these growths. Further studies are necessary to resolve whether $CeCoSi_3$ is a superconductor and this work is currently in progress. In particular powder diffraction studies and compositional analysis of a large number of samples will be useful methods of determining whether an impurity superconducting phase is present. Large single crystals would also be desirable to check the reproducibility of previous reported results where they do not show superconductivity [8].

References

[1]　Pfleiderer C 2009 *Rev. Mod. Phys.* **81** 1551-1624

[2]　Kimura N, Ito K, Saitoh K, Umeda Y, Aoki H and Terashima T 2005 *Phys. Rev. Lett.* **95** 247004

[3]　Sugitani I *et al*. 2006 *J. Phys. Soc. Jpn.* **75** 043703

[4]　Haen P, Lejay P, Chevalier B, Lloret B, Etourneau J and Sera M 1985 *J. Less-Common Met.* **110** 321-5

[5]　Iwamoto Y, Ueda K, Kohara T and Yamada Y 1995 *Physica* B **206 & 207** 276-8

[6]　Eom D, Ishikawa M, Kitagawa J and Takeda N 1998 *J. Phys. Soc. Jpn.* **67** 2495-500

[7]　Okuda Y *et al.* 2007 *J. Phys. Soc. Jpn.* **76** 044708

[8]　Shimoda T *et al.* 2007 *J. Magn. Magn. Mater.* **310** 308-9

[9]　Iida H, Kadota Y, Kogure M, Sugawara T, Aoki H and Kimura N 2011 *J. Phys. Soc. Jpn.* **80** 083701