**Institution:** Imperial College London

**Unit of Assessment:** 9 Physics

**Title of case study:** P5 - Successful commercialisation of microcalorimeter for ultrasensitive heat capacity measurements of magnetic materials

**1. Summary of the impact** (indicative maximum 100 words)

Heat capacity is the measurable physical quantity that specifies the amount of heat required to change the temperature of an object or body by a given amount and is an important quantity to establish in any application that requires knowledge of the thermal response of a material. It is quite usual in the development of new materials that the volume of material available in single crystalline form is limited, and the ability to measure small samples sensitively has particular importance for this reason. We claim a dominant influence on the design of an ultrasensitive heat capacity microcalorimeter that is now sold by the UK company Cryogenic Ltd as a heat capacity option for their cryogenic measurement systems. The microcalorimeter makes it possible to measure ultra- small samples, particularly magnetic samples that are invisible to other commercial probes. Research was carried out within Imperial's Physics Department in 2003-04 to develop the instrumentation; the design was published in 2005 after which it transferred to UK company Cryogenic Ltd. In the past three years the approximate total sales of the heat capacity option at Cryogenics amount to £500K, as a valuable component of a physical properties measurement system with a total sale value in the region of £2M [section 5, source E].

**2. Underpinning research** (indicative maximum 500 words)

Imperial College has a world leading activity on the study of magnetic materials for energy applications with a current grant portfolio in this area of the order of £5-6M (current grants are listed below). The particular emphasis of our research relates to the development of materials for room temperature magnetic refrigeration using the magnetocaloric effect (the change of temperature of a material in the presence of a magnetic field). Development of unique instrumentation has always been at the forefront of the group's strengths. The group had begun to study magnetocaloric materials in 2003, and needed to measure the specific heat capacity of small samples as a function of magnetic field. Instrumentation to carry out these types of measurements was not available commercially.

Prof Minakov (employed on a Royal Society International Collaboration grant with the group for several months in 2003 [G1]) and Dr Yuri Bugoslavsky (post-doctoral researcher supported by the EPSRC [G2]) built on Minakov's prior experience using a commercially available Si nitride membrane to perform scanning calorimetry over very large temperature excursions. Minakov had already studied the device's response to small temperature oscillations but not to magnetic field.

The development of the microcalorimeter as a working instrument to determine heat capacity as a function of swept magnetic field took place at Imperial College [1]. It required thorough analysis of heat transfer through the device to the sample and to its surroundings, establishment of protocols for reliable measurement, and experimental verification of their accuracy. The work performed at Imperial College is published in reference [1] and can be summarised as:

A) Heat transfer analysis
B) Establishment of protocols for use of the probe

C) Development of the analysis for magnetic field dependence of calorimetry

Imperial Innovations was consulted about intellectual property rights protection in 2005 but the research was deemed unsuitable because the silicon nitride membrane was a commercially available device (from Xensor Integration) and Minakov had published aspects of its use for ac calorimetry prior to the development work at Imperial College (and hence making patent protection ineligible). Nonetheless, the inventors were keen to see the technique translated into a commercial product and from 2005 worked with Cryogenic Ltd to pursue this.

**Key Researchers:**

- Prof A. A. Minakov – Royal Society International Academic visitor, Jan-March 2003 & Jan-Feb 2004 (supported on a travel grant [G1])
- Dr Y. V. Bugoslavsky – EPSRC Post-doctoral researcher, 1/2000-10/2005, Academic Visitor, 10/2005-4/2008.
- Prof L. F. Cohen – Academic staff, 1991 – present

**Current Grants in magnetocalorics:**

- A Platform to Develop and Utilise Characterisation Tools for Functional Magnetic Materials – PI Prof Lesley Cohen**.** Grant **"**EPSRC EP/E016243/1". Period**:** 01/06/07–31/05/2012. Value: £780**,**791.
- Solid State Energy Efficient Cooling – SSEEC – PI Prof Lesley Cohen. Grant "EC FP7-NMP-214864". Period: 01/10/09 - 30/09/11. Value: £210,000.
- Nanostructured Functional Materials for Energy Efficient Refrigeration, Energy Harvesting and Production of Hydrogen from Water. PI Prof Neil Alford. Grant "EPSRC Programme grant EP/G060940/1". Period: 01/10/2009 – 31/03/2015. Value: £3,868,581 (Cohen has 25% financial and scientific responsibility of budget - £965,865)
- Drastically Reduced Rare Earth use in Applications of Magnetocalorics- DDREAMS, PI Dr K. Sandeman. Grant: "EC 310748-2 DRREAM CP-FP" Period: 01/04/2013 – 30/03/2016. Value: £600,000.

**3. References to the research** (* References that best indicate quality of underpinning research)

There is one paper that describes the underpinning research leading to the design of the probe. Papers are only published in Rev Sci Instruments after a rigorous peer review process.

[1] * A.A. Minakov, S.B Roy, Y.V.Bugoslavsky and L.F. Cohen, "*Thin-film alternating current nanocalorimeter for low temperatures and high magnetic fields*", Review of Scientific Instruments, 76, 43906 (2005). DOI**, 41 citations (as at 01/04/13)**

**Selected grants that supported the research that underpinned the impact**

[G1] Royal Society Travel Grant, REF: RS 15095, to A. A. Minakov, 1/5/03-31/7/03, £4,110

[G2] EPSRC, GR/T03802/01, 1/10/04-31/1/08, "Spatially resolved spin-polarisation spectroscopy for improved characterisation of spintronic materials", PI: L Cohen, £257,461.

**4. Details of the impact** (indicative maximum 750 words)

Heat capacity is an important quantity to establish for the development of new materials in areas as diverse as energy storage, energy generation, optoelectronic communications or magnetism. New materials studied in single crystalline form are often available in only very small quantities and therefore the creation of an instrument that provides the ability to measure small samples, in

particular magnetic samples, sensitively has particular importance for this reason.

The direct derivative of the swept field ac calorimetric probe developed at Imperial College is currently being sold at Cryogenic Ltd. Cryogenic Ltd is a leading supplier of high field superconducting magnets and low temperature measurement systems which operate without liquid helium. Cryogenic Ltd has offices in the UK, USA and Australia, and is partnered with distribution companies in thirteen other countries [A]. The system was designed, tested and optimised within the Solid State Physics Labs at Imperial College in 2003-4 and was published as a scientific instrument design in 2005 [1]. That was the primary method by which the research was disseminated. The technical know-how was transferred to Cryogenic Ltd in 2005, by direct discussions with the company (discussions that were facilitated by Imperial Innovations in the first instance and later by Cryogenic's employment of Dr. Bugoslavsky).

Throughout the following years the Imperial College research on magnetocalorics has gained worldwide interest and through presentation at international meetings and journal publication we have continued to disseminate the use of the microcalorimeter. In this sense the research undertaken at Imperial College has helped to underpin the commercial impact of the probe that is being sold by Cryogenic Ltd.

Since 2006, Cryogenic have been selling developments of the Imperial designed microcalorimeter as part of its Measurement Systems range (Cryogenic product range webpage [B]). The system allows for specific heat measurements to be made for samples with microgram weights using a miniature calorimeter fabricated on a silicon nitride membrane with thermometer and heater. This technique offers unsurpassed sensitivity combined with simplicity of operation [C]. The normal temperature range is 2 to 300K, and high magnetic fields can be applied. The Cryogenic Specific Heat measurement system features: l*ow* amplitude of temperature oscillations and hence high temperature resolution (typically 0.1K); fast measurements as the frequency of the temperature modulation is of the order of 10 to 100 Hertz; *h*igh sensitivity of 1 nJ/K throughout the temperature range 2-300K [B, D]. The system is robust and durable; with reasonable care the lifetime of a single sensor can span over tens of sample replacements [B, C]. The method used by the microcalorimeter is "*fast and capable of resolving details that would be very difficult if not impossible to see using other methods such as relaxation calorimetry"* [E].

The Cryogenic Ltd microcalorimetry heat capacity probe provides a useful alternative method to the relaxation method offered by other manufacturers, making it possible to measure small samples that are invisible to other commercial probes. An additional advantage is the possibility to make rapid measurements at varying temperature or applied magnetic field. The small size of the measurement cell makes it easy to adapt the experiment to the user's requirements (e.g. mounting on a rotating stage, in small applied AC magnetic field, or illuminating with light).

The contribution and importance of the ac microcalorimeter to Cryogenic Ltd has been confirmed in a letter from the Managing Director of Cryogenic Ltd [F]. He confirms that the company offers a heat capacity option that was "*developed at Cryogenic based on a prototype originally devised at Imperial College…published in Review of Scientific Instruments in 2005*" [F]. The company "*understood the competitive advantage of this method and commercialised it, making it compatible with cryogen-free and liquid-helium based magnetic systems*" [F].

Cryogenic trades internationally and many of its customers "*are based in countries where liquid helium is of limited availability*" [F]. In countries such as "*Brazil, India, the Middle East, China and…Japan"* [F] liquid helium is very hard or extremely expensive to obtain making cryogen free

equipment attractive.

The probe is ideally suited to the characterisation and therefore the development of magnetic materials. Magnetic materials play a dominant role in many key areas of technology (renewable energy, transport, sensors, information storage). The highly sensitive probe also has potential for use in a wide range of applications, where only small samples are available, including biochemical and biomedical diagnostics, for which samples are functionalised with magnetic beads or undergo changes of state in magnetic field. End users primarily reside in research laboratories.

Cryogenic Ltd report that in the last 3 years sales of the heat capacity option, which is priced at about £[text removed for publication] [C, F], amount to approximately £500K. The specific heat option is sold as "*a valued component in about 20% (£2M worth) of the larger integrated measurement systems* [which are worth £12M]…*95% of [the] Company's products are exported overseas and 75% goes outside Europe*" [F]. They further note that adding "*measurement options for heat capacity and thermal conductivity has greatly benefited the market acceptance of [their] instruments*" [F].

**5. Sources to corroborate the impact** (indicative maximum of 10 references)


[A] Cryogenic Ltd webpage, http://www.cryogenic.co.uk/ (archived at https://www.imperial.ac.uk/ref/webarchive/lkf on 2/5/13)

[B] Cryogenic Ltd 'Heat Measurement' product page, http://www.cryogenic.co.uk/products/specific-heat-capacity (archived at https://www.imperial.ac.uk/ref/webarchive/c8f on 18/11/13)

[C] [text removed for publication]

[D] Cryogenic Ltd 'Specific Heat' specifications page, http://www.cryogenic.co.uk/sites/default/files/product_files/specific_heat_capacity_specification.pdf (archived here)

[E] Cryogenic Ltd, 'Application Note: Studying phase transitions using AC calorimetry', http://www.cryogenic.co.uk/sites/default/files/product_files/heat_capacity_data_combined_310713.pdf (archived here)

[F] Letter of support from Managing Director, Cryogenics Ltd, 3 Dec 2012 (available from Imperial on request)