# Materials Analysis with Cryogenic Sensors

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Abstract Low temperature photon detectors are increasingly attractive tools for materials analysis. Their range of applications has broadened from early work on x-ray fluorescence and now spans the electromagnetic spectrum from terahertz to gammaray energies. In addition, low temperature detectors (LTD's) show promise for measuring the energy of neutrons, alpha particles, simple ions, and complex biomolecules. LTD's are emerging from low temperature laboratories and can now be found at a growing range of analytical facilities including electron microscopes, mass spectrometers, ion traps, and synchrotrons. Here, we review these uses of LTD's. Despite the remarkable capabilities of LTD's, they are still at the stage of demonstration measurements for some applications. We discuss obstacles to the more widespread use of LTD's and some emerging solutions to these obstacles.

Keywords Low temperature detectors · Cryogenic sensors · Materials analysis

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## 1 Introduction

Low Temperature Detectors (LTD's) are a promising technology for precision measurements of particles and photons because of the exquisite sensitivity possible at operating temperatures near 0.1 K. We discuss the use of LTD's for the analysis of industrial, biological, and nuclear materials. The discussion emphasizes the use of LTD's for biomolecule mass spectrometry and x-ray fluorescence measurements on electron microscopes because these are applications with potential for wide dissemination of LTD technology, even if significant obstacles to such dissemination remain.

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Other successful work, for instance at specialized facilities such as ion traps and synchrotrons, is treated with unfair brevity.

### 2 Mass Spectrometry

The use of LTD's for mass spectrometry of biological molecules was presented at the 6<sup>th</sup> International Workshop on Low Temperature Detectors held in 1995 [1]. The chief attraction of LTD's for this application is that their sensitivity is independent of the mass of the incident ion. In contrast, the efficiency of microchannel plates traditionally used for mass spectrometry decreases sharply for molecule masses above  $10^4$  Da (proton masses) [2]. In linear time-of-flight mass spectrometry, molecules are launched and ionized, usually by a laser pulse. They are then accelerated through a potential difference  $V_{acc}$  of 10–30 keV. The time interval between launch and detection at the end of a flight tube of length L is  $L/\sqrt{(2qV_{acc}/m)}$  and thus reveals the charge-to-mass ratio q/m of the molecule. The energy sensitivity of LTD's provides additional diagnostic capabilities. For instance, simultaneous hits by several molecules and molecules in different charge states can be directly identified. Relatively little information can be obtained from microchannel plate pulse heights [3].

Demonstration measurements have been performed with both superconductorinsulator-superconductor tunnel junctions (STJ's) and normal-insulator-superconductor tunnel junctions (NIS's). Since the LTD's must stare into a 300 K flight tube without intervening filters, infrared loading is a challenge and most measurements were conducted at temperatures of 0.3–1 K. Early results confirmed the efficiency advantage of LTD's for massive molecules and showed some ability to clarify and enhance signals of interest [2, 4].

In addition to the advantages described above, LTD's have several disadvantages for mass spectrometry. First, the area of a single tunnel junction is approximately  $10^{-1}$  cm<sup>2</sup> whereas the area of a microchannel plate can easily be 4 cm<sup>2</sup>. The increased area of microchannel plates reduces the time and source material needed to perform an analysis. Second, both the rise and fall times of microchannel plates are significantly faster. A fast rise time allows more accurate measurements of molecule mass since the mass uncertainty  $\Delta m$  scales as t $\Delta t$  where t is the flight time. A fast fall time allows the detector to respond to molecules with similar masses that arrive in rapid succession. The rise (fall) time of a microchannel plate can be a few hundred picoseconds (a nanosecond), whereas the rise (fall) time of a tunnel junction is typically a few microseconds (10–100 microseconds).

In addition to the technical disadvantages listed above, the initial motivation for the use of LTD's was overly simplified. Most importantly, the difficulty of launching and ionizing large molecules such as DNA with laser desorption is at least as significant a limitation on the use of mass spectrometry as detector efficiency. Electrospray techniques can be used to launch large molecules but the absence of a well-defined launch time in electrospray systems necessitates either mass separation by magnetic or orthogonal deflection. Electrospray ionization also produces ions with a broad distribution over several tens of charges and the energy resolution of cryogenic detectors has so far not been sufficient to separate nearby charge states at these high charges





[5]. Sensor resolution is significantly worse for complex ions than for photons or simple particles, presumably due to fragmentation on impact. Overcoming this limitation could make electrospray launch an attractive technique. Finally, the sensitivity of conventional detectors to high mass molecules can be increased at the price of degraded time resolution by fragmenting and post-accelerating the ions at the end of the flight tube. A thorough review of early work on mass spectrometry is given in Ref. [6].

A recent development that may overcome some of the limitations described above is the use of thresholding cryogenic detectors similar to sensors developed for dark matter detection and optical photon counting [7, 8]. These devices consist of a narrow superconducting meander with a direct current bias that is locally driven normal by the impact of an ion. A GHz-bandwidth voltage amplifier is used to measure the resulting signal pulse. Such devices can provide greatly improved collection area and response speed over earlier efforts. These devices sacrifice energy resolution but this parameter provides little information for the low charge states produced by laser desorption. Prototype Nb meanders are shown in Fig. 1 with 50% fill factors. The rise time of a device is given by  $L/R_{circ}$  where the inductance L is the sum of geometric/magnetic and kinetic contributions and the circuit resistance R<sub>circ</sub> is the sum of the hot spot resistance and any shunting resistor. For a 0.3 mm  $\times$  0.3 mm device similar to those of Fig.1, the calculated rise time is 400 ps. A target device area for the future is 3 mm by 3 mm which, while still smaller than a microchannel plate, will occupy much of the beam spot in a typical mass spectrometer. Devices made of Nb, NbN, or another Nb compound can operate at 4 K, greatly simplifying the required cryogenics. Hence, meander-type devices with high efficiency for massive molecules may in the future provide mass/time resolution comparable to microchannel plates and useful collecting areas. Two similar efforts are described in Refs. [9] and [10].

## 3 X-Ray Detection on Electron Microscopes

One of the earliest applications envisioned for LTD's was the measurement of x-rays fluoresced by the electron beam in a Scanning Electron Microscope (SEM). Since the energy resolution of LTD's can be one to two orders of magnitude better than silicon-based sensors in the 1 to 10 keV range, LTD's can resolve numerous x-ray line overlaps in technologically interesting materials. The problem of line overlaps is

particularly severe in thin samples that can only be excited by weakly penetrating low energy electron beams that produce fluorescence below 2 keV from both the target and substrate. Higher energy electron beams interact mostly with the underlying substrate in thin samples so their ability to produce widely separated fluorescence from deep electronic shells is wasted. Hence, LTD's are a means to extend x-ray fluorescence analysis to nanometer-scale samples. Examples of nearby x-ray lines include Si K (1740 eV), W M (1775 eV), Ta M (1710 eV), Hf M (1645 eV), Al K (1486 eV) and P K (2014 eV). These lines can all be easily separated by microcalorimeters that have demonstrated an energy resolution of 2.0 eV FWHM at 1486 eV [11].

Several results have shown the ability of LTD's to perform novel analyses. For example, microcalorimeter measurements of TaSiN films suitable for diffusion barriers have shown that stoichiometry and thickness information can be obtained from films as thin as 3.5 nm [12]. Microcalorimeters have also been used to measure P doping levels in Si [13]. Impressively, microcalorimeters have been used to detect sub-eV chemical shifts in the position of Al and Fe elemental lines due to the bonding state of the material [14, 15].

The ability of LTD's to perform quantitative analyses has also been demonstrated. Isaila et al used spectra from reference samples to accurately determine the elemental ratio in a WSi<sub>2</sub> sample [13]. More recently, Jach et al. demonstrated quantitation of a multielement glass to about 1% absolute or 8% relative [16]. These results show that LTD's can yield accurate compositional information in systems where silicon-based sensors are stymied by overlapping x-ray lines.

Given the performance levels described above, system design and cost will ultimately determine whether LTD's become widely used on electron microscopes. The advent of 4 K cryocoolers, especially pulse tubes, has eliminated the need to replenish liquid cryogens. Cryocooler vibration has the potential to degrade microscope imaging but can be almost eliminated with careful engineering. An alternative scheme is to use a floor-mounted cryocooler to maintain a sealed charge of liquid cryogens [17]. For detectors with a resolution of one part in 500–2500, calibration and temporal stability are critical. Some discussion is given in Refs. [18] and [19].

Acquisition speed is another important component of system performance. The area and count rate of individual LTD's compare unfavorably to competing siliconbased sensors. Recently developed Si drift detectors have an area of 50 mm<sup>2</sup> and can count at 100 kHz or faster whereas a single transition-edge microcalorimeter has an area of  $\sim 0.16 \text{ mm}^2$  and can count at  $\sim 0.8 \text{ kHz}$ . As a result, the drift detector will attain statistical significance more rapidly, except in spectra with lines spaced by much less than the resolution of the drift detector [20]. One compensating strategy is to couple a cryogenic detector to a polycapillary x-ray optic in order increase its effective collecting area. Collecting area can be improved by a factor of  $\sim 30$ , but since the count rate capability of a single sensor is limited, this improvement is only applicable for faint sources [11]. The combination of an x-ray optic with a fast cryogenic sensor such as a tunnel junction is attractive although the resolution and efficiency of tunnel junction x-ray sensors lag those of microcalorimeters.

Arrays of cryogenic sensors provide both increased collecting area and count rate. For a detector system that uses the regular EDS port on an electron microscope, the cold finger diameter is limited to 3 cm or less. After space is allocated for a 300 K vacuum shell and 77 K and 4 K radiation shields, there is only room for a few tens of sensors. However, even 20 microcalorimeters can provide a collecting area of  $3.2 \text{ mm}^2$  and count rate of 16 kHz. An 8:1 multiplexing demonstration with 3.7 eV resolution at 5.9 keV using 150 µs microcalorimeters is described in Ref. [21].

The number of LTD systems installed on electron microscopes worldwide is modest; certainly fewer than ten. However, the maturation of the technology is incomplete. The deployment of even small arrays will significantly improve the attractiveness of cryogenic systems. Improvements in price and simplicity are also likely required for widespread dissemination of LTD technology.

#### 4 Nuclear Materials Analysis

LTD's can be used to characterize materials based on their natural radioactivity. While gamma-ray spectroscopy at 100 keV and above is the most common application, useful information can also be obtained from alpha and neutron spectroscopy.

Gamma-ray spectroscopy requires bulk absorbers for useful efficiencies. Typically, a superconducting or insulating absorber is attached to a thermometer such as a transition-edge sensor. One such device has achieved a resolution of 25 eV FWHM at 103 keV compared to ~450 eV for a planar germanium sensor [22]. The number of line overlaps above 100 keV is fewer than at x-ray energies, but overlaps occur in materials related to the nuclear fuel cycle that are of considerable analytical interest. Measurements where cryogenic detectors can provide useful information include Pu isotopics, separation of <sup>235</sup>U from <sup>226</sup>Ra, U enrichment, and Pu in spent reactor fuel. Since individual cryogenic gamma sensors are 1–2 mm on a side, arrays are required for practical application. We have recently delivered to Los Alamos National Laboratory a liquid cryogen-free system for real-time gamma spectroscopy with 61 pixels. When fully populated, the system will hold 256 pixels and have an active area of 5.75 cm<sup>2</sup>, comparable to a planar germanium sensor.

Alpha particle spectroscopy is widely used to analyze trace quantities of radioactive material. Alpha spectroscopy is often preferred over gamma-ray spectroscopy for trace analysis because the alpha branching ratios can be significantly higher. Alpha spectroscopy is usually performed with silicon-based detectors whose resolution is limited to  $\sim$ 8.5 keV at 5.5 MeV [23].

The finite resolution of silicon sensors has analytical consequences. For instance, the most intense emission lines from  $^{239}$ Pu and  $^{240}$ Pu are at 5.1554 MeV and 5.1683 MeV, respectively, a difference of only 12.9 keV. Quantitative analyses can be performed in the presence of these overlaps using deconvolution algorithms, but the error bars are significant and long counting times are required. As a result, mass spectrometry is usually used to determine the  $^{239}$ Pu/ $^{240}$ Pu isotopic ratios in trace samples.

LTD's have recently demonstrated resolutions as good as 2.5 keV for 5.3 MeV alpha particles [24–26]. The devices are similar to the gamma-ray detectors described above but with increased area and heat capacity. These devices have demonstrated accurate measurements of Pu isotopic ratios without peak fitting.

Alpha sources must be mounted inside the cryostat in order to eliminate energy straggling in intervening windows. Rapid sample introduction or fast cooldown is

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required to process large numbers of samples. Since alpha analysis is typically performed on trace samples, source area is small. With the detectors located 1–2 mm from the source, an array of 9–25 pixels each 1–4 mm<sup>2</sup> will fill close to  $2\pi$  solid angle. Hence, microcalorimeter technology is especially well matched to alpha spectroscopy.

Semiconductor and transition-edge microcalorimeters as well as tunnel junctions have been applied recently to neutron spectroscopy [27–29]. Neutrons are typically stopped in an absorber rich in <sup>6</sup>Li or <sup>10</sup>B where (n, $\alpha$ ) reactions release energies of several MeV plus the kinetic energy of the neutron.

#### 5 Exotic Sources

LTD's are finding applications at electron-beam ion traps, synchrotrons, and other exotic photon sources. These sources are often good points of deployment because their users tolerate complexity, the incremental cost of a cryogenic detector system is small, and their focus is more on research than routine analyses.

Electron-beam ion traps (EBITs) provide a controlled mechanism for creating and studying almost any ionization state of the naturally occurring elements. The broadband response, high efficiency, and good energy resolution of microcalorimeters are well matched to studies of atomic structure and plasma behavior at EBITs. Semiconductor microcalorimeter systems are presently in use at EBITs at NIST Gaithersburg and Lawrence Livermore National Laboratory [30, 31].

Synchrotrons provide intense beams of monochromatic x-rays that can be used to probe a wide range of materials. LTD's so far have been used at synchrotrons for fluorescence-detected x-ray absorption spectroscopy (XAS). The beam energy is scanned through an absorption edge of a dilute element present in a more plentiful matrix. Excitations are created in the analyte at rates related to the availability of electronic states elevated by the beam energy. The intensity of fluorescence x-rays produced as these excitations are filled can reveal the bonding state and other information about the analyte. This technique provides information on energy scales of the beam width (sub-eV) provided the detector system can distinguish between fluorescence from the analyte and matrix (typically separated by 10s of eV). The high count rate of STJs is well matched to the high x-ray intensities possible. A number of demonstration experiments have been performed and an STJ system is resident at the Advanced Light Source. This system has analyzed the effects of nitrogen doping in ZnO and annealing in GaInNAs [32, 33]. An overview of possible synchrotron measurements is given in Ref. [34].

Doubtless, other sources of interest will emerge. For instance, TES microcalorimeters have already been used for demonstration measurements at a fusion machine [35].

#### 6 Biological Optical Fluorescence

A recent application of LTD's is Fluorescence Resonance Energy Transfer (FRET) of biological molecules. In FRET, at least two fluorescent probes (fluorophores) are

attached to molecules of interest. One of the fluorophores, the donor, is then optically excited. If the second fluorophore, the acceptor, is in close proximity to the donor, for instance as a result of molecular binding, energy will be transferred to the acceptor which fluoresces at a second characteristic wavelength. The intensity of the acceptor signal can be used to measure the donor-acceptor distance and certain environmental parameters. LTD's of optical photons can potentially provide higher quantum efficiency and lower background rates than photomultiplier tubes used presently. In addition, the resolving power of LTD's may allow fluorophores at multiple wavelengths to be analyzed in parallel. A demonstration measurement has been conducted with optical tunnel junctions [36].

#### 7 Conclusions

LTD's are in the early stages of application for numerous types of material analysis. Arrays of LTD's will greatly enhance the utility of the technology for x-ray and gamma-ray measurements. Meander detectors may bring new capabilities to mass spectroscopy. Additional applications will likely emerge, for instance in THz spectroscopy [37].

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