Promising X-Ray Fluorescence Tests for Superconducting Tunnel Junction Detector

Scientists in the Physical Biosciences Division of the Ernest Orlando Berkeley National Laboratory (Berkeley Lab) studying transition metals in proteins with fluorescence-detected L-edge absorption spectroscopy have found the measurements to be extremely challenging. The difficulty is that the metal centers are present in very dilute concentrations so that their weak fluorescence is often obscured by strong background signals carbon and oxygen.

To solve this problem, the Berkeley group has been working with researchers from the Advanced Detector Group at the Lawrence Livermore National Laboratory on an energy-dispersive superconducting tunnel junction x-ray detector. These devices in principle have the energy resolution needed to reveal the metal signal. The most recent results with the latest version of the detector on Beamline 4.0.1-2 at the Advanced Light Source (ALS) illustrate the promise of the cryogenic detector strategy not only for this application but also for spectroscopy of other types of dilute samples.

Transition-metal complexes are key elements in many biologically important processes that are catalyzed by proteins (enzymes), photosynthesis being a prime example. The changes in that occur in electronic structure throughout a catalytic cycle are the subject of much research aimed at understanding the mechanisms of these processes. L-edge x-ray spectroscopy offers several advantages relative to the more common K-edge techniques, since it involves allowed transitions to the d-orbitals associated with metal-ligand bonding. It also has a rich multiplet structure interpretable by theory and higher spectral resolution.

Along with the advantages come the challenges. The concentrations of the transition-metal complexes in enzymes are typically low, around 100 parts per million, so that the

metal signal rides on top of a very large background absorption from the protein and water background. Fluorescence-yield detection can in principle remove this background, by selecting only emission at the metal fluorescence energy. But even with this technique, spectroscopy remains a formidable task because the weak fluorescence from transition-metal L lines is often buried in the wings of much stronger neighboring lines unless the detector resolution is very good. For example, manganese in biological molecules, such as the photosynthetic oxygen-evolving complex, has weak fluorescence lines at 637and 649 eV that are obscured by the strong oxygen K emission line at 525 eV.

What is needed is an x-ray fluorescence detector with sufficient energy resolution to reveal the transition-metal lines and sufficient efficiency to record spectra in a reasonable time. Grating spectrometers have the resolution but not the efficiency; energy-dispersive semiconductor detectors have the efficiency but not the energy resolution. To bridge this impasse, the Berkeley researchers joined with the Livermore group, which had been developing energy-dispersive superconducting tunnel junction (STJ) detectors for x-ray astrophysics applications.

The operating principle for SJT x-ray detectors parallels that of semiconductor (lithium-drifted silicon or germanium) detectors. Absorption of an x ray stimulates a cascade of processes, with the end result being a large number of charge carriers that generate a current proportional to the energy of the x ray. In superconductors, absorption breaks Cooper pairs and creates free electrons; in semiconductors, absorption creates free electrons and/or holes. In either case, the number of charge carriers created per photon absorbed is determined by the energy gap of the absorbing material. For superconductors, the energy gap is in the milli-electron-volt range, in contrast to electron volts for semiconductors, with the result being roughly a thousand-fold increase in the number of carriers and, in theory, an improvement of $(1000)^{1/2}$ in the energy resolution. However, the statistics of the carrier generation tend to degrade the resolution somewhat.

Speed is an issue for all detectors. For STJ devices, the time for the excess carriers to decay (e.g., re-form Cooper pairs in superconductors) determines the maximum count

rate without affecting the energy resolution. If carriers from an earlier absorption event are still present when the next event occurs, a condition called pile-up occurs. With pile-up, the current does not accurately reflect the energy of either photon, and the resolution of the spectrum is degraded. The relatively slow recombination times in superconductors of several microseconds restrict the maximum count rate to around 10 kHz in contrast to a few hundred kHz for semiconductor detectors.

Another cryogenic detector, the microcalorimeter, which measures the temperature rise in a semiconductor or superconductor resulting from x-ray absorption, provides the chief competitor for STJs. These devices have even better energy resolution, more than twice as good as that of the STJs, but this advantage is counterbalanced by a count rate around a factor of 10 lower. The pluses and minuses for the various detectors suggest that the 'best' device will depend on the particular requirements of a given experiment.

The STJ detector system, based on a design originally developed at Livermore [1], has three main components: the superconducting tunnel junction, a refrigerator to cool it, and a structure to place the tunnel junction close to the x-ray emitting sample. The tunnel junction is a multilayer sandwich of superconductors on an oxidized silicon substrate separated by a 15-Å aluminum oxide barrier. The sandwich combines a moderately thick niobium absorber film for high efficiency with a thin aluminum trapping layer for fast tunneling. X-rays are absorbed in the upper niobium layer. Because the energy gap of niobium is greater than that of aluminum, the charge carriers migrate into the aluminum where they are confined until they tunnel through the barrier. After tunneling, they either reform Cooper pairs or participate in a back-tunneling process that effectively amplifies the current induced by each photon absorption.

To cool the superconducting tunnel junction to its operating temperature of 0.4K or less, the Livermore group utilizes adiabatic demagnetization refrigeration (ADR). In brief, an applied magnetic field first magnetizes a paramagnetic material cooled to liquid-helium temperature, lowering its entropy (increasing its magnetic order) while the liquid-helium bath carries away the heat of magnetization and keeps the temperature constant. After the

paramagnet is isolated from the helium bath, the magnetic field is decreased slowly enough to keep the entropy of the paramagnet constant, thereby lowering the effective temperature of the electron spins. The lattice, which is already cooled to liquid helium temperature and has a very low entropy at the start, is then readily cooled further by receiving a small amount of the spin entropy.

As originally implemented at Livermore, the refrigeration system was based on a single-stage ADR to cool below 0.4K for times up to six hours per demagnetization cycle (it is not necessary to warm up between cycle). In the latest instrument, the refrigerator is a two-stage device that makes use of two different paramagnetic materials (gadolinium gallium garnet and ferric ammonium alum or $Fe(NH_4)(SO_4)_2 \times 12\ H_2O$), which cool to 1K and 0.1K, respectively.

Other improvements have also been made. Originally, a single small STJ detector ($50 \times 50\ \mu m^2$) was used, which reduced the practical solid angle of the fluorescence that can be detected. Making very large detectors is not an option because of the large capacitance associated with the thin tunnel junction, which reduces the energy resolution at a given count rate. Detector arrays provide a way around the problem. Preliminary results with two detectors, each $200 \times 200\ \mu m^2$, showed that it is possible to operate two detectors together without significant loss in energy resolution [2]. Future plans include fabrication of 3×3 array and the use of x-ray collection optics to achieve a total count rate above 100 kHz.

The cryostat was also modified to bring the detector closer to the sample [3]. The detector now resides on cold finger that protrudes 40 cm from the cryostat wall. It fits through a standard gate valve and is inserted into the UHV sample chamber on the EPU beamline.

In tests at ALS Beamline 4.1-2, with detectors $100 \times 100\ \mu m^2$ in area, the resolution over the photon-energy range from 277 to 850 eV was 11 to 25 eV, more than sufficient to separate weak transition-metal L lines from a strong oxygen K line in metalloenzymes. This is somewhat less than nominally identical detectors mounted in the center of the

ADR. In sum, the new detector system, which is also quite easy to operate, significantly improves the sensitivity in high-resolution soft x-ray spectroscopy of dilute samples.

[references]

1. "Energy resolution and high count rate performance of superconducting tunnel junction x-ray spectrometers," M. Frank, L.J. Hiller, J.B. LeGrand, C.A. Mears, S.E. Labov, M.A. Lindeman, H. Netel, D. Chow, and A.T. Barfknecht, *Rev. Sci. Inst.* **69**, 25 (1998).

2. "Superconducting tunnel junction array development for high-resolution energy-dispersive X-ray spectroscopy," S. Friedrich, C.A. Mears, B. Nideröst, L.J. Hiller, M. Frank, S.E. Labov, A.T. Barfknecht, and S.P. Cramer, *Microsc. Microanal.* **4**, 616 (1999).

3. "A superconducting detector endstation for high-resolution energy-dispersive SR-XRF," S. Friedrich, T. Niedermayr, O. Drury, M.F. Cunningham, M.L. van den Berg, J.N. Ullom, A. Loshak, T. Funk, S.P. Cramer, J.D. Batteux, E. See, M. Frank, S.E. Labov, *Nucl. Inst. Meth.* (accepted for 2001).

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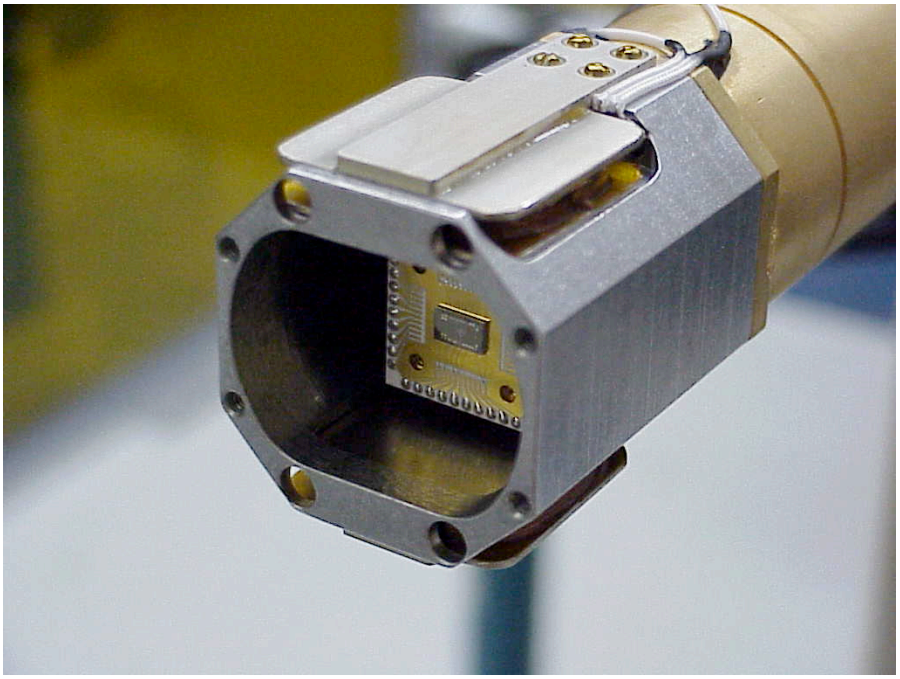

Figure 1: Photograph of the superconducting tunnel junction x-ray detector. The STJ chip sits at 0.1 K the end of the 40-cm-long cold finger for insertion into a UHV sample chamber. It is surrounded by a liquid He cooled radiation shield. The secondary liquid N2 cooled shield and the IR blocking windows are not shown here.

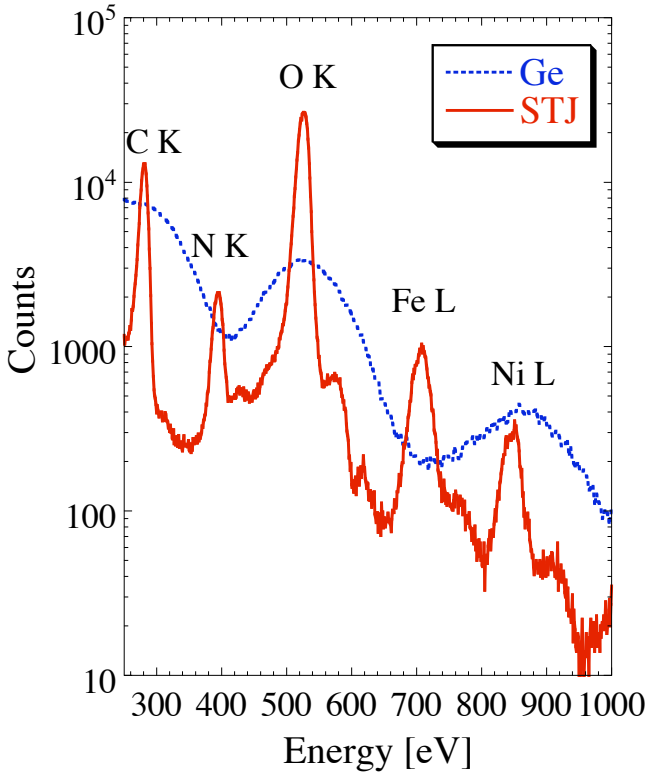

Figure 2: Soft x-ray emission spectra at ALS Beamline 4.1-2 of the metalloprotein hydrogenase containing about 480 ppm nickel and about 5800 ppm iron taken with the superconducting tunnel junction (STJ) detector (red curve) and for comparison a commercial 32-element germanium detector (blue curve). The nickel fluorescence is enhanced in the case of germanium because of resonant excitation at the nickel L edge, whereas the spectrum recorded by the STJ was excited well above the nickel edge.