

## THE SINGLE CRYSTAL DIFFRACTOMETER (SCD)

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The first experimental demonstration of the time-of-flight (TOF) method for determining single-crystal structures, using chopped beams at steady state reactor sources, was reported by Buras *et al.* in 1965.<sup>1</sup> It had been only 13 years earlier, in 1952, when Selmer Peterson and Henri Levy reported the first structure determined by single crystal neutron diffraction using a monochromatic steady-state incident beam.<sup>2</sup> In the late 1960's Peterson joined his former student, Jack Williams, here at Argonne to design and build a single crystal diffractometer at the CP-5 reactor. Then, in the 1970's Peterson led the effort to develop a single crystal TOF Laue instrument for the proposed pulsed spallation neutron source.

The prototype instrument for ZING-P' was designed by Peterson and Art Reis, Jr., of the ANL Chemistry Division.<sup>3</sup> The detector was a <sup>3</sup>He-filled, multiwire area position-sensitive detector which was shared with the small angle scattering group and is still in use on SAD. I believe it was sometime in the spring of 1979 that a NaCl crystal was used to obtain the first time-of-flight Laue diffraction pattern on a pulsed spallation neutron source. In September of that year, Reis left Argonne for Brandeis University, and with Peterson planning to retire in 1980, I acquired the role of instrument scientist for the SCD. Ray Teller worked with me for about the first 2 years of IPNS, followed by Peter Leung for 3 years. A large part of the work during those years involved the development of a program library for data analysis. In June of 1989 Rick Goyette became the scientific assistant for both SCD and the POSY instruments.

In 1981 the SCD was set up on beam line H1 with an initial flight path of 6.5 m. An entry in my notebook dated April 1, 1981, (not an April fools joke) reads: "Called Al Knox — we will have to fill 500 downspouts with 18,000 pounds of anhydrous borax." With help from the entire Chemical and Electronic Structure Group [Ray Teller, Mark Beno, Jack Williams and others], we filled the downspouts and constructed a shielded hutch and the SCD was ready for testing by July of that year. In 1986, the SCD was moved to its present location on beam line F6 with an initial flight path of 9.5 m to provide higher resolution and avoid dead time losses in anticipation of the installation of the Booster target.

The most important component of the IPNS SCD is the area position-sensitive <sup>6</sup>Li-glass scintillation detector designed and constructed by Raul Brenner and Mike Strauss of Argonne's Electronics Division. A scintillation detector based on the principles of the Anger  $\gamma$ -ray camera seemed most promising in terms of overcoming some of the limitations of the <sup>3</sup>He-gas filled multiwire detector for single crystal diffraction. In particular, without the need to contain a large volume of gas under high pressure, a scintillator detector could have high efficiency, thin windows

and minimum parallax due to the thin scintillation glass. A 22-cm diameter circular prototype detector was successfully tested on the ZING-P' SCD.<sup>4</sup> The detector currently in use for the past 10 years at IPNS is square with an active area of 30x30 cm<sup>2</sup> and was ready for testing on the SCD by August, 1981.<sup>5,6</sup> In 1983, Brenner and Strauss received an IR100 Award for their work in developing the detector.

A number of outside collaborators have made important contributions to the development of the single crystal TOF Laue technique. Bob Jacobson from Iowa State University assisted us in 1981 by adapting his autoindexing program BLIND for TOF Laue data obtained with the SCD.<sup>7</sup> Wolfgang Jauch of the Hahn-Meitner Institut in Berlin collaborated on a series of studies designed to compare the results from the SCD with those from monochromatic neutron and  $\gamma$ -ray techniques using the same crystal.<sup>8-10</sup> The analyses included testing various extinction models, spectral corrections and integration procedures. In these studies, the accuracy of the TOF Laue technique was shown to be equivalent to the conventional monochromatic techniques. Clive Wilkinson of Kings College, London, examined procedures for integrating Bragg peaks in the three-dimensional histograms.<sup>11</sup>

Ancillary equipment for varying temperature and pressure is required for most experiments. The Displex closed-cycle helium refrigerator (10-300 K) mounts through the  $\phi$ -circle of the diffractometer. In order to overcome the problems of shielding the large area detector from the aluminum scattering of the vacuum container, Bob Kleb (Materials Science Division) designed and fabricated a unique vacuum container with two rotating vacuum seals. Recently, low temperatures approaching 4 K have been achieved with a liquid helium cryostat. The first SCD furnace was designed and constructed by Hiroyuki Horiuchi, currently at the University of Tokyo, in order to study yttria-stabilized zirconia,  $Zr(Y)O_{1.862}$ , at 1040 K with a voltage across the crystal to generate an  $O^{2-}$  ionic current.<sup>12</sup> A furnace of a different design was used to characterize the crystal structure of the nonlinear optical material thallium titanate phosphate,  $TlTiOPO_4$ , at 650°C, well-above its ferroelectric to paraelectric phase transition ( $T_c = 583^\circ C$ ).<sup>13</sup> The helium pressure cells (0-5 kbar) which mount on the Displex cold stage were designed by Bob Kleb for the study of the organic superconductor  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> as described below.

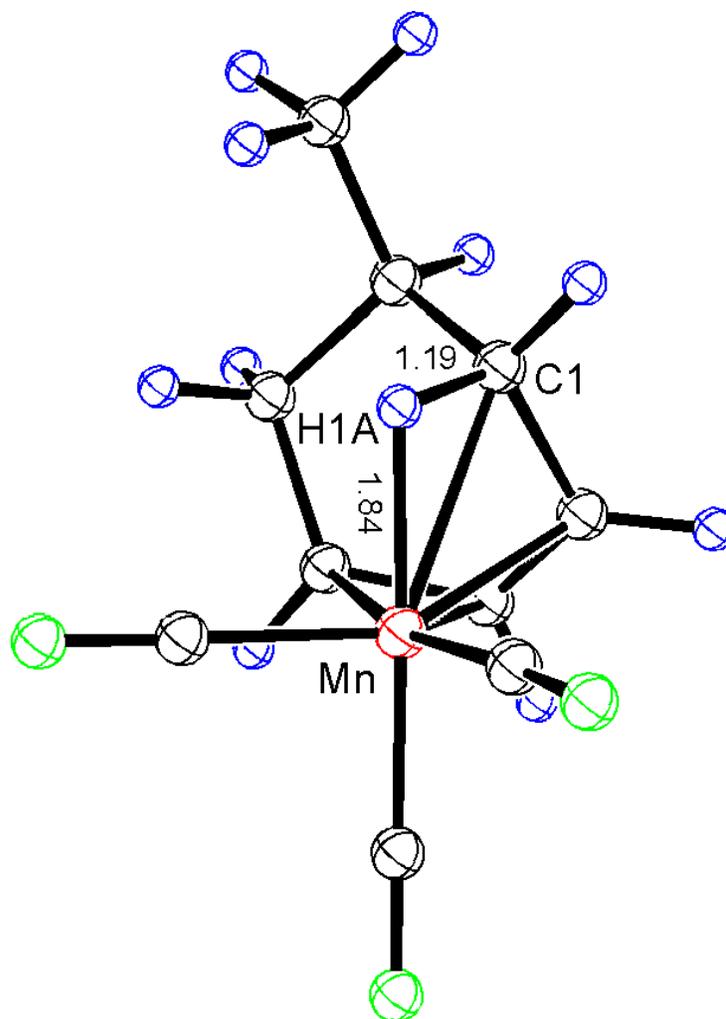
During the past decade a related single crystal time-of-flight Laue instrument was under development at Los Alamos by Phil Vergamini and Allen Larson. The exchange of ideas, software and hardware designs has been extremely beneficial for both groups.

The following sections describe a few SCD experiments selected for their historical and scientific significance.

## THE FIRST EXPERIMENT: C—H··METAL INTERACTIONS

The activation of a C—H bond by a metal is a critical step in many catalytic reactions. The nature of the C—H··metal intermediate had been investigated by various spectroscopic methods, but the arrangement of the three atoms in the bond and the degree of electron delocalization could only be ascertained from high precision neutron structures. In the fall of 1981, only four stable molecules containing 3-center C—H··metal bonds had been unambiguously characterized by single crystal neutron diffraction.<sup>14-17</sup> For the first scientific experiment using the SCD, Jack Williams proposed the structure determination of  $\text{Mn}(\text{CO})_3(\text{C}_7\text{H}_{11})$  with crystals obtained from Maurice Brookhart of the University of North Carolina. Data were collected with a sample at 25 K in November and December of 1981, but all attempts to phase the data with the previously determined room temperature X-ray structure met with failure. This being the first SCD experiment, Ray Teller and I examined in detail every step of the data analysis procedure for possible errors. We also provided Mark Beno with Bragg data within a limited wavelength range to reduce the effects of extinction, and he was able to obtain a structure solution using the direct methods program MULTAN. It then became clear that we had actually chosen a different monoclinic unit cell, with  $\mathbf{a}_n = -\mathbf{a}_x$ ,  $\mathbf{b}_n = -\mathbf{b}_x$ , and  $\mathbf{c}_n = 2\mathbf{a}_x + \mathbf{c}_x$ , where the subscripts n and x refer to the original neutron and X-ray unit-cell vectors, respectively. We initially thought the unit cells were equivalent because of the fortuitous near equivalencies of the magnitudes of  $c_n = 17.132 \text{ \AA}$  and  $\beta_n = 113.21^\circ$  with  $c_x = 17.250 \text{ \AA}$  and  $\beta_x = 112.00^\circ$ . Thus, the first single-crystal time-of-flight structure determination was solved by direct methods independent of the X-ray structure.

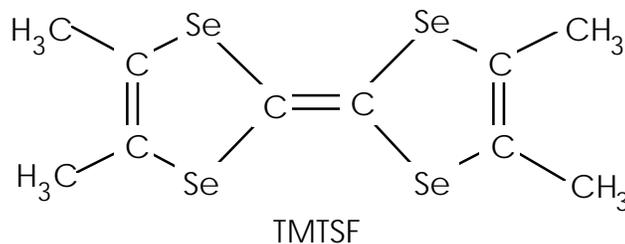
The most important feature of the structure is the C(1)—H(1A)—Mn interaction with H(1A) located almost exactly in an octahedral site about the manganese atoms and with a very long C(1)—H(1A) distance of  $1.19(1) \text{ \AA}$  (Fig. 1). The average value for the other C—H distances in the structure is, as expected,  $1.09(1) \text{ \AA}$ . This same type of interaction was structurally characterized in a related isoelectronic cationic iron complex with C—H =  $1.164(3) \text{ \AA}$ .<sup>14</sup> In both of these molecules, an 18-electron configuration is achieved only by delocalization of the two electrons in the C—H bond to form a 3-center, 2-electron C—H··metal bond.



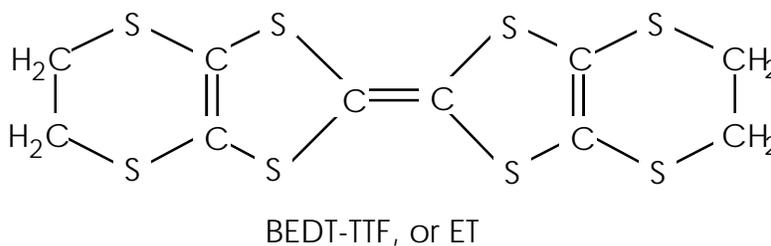
**Figure 1.** The structure of Mn(CO)<sub>3</sub>(C<sub>7</sub>H<sub>11</sub>) at 25 K.

## ORGANIC SUPERCONDUCTORS: THE DEVELOPMENT OF THE HIGH PRESSURE APPARATUS

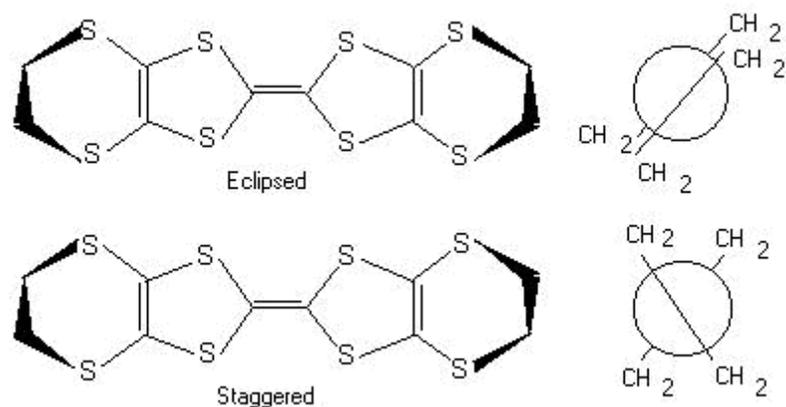
Organic superconductors have been the subject of a number of investigations on the SCD. The first of these involved the characterizations of the low temperature commensurate superlattices in the quasi-one-dimensional charge transfer salts (TMTSF)<sub>2</sub>X, where X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup>, both of which have  $T_c$ 's of 1–2 K.<sup>18</sup> The superlattices are due to ordering of the tetrahedral anions which are located on centers of inversion in the high temperature structural phases. This was the first demonstration using the SCD of the importance of crystallographic order to superconductivity in the organic metals.



The largest number of organic superconductors and those with the highest  $T_c$  values known to date are based on the donor molecule BEDT-TTF, or simply ET.<sup>19</sup> Whereas the TMTSF salts are all nearly isostructural, ET salts crystallize with many different structural phases, even with the same anion and stoichiometry. Most of the salts are layered materials with layers of conducting donor molecules sandwiched between layers of anions.

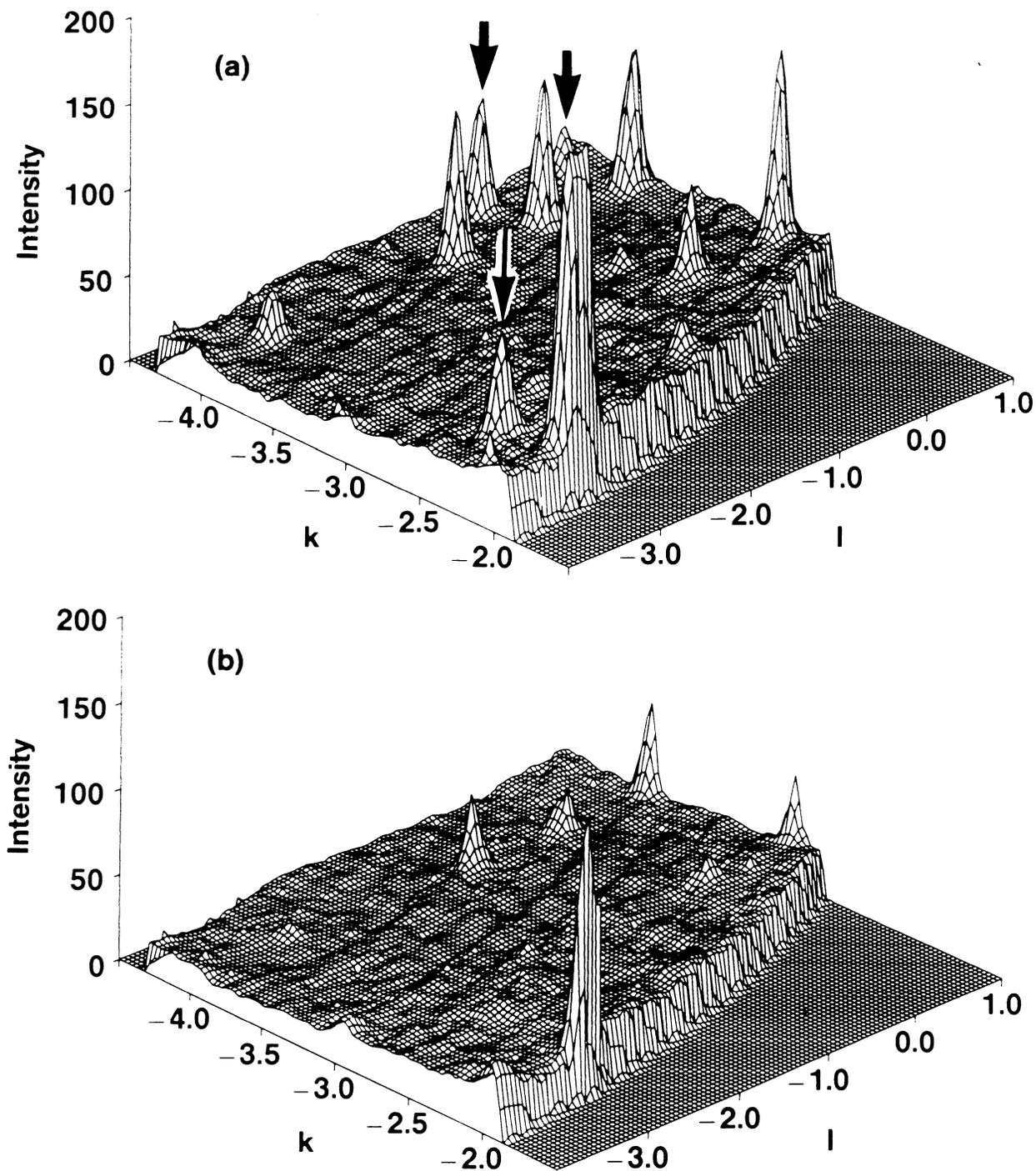


One of the most interesting features of the ET molecule is the occurrence of different conformations as depicted in Figure 2, and the relation of these conformations to lattice softness, disorder, and  $T_c$ . In the case of  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub>, we have characterized three distinct structural phases. At room temperature and ambient pressure, each ET molecule assumes a random orientation with either an eclipsed or staggered conformation of their ethylene groups. In 1984, the observation of incommensurate superlattice satellite reflections with X-rays and with neutrons on the SCD from crystals of  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> below ~200 K was reported.<sup>20</sup> These satellite reflections were shown to be due to (i) displacive modulations of the I<sub>3</sub><sup>-</sup> anions and the ET molecules as rigid groups and (ii) modulation of the above-mentioned conformational disorder.<sup>21</sup> Upon further cooling,  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> becomes superconducting at  $T_c = 1.4$  K. This compares to salts in which the ET molecules are in ordered eclipsed conformations with  $T_c = 2.8$  K for  $\beta$ -(ET)<sub>2</sub>IBr<sub>2</sub> and  $T_c = 4.98$  K for  $\beta$ -(ET)<sub>2</sub>AuI<sub>2</sub>. The low  $T_c$  for  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> was attributed to its partial disorder (incommensurate modulation) although band calculations of the density of states at the Fermi energy indicated it should have the highest  $T_c$ .



**Figure 2.** Schematic view of the two possible ethylene group arrangements of ET where the C–S and C–C bonds of the ethylenedithio units ( $-\text{S}-\text{CH}_2-\text{CH}_2-\text{S}-$ ) are represented by wedges to distinguish the C atoms lying above and below the molecular  $\pi$ -framework. The diagram on the right of each molecule depicts the eclipsed and staggered arrangements of the ethylene groups when viewed parallel to the central C=C double bond.

Then, in 1985 Soviet and Japanese scientists reported that the superconducting transition temperature  $T_c$  for  $\beta\text{-(ET)}_2\text{I}_3$  rises from  $\sim 1$  K at ambient pressure to  $\sim 8$  K with applied pressures above 1.2-1.3 kbar.<sup>22,23</sup> I simultaneously sent off a proposal to the ILL and discussed with Bob Kleb the possibility of obtaining pressure capabilities on the SCD. Kleb came through first with the design and construction of the high pressure sample cell which mounts on the Displex cold stage of the SCD. To complete the instrumentation, Jim Jorgensen helped us locate a helium pumping station which had been stored in the basement of building 223 since the shutdown of CP-5 in 1981. Using this equipment, it was observed that the satellite reflections, which are present at ambient pressure below 200 K, are absent above a critical pressure of 0.5 kbar applied at room temperature and followed by cooling (Fig. 3).<sup>24</sup> The satellite reflections remained absent if the pressure was released while the temperature was maintained at 20 K. It was proposed that the high pressure structural phase was ordered and the transition from the modulated structure to the completely ordered phase accounted for the rise in  $T_c$ . The ordered structure was later confirmed with data obtained at the ILL.<sup>25</sup>

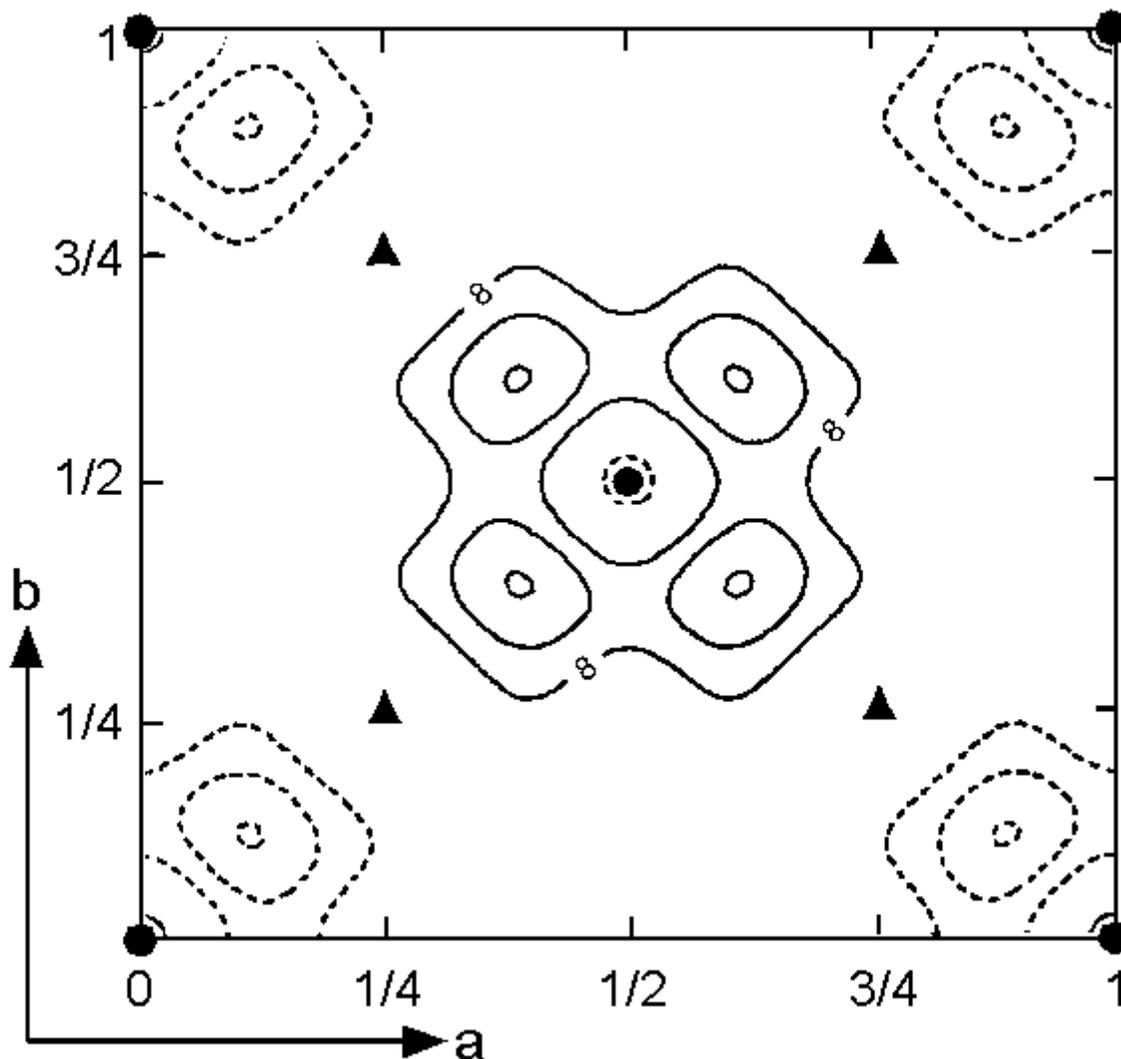


**Figure 3.** (a) Plot of the neutron-diffraction intensity distribution in the  $h = 4.92$  reciprocal lattice plane of  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> at 20 K and with zero pressure. Satellite peaks at  $(5 \bar{2} \bar{3})-\mathbf{q}$ ,  $(5 \bar{4} 0)-\mathbf{q}$ , and  $(5 \bar{4} 1)-\mathbf{q}$ , where  $\mathbf{q} = 0.08\mathbf{a}^* + 0.27\mathbf{b}^* + 0.21\mathbf{c}^*$ , are clearly observable. (b) The same  $h = 4.92$  plane after applying a pressure of 1.4 kbar, warming to room temperature, and cooling back down to 20 K.

## HIGH- $T_c$ AND RELATED MATERIALS: STUDIES OF MAGNETIC PROPERTIES

Materials related to the high- $T_c$  superconductor  $\text{La}_2\text{CuO}_4$  were the subject of the first *quantitative* investigation of magnetic properties using SCD data.  $\text{La}_2\text{CuO}_{4-\delta}$  is antiferromagnetic with a Néel temperature that depends on  $\delta$  and a magnetic form factor in the ordered state which is not in very good agreement with that of the  $\text{Cu}^{2+}$  free ion due to a plateau at low  $Q$ . The two reasons suggested for this discrepancy are either anisotropic magnetization density of the copper site or some small magnetic moment on the out-of-plane oxygen sites. In order to test these theories, measurements on a material in which the out-of-plane oxygen atoms are replaced by chlorine atoms,  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , were carried out by Xunli Wang from Iowa State University in a collaboration with scientists from Argonne and other laboratories.<sup>26</sup> Using the SCD, it was found that the form factor of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  is quite similar to that of  $\text{La}_2\text{CuO}_4$  and it is therefore unlikely that any significant moments exist on the out-of-plane oxygen (or Cl) ions. A reasonable fit to the experimental form factor data is obtained if a dipolar spin polarization on the in-plane oxygen ions is assumed. In this model, the in-plane oxygen 2p orbital which overlaps with the two nearest neighbor Cu  $d_{x^2-y^2}$  orbitals is spin-up on one side and spin down on the other side.

In another series of experiments the magnetic form factor of  $\text{La}_2\text{NiO}_4$  was examined.<sup>26</sup> Since  $\text{Ni}^{2+}$  has a much larger moment than  $\text{Cu}^{2+}$ , measurements on  $\text{La}_2\text{NiO}_4$  should be more precise than those on  $\text{La}_2\text{CuO}_4$  and  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ . Attempts to measure the magnetic reflections of  $\text{La}_2\text{NiO}_4$  at a steady state reactor source were not successful due to contamination by multiple Bragg scattering. Using the IPNS SCD, each reflection was measured many times ( $\sim 10$ ) over a wide range of neutron wavelengths so that anomalous intensities could be easily identified and discarded. Again, the experimentally determined data for  $\text{La}_2\text{NiO}_4$  exhibit a plateau at low  $Q$  similar to  $\text{La}_2\text{CuO}_4$  and  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ . With  $\text{La}_2\text{NiO}_4$ , the larger number of measured magnetic reflections permits the evaluation of the spin density Fourier map corresponding to the difference between the observed density and that obtained by fitting the data to an isotropic  $\text{Ni}^{2+}$  form factor. No significant density is observed away from the Ni-O plane. As shown in Fig. 4, in the Ni-O plane there is spin density extending from each copper in the direction of the four in-plane oxygen atoms.



**Figure 4.** The difference magnetization density in the Ni-O plane of La<sub>2</sub>NiO<sub>4</sub>. The atoms symbols are circles for Ni and triangles for O. The solid and dashed contours denote positive and negative densities, respectively. Each contour is  $8 \times 10^{-3} \mu_B/\text{\AA}^3$ . The Ni atoms at the corner positions have been defined to have positive densities.

### TEXTURE STUDIES OF POLYCRYSTALLINE SAMPLES

Although the SCD was designed for measurements of single crystal samples, over the years we have found that it is also ideally suited for determining the texture (preferred orientation) of polycrystalline materials. A major advantage of using the SCD, with its large area detector and range of wavelengths, is the ability to measure large portions of the pole figures of many d-spacings with a single sample orientation in the case of fine-grained polycrystalline material. For coarse-grained material, single crystal orientations for several grains can be derived from one sample setting.

An example of determining preferred orientation of a coarse-grained material is that of mineral grain orientations in earth mantle samples [J. R. Smyth (University of Colorado), P. J. Vergamini (LANL), A. J. Schultz (ANL)].<sup>27</sup> In this experiment, slabs approximately 80x25x3 mm were attached to an x-y linear drive stepping motor assembly which was mounted in the sample position of the SCD. The x-y translator also includes one rotation axis and had been originally constructed by Bob Kleb, Sherman Sussman and Torben Brun (Materials Science Division) for searching for single crystals in boules of LiAl and LiGa obtained from a melt. For the earth mantle experiment, a single histogram of data was recorded for about 35 minutes at one spot, the sample was then translated a few millimeters, and data from another spot was recorded. In this manner, data from as many as 48 spots were collected from each sample. Bragg peaks were indexed for garnet and clinopyroxene using the multiple phase and crystallite features of Larson and Von Dreele's GSAS program. Significant preferred orientation was revealed with respect to the observed foliation of the rocks which may account for seismic velocity anisotropy.

The development of pole figure analysis software was initiated in 1987 in order to study the texture of high- $T_c$  samples. The pole figure analysis software developed here at Argonne also produces the input required to calculate the orientational distribution function (ODF) using software provided by John Kallend of the Illinois Institute of Technology (IIT). In a round-robin experiment using a highly textured calcite sample, the results from both the IPNS and LANSCE SCDs compared well with the results from instruments at steady state reactor sources.<sup>28</sup>

During the fabrication of wires, rods or films from high- $T_c$  copper oxide superconductors, the high aspect ratio of the crystallites leads to preferred orientation. In the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , this texturing can give rise to significant increases in the critical current density ( $J_c$ ) if the a-b planes of the crystallites are aligned in the direction of the electrical conductivity. In an ongoing program with Ken Goretta (Material and Components Technology Division), Tony Biondo and John Kallend (IIT), various processing techniques ranging from slip casting to sinter forging have been evaluated.<sup>29,30</sup> We are currently extending these investigations to samples of the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  superconductor.

## LOOKING AHEAD

In the past ten years the single crystal time-of-flight Laue technique has progressed from the proof-of-principle stage to being a valuable scientific tool of proven capabilities. Of course, the entire IPNS staff need to be acknowledged for the design and construction of everything from the beam line to the data acquisition system. In the near future, plans for installing a chopper to reduce delayed neutron background, obtaining a closed cycle helium refrigerator capable of cooling to 4 K, and the addition of a second detector, will be evaluated. These improvements could lead to better measurements of low  $Q$  data (e.g., first order magnetic reflections) at lower angles and shorter

wavelengths where there is a higher incident neutron flux and less secondary extinction. A second area detector will also reduce data collection times and allow the use of smaller samples and the study of larger crystal structures.

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