Progress Report

NEUTRON SCATTERING IN LIQUIDS AND SOLIDS
(Covering Period March 25, 1963, to March 24, 1964)

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A. OUTLINE OF PROJECT OBJECTIVES AND PROGRESS

1. REVIEW OF OBJECTIVES

This is the first annual progress report on "Neutron Scattering in Liquids and Solids," sponsored by the National Science Foundation under Grant No. GP-1032, effective March 25, 1963, to March 24, 1965. The objectives of this project, as set forth in the original three-year project proposal, are:

a. To construct and calibrate Model II of The University of Michigan Triple Axis Crystal Spectrometer. Model I was constructed and operated under NSF Grant G-12147, and a new design was conceived out of operating experience on that project. Need for a substantial increase in counting intensity dominates the Model II design.

b. To perform experimental investigations of (1) inelastic scattering from hydrogenous liquids such as HCl, HF, (2) inelastic scattering spectra from selected molecules for comparison with well known infrared or Raman spectra, (3) Debye-Waller factors for liquids, and (4) multiple scattering phenomena.

The feasibility of the experimental program rests not only upon the success of the spectrometer redesign but also on the usefulness of any fixed-crystal spectrometer operating in the neutron energy region of .02 to .2 electron volts using a conventional swimming pool reactor neutron source.

2. PROGRESS TOWARD OBJECTIVES

The construction and calibration of Model II was completed between March 24, 1963, and December 24, 1963. In brief, the new system provides an increase in counting rate of a factor of 180 as compared to Model I, at a cost in resolution of 2.3% in ΔE/E, an increase in beam dimensions, and an increase of a factor of 16 in background count rate. This performance was considered more than satisfactory from an intensity standpoint and somewhat marginal in resolution. Also during this period, the system was completely automated to provide round-the-clock programmed operation.

Experimental measurements, using this improved spectrometer, were begun December 30, 1963. It was decided that the comparison of neutron spectra with infrared spectra on selected molecules should be the first and perhaps most fruitful area of study. An extensive examination of scattering from solid polyethylene (CH2)n was begun first, for many reasons, with the intent of completing a six-month program by July 1, 1964. This work constitutes the doctoral thesis of one graduate student, John L. Donovan. Ethane gas was selected as a second
target material. A rather elaborate, high pressure (50 atmospheres) ethane target chamber gas was designed during this period. Study of this target as a function of pressure, both in the Model II crystal spectrometer and in The University of Michigan phased rotor facility, is intended to be the doctoral thesis for a second graduate student, Edward Straker. Both projects should be essentially completed in calendar year 1964.

So many interesting and, we believe, worthwhile ramifications of the \((\text{CH}_2)_n\) study have revealed themselves during our initial experiments that it now appears desirable to extend these measurements at the expense of other parts of the proposed program. In particular, we hope to examine the scattering at low temperature from \((\text{CH}_2)_n\) targets with such special features as chain orientation, deuteration, and 100% crystallinity.
B. CONSTRUCTION AND PERFORMANCE
OF MODEL II TRIPLE AXIS CRYSTAL SPECTROMETER

1. NEW DESIGN FEATURES

As detailed in progress reports on Grant G-12147, University of Michigan ORA reports 03671-1-P, 2-P, 3-T, and 4-P, the original design, Model I, was found to be very low in counting intensity although good in energy resolution. (Typical performance parameters, obtained by scattering from 1/4 in. vanadium calibration targets, are listed in Table I.) It was impractical to perform sound experiments with the low intensity. Consequently, Model II was designed in an effort to obtain adequate counting statistics, even with reduced resolution. A number of design features were exploited; some of these, we believe, are unique in neutron crystal spectrometry, while others are of a "brute force" nature. We list briefly the new features:

a. Vertical focusing of the primary beam. This was accomplished by using a very large, tapered vertical aperture in the primary collimator, and by a split copper crystal monochromator. Rather gross lack of vertical resolution produces only a second order horizontal (Bragg angle) resolution effect while the intensity increases linearly with the vertical aperture dimension. The collimator is 10 ft long with a 5-1/2 in. vertical aperture at the reactor source plane.

b. Multiple analyzers to increase the scattering solid angle seen by the detectors. Four complete analyzers including second collimator, second crystal, second Bragg arm drive, detector, and preamplifier, are operated in parallel into a common amplifier-high voltage channel. This requires four large copper analyzers but these were slabs cut from the original 3-in. x 7-in. cylindrical copper ingot. Specially built 3-in. x 6-in. ceramic end window BF₃ detectors were successfully supplied by the Reuter-Stokes Company. These detectors are noise free when the high voltage (5000 volts) input lines are sealed against humidity. Inherent background of the parallel system is less than 1 cpm. (The preamplifiers were built by a graduate student.) It should be noted that the spectrometer operates with a fixed final energy so that simultaneous analysis is quite simple.

c. Crystal surface scoring. Surface roughening by milling .005 in. grooves in the copper (200) faces produced a surprisingly large enhancement in integrated reflectivity (and, of course, broadening of crystal resolution). This effect improved the crystal-collimator...
resolution matching. The effect is not well investigated or understood at present. It appears that the mosaic recovers its original width when remilled smooth, but a systematic study is needed.

Other improvements include a doubling of the reactor power, and greatly increased fast neutron shielding. Figure 1 shows the present shielding arrangement: large water and paraffin tanks surround the analyzer system and ride on a "railroad car" platform attached to the main Bragg arm. The overall performance of the Model II relative to the Model I system is itemized in Table I.

### TABLE I

**MEASURED INTENSITY IMPROVEMENT AND RESOLUTION LOSS**

<table>
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<th></th>
<th>Model I (1962)</th>
<th>Model II (1963)</th>
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<tr>
<td><strong>A. Intensity Improvement:</strong></td>
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<td></td>
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<tr>
<td>1. Higher Reactor Power Level</td>
<td></td>
<td>2.0</td>
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<tr>
<td>2. Primary Collimator Vertical Focusing and Increased Aperture</td>
<td></td>
<td>4.0</td>
</tr>
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<td></td>
<td>1.7</td>
</tr>
<tr>
<td>4. Crystal Surface Treatment</td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>5. Increased Analyzer Aperture</td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>6. Simultaneous Use of (3) Analyzers</td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td><strong>B. Total Intensity Ratio</strong></td>
<td></td>
<td>180.0</td>
</tr>
<tr>
<td><strong>C. Total Count Rate (1/4-in. V target, elastic peak at .05 ev)</strong></td>
<td>7 cpm</td>
<td>1260 cpm</td>
</tr>
<tr>
<td><strong>D. Background Count Rate (.05 ev)</strong></td>
<td>0.9 cpm</td>
<td>15 cpm</td>
</tr>
<tr>
<td><strong>E. Total Signal to Background Ratio</strong></td>
<td>8</td>
<td>84</td>
</tr>
<tr>
<td><strong>F. Resolution, FWHM at .05 ev</strong></td>
<td>5.4%</td>
<td>7.8%</td>
</tr>
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While the intensity increase is most satisfactory, the loss in resolution is a serious disadvantage and rules out "high resolution" experiments in this energy range. Furthermore, the high intensity also exists for second order contamination from both monochromators. This can be effectively eliminated in the primary beam by exploiting the Maxwellian source spectrum (which, for us, means keeping the incident beam energy above about .027 ev), but no such advantage occurs in the scattered beam. Various alternatives, including "order rotors," filters, multiple crystal reflections, and use of monochromators such as Si or Ge with no second order reflection have been carefully considered to eliminate order
Fig. 1. Triple axis crystal spectrometer.
contamination. Thus far, no solution has been found practical for this spectrometer. Consequently, analyzer order contamination is measured and subtracted from the total count. This requires duplicating each run with analyzers set at \( E_f \) and \( 4E_f \), where \( E_f \) is the final neutron energy. This technique is time consuming and only moderately reliable in certain experiments. Furthermore, restriction of the primary energy to values above .027 ev seriously limits the experimental region of interest (the region between the source energy, .006 ev, in the "cold neutron" technique, and .027 ev is a most valuable area to cross check experimental methods). It is clear that order contamination is the foremost problem of the present spectrometer.

2. PROGRAMMED OPERATION

The spectrometer is now automated for 24-hour operation without manual adjustment. This includes, presently, arbitrary motions of the target table and primary Bragg arm, but could, with little effort, include scattering angle for constant momentum experiments. The system relies on "Slo-Syn" dc impulse motors, driven from preset scalers. Figure 2 is a block diagram of the logic sequence. This sequence was designed, built, and installed by William Myers of our group. Currently, data are accumulated by a sequence of uniform Bragg angle advances, with a total count followed by a background count (180° target rotation to a cadmium backing) at each arm position. Each count is printed out on paper tape. These numbers are transcribed to card input for The University of Michigan IBM 7090 computer. All necessary corrections and conversions of data are then calculated by the computer, i.e., corrections for background, second order, and beam monitor efficiency. Data can be converted to energy cross sections and, in the case of solids, phonon frequency distributions.
Fig. 2. Triple axis crystal spectrometer data collection programmer.
C. EXPERIMENTS ON POLYETHYLENE \((\text{CH}_2)_n\)

A six-month study of \((\text{CH}_2)_n\) was begun December 20, 1963. The objectives of this study were:

1. To determine, by direct comparison with published "cold neutron" data and with University of Michigan phased rotor data, whether crystal spectrometer results are indeed equivalent to other techniques in detail.

2. To verify, both at room temperature \((298^\circ \text{K})\) and liquid nitrogen temperatures \((90^\circ \text{K})\), published phonon frequency spectra.

3. To determine the multiple phonon effect on these spectra and its theoretical predictability.

This program constitutes the Ph.D. thesis effort for Mr. John Donovan, and was well underway at the end of this report period. Preliminary results indicate some differences between our crystal data and "cold neutron" results for \(298^\circ \text{K}\) targets. These differences are expected to be strongly reduced at low temperatures, when multiphonon effects are minimized. Figure 3 is a typical comparison of frequency spectra, \(g(\epsilon)\), where \(\epsilon\) is the phonon energy and \(g(\epsilon)d\epsilon\) is the number of phonons between \(\epsilon\) and \(\epsilon+d\epsilon\) for the two methods. \(g(\epsilon)\) is extracted from the measured differential scattering cross sections according to the one phonon, incoherent approximation, with the Debye-Waller factor set equal to unity. Figure 4 shows the reproducibility of these results as a function of final energy setting.

The same target was used for both the cold neutron and crystal spectrometer experiments, through the kindness of Dr. D. M. Danner. Preliminary University of Michigan chopper data have been taken also, but unfortunately not on the same target as yet. A comparison of low temperature results at \(90^\circ \text{K}\) for all three experiments will be a valuable and publishable by-product of this study.

It must be noted here that this is a study of internal acoustic vibrations in high-polymer crystals. This, we believe, is a fruitful area for neutron experiments because some of these motions are not infrared nor Raman active because of selection rules; these motions are observable by neutron interactions only (which have no selection rules).

Additional measurements are underway for various target conditions, i.e., low temperature variation, multiple scattering effect from variation in target thickness, and the influence of amorphous regions of the polyethylene. A simple low temperature cryostat is under construction and a large number of \((\text{CH}_2)_n\)
Fig. 3. Comparison of frequency spectra for room temperature Marlex 6050; .033 in.; crystallinity, 89.7%; $\theta = 90^\circ$. 

Donovan and King (298° K), $E_f = .0268$ ev

Danner et al (293° K)
$E_0 = .005$ ev
Fig. 4. Frequency spectra vs. $E_f$ for Marlex 6050 polyethylene; $T = 289^\circ K; 33~\text{mil}; \theta = 90^\circ$. 

$E_f = 0.0595~\text{ev}$

$E_f = 0.0341~\text{ev}$

$E_f = 0.0268~\text{ev}$
samples of varying crystallinity have been accumulated. There is some hope of obtaining polyethylene pellets with 100% crystallinity as grown from the melt.
Personnel conducting the experimental program include the principal investigator and four doctoral candidates. Financial assistance was provided as follows according to approximate percentage of full time:

J. S. King, Professor
Department of Nuclear Engineering 18%
Sanford Cohen, Ph.D. Candidate 10%
John Donovan, Ph.D. Candidate 50%
William Myers, Ph.D. Candidate 80%
Edward Straker, Ph.D. Candidate 20%

In addition to the experimental group, several members of the theoretical group in the Department of Nuclear Engineering have contributed much effort to the program, without financial support. These are Assistant Professor George Summerfield and graduate students Jon Erickson and Kenji Takeuchi.

Our financial status is approximately on schedule. Principal expense items which have differed from the original proposed budget include "savings" roughly as follows:

Fast Neutron Filter for Beam Port Plug
(in Collimator) +$1000
Order Rotor and Rotor Drive + 2550
Crystal Growing Laboratory + 600

$4150

These items have proved impractical for the present spectrometer system and have not been undertaken. Principal unplanned expenses include:

Additional Analyzer Housing, Drives, and Shielding - $2000
Additional Cost of 3-in. Detectors - 500
Temperature and Humidity Control of Experimental Area - 410

$2910