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February 18, 1991

**UNIDO FINAL REPORT**

**FINAL REPORT ON DP/IND/87/007** **AGENCY AWARD NO.** 89/10

**UCSB Proposal Number** 08 004490 **Amount Awarded:**$10,000

**Period of Performance:** February 21, 1990 through February 20, 1991.

**Title:** "DEVELOPMENT OF NOVEL SHAPE SELECTIVE ZEOLITE CATALYSTS"

**P.I.:** Professor Galen D. Stucky, Department of Chemistry
University of California, Santa Barbara, California, 93106

Characterization of UN-1

The purpose of this research was to assist in the characterization of the unkown zeolite phase, "UN-1" (sample code, ZANK-5(34) Na form, calcined in air at 550 °C for 10 hours, synthesized at NCL). Powder diffraction studies on a Scintag PAD X diffractometer (Figure 1) were carried out at the University of California at Santa Barbara by William Harrison, a postdoctoral associate of Professor Galen Stucky. The X-ray lines were relatively broad (0.5 ° full width at half maximum intensity at 10 ° in 2Θ). A substantial amorphous component is indicated by broad diffraction peaks centered at 12 ° and 24 ° 2Θ.

A search of JCPDS --International Centre for Diffraction Data-- files suggests that ZANK-5(34) (UN-1) is an $SiO_2$ isomorph, Silica X, previously reported by C. Frondel, Am. Mineral. 64, 799 (1979) (Figure 2 and Table I). Frondel's sample was made by treating gmelinite or scolecite in acid and adding the residue to KOH solution, then heating to

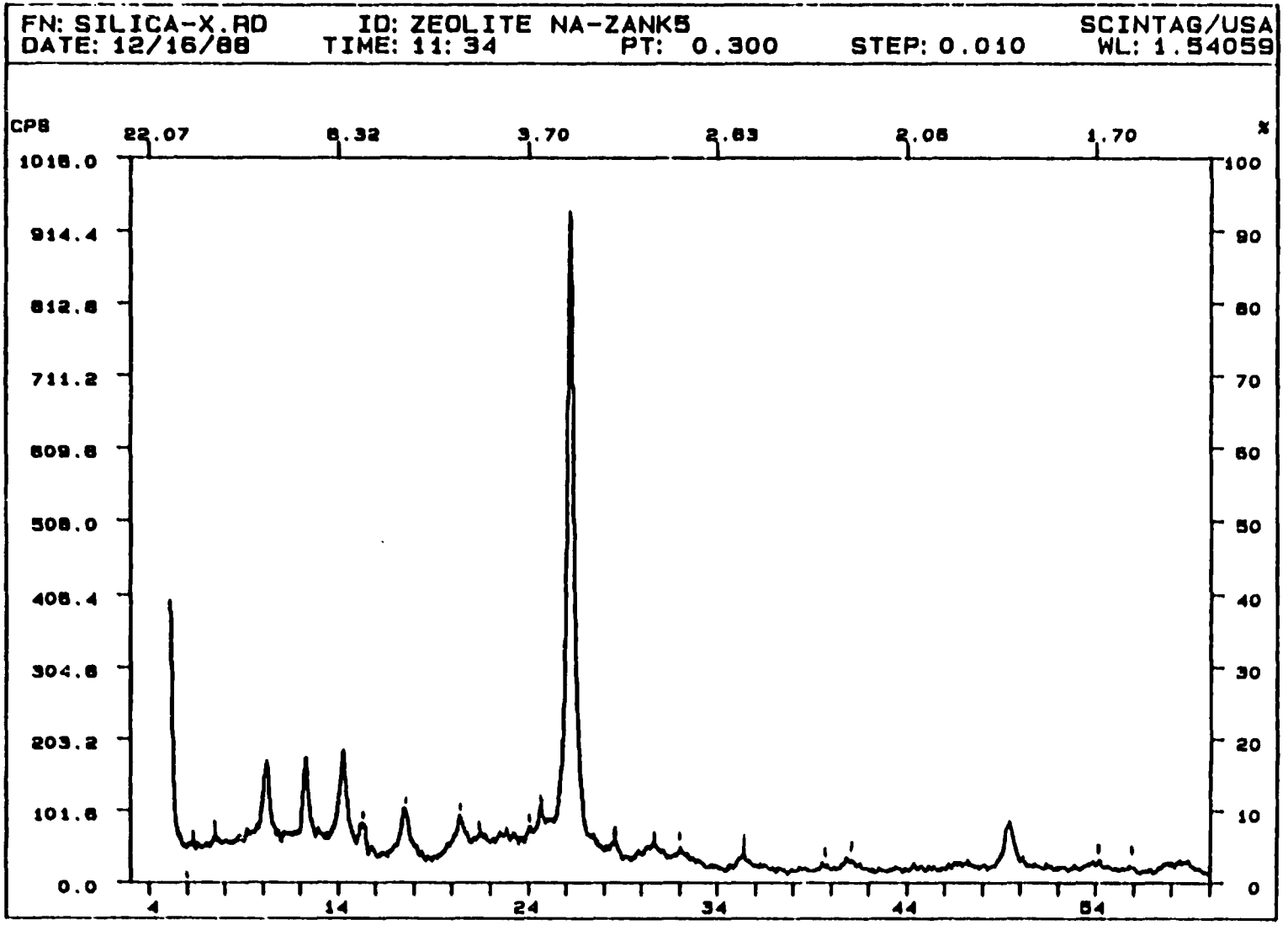
175 °C for 3 to 10 days. It has also been formed from amorphous silica by heating to 180 °C with a KOH solution. The phase goes to cristobalite than quartz in 5 days (B. Hedemann, Min. Petrog. 10, 242 (1964). The sorption, catalytic and structural details of Frondel's phases are currently unknown.

The computer program, TREOR (P.-E. Werner, University of Stockholm), was used to index the diffraction pattern of UN-1 and the reported pattern of Frondel. The indexing output is given in Table II for UN-1. Because of the broad diffraction peaks and the large unit cell, the assignment is tentative but consistent with the identification of UN-1 as being Silica-X. Unit cell parameters which best fit UN-1 also are given in Table II. These parameters assume a pure phase, and as noted above are also tentative because of sample crystallinity.

There is no obvious structural model suggested by the unit cell parameters so that an ab initio structural determination would be required. Such a structural analysis of UN-1 would require 1) a more crystalline sample, 2) transmission electron microscopy diffraction data (Dr. Singh of Pune) to obtain as much symmetry information as possible and 3) high resolution neutron diffraction powder data on the dehydrated sample in order to obtain the maximum possible number of Bragg peaks. The Bragg peaks would be deconvoluted and the structure analysis attempted using a combination of direct method, Patterson, and tetrahedral annealing analysis. The latter approach is unpublished and recently developed by John Newsam of Biosym corporation. Solid state magic angle spinning experiments using $^{29}Si$ would be an important asset in this analysis.

The above references have been given to Dr. Kotasthane of the National Chemical Laboratory at Pune. If it is felt that the more detailed structural analysis described above would be beneficial to NCL, we would be happy to continue this collaboration. The ab initio solution of structures from powder diffraction techniques is a non-trivial exercise and should only be pursued for important, new molecular sieves which might have a substantial impact on the NCL zeolite research program.

Conclusion: The identity of the sample ZANK-5(34) Na, also referred to here as UN-1, has been determined to be that of Silica-X. The diffraction pattern shows considerable amorphous component with relatively broad Bragg diffraction peaks. TREOR software was used to determine the most probable unit cell parameters for ZANK-5(34) Na and Silica-X (Table II). An ab initio structural determination to obtain atomic positional coordinates would require 1) a more crystalline sample, 2) high resolution neutron diffraction data 3) electron diffraction information and 4) auxillary NMR data for modelling purposes.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609.6
508.0
406.4
304.8
203.2
101.6
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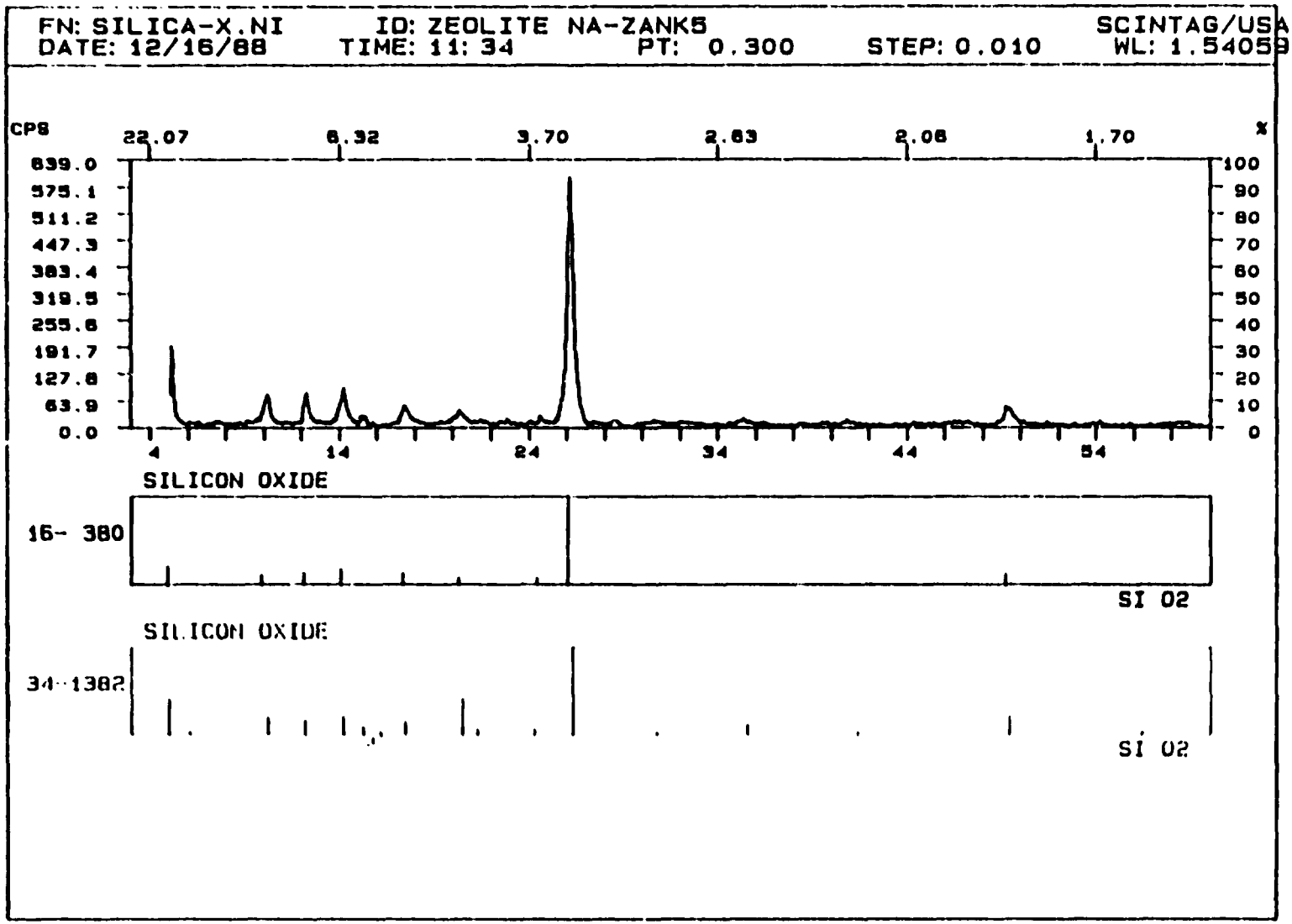
40
30
20
10
0
4
14
24
34
44
54

FIGURE 1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6.32
3.70
2.63
2.08
1.70
X
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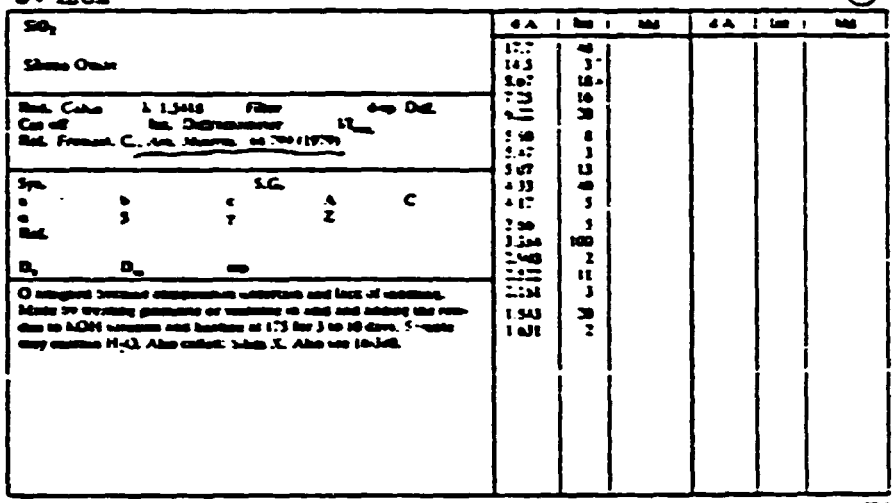
575.1
511.2
447.3
383.4
319.5
255.6
191.7
127.8
63.9
0.0
100
90
80
70
60
50
40
30
20
10
0
4
14
24
34
44
54
SILICON OXIDE
16- 380
SI 02
SILICON OXIDE
34-1382
SI 02

FIGURE 2

34-1382



16-380

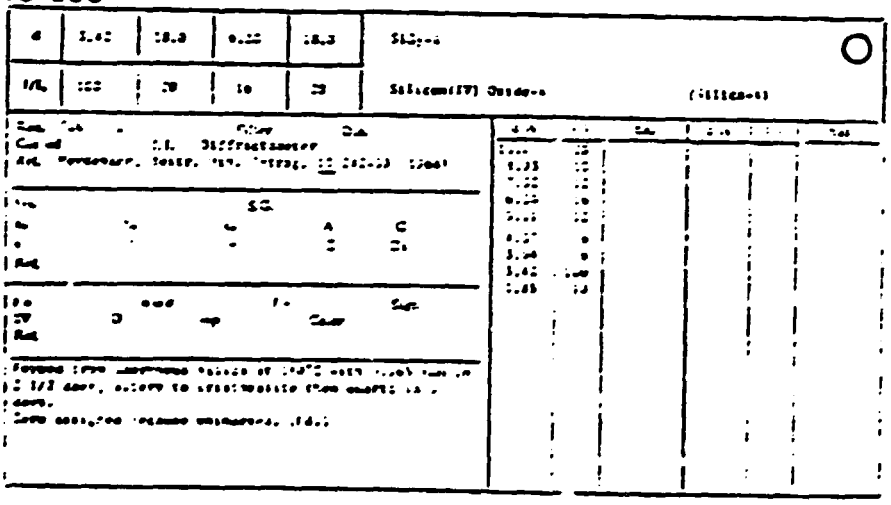


TABLE 1

## Table 2

```
CYCLE RESULTS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 0.001965  0.002358  0.013429  0.00C000  0.000000  0.000000


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 NUMBER OF SINGLE INDEXED LINES =    10
  TOTAL NUMBER OF LINES =    18
  A = 17.378817  0.018944 A    ALFA = 90 000000  0.000000 DEG
  B = 15.864689  0 021135 A    BETA = 90.000000  0 000000 DEG
  C =  6.647115  0 004484 A   GAMMA = 90.000000  0 000000 DEG
  UNIT CELL VOLUME =    1832.67 A**3
   H   K   L SST-OBS  SST-CALC    DELTA   2TH-OBS 2TH-CALC D-OBS   FREE PARAM.
   1   0   0 0.002028 0 001965  0 000063   5.162    5 081 17 1060
   2   0   C 0.007861 0 007858  0 000002  10 173   10.172  8 6881
   1   2   0 0.011443 0 011395  0 000048  12.282   12.256  7 2009
   1   0   1 0.015360 0.015394 -0 000034  14.239   14 254  6 2153
   3   0   0 0.017639 0.017682 -0 000043  15 264   15.283  5 8000
   1   1   1          0.017751                    15 313
   0   2   1 0.022983 0 022859  0 000124  17 440   17 392  5 0811
   1   3   0          0 023182                    17 516
   4   0   0 0.031443 0 031434  0.000009  20 428   20 425  4 3441
   0   3   1 0.034707 0 034647  0.000060  21.474   21.455  4 1348
   2   4   0 0.045457 0 045579 -0.000121  24 621   24 654  3.6129
   0   4   1          0.051150                    26 143
   5   1   0 0.051352 0.051473 -0.000121  26 175   26 227  3 3992
   1   5   0 0.060534 0.060903 -0.000369  28.486   28.575  3.1308
               0.077304                    32 286           2.7705
   6   3   0 0.091932 0 091944 -0.000012  35 300   35.303  2 5405
               0.114156                    39.494           2.2799
   5   5   1 0.121523 0 121483  0.000041  40 804   40 797  2.2097.
   6   4   1          0.121876                    40.865
   4   3   3 0.173494 0 173515 -0.000021  49 231   49 234  1.8493
  10   2   0          0 205892                    53 969
   1   9   1 0.206271 0 206353 -0.000083  54 023   54 035  1 6961
   1   8   2          0 206563                    54 065
   9   5   0          0 218072                    55.677
   5   7   2 0.218413 0.218331  0.000062  55.724   55.716  1.6482
NUMBER OF OBS. LINES =    18
NUMBER OF CALC. LINES =    23
M( 18)=    5  AV EPS. = 0 0000758
F 18 =    3 (0 024895,   292)

 M   CF  J APPL CRYST  1(1968)108
 F  CF  J APPL CRYST  12(1979)60
    2  LINES ARE UNINDEXED
MONOCLINIC TEST
MAX BETA ALLOWED=     1 DEG
(020)-SEARCH
K= 18 XYZU=  0.005746  0 001965  0 013395  0.012467


CYCLE RESULTS


 0 005714  0 001963  0 013308  0 012392  0 000000  0.000000
 0 005714  0 001964  0 013390  0 012394  0 000000  0.000000
 0 005714  0 001964  0 013390  0 012394  0 000000  0 000000
```

## Table 2 Continued

```
CYCLE RESULTS


 0 002023  0 003923  0 008324  0 002496  0 000000  0 000000
 0.002023  0.003923  0 008324  0.002496  0.000000  0 000000
 0 002023  0.003923  0.008324  0 002496  0.000000  0.000000


NUMBER OF SINGLE INDEXED LINES=   10 TOTAL NUMBEROF LINES=.   18
 NUMBER OF SINGLE INDEXED LINES =   10
  TOTAL NUMBER OF LINES =   18
  A = 17 978277  0 023620 A   ALFA = 90 000000  0 000000 DEG
  B = 12.298343  0 005284 A   BETA =107 703482  0 027954 DEG
  C =  8.862907  0 004030 A  GAMMA = 90 000000  0 000000 DEG
  UNIT CELL VOLUME =   1866 79 A**3
   H   K   L SST-OBS  SST-CALC    DELTA   2TH-OBS 2TH-CALC D-OBS   FREE PARAM
   1   0   0 0 002028 0.002023  0 000005   5 162   5 156 17 1060
  -1   0   1 0 007861 0 007851  0 000010  10 173  10 167  8 6881
  -2   0   1 0 011443 0 011423  0 000020  12 282  12 271  7 2009
  -2   1   1 0.015360 0 015347  0 000013  14 239  14 232  6 2153
   1   2   0 0 017639 0.017715 -0 000076  15 264  15 297  5 8000
  -3   1   1 0 022983 0 022965  0 000018  17 440  17 433  5 0811
  -2   0   2 0 031443 0 031403  0 000040  20 428  20 414  4 3441
  -4   1   1           0.034629                  21 449
  -3   2   1 0 034707 0.034734 -0 000028  21 474  21 482  4 1348
               0.045457                  24 621          3 6129
   2   0   2 0.051352 0.051370 -0 000018  26 195  26.200  3 3992
               0 060534                  28 486          3 1308
  -4   0   3 0 077304 0 077327 -0 000024  32.286  32 291  2 7705
  -6   2   2           0 091860                  35 286
  -5   1   3 0 091932 0 091970 -0 000038  35 300  35 308  2 5405
   2   4   2 0.114156 0 114139  0 000017  39 494  39 491  2 2799
  -2   0   4           0.121303                  40 765
  -3   0   4 0.121523 0.121434  0 000089  40 804  40 788  2 2097
  -7   0   3           0.121621                  40.821
  -5   4   2           0 121677                  40.831          -
  -8   1   1           0 121745                  40 842
   8   2   1 0 173494 0 173448  0 000046  49 231  49 224  1 8493
   4   6   0           0 173597                  49 246
  -6   0   5           0 206040                  53 990
  10   1   0           0 206212                  54 015
  -4   2   5           0 206233                  54 018
 -10   1   3 0 206271 0 206249  0 000022  54 023  54 020  1 6961
   8   1   2           0 206617                  54 072
 -10   2   3           0 218018                  55 670
  -8   3   4           0 218093                  55 679
   8   2   2 0 218413 0 218396  0 000027  55 724  55 721  1 6482
  -4   6   3           0 218539                  55 745
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NUMBER OF CALC. LINES =   30
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 F  CF  J APPL CRYST  12(11979)60
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CYCLE RESULTS


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 0 001980  0 009349  0 006053  0 000000  0 000000  0 000000
```

## Table 2 Continued

```
CYCLE RESULTS


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 0.002025  0.009464  0 006327  0.000480  0.000000  0 000000


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 NUMBER OF SINGLE INDEXED LINES =   12
  TOTAL NUMBER OF LINES =   18
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  B =  7 719109  0 007266 A    BETA = 79 841376  0 005554 DEC
  C =  9 706100  0 005611 A   GAMMA = 90 000000  0 000000 DEC
  UNIT CELL VOLUME =   1315 55 A**3
   H   K   L SST-OBS  SST-CALC    DELTA   2TH-OBS 2TH-CALC D-OBS   FREE PARAM.
   1   0   0 0.002028 0.002025  0 000003   5 162   5 158 17 1060
  -1   0   1 0 007861 0.007872 -0.000011  10 173  10 181  8 6881
   1   1   0 0 011443 0.011489 -0 000046  12.282  12.306  7 2009
   2   0   1 0.015360 0 015386 -0.000026  14.239  14 251  6 2153
   2   1   0 0.017639 0 017564  0.000075  15.264  15 232  5 8000
  -2   1   1 0.022983 0 022932  0.000051  17.440  17 420  5 0811
  -3   0   1           0 023113                  17 489
  -2   0   2 0.031443 0 031489 -0 000046  20.428  20 443  4 3441
   0   1   2 0.034707 0 034771 -0.000064  21.474  21.494  4 1348
             0.045457                     24 621          3.6129
  -2   2   1 0.051352 0 051324  0.000028  26.195  26 188  3 3992
   1   0   3 0.060534 0 060405  0.000129  28.486  28.455  3 1308
   2   1   3 0.077304 0 077383 -0.000079  32.286  32.303  2 7705
   6   1   1           0 091570                  33 228
  -4   2   2 0.091932 0 091727  0 000205  33 300  33 259  2 5405
  -6   2   1 0 114156 0 114207 -0 000051  39 494  39 503  2 2799
  -6   0   3           0 121209                  40 749
  -4   2   3 0.121523 0 121442  0 000081  40.804  40 787  2 2097
   7   1   0 0.173494 0 173492  0 000001  49 231  49 231  1 8493
  -5   4   1           0 205979                  53 982
  -5   1   3 0.206271 0 206269  0 000001  54 023  54 023  1 6961
  -6   3   3           0 206386                  54 039
 -10   0   2           0 218219                  55 698
  -9   2   2 0.218413 0.218559 -0 000146  55.724  55 745  1.6482
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 F  CF.  J. APPL. CRYST  12(1979)60
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CYCLE RESULTS


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 0.001996  0 009306  0.006045  0 000185  0 000000  0 000000
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