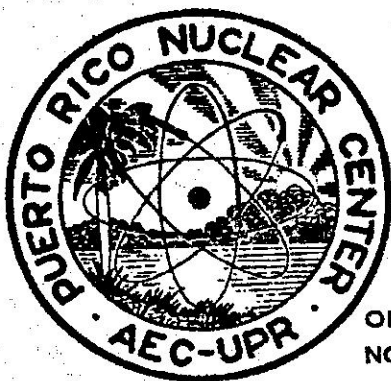


PRNC 30

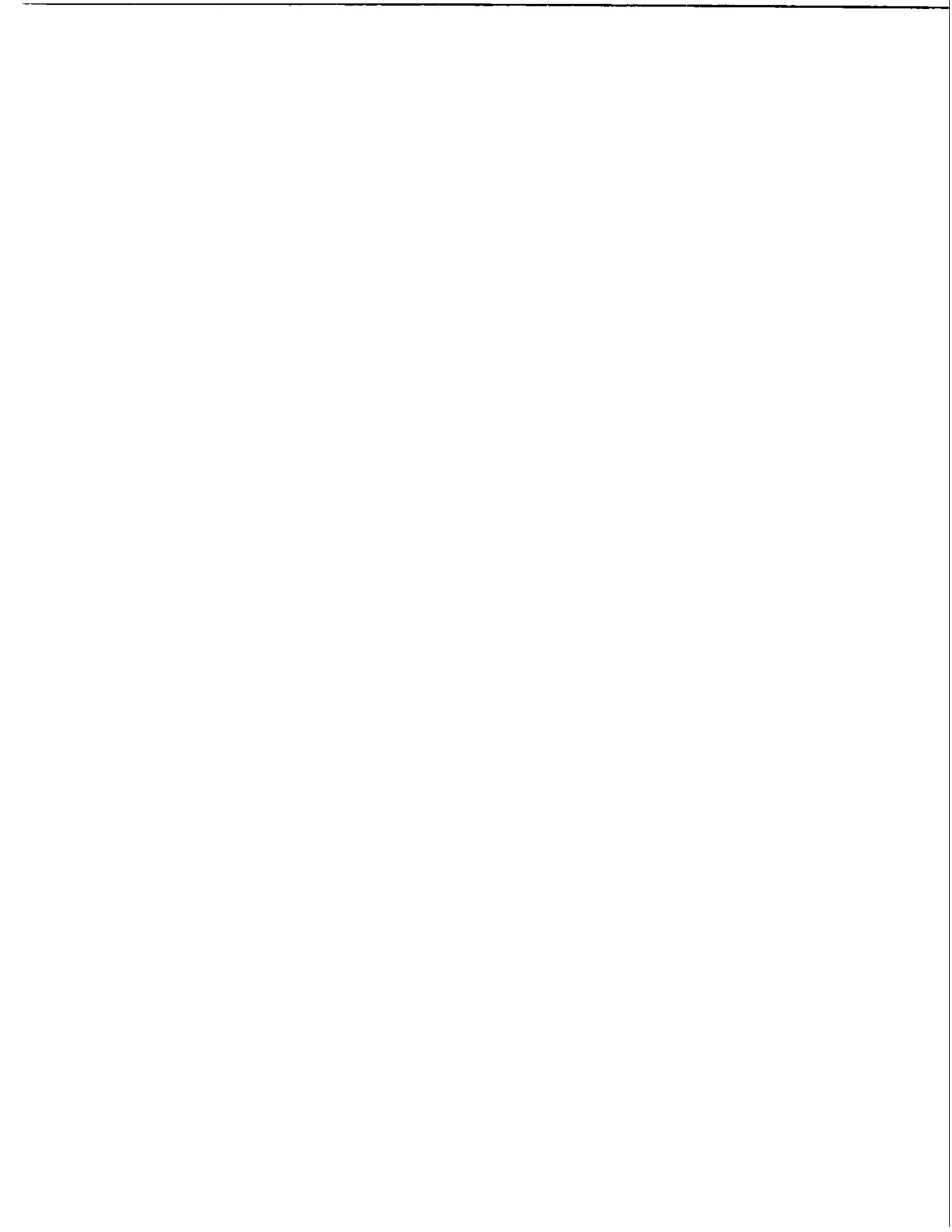
PUERTO RICO NUCLEAR CENTER

PROGRESS SUMMARY REPORT NO. 2

NEUTRON DIFFRACTION PROGRAM



OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT
NO. AT (40-1)-1833 FOR U. S. ATOMIC ENERGY COMMISSION



NEUTRON DIFFRACTION

PROGRESS SUMMARY REPORT No. 2

Ismael Almodóvar — Principal Investigator

with Guest Scientists

B. Chalmers Frazer, H. J. Bielen,
K. Okada, and M. I. Kay

March 1964

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100

TABLE OF CONTENTS

List of Tables and Figures	ii
INTRODUCTION	1
SUMMARY OF RESULTS	1
Calcium Tungstate	1
Copper Sulfate	2
Iron Orthosilicate	3
Barium Nickelate	5
OTHER CURRENT RESEARCH PROBLEMS	6
Copper Formate	6
Crystal Structure Analysis at low temperatures	6
EQUIPMENT	7
References	8
Tables	9
Figures	11

LIST OF TABLES AND FIGURES

TABLES

I	Positional and temperature coordinates for CaWO_4 with standard deviations	9
II	Short distances and angles in CaWO_4	10

FIGURES

1	b axis projection of CaWO_4	11
2	c axis projection of CuSO_4	12
3	Neutron diffraction patterns for CuSO_4 . The only obvious change is a new peak at 8.9°	13
4	Difference pattern for CuSO_4 . Peak distortions are caused by imperfect matching of He and N_2 data	14
5	c axis projection of olivine (Mg_2SiO_4)	15
6	Difference powder pattern for Fe_2SiO_4	16
7	Modern (U.S.I.) neutron spectrometer designed and constructed by BNL for PRNC . .	17
8	Second neutron spectrometer in operation at PRNC. The diffractometer assembly was donated to the UPR by the Westinghouse Electric Corporation	18
9	X-ray diffraction equipment and accesories now in operation for research at PRNC . .	19
10	Equipment and area designated for microscopic studies of crystals	20

INTRODUCTION

The neutron diffraction group at the Puerto Rico Nuclear Center has worked on essentially two types of problems. The first is concerned with the chemical binding of atoms in crystals and molecules, and the second with the nature of ferromagnetism and antiferromagnetism.

Both problems are related to the spatial arrangement of atoms in molecules. If either x-rays or neutrons are scattered from crystals, patterns can sometimes be analyzed which show the arrangement of atoms in the crystal. The amplitude of x-rays diffracted from atoms is proportional to the atomic number of the scattering atoms. Thus, if there are light and heavy atoms in the same compound, the contribution of the light atom is very weak and its position can be determined only with great difficulty. If neutrons are used, however, they are scattered by the nuclei of the atoms, and as a result, diffraction of neutrons by light elements compares favorably with that from heavier elements.

There also is a neutron-electron spin interaction in compounds which possess atoms with unpaired electrons. Since the magnetic properties of substances are related to the way the electron spins are arranged within the crystal, neutron diffraction provides an accurate method for determining such spin arrangements (magnetic structures).

SUMMARY OF RESULTS

Calcium Tungstate (CaWO_4)*

The first neutron diffraction problem investigated at the Nuclear Center was a single crystal structure analysis of CaWO_4 . Preliminary results of this study were included in Progress Summary Report No. 1, March 1963. Final results are summarized here.

While the CaWO_4 structure is usually considered to be typical of that adopted by an important series of ABO_4 compounds, the oxygen coordinates have been known¹ with an accuracy of only about 0.1 \AA . The reason for this is that the B atom is always one of rather high atomic number, relative to oxygen, and hence the oxygen contributions to x-ray structure factors are comparatively small. In the neutron case, the oxygen scattering length does not differ greatly from that of the other atoms. Accordingly, neutron structure analysis was undertaken. In the course of our work, it was learnt that Zalkin and Templeton² have been engaged in an independent study of the structure using very accurate x-ray data and modern refinement techniques. Their results are in excellent agreement with those reported here.

* "A Neutron Diffraction Refinement of CaWO_4 ", M.I. Kay, B.C. Frazer, and I. Almodóvar, J. Chem. Phys. 40, 504 (1964)

CaWO_4 crystallizes in the tetragonal space group $I4_1/a$ and has cell dimension values² of $a = 5.243 \pm 0.002 \text{ \AA}$ and $c = 11.376 \pm 0.003 \text{ \AA}$. The Ca and W atoms are in the four-fold symmetry fixed positions 4(b) and 4(a), respectively, and oxygen is in the 16(f) general position. A diagram of the structure is given in fig. 1.

Least squares refinement calculations, carried out on (h o l) and (h h l) data collected from samples cut from a large synthetic crystal, led to a final R value of 0.041. The final parameters (with the cell origin chosen at the tungsten site) are listed in Table I and compared with the values obtained from x-ray studies. Table II shows the important interatomic distances and bond angles. The WO_4^{2-} group is nearly regular but the small distortion is outside of experimental error.

Anhydrous Copper Sulfate (CuSO_4)

The anhydrous sulfates of the divalent transition elements form an interesting group of magnetic compounds. Magnetic structures have already been determined for FeSO_4 , NiSO_4 , $\alpha\text{-CoSO}_4$ and $\beta\text{-CoSO}_4$ ⁽³⁻⁵⁾. Discussed here are the results of a neutron diffraction study of CuSO_4 , undertaken in continuation of an investigation by two of the present authors (I.A. and B.C.F.) at Brookhaven with Dr. P. J. Brown.

Because of the low Cu^{+2} moment, and because of troublesome peak overlaps in a neutron powder pattern, the magnetic structure of CuSO_4 should be investigated using single crystals. Single crystals of suitable size are not easily grown, although the polycrystalline anhydrous sulfate is easily obtained from the pentahydrate salt. Accordingly, the problem has been approached by the analysis of powder data. If these data are considered along with the magnetic measurements of Kreines⁶, a complete determination of the magnetic structure is possible.

CuSO_4 has the orthorhombic ZnSO_4 type crystal structure⁷ with space group Pbnm. See fig. 2. The four crystallographically equivalent Cu^{+2} ions are located on the 0 0 0, 0 0 $\frac{1}{2}$, $\frac{1}{2}$ $\frac{1}{2}$ 0, and $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ sites. For the case where the magnetic cell is identical with the chemical cell, the possible collinear spin configurations for antiferromagnetic ordering are + - - +, + + - -, and + - + -. In the Wollan - Koehler - Bertcut notation these arrangements are labelled G, C, and A, respectively.⁶ Each of them leads to a distinct set of magnetic reflections.

In comparing diffraction patterns taken at 4.2° K and 77° K, only one clearly resolved new peak was found in the low temperature pattern. See figs. 3 and 4. This indexed as the (0 0 1) reflection, which is characteristic of type A ordering. A change in intensity was also found for the combination (0 2 1), (1 1 1) peak, again characteristic of type A. The other

intensity changes shown in fig. 4 are not reliable, due to overlap with residual aluminum lines from the cryostat.

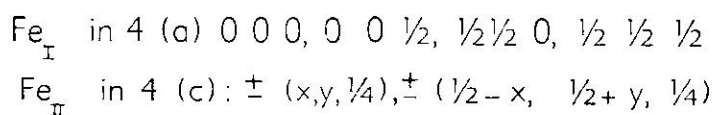
While this small amount of information is sufficient to identify the ordering scheme, it does not yield reliable information on the magnitude and orientation of the Cu^{+2} moment. Here it is useful to consider the magnetic measurements of Kreines.⁶ Kreines used small single crystals which were oriented by morphology and x-rays. While the setting was not specified in her paper, it can be identified from the cell dimensions as Pcmn. Her fig. 4 is drawn incorrectly, since the Cu sites are improperly assigned for this setting, but this does not affect the conclusions which may be drawn from the measurements. According to Kreines $X_a = X_b = X_c$ and $X_{II} = X_a$. This of course suggests a collinear spin structure with the spin axis parallel to \underline{a} . With this assumption the Cu^{+2} moment calculated from the neutron diffraction data is $1\mu_B$, as expected for this ion. The spin ordering mode is A_x , i.e., $+ - + -$ on the $000, 00\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}\frac{1}{2}\frac{1}{2}$ sites, with the moment orientations along the \underline{g} axis of the Pbnm cell.

Iron Orthosilicate (Fe_2SiO_4)

Until quite recently, very little has been known about the magnetic properties of the transition metal olivine type compounds. See fig. 5. Early this year, Kondo and Miyahara⁹ published magnetic susceptibility data on the orthosilicates of divalent Mn, Fe, Co, and Ni between 77°K and 300°K . The curves suggest that magnetic transitions will be found in all of these compounds at lower temperatures. A transition in polycrystalline Fe_2SiO_4 has been found by the present authors by neutron diffraction measurements, and by Takei and Cox¹⁰ by magnetic susceptibility measurements. Subsequent work on single crystals has shown that there are in fact two transitions, one at about 35°K and one at about 55°K . Fayalite mineral samples kindly supplied by Dr. Clifford Frondel, of Harvard University, were used for all of these measurements. The neutron analysis of the magnetic ordering is now in progress with the collection of accurate single crystal data. Some preliminary results derived from powder data are already included at this time.

In the orthorhombic olivine structure¹¹, space group Pbnm (D_{2h}^{16}), there are four formula units per unit cell. The cell of Fe_2SiO_4 has dimension values¹² of,
 $a = 4.82\text{\AA}$ $b = 10.48\text{\AA}$ $c = 6.09\text{\AA}$.

There are two four-fold set of Fe^{+2} ions:



In the ideal olivine structure $x = 0$ and $y = 1/4$, but the values observed in olivine itself are 0.99 and 0.281, respectively. Each of the Fe^{+2} ions is octahedral coordination with oxygen and one may expect magnetic interactions of the same nature as the B-B interaction in spinel structures. In addition there are superexchange paths available via the covalent SiO_4^{-4} groups.

If the magnetic and chemical cells are identical, as proves to be the case in Fe_2SiO_4 , there are eight spin vectors in the cell, and hence a large number of antiferromagnetic configurations. These can be reduced considerably by symmetry considerations, but even then there are 19 possible collinear spin ordering modes, and of course there are many more combination modes that become possible for canted spin structures. The problem of sorting through all these possibilities to satisfy observed neutron intensities is complicated by the free x and y parameters of Fe_{II} . For one thing, these parameters must be accurately determined as part of the analysis, but more important difficulty is that the magnetic extinction rules which would apply for Fe_{II} spins in the ideal olivine structure are no longer valid. At this preliminary stage, however, the ideal structure is being assumed. This should be reasonably safe for determining the principal features of the magnetic structure, since the intensity contributions arising from non-ideal shifts should be small.

Let the spins on the Fe_I 4(a) sites be numbered 1 through 4 in the same order as given above. Assuming ideal positions for Fe_{II} , let the spins on the 4(c) sites be numbered 5 through 8 in the following order:

$$0 \frac{1}{4} \frac{1}{4}, 0 \frac{3}{4} \frac{3}{4}, \frac{1}{2} \frac{1}{4} \frac{3}{4}, \frac{1}{2} \frac{3}{4} \frac{1}{4}$$

If one calculates magnetic extinction conditions for the various possible collinear antiferromagnetic spin configurations it is found that none of these can account for the observed data. Hence there must be at least two spin directions in the structure. The proper spin vectors may be constructed from their components by using combinations of the collinear ordering modes.

The most intense reflection in the pattern is the (100). See fig. 6. This peak can arise from two different modes but only one of them can yield a high intensity:

$$\begin{array}{ccccccccc} 1 & 2 & 3 & 4 & & 5 & 6 & 7 & 8 \\ + & + & - & - & & + & + & - & - \end{array}$$

In this ordering scheme the spin components form alternating parallel sheets on the (200) planes. This mode, which is the dominant one in the structure, is associated with the crystal-

lographic \underline{b} axis. Analysis of the data indicates a + - + - + - + - arrangement of spin components parallel to \underline{a} .

The components in the \underline{c} direction are small, if indeed they exist at all. The Fe^{+2} moment was found to be approximately $4 \mu_{\text{B}}$ for both Fe_{I} and Fe_{II} . In both cases the spin vectors are approximately parallel to the XY plane and are tilted from the \underline{b} axis by about 30° , with the tilt alternating in sign as prescribed by the \underline{a} axis ordering mode.

It should be pointed out that these are preliminary results only. While they yield a very good agreement with the observed data, the structure is too complex for a completely reliable solution by powder methods.

Data collection from single crystals is progressing rapidly. Measurements on an \underline{a} axis oriented crystal (h o k l data) have been completed at 77° K and 4.2° K. Intensity measurements of several reflections as a function of crystal temperature have also been completed. Collection of (h o l) data is now in progress. Single crystal x-ray measurements are also in progress in order to complement and aid in the interpretation of neutron patterns.

Barium Nickelate (BaNiO_2)

The results obtained on BaNiO_2 have been largely negative; however, it may be worthwhile to make a few remarks on this rather unusual compound. There were several reasons why it was chosen for study. In the first place, Lander's trial-and-error determination of the oxygen positions from visually estimated x-ray data did not seem overly convincing since the atomic number of Ba is quite high and even that of Ni is relatively high.¹³ Some preliminary packing calculations revealed other possible structures which were not mentioned by Lander, and one of these in particular seemed as likely as the one he reported. Also, the square planar oxygen coordination by Ni^{+2} was most unusual in view of Lander's observation of a nearly "normal" paramagnetic moment corresponding to 1.8 unpaired electrons. The explanation suggested by Lander for the observed moment is that there are additional bonds between neighboring nickel ions, as evidenced by the very short Ni-Ni distance of 2.36 \AA . Finally, the orthorhombic Cmcm structure is similar in many respects to the anhydrous sulfate structures, and it was of interest to investigate possible magnetic ordering at low temperatures.

Essentially, the structure investigation led to a confirmation of Lander's structure. It may be that some significant parameter changes can be found (this seems to be the case with the oxygen y parameter), but there is no doubt that Lander's general configuration is correct.

The magnetic studies have not been so conclusive. In a paper separate from his

report on the BaNiO_2 structure, Lander quotes unpublished susceptibility measurements of F. Morin.¹⁴ The temperature range is not given, but it is stated that the Curie-Weiss law is obeyed with $\Delta = 180^\circ$, and that the calculated number of unpaired electrons per nickel ion is 1.83. From this one might expect to find a Néel point well above the temperature of liquid helium. However, there are no obvious changes in the neutron powder patterns in going down to this temperature. Through the courtesy of Drs. W.J. Takei and D.E. Cox,¹⁰ of the Westinghouse Research Laboratories, the authors were able to obtain magnetic susceptibility data down to 4.2° K. These data disagreed somewhat with Morin's in giving $\Delta = 72^\circ$ and approximately one unpaired electron per nickel ion. The Curie-Weiss law was obeyed very well down to liquid N_2 , but the $1/\chi$ curve began to fall off from a straight line at lower temperatures, suggestive of an approaching transition. Unfortunately, Takei and Cox were unable to take data between 4.2°K and approximately 50°K , so there was no definite evidence of a transition. Also, the magnetic sample was found to be somewhat impure, so not too much faith can be placed in the differences from Morin's measurements. If the Ni moment is as low as $1\mu_B$, as indicated by the data of Takei and Cox, it is possible that the neutron diffraction statistics were not sufficiently good to observe ordering. This would be particularly true if the ordering is type A, since peak overlaps happen to be very bad for this case.

This is as much as can be said on this problem for the moment. Further magnetic measurements must be made at low temperatures on a pure sample before continuing with neutron diffraction work.

OTHER CURRENT RESEARCH PROBLEMS

Copper Formate Tetrahydrate $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$

Large single crystals of this compound have been grown from saturated solutions of copper carbonate in 30% formic acid. The crystals decompose rapidly on contact with air and therefore have been cut and mounted inside thin-wall glass containers. Collection of (o k l and o o l) data have been completed as part of the crystal structure analysis now in progress. The structure has been examined previously by x-rays¹⁵ but this study did not yield hydrogen positions.

Copper formate also shows very interesting magnetic properties at low temperatures,^{16,17} becoming anti-ferromagnetic below 17°K . An investigation of the magnetic structure of this compound will follow its structure analysis.

Crystal Structure Analysis at Low Temperatures

Refinement of the techniques of single crystal growth at low temperatures is in progress. Although small crystals for x-ray analysis have been grown we have found a series of difficulties, mainly ice formation on the larger capillaries used to enclose the sample. The use of a dry-box type enclosure fitted with a mylar window through which the neutron beam passes seems promising. No work has previously been reported on structure analysis by neutron diffraction at low temperatures. Among others, we are interested in the structure refinement of methanol, dimethyl acetylene, formamide, and diamonia hydrate.

EQUIPMENT

A modern spectrometer designed and constructed at the Brookhaven National Laboratory has been installed and is now in operation. See fig. 7. This excellent versatile machine permits continuous variation of the neutron wavelength. It has been designed for work with heavy magnets and cryostats, and features a rotating collimator assembly which allows the operator to change collimators in a few minutes without removing the monochromator housing assembly. Furthermore, a programming unit can easily be attached to the spectrometer without modification.

The somewhat primitive diffractometer donated to PRNC by BNL has been sent to the Georgia Institute of Technology. A more advanced and precise instrument donated to the University by the Westinghouse Electric Corporation is now in operation. A photograph of this machine is shown in fig. 8.

X-ray diffraction equipment has been acquired during the period covered by this report to complement the diffraction apparatus described above. The powder diffractometer and associated equipment are shown in fig. 9. Figure 10 shows the microscope facilities used to mount crystals and to study some of their properties.

REFERENCES

1. L.G. Sillén and A. Nylander, *Arkiv Kemi Min. Geol.* 17A, No. 4 (1943).
2. A. Zalkin and D.H. Templeton (private communication).
3. B.C. Frazer and P. J. Brown, *Phys. Rev.* 125, 1283 (1962).
4. P.J. Brown and B.C. Frazer, *Phys. Rev.* 129, 1145 (1963).
5. E.F. Bertaut, J. Coing-Boyot, and A. De la Palme, *Phys. Letters* 3, 178 (1963).
6. N.M. Kreines, *Zhur. Eksp. i Teoret. Fiz.* 35, 1391 (1958).
Eng. transl: *Sov. Phys. JETP* 8, 971 (1959).
7. P.A. Kokkoros and P.J. Rentzperis, *Acta Cryst.* 11, 361 (1953).
8. E.F. Bertaut, *J. Appl. Phys., Suppl.*, 33, 1138 (1962).
9. H. Kondo and S. Miyahara, *J. Phys. Soc. Japan* 18, 305 (1963).
10. W.J. Takei and D.E. Cox (unpublished data).
11. N.V. Belov, E.N. Belova, N.H. Andrianova, and P. F. Smirnova, *Dokl. Akad. Nauk SSSR* 81, 399 (1951).
12. H. Winchell, *Amer. Cryst. Assoc. Meeting Abstr.* p 14 (Apr. 10-12, 1950).
13. J.J. Lander, *Acta Cryst.* 4, 148 (1951).
14. J.J. Lander, *J. Am. Chem. Soc.* 73, 2450 (1951).
15. R. Kiriyaama, H. Ibamoto and K. Matsuo *Acta. Cryst.* 7, 482 (1954).
16. J. Itoh and Y. Kamiya, *J. Phys. Soc. Japan* 17, Suppl. B-1, 512 (1962).
17. T. Haseda and R. Miedema, *J. Phys. Soc. Japan* 17, Suppl. B-1, 518 (1962).

Table I - Positional and temperature coordinates for CaWO_4
with standard deviations.

Oxygen	S & N ¹		Z & T ²		K, F, A,	
x	0.25	0.02	0.2415	0.0014	0.2413	0.0005
y	0.15	0.02	0.1504	0.0013	0.1511	0.0006
z	0.075	0.015	0.0861	0.0006	0.0861	0.0001
β_{11}			0.0115	0.0016	0.0073	0.0014
β_{22}			0.0100	0.0016	0.0057	0.0012
β_{33}			0.0016	0.0003	0.0016	0.0003
β_{12}			-0.0016	0.0013	-0.0014	0.0007
β_{13}			-0.0008	0.0006	-0.0005	0.0002
β_{23}			0.0004	0.0006	0.0004	0.0002
Calcium						
β_{11}			0.0071	0.0004	0.0051	0.0022
β_{33}			0.0011	0.0001	0.0019	0.0006
Tungsten						
β_{11}			0.0036	0.0001	0.0038	0.0022
β_{33}			0.00095	0.00003	0.00038	0.0005

Table II - Short distances and angles in CaWO_4^a

WO_4 Group	Distance or angle	Standard deviation
$\text{W} - \text{O}^b$	1.788 Å	0.003
$\angle \text{O}_1 - \text{W} - \text{O}_2$	113 27'	14'
$\angle \text{O}_1 - \text{W} - \text{O}_2$	107 56'	09'
$\text{O}_1 - \text{O}_2$	2.985 Å	0.004
$\text{O}_2 - \text{O}_{3,3'}$	2.690	0.003
Other Close approaches		
$\text{Ca}_1 - \text{O}_1$	2.479	0.005
$\text{Ca}_2 - \text{O}_1$	2.433	0.002
$\text{O}_1 - \text{O}_{4,4'}$	2.767	0.002
$\text{O}_1 - \text{O}_5$	2.874	0.004
$\text{O}_1 - \text{O}_{6,6'}$	2.938	0.004
$\text{O}_1 - \text{O}_7$	3.036	0.004
$\text{O}_1 - \text{O}_8$	3.142	0.004

a- For numbering scheme, see fig. 1

b- 0.003 Å added for torsional oscillation.

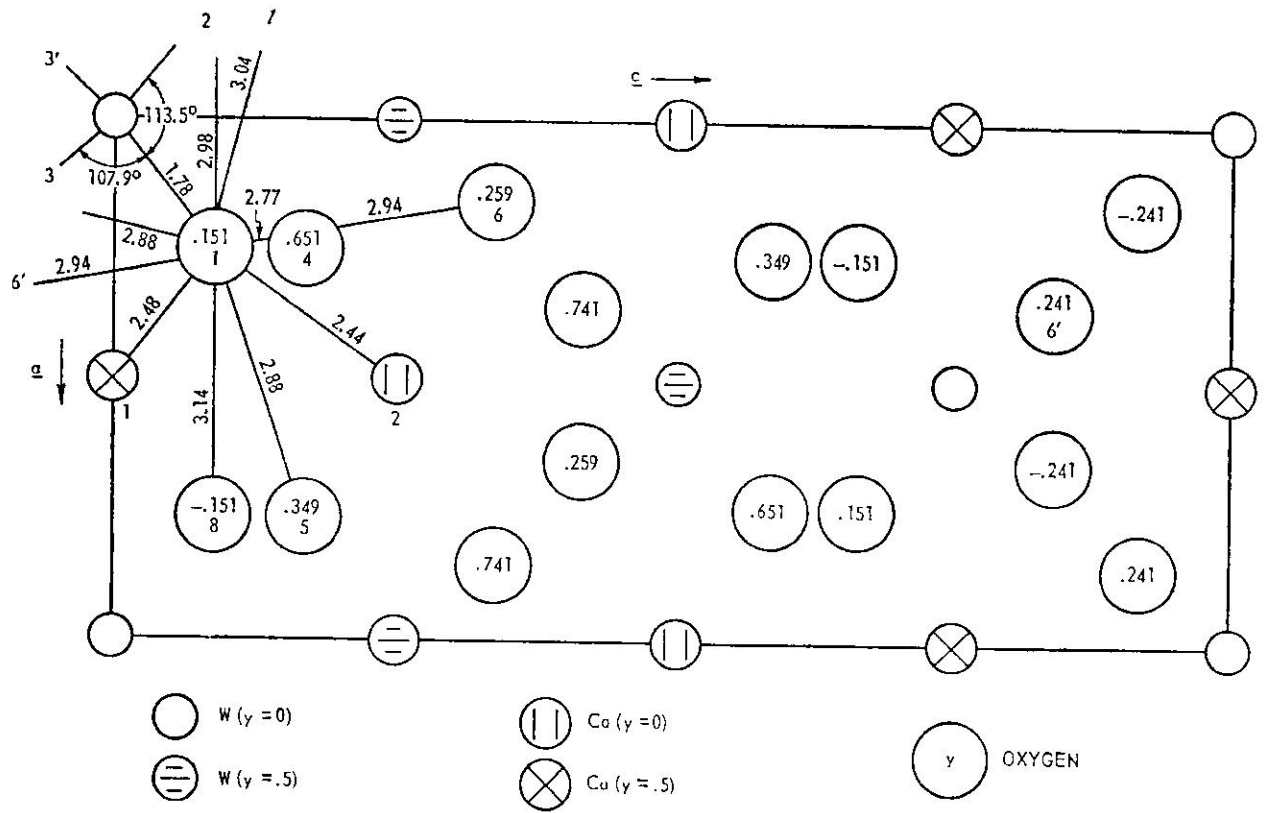


Fig. 1 b axis projection of CaWO_4

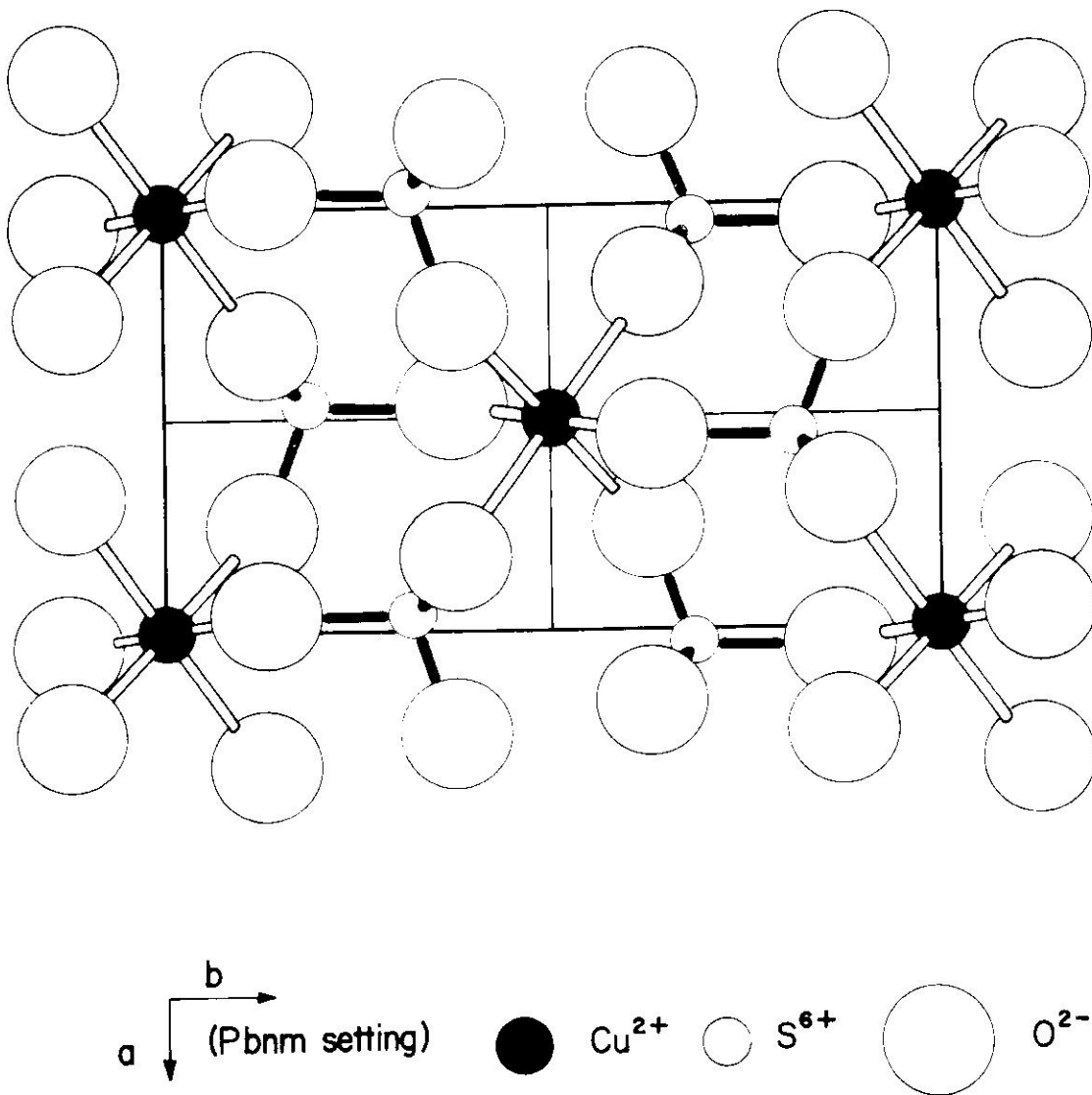


Fig. 2 c axis projection of CuSO_4

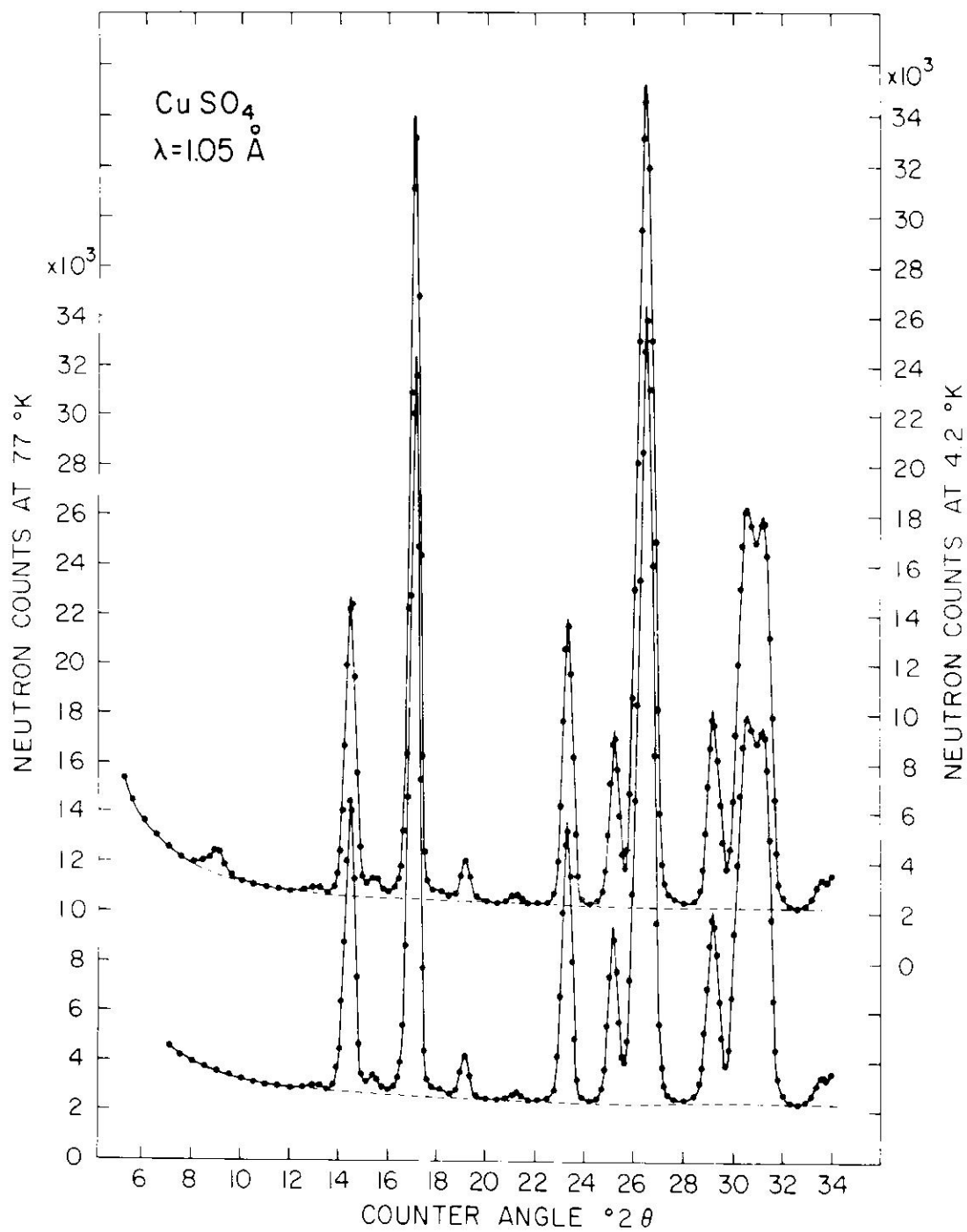


Fig. 3 Neutron diffraction patterns for CuSO_4 . The only obvious change is a new peak at 8.9° .

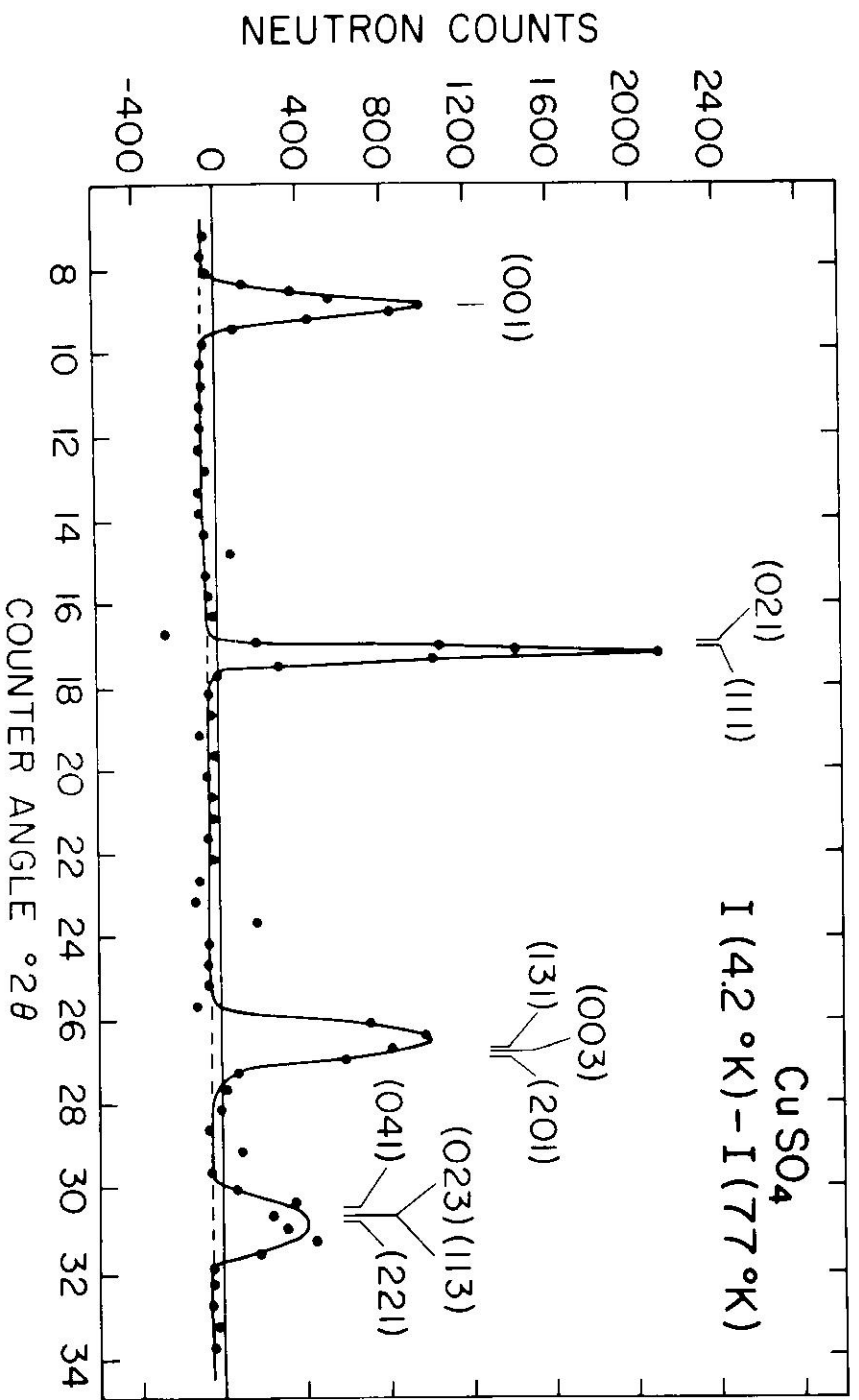


Fig. 4 Difference pattern for CuSO_4 . Peak distortions are caused by imperfect matching of He and N_2 data.

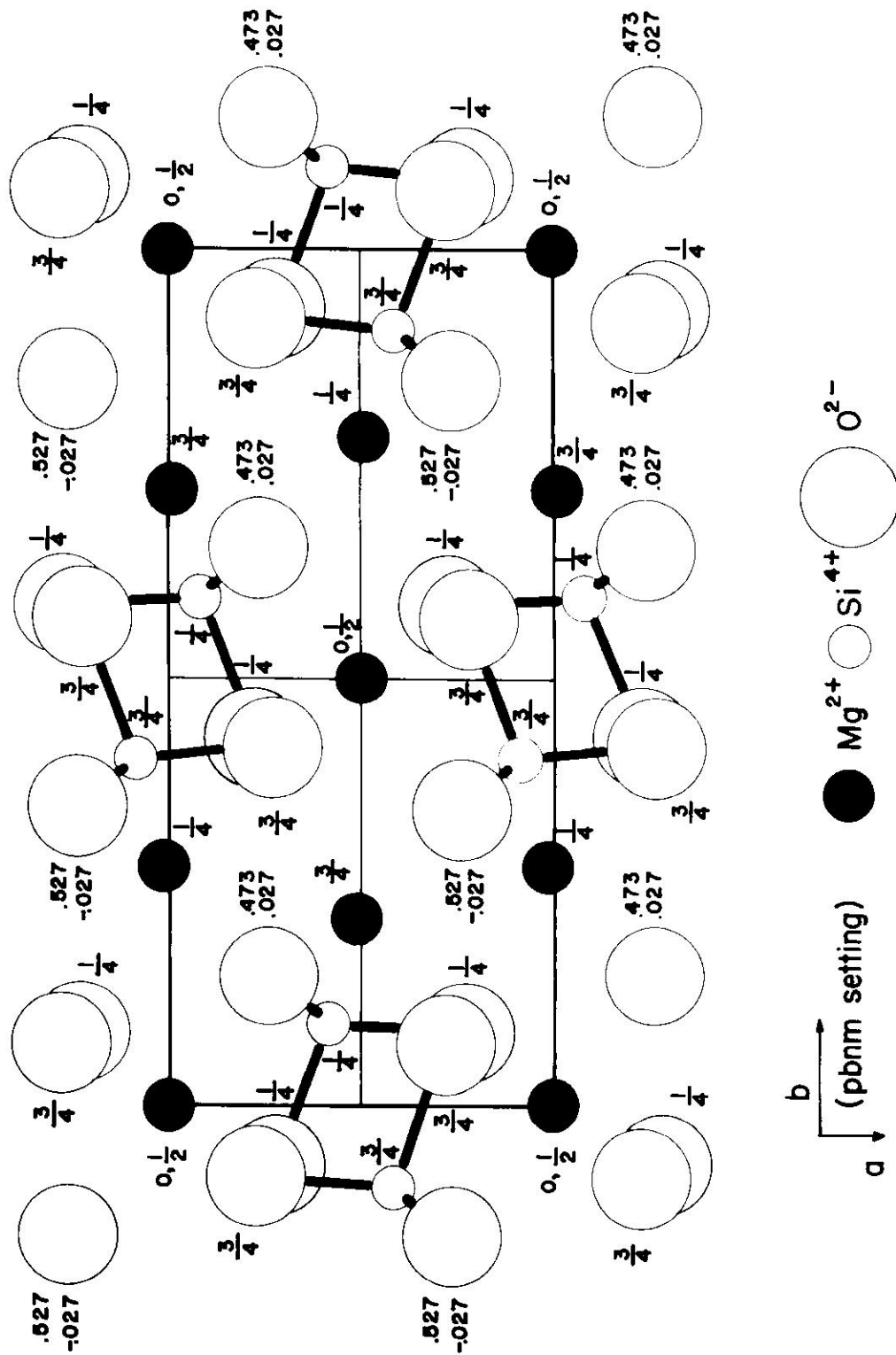


Fig. 5 c axis projection of olivine (Mg_2SiO_4).

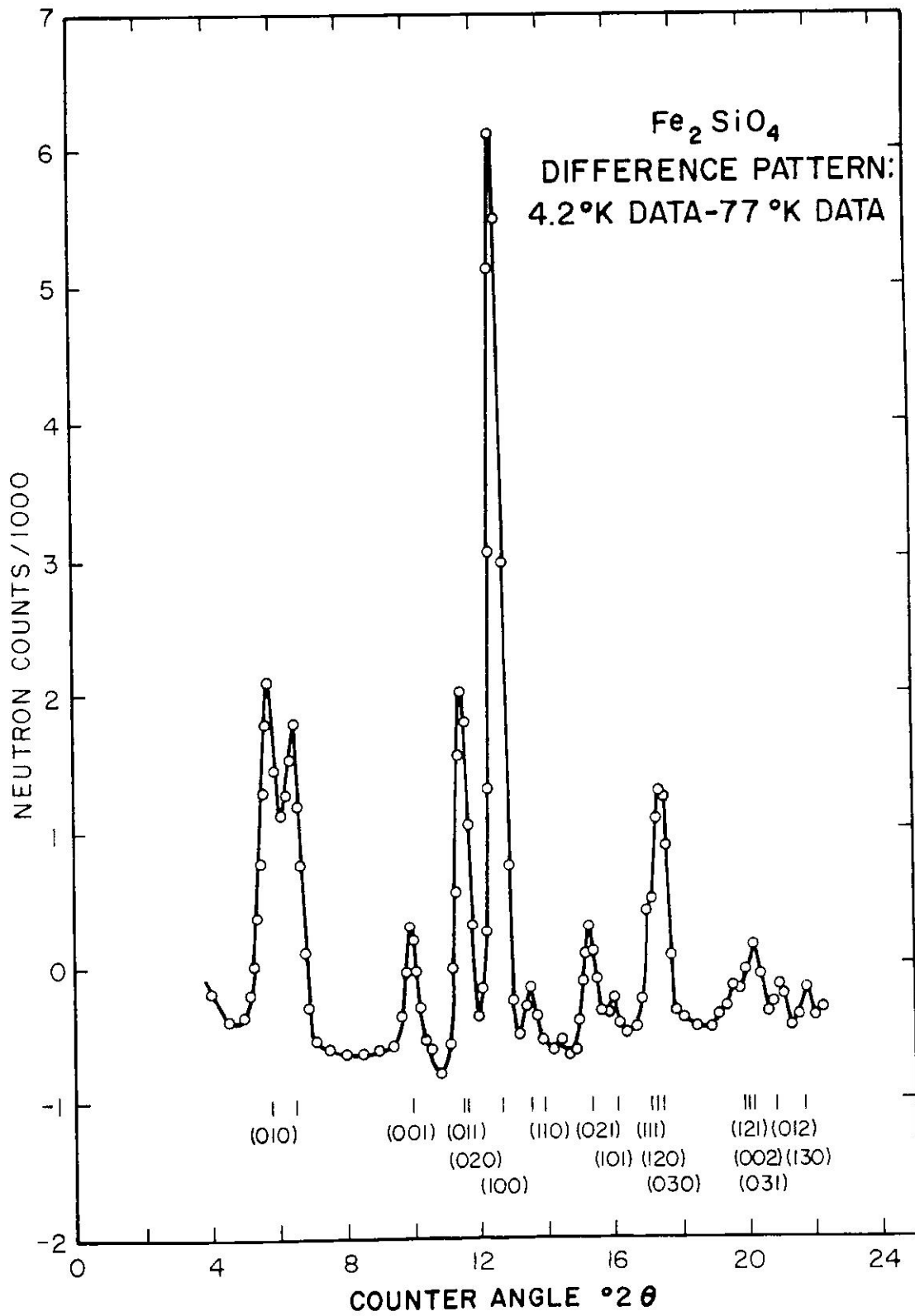


Fig. 6 Difference powder pattern for Fe_2SiO_4

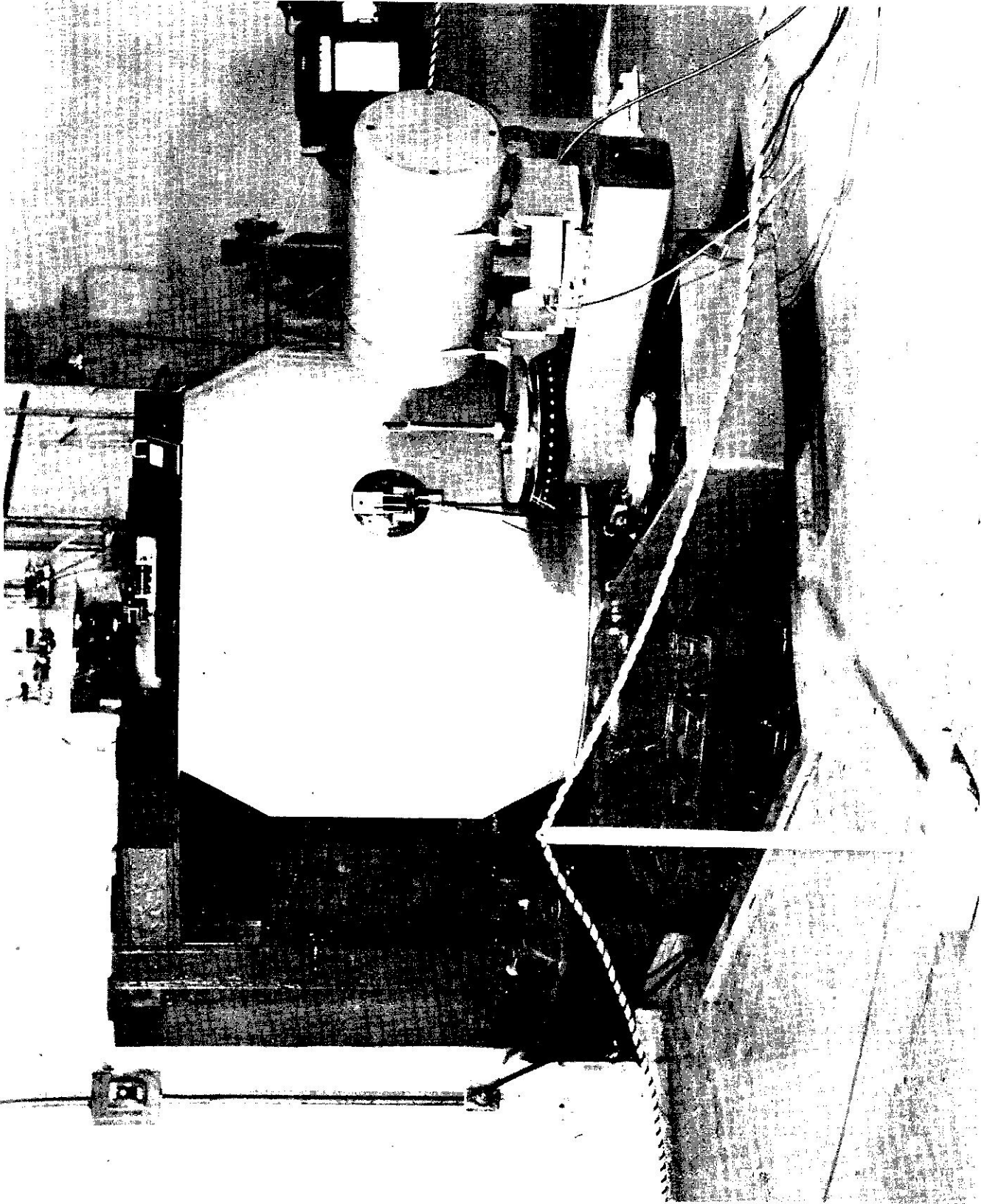


Fig. 7 Modern (U.S.I.) neutron spectrometer designed and constructed by BNL for PRNC.

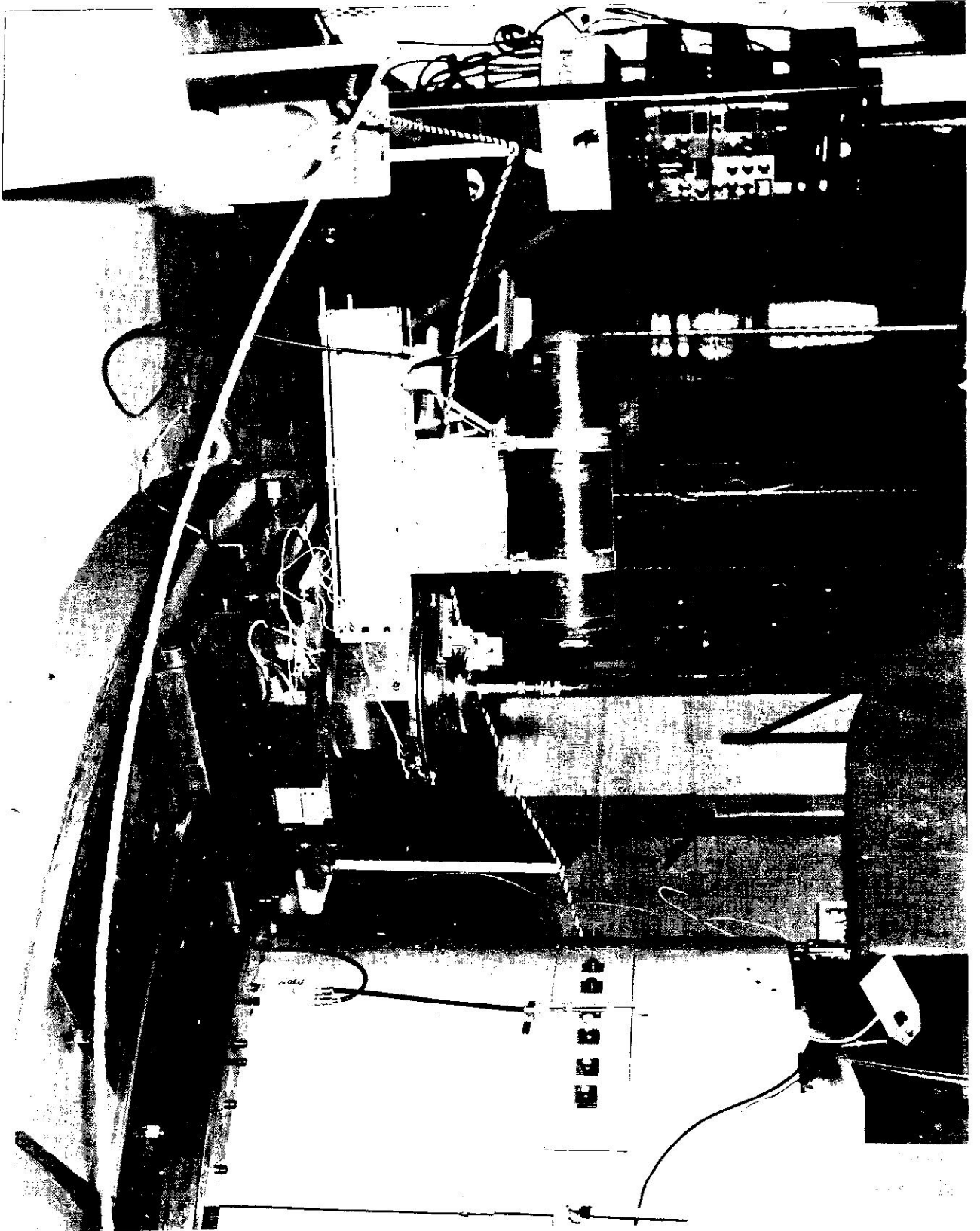


Fig. 8 Second neutron spectrometer in operation at PRNC. The diffractometer assembly was donated to the UPR by the Westinghouse Electric Corporation.

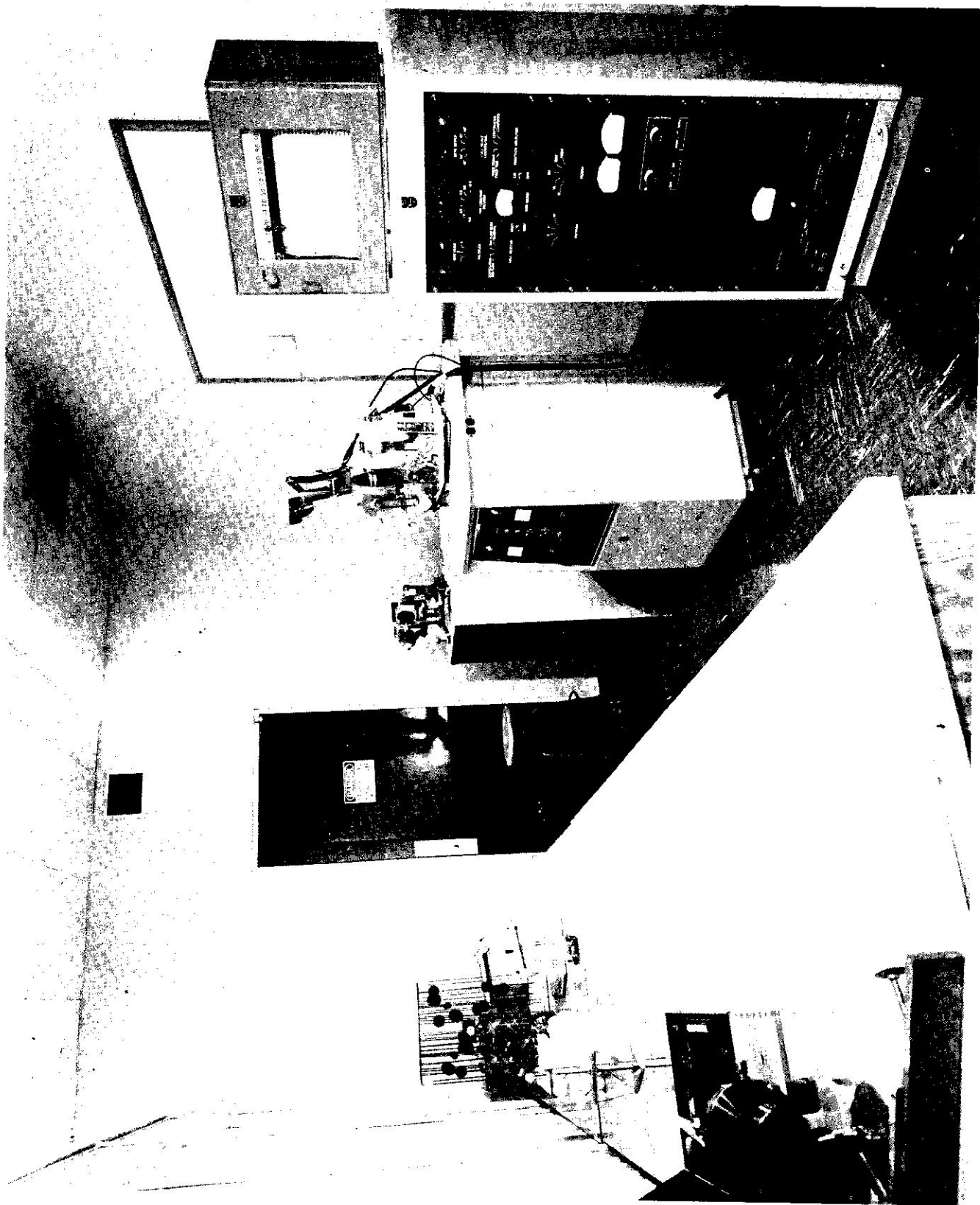


Fig. 9 X-ray diffraction equipment and accessories now in operation for research at PRNC.

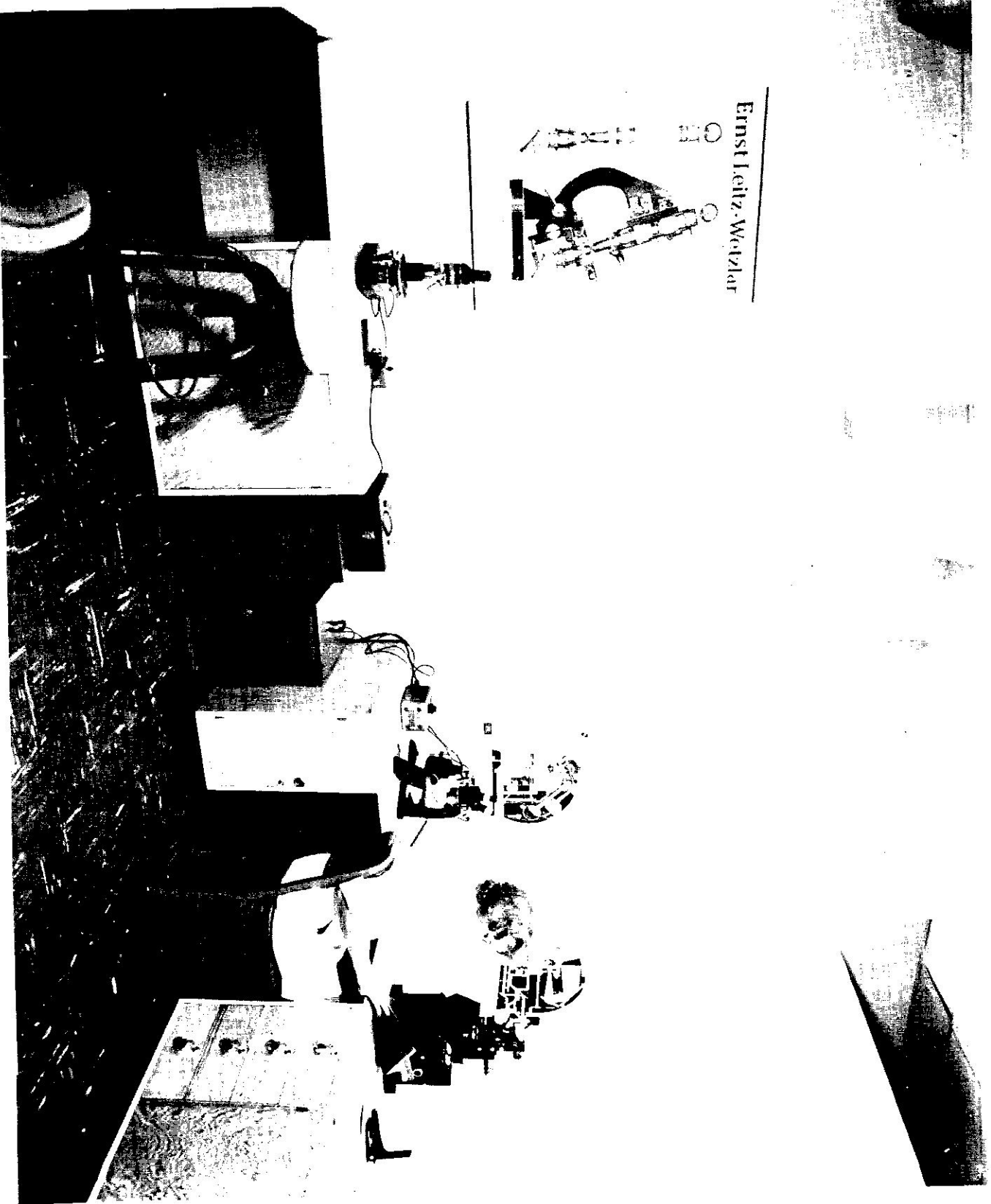


Fig. 10 Equipment and area designated for microscopic studies of crystals.