PRNC 16

PUERTO RICO NUCLEAR CENTER

NEUTRON DIFFRACTION PROGRAM

Progress Summary Report No. 1

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

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March 1963

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Puerto Rico Nuclear Center
operated by
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One of the major uses of a research reactor in basic investigation in the physical sciences is for neutron diffraction studies. The establishment of a program in this field during the past year is expected to be of key importance in the future development of research in the physical sciences at the Nuclear Center. A brief summary of program accomplishments in FY-1963 is presented in this report.

1. Spectrometer Installation

Since this was the first year of the project, a considerable fraction of FY-1963 was taken up with the construction, installation, and testing of equipment. One of the two double-crystal neutron spectrometers to be used in the program went into research operation in January 1963. A view of this machine is shown in Figure 1. A liquid helium research cryostat is mounted on the sample table. Figure 2 shows a test pattern of powdered iron. This was the first neutron diffraction data taken in Puerto Rico.

Installation of the other spectrometer is expected very soon. This will be a high quality, versatile instrument of the same basic design being used by Brookhaven in its spectrometer construction program for the new High Flux Beam Reactor. The construction is being done at Brookhaven in parallel with that program.

The spectrometer which is now in use at the Nuclear Center was also acquired under a cooperative arrangement with Brookhaven. The in-pile collimation, shutter, monochromator plug, and basic out-pile shielding were constructed there on a cost reimbursement basis. The diffractometer portion was already available and was transferred to the Nuclear Center without charge. This latter portion of the spectrometer is an old, relatively simple machine, which had become obsolescent at

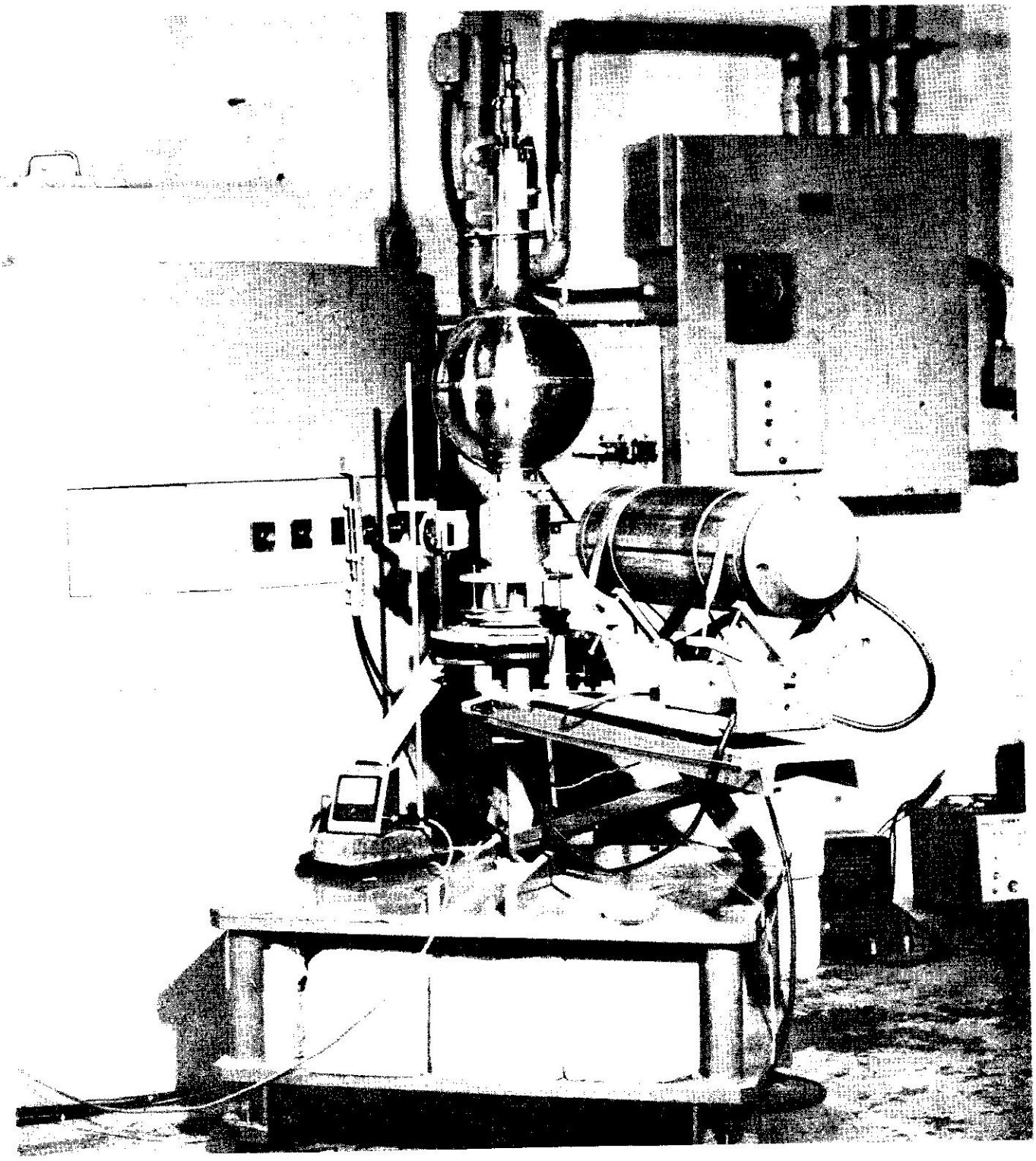

Figure 1. Neutron spectrometer now in research operation at the Puerto Rico Nuclear Center. A liquid helium cryostat is mounted in the sample position.

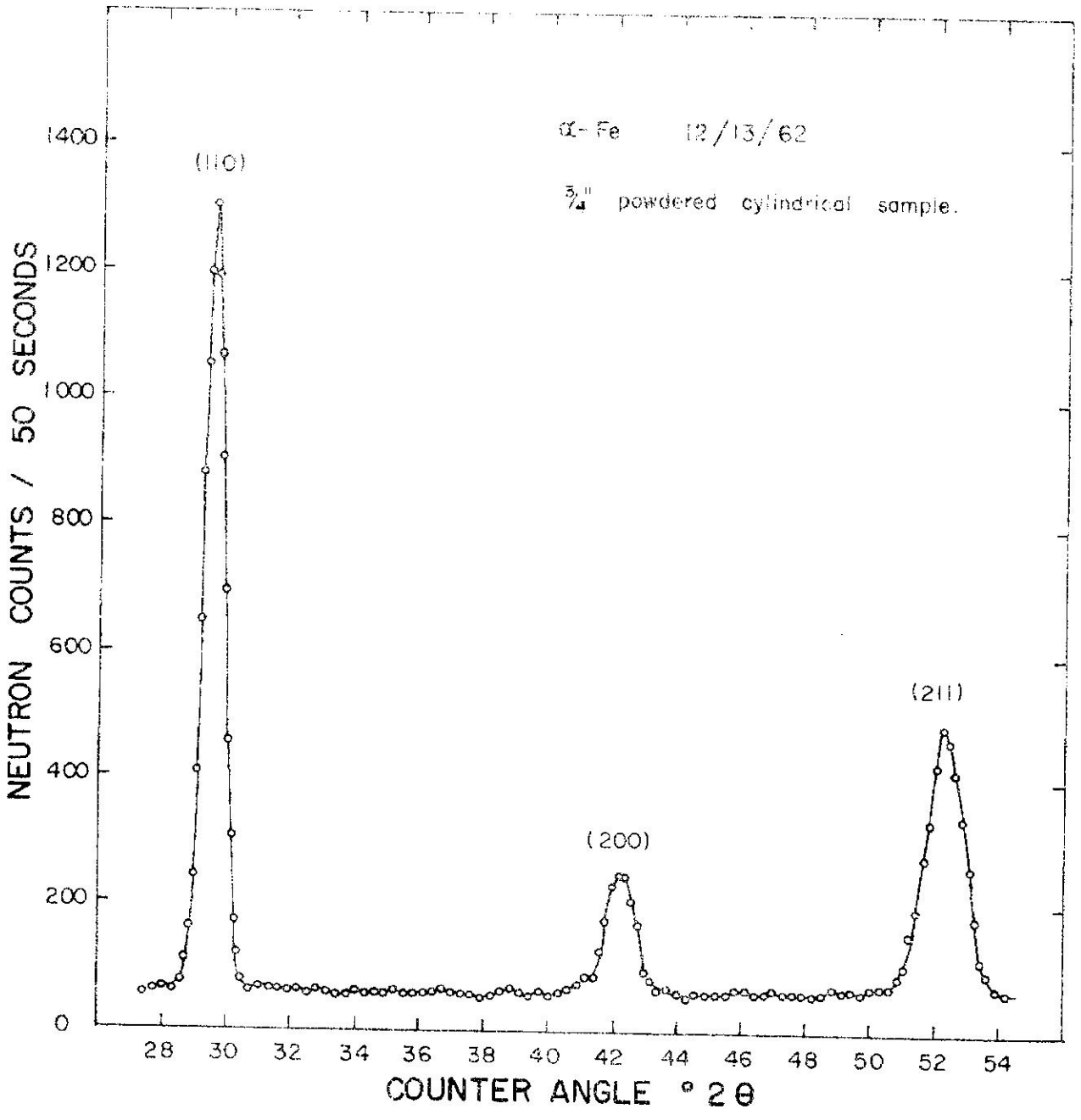

Figure 2. Neutron diffraction test pattern of powdered iron. The first data taken on the spectrometer.

Brookhaven, and was literally rescued from the scrap heap. In February an excellent neutron diffractometer was donated to the University of Puerto Rico by the Westinghouse Research Laboratories, and an arrangement is being made with the University to replace the older simple machine with the new Westinghouse unit. The old unit will probably be transferred at cost to AEC contract research at the Georgia Institute of Technology.

2. $CaWO_4$

The structure of $CaWO_4$ (scheelite) was the first neutron diffraction search problem undertaken at the Nuclear Center. Work was done in collaboration with Dr. M. I. Kay of the Georgia Institute of Technology.(1)

A number of crystals having the tetragonal-scheelite structure have been examined by X-rays. These studies have yielded the heavy atom positions, but in most cases the oxygens could be located only from packing considerations, and in all cases the uncertainties in the oxygen parameters are quite large. The discrepancies between the structures reported for various scheelite-type compounds are larger than one would expect in an isomorphous series.

With neutron diffraction data an accurate direct refinement of all parameters is possible. Starting with oxygen coordinate parameters of Sillen and Nylander,(2) a set of single crystal (hOl)

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(1) Paper submitted by M. I. Kay, B. C. Frazer and I. Almodóvar for presentation at the Int'l Union of Crystallography, Rome, Italy. Sept. 9-18, 1963.

(2) L. G. Sillen and A. L. Nylander, Arkiv Kemi, Min. Geol. 17A, No. 4 (1943).

neutron data was refined by least squares to yield = 0.2417 ± 0.0007, y = 0.1522 ± 0.0009, and z = 0.0861 ± 0.0002. These may be compared with the set proposed in the X-ray study of Sillen and Nyllander: = 0.25 ± 0.02, y = 0.15 ± 0.02, z = 0.075 ± 0.015. Here oxygen is in the 16 (f) general position of space group I $4_1/a$. An appreciable change is noted in the z parameter, although the neutron value falls within the rather large estimated error limits.

3. $BaNiO_2$ and Fe_2SiO_4

Preliminary neutron data have been taken on these two compounds using powder diffraction techniques. The magnetic spin structures of these crystals are of principal interest, although the chemical structure of $BaNiO_2$ is also of considerable interest.

According to the X-ray study of Lander[3], the Ni^{2+} ion in $BaNiO_2$ is surrounded by oxygens in approximately square planar coordination. The oxygen squares share edges to form zig-zag chains in the c direction of the orthorhombic Cmcm unit cell. Ordinarily, one would not expect Ni^{2+} to have a magnetic moment when in square planar coordination, but in this compound the moment appears to have nearly the "normal" moment of the divalent ion (approximately $2\mu_B$). Lander points out that this is undoubtedly due to the unusually short Ni-Ni distance in the chains. This distance is only slightly larger than in metallic nickel.

The structure determination of Lander was not carried out with high precision, and the oxygen positions were located mostly on the basis of packing considerations. Neutron data collected at room and liquid nitrogen temperatures did not agree very well with Lander's proposed structure, although preliminary analysis indicates that his

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(3) J. J. Lander, Acta Cryst. 4, 148 (1951).

general model is correct. The alternate model one can derive from packing considerations is definitely incorrect. Adjustment of the oxygen and barium parameters is now in progress, and preparations are underway to examine the crystal for magnetic order at liquid helium temperature.

Fe_2SiO_4 has been studied so far only at room temperature. The observed and calculated intensities for the chemical structure agree fairly well using the parameters of Mg_2SiO_4 (olivine)[4] although some adjustment may be necessary. An accurate chemical structure is especially important in this case, for only half of the iron atoms are in symmetry-fixed positions. Low temperature experimental studies are planned for the near future.

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(4) N. V. Belov, E. N. Belova, N. H. Andrianova, and P. R. Smirnova; Dokl. Akad. Nauk SSSR 81, 399 (1951).