PUERTO RICO NUCLEAR CENTER NEUTRON DIFFRACTION PROGRAM Progress Summary Report No. 1 by UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT(40-1-183) FOR U.S. ATOMIC ENERGY COMMISSION NEUTRON DIFFRACTION Progress Summary Report No. March 1963 Tomsel Almodóvar - Principal Investigator with Guest Scientists B. Chalmers Frazer, Helmut J. Bielen, and M.T. Kay Puerto Rico Nuclear Center operated by University of Puerto Rico for the U.S. Atomic Energy Commission under Contract No. AT-(40-1)-1833, PRNC 16 sa. 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-1964 is presented in this report. 1. Spectrometer Installation Since this was the first year of the project, a considerable fraction of FY-1965 was taken up with the construction, installation, and testing of equipment. One of the two 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 couple 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, conchstonator 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 ---Page Break--- Figure 1, Neutron spectrometer now in research operation at the Puerto Rico Nuclear Center. A liquid helium cryostat is mounted in the sample position. ---Page Break--- - NEUTRON COUNTS / 50 SECONDS 8 é 8 8 8 r | i { ' i \ ' i] { 28 30 Figure 2. Me ponderes cytinavicai samp. rau (200) re 3234 36 38 40 42 44 48 48 50 52 COUNTER ANGLE °2@ Neutron diffraction test patterns of powdered iron. First data taken on the spectrometer. 34 the ---Page Break--- was 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 arrangements are being made with the University to replace the older simple machine with the new Westinghouse unit. The old unit will probably be re-manufactured at cost to ABC contract research at the Georgia Institute of Technology. The structure of CaWO4 (scheelite) vs the first neutron diffraction research problem undertaken at the Nuclear Center. Work was done in collaboration with Dr. H. 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 greater 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 Haylander, (2) a set of single crystal (KOL) (1) Paper submitted by H. I. Kay, B.C. Frazer and T. Almodóvar for Presentation at the int'l

Union of Crystallography, tome, Italy. Sept. 9-18, 1963. (2) L. G. Eitlen and A. I. Tylander, Arkiv Kemi, Min. Geol. 17A, No. 4 (1943). ---Page Break--- Neutron data was refined by least squares to

yield x = 0.2617 ± 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 Tylander: x = 0.25 ± 0.02, y = 0.15 ± 0.02, z = 0.075 ± 0.015. Here oxygen is at the 16 (6) general position of space group I 4j/a. An appreciable change is noted in the z parameter, although the neutron value falls within the rather large estimated error limits. Balio and FopSiO, 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 BaF2 is also of considerable interest. According to the X-ray study of Lander, the 112 ion in BaF2 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 crystal unit cell. Ordinarily, one would not expect Mn 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 μB). Lander points out that this is undoubtedly due to the unusually short Mn 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 model is correct. The alternate model one can derive from packing considerations is definitely incorrect. Adjustment of the oxygen and

Barium parameters are now in progress, and preparations are underway to examine the crystal for magnetic order at 1:quid helium temperature. FeP8O 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 FeP10 (olivine), 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. (4) YL v. Botov, BM. Belova, HH. Andeianové Dokl: Akad. ‘vauk $852 81,399 (1951). and P. R. Sufrnova; ---Page Break---