PRNC 30 PUERTO RICO NUCLEAR CENTER PROGRESS SUMMARY REPORT NO. 2 NEUTRON DIFFRACTION PROGRAM [OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NNO, AT (40-1}-1833 FOR U. S. ATOMIC ENERGY COMMISSION ---Page Break--- ---Page Break--- NEUTRON DIFFRACTION PROGRESS SUMMARY REPORT No. 2 Ismael Almodivar — Principal Investigator with Guest Scientists B. Chalmers Frazer, H. J. Bielen, K. Okado, and M. I. Koy March 1964 ---Page Break--- ---Page Break--- TABLE OF CONTENTS. List of Tables and Figures INTRODUCTION 2.0.20. SUMMARY OF RESULTS . Calcium Tungstate ..... Copper Sulfate .... 2 Iron Orthosilicate .. .. 3 Boron Nickelate - 5 OTHER CURRENT RESEARCH PROBLEMS ..... 6 Copper Formate 6 Crystal Structure Analysis at low temperatures. ... 6 EQUIPMENT .. 7 References ... 8 Tables ... 9 Figures ... ---Page Break--- 7 10 LIST OF TABLES AND FIGURES TABLES Positional and temperature coordinates for $CoWO_4$ with standard deviations .... 9 Short distances and angles in $CoWO_4$. FIGURES b axis projection of $CoWO_4$ ... axis projection of $CuSO_4$ Neutron diffraction patterns for $CuSO_4$ The only obvious change is a new peak, at 9° 3 Difference pattern for $CuSO_4$. Peak distortions are caused by imperfect matching of He and N2 data . 14 c axis projection of olivine (Mg_2SiO_4) .. 15 Difference powder pattern for Fe_2SiO_4 .... 16 Modern (US) neutron spectrometer designed and constructed by BNL for PRNC .. 17 Second neutron spectrometer in operation at PRNC. The diffractometer assembly was donated to the UPR by the Westinghouse Electric Corporation 18 X-ray diffraction equipment and accessories now in operation for research at PRNC .. 19 Equipment and area designated for microscopic studies of crystals .... 20 ---Page Break--- 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 ($CaWO_■$) The first neutron diffraction problem investigated at the Nuclear Center was a single crystal structure analysis of $CaWO_■$. Preliminary results of this study were included in Progress Summary Report No. 1, March 1963. Final results are summarized here. While the $CaWO_■$ structure is usually considered to be typical of that adopted by 180 compounds, the oxygen coordinates have been known with an accuracy of only about 0.1 Å. The reason for this is that the W 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 Templeton 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, important series of * "A Neutron

Diffraction Refinement of CaWO4," M. Koy, B.C. Frzer, and J. Almoier, J. Chem. Phys. 40, 504 (1964) ---Page Break--- CaWO4 crystallizes in the tetragonal space group I4/a and has cell dimension values of a = 5.243 + 0.002 and c = 11.376 ± 0.003 Å. The Ca and W atoms are in the fourfold 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 of) and (hh) data collected from samples cut from a large synthetic crystal, led to a final R value of 0.041. The refined 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 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 $FeSO_4$, $NiSO_4$, $CoSO_4$, and $CoSO_4$." 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 (L.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 Kreines, a complete determination of the magnetic structure is possible. $CuSO_4$ has the orthorhombic 2°80 type crystal structure.

with space group Porm. See fig 2. The four crystallographically equivalent Cu^{2}■ ions are located on the (0 0 0), (0 0 ½), (½ 0 0), and (½ ½ ½) sites. For the case where the magnetic cell is identical to the chemical cell, the possible collinear spin configurations for antiferromagnetic ordering are ±4 0, ±4 -7, 0 0 and ± 0. In the Weller - Koehler - Berteut notation these arrangements are labelled G, C, and A, respectively. Each of them leads to a distinct set of magnetic reflections. In comparing diffraction patterns taken at 42° K and 77°, 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. 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 Pnma. 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■ = X■ = X■ and X■ = X■. This of course suggests a collinear spin structure with the spin axis parallel to c. With this assumption, the Cu^{2}■ moment calculated from the neutron diffraction data is roughly 0.8 expected for this ion. The spin ordering mode is A, +++ - on the (0 0 0), (0 0 ½), (½ 0 0), (½ ½ ½) sites, with the moment orientations along the c axis of the Pnma cell, i.e., Iron Orthosilicate (Fe■ SiO■). Until quite recently, very little has been known about the

magnetic properties of the transition metal clivine type compounds. See fig. 5. Early this year, Kondo and Miychora® 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, SiO, has

been found by the present authors by neutron diffraction measurements, and by Tokei and Cox!® 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 85°K. Foyalite 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 collection of accurate single crystal data, some preliminary results derived from powder data are already included at this time is now in progress with the orthorhombic olivine structure, space group Pbnm (0,"*), there are four formula units per unit cell. The cell of Fe,SiO, has dimension values a= 482Å b= 1048Å c= 600Å. There are two four-fold sets of Fe^{2}■ ions. Fe, in 4 (ce) 000,904, 440, % Fe, in 4 (cd) yttrium Van, Vary, ---Page Break --- 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^{3}■ ions is in 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 O^{2}■ groups. If the magnetic and chemical cells are identical, as proves to be the case in Fe,SiO, 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 three x and y parameters of Fe. For one thing, these parameters must be accurately determined as part of the analysis, but a more important difficulty is that the magnetic extinction rules which would apply for Fe 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, 4(a) sites be numbered 1 through 4 in the same order as given above. Assuming ideal positions for Fe, let the spins on the 4(c) sites be numbered 5 through 8 in the following order: 0 M4 Va, 0% %, eh %, Ve HV. If one calculates magnetic extinction conditions for the various possible collinear anti-ferromagnetic 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 1234 5678. 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 logographic b axis. Analysis of the data indicates a + - + - - + - arrangement of spin components parallel to 9. The components in the c direction are small, if indeed they exist at all. The Fe moment was found to be approximately 4 µB for both Fe, and Fe. In both cases, the spin vectors are approximately parallel to the XY plane and are tilted from the b axis by about 30°, with the

tit alternating in sign is prescribed by the ¢ axis ordering made. 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 axis-oriented crystal (0 k R data) have been completed at 77° K and 42° K. Intensity measurements of several reflections as a function of crystal temperature have also been completed. Collection of (ho 2) 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■) The results obtained on BaNiO■ 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. 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 236 Å. Finally, the orthorhombic Cmme 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 BoNiO structure, Lender quotes unpublished susceptibility measurements of F. Morin. The temperature range is not given, but it is stated that the Curie-Weiss law is obeyed with A = 180°, and that the calculated number of unpaired electrons per nickel ion is 183. 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 of the Westinghouse Research Laboratories, the authors were able to obtain magnetic susceptibility data down to 42° K. These data disagreed somewhat with Morin's in that & = 72° and approximately one unpaired electron per nickel ion. The Curie-Weiss law was obeyed very well down to liquid N2, 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 42° K and approximately 0 K, so there was no definite evidence of a transition. Also, the magnetic sample was found to be somewhat impure, so not much can be placed in the difference from Morin's measurements. If the Ni data by Takei and Cox, it is possible that the statistics were not sufficiently good to observe ordering. This was true if the ordering is type A, since peak overlap happens to be very bad for this case particularly. 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 Cu(HCOO)2·4H2O 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 & tend 9.0.2) data have been completed as part of the crystal structure analysis now in progress. The structure has been examined previously by x-rays, but this study did not yield hydrogen positions. Copper formate also shows very interesting magnetic properties at low temperatures, becoming anti-ferromagnetic below 17°K. An investigation of the magnetic structure of this compound will follow its structure analysis. ---Page Break--- 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 cry-box type enclosure fitted with a mylar window through which the neutron beam passes seems promising. No work has previously been reported on structural analysis by neutron diffraction at low temperatures. Among others, we are interested in the structure refinement of methanol, dimethyl acetylene, formamide, and diamine 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 high aperture 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, by magnets and cryostats, and features a rotating cell meter assembly which allows the somewhat primitive diffractometer donated to PRNC by BNL has been sent to the Georgia Institute of Technology. A more advanced and precise instrument connected 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 conduct installs and to study some of their properties. ---Page Break--- REFERENCES LG Sin and A. Nylender, Arkiv Kemi Min. Geol, 17A, No. 4 (1943) A Zalkin and DH. Templeton (private communication). BC. Frazer and P. J. Brown, Phys. Rev. 125, 1283 (1952), PL. Brown and BC. Frazer, Phys. Rev. 129, 1145 (1963) EF. Bertaut, J. Coing-Boyat, and A. De la Polme, Phys Letters 2, 178 (1563). NM. Kreines, Zhur. Eksp. i Teoret, Fiz (1958. Eng, tons" Sov. Phys. JETP 8, 971 (1959) PA. Kokkeres and PJ, Rentzperis, Acta Cryst. 11, 361 (1953) EF. Berreut, J. Appl. Phys, Suppl. 33, 1138 (1962) H. Konda and S. Miyahara, J. Phys. Soc. Japon 18, 305 (1963) W.J. Tekei and DE Cox (unpublished data) NV. Belov, ENN. Belova, NH. Andricnova and P. F Smirnova, Dokl, Akad, Nouk SSSR 81, 399 (1951), H Winchell, Amer. Cryst. Assoc. Meeting Abstr. p 14 (Apr. 10-12, 1950). JJ. Londer, Acta Cryst. 4, 148 (1951) JJ. Lender, J. Am, Chem, Soc. 73, 2450 (1951). R. Kiriyoma, H. Shibamoto and K. Matsuo Acta. Cryst 7, 482 (1954) J. Tah and Y. Kemiya, J. Phys. Soc. Japon 17, Suppl, B-1, 512 (1962) THosedo and R. Miedema, J. Phys. Soc. Japon 17, Suppl. B-1, 518 (1962). ---Page Break--- Table I Positional and temperature coordinates for CaWO4, with standard deviations. Origin SGN zero KFA, x 0.2 om OIS cong 0.2m3 0.05 y 0.015 0.20504 0.0013 dust 0.0006 z 0.05 0.0015 0.0001 0.0006 0.001 ny 0.115 0.0073 0.0014 Pa 0.100 0.016 0.0057 0.0012 P33 ons 0.0003 0.00016 0.001 Fiz 0.00016 cos = -0.00014 0.007 Fig 0.0008 'coos 0.0005 0.0002 Pa 0.00 0.0005 aos 0.001 Calcium Fn 0.071 0.0004 0.00051 0.0022 P33 0.001 0.00019 c.0005 Tungsten Fu 0.0036 coco 0.00038 0.0022 ---Page Break--- ° Table II - Short distances and angles in CaWO4.

WO, Group Distance Standard congle 0.003, ry ov 004 a-ay 220 003 Otter Close pproacives C—-9 2579 0.005 Ca,— 0, cou O-Oy oo 9-0, 274 oom 0-2 9 2938 coos 0-90, 6 com Q-o an com + For numbering scheme, see fig. 1 » 0.003 A added for torsional oscillation ---Page Break--- b axis projection of CoWO, ---Page Break--- b a | orm setting) @ at Cs ig 2 € ax's projection of CuSQ, ---Page Break--- NEUTRON COUNTS AT 77 °« 10 Cu SO 34 n=105 © x0 we = " 2 xh x zof 22 wl 20° 26 18 S 2a 16 5 2 4s 2 ee . we 16 8? 14 6 e+ ' 3 ° : | Ny 2 OS SW Rw 1 20 2 28 26 2B 0B Ba COUNTER ANGLE +28 Fig 3 Neutron diffraction pattems for cus The only obvious change iso new peck at 39° ---Page Break--- NEUTRON COUNTS on ' cu SO4 ~ 2400+ 1(42 °K)-1(77°K) | 2000 + 4 (003) 1600 F g91) wan) (200 1 Woop! (023)(13) 7 800+ oan teen 4 - i bea -400 L ee 8 10 2 14 16 8 20 22 24 2 28 30 32 34 COUNTER ANGLE °28 Fig. 4 Difference p coused by impertect mate

---Page Break--- 420 te a0 a ---Page Break--- NEUTRON COUNTS /1000 Fe, Sid, DIFFERENCE PATTERN: 4.2°K DATA-77 °K DATA ui tone momar (010) on on (en un) canoe) (020) '90H 120) 190234130) (00) (030) (030) pe 4 8 12 6 20 24 COUNTER ANGLE 26 Fig 6 Difference powder pattern for Fe, SiO, ---Page Break--- ---Page Break--- ---Page Break--- 2 uoyroyyp foxx 6 Sig ---Page Break--- ---Page Break---