PRNG-84 PUERTO RICO NUCLEAR CENTER NEUTRON DIFFRACTION PROGRAM PROGRESS SUMMARY REPORT NO. 4 M. I. KAY, T. ALMODOVAR, J. A. GONZALO, D. T. CROMER, K. OKADA MAY 1965 — APRIL 1966 ‘OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT (40-1)-1833 FOR U. S. ATOMIC ENERGY COMMISSION ---Page Break--- PUERTO RICO NUCLEAR CENTER NEUTRON DIFFRACTION PROGRAM PROGRESS SUMMARY REPORT NO. M. I. KAY, T. ALMODOVAR, J. A. GONZALO, D. T. CROMER, K. OKADA APRIL 1966 ---Page Break--- TABLE OF CONTENTS Introduction • Copper Formate Tetrahydrate • Tartaric Acid • The Magnetic Structure of Palladium • Magnetic Intensity Program • Conclusions • References • Tables • Figures • ---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. 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 scattering atoms. Thus, if there are light and heavy atoms in the same compound, the contribution of the light atoms 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 is also a neutron-electron spin interaction in compounds which possess spins 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). ---Page Break--- Copper Formate Tetrahydrate Introduction ‘The physical

Properties of copper formate tetrahydrate have been extensively studied. Phase transitions to a partially ordered magnetic state at 50% and to an antiferromagnetic state at about 17% have been reported. The crystal structure has been determined with X-rays by Kiriyena, Toanoto, and Vateuo, who found the crystal to be sonoslinic, space group P2/a with a= 8.25, b= 0.28, and c = 6.35 Å, 101°5' and with two formula units per unit cell. A dielectric anomaly at -38.9°C has been reported by Kiriyama and independently by this laboratory. In this report we give the results of a neutron diffraction analysis of the room temperature phase of copper formate tetrahydrate and an account of the dielectric analysis. The structure of this compound can be described as two alternating layers, one of copper formate near z = 0, see Fig. 1, and one of water near z = 1/2, see Fig. 2. It has been proposed that the magnetic ordering arises from exchange through the formate groups. The Cu-Cu distance within the copper formate layers is 5.77 Å. The shortest Cu-Cu distance between layers is 6.35 Å, which is the c axis. A path through oxygen neighbors exists, but includes hydrogen bonds. Thus it is not surprising that a partial ordering which may be two dimensional occurs at a higher temperature than antiferromagnetism. ---Page Break--- Preparation of Specimens Saturated solutions of copper formate were prepared by dissolving CuO in 30% aqueous formic acid. Large single crystals were readily grown by suspending seed crystals in the solution and slowly evaporating at constant temperature (50.5%). Crystals were cut using a wet string saw. For dielectric measurements, thin plates of dimensions 5 x 5 x 0.5 mm were cut perpendicular to the b axis. A drying silver paint (Dupont Conductive Silver Coating Material No. 4627) was applied to serve as electrodes and then the crystal and electrodes were covered by a plastic spray to avoid dehydration. For the neutron diffraction work, parallelepipeds about 2 x 2 x 6 mm were used.

wore feut along each of the three crystallographic axes. These crystals were sealed in thin glass tubes. A growing showing the crystal habit is given in Fig. 3. The phase transition is noted in a preliminary report by Kacada, an antiferroelectric transition occurs in copper formate tetrahydrate at -30.9°C. At this temperature, the crystal shows a discontinuous decrease in dielectric constant as the temperature is lowered. A peak value of the dielectric constant 50 times as great as that observed by Xérayana was measured (Fig. a). Below the Curie point, the crystal shows a double hysteresis loop in the curve of electric field versus polarization, within a small temperature range. ---Page Break--- Figure ta also shows the dielectric constant at low AC amplitude and 1000 eps versus temperature. As the temperature is decreased, the dielectric constant of the (C10) plate rises to a peak of 1500 at -38.9°C, and a large discontinuous decrease occurs at this temperature. Above this transition point, T, the Curie-Weiss law, $\varepsilon = C/(t{\sim}2)$, is satisfied, and a plot of the reciprocal dielectric constant versus temperature is a straight line, as seen in the figure with T, = -58°C and C = 3.2×10^6°C. The (001) plate has a low dielectric constant varying gradually from 20 at room temperature to 5 at liquid-nitrogen temperature without any anomaly. The (100) plate gave a small discontinuity at T as shown in Fig. ba. This might be attributed to a small component of the large anomaly in the [010] direction owing to the cutting error of the crystal plate, in contrast to the perfect orientation of the (001) crystal plate. This high anisotropy can be expected from the predominance of layer structure of this crystal. A clear double E-D hysteresis loop was observed within a certain temperature region below the transition point with the ordinary Sawyer-Tower hysteresis-loop circuit with a high AC amplitude of 19 kV/cm and 60 cps. At low temperature, the E-D relation is a straight line. With rising temperature, nonlinearities.

appear at the ends of the straight line. A double hysteresis loop comes out with further warming. (see Fig. 6). On passing through the transition point, the loop disappears. The double hysteresis loop was observed only in a narrow temperature region from -42.6°C to the transition point. This range seemed to depend upon the applied AC amplitude. ---Page Break--- An attempt was made to obtain saturated branches at both ends of the double loops. However, saturation in the curve of polarization versus electric field could not be obtained. When the sweeping amplitude of the AC field was not very strong, say 19 kV/m, the double loop was quite stable. When a strong field was applied, instead of saturation, an unusual effect appeared in the critical field. The critical field decreased gradually and both loops became larger. In about one minute the loops coalesced to become a single loop similar to a distorted ferroelectric hysteresis loop. After decreasing the AC field to the field strength that had given the stable loop, this procedure could be repeated. This phenomenon is similar in appearance to the AC annealing effect in a damaged ferroelectric crystal irradiated above the Curie point (202,12,13). We, as yet, have no interpretation of this phenomenon and more experiments are required. Figure 5 illustrates the thermal hysteresis in the transition. The rate of change in temperature was about 0.07°C/min, and the accuracy of temperature measurement was ± 0.05°C. The temperature was first lowered from room temperature to -63°C and then raised. A thermal hysteresis of 0.3°C occurs in the transition. Although small, this hysteresis is definitely larger than experimental error. Effects of DC biasing fields on the transition are shown in Fig. 6. Superimposing a DC field on the 1000 cycle AC field of nominal amplitude used for the dielectric constant measurement moved the transition point to a lower temperature. This behavior is usual for a first order antiferroelectric phase transition. ---Page Break--- X-ray photographs,

Using precession camera and Cuky radiation, were ‘taken at various temperatures from room temperature, about 20°C, to -50°C. ‘The photographs were recorded on the same film by moving the cassette a small ‘out for each exposure. Although no special care was taken to achieve precise measurements of the absolute lattice constants, relative values accurate ‘to at least 0.5% were obtained, No discontinuous change, either in diffraction intensity or in lattice constants was detectable by this technique, nor did any reflections appear that violate the systematic extinctions of space group ee (8,18) results are in agreement with Kiriyama and indicate that ‘the transition probably results from hydrogen motion. ‘The thermal expansion coefficients are 5 x 10^-5, -2 x 10^-7 and 8 x 10^-6/°C along a, b, and c respectively. Some hk0 neutron reflections were measured below the Curie point. No reflections which should be absent in space group P2,/ a were observed, but small to moderate intensity changes were noted, indicating further that the transition is caused by hydrogen motion. Neutron Diffraction Study of the Crystal Structure Single crystal neutron diffraction intensity measurements were made on ‘the three principal zones of copper formate tetrahydrate at room temperature, Lorentz corrections, and in the final stages of the analysis, empirical extinction corrections were applied. Full matrix Least squares refinements using anisotropic temperature factors and with separate scale factors for each zone minimized χ^2 (984) where w = 1/(6P + 0.005F) and sP was based on counting statistics. For unobserved reflections w = 0. The OO reflections from the OK and nO zones also had w = 0 because they were so strongly influenced by extinction. Discrepancy indices quoted are R_e = |ΣF_o|/|ΣF_o| and R_y = Σ|F_o| with unobserved reflections omitted. These values are listed in Table 1. The x-ray data of Kiriyama et al. were refined by least squares using anisotropic temperature factors and with weights w = 1/(P_o + 0.0272).

The original parameters, the least squares parameters and our final heavy atom parameters are given in Table 2. Difference Fourier projections were computed from the neutron data with the heavy atoms removed by using the x-ray parameters of the non-hydrogen atoms found by Kiriyama et al. In these difference Fouriers we expected to find the formate hydrogen and four water hydrogens. The formate hydrogen and three of the four water hydrogens were fairly evident, but no definite indication of the fourth water hydrogen was observed. Least squares refinement, followed by further difference Fouriers, was made with all atoms except the fourth hydrogen included. These difference Fouriers had negative regions (hydrogen has a negative scattering amplitude) near two of the symmetry centers. Neither of these positions was far enough from the center to accommodate a hydrogen atom. Placing a disordered half hydrogen in each position would result in a structure having an average of MeO and OH" in one position and H2O and H2O+ in the other position. The latter pair in the water coordinated to the copper ion and the notion of a positive hydronium ion being coordinated to a positive copper ion is untenable. However, the existence of negative scattering regions near the symmetry centers was undeniable. ---Page Break--- We were then led, partly by small features in the difference Fouriers and partly by the known geometry of water, to a scheme of statistically disordered water molecules. It was disordered water molecules. It was this disorder that led us to examine the dielectric properties of the material. This disordered structure may be regarded as a superposition of the four structures shown in Fig. 7. These are actually two similar structures and the same structures related by a center of symmetry. The hydrogen atoms (2) and H(2) in Fig. 2 have weight 3/4 and H(3) has weight 1/2. In half of the unit cells, water (1) has the orientation H(1)-OH(2), in one fourth H(2)-O-H(3) and in one fourth H(2)~(5). Thus, water (1) assumes

either of three positions. Water (2) also assumes either of three positions, but one bond, O-H(4), remains fixed. H(3) has unit weight, H(5) has weight 1/2 and H(6) and H(7) have weight Wi. In half of the unit cells the orientation is H(4)-O-H(5), in one fourth H(4)-O-H(6) and in one fourth H(4)-O-H(7). This model was refined by least squares leading to R = 0.10 and R, = 0.066. The resulting hydrogen parameters are given in Table 5. From PMR measurements Kiriyana (3) assigned positions for three of the water hydrogens. She concluded that the fourth hydrogen was freely rotating about a fixed O(4). Her description of water (1) corresponds to our orientation H(1)-O-H(2). Her model, with the rotating water molecule, was refined by least squares resulting in R= 0.270 and R, = 0.356. The agreement is clearly less satisfactory than for our disordered model. One might argue that the positions of H(5), H(6) and H(7) are approximations to a free rotation of minima in a hindered rotation. However, the presence of H(5), omitted in Kiriyana's model, does seem to be necessary for good refinement of the neutron diffraction data. The phase transition and the ease of dehydration suggest that the water molecules are not firmly bound. Bond distances and angles are given in Table 1b. Standard deviations have been calculated using the entire correlation matrix and include estimates of unit cell errors. The results for the heavy atoms are the same as obtained from the x-ray measurements within experimental error. Some of the bond lengths and angles for water appear to be in disagreement with other studies of hydrated crystals. However, the accuracy of hydrogen positions is not great. Reasons for this low accuracy are that the ratio of observations to parameters is low, high background from inelastic hydrogen scattering, and because fractional hydrogen atoms have a small scattering length, even for neutrons. Also, most of the hydrogen parameters are near 0 or 1/2 and thus only half of the reflections,

Those with Yoda are sensitive to the z parameters. Finally, we have postulated that the positions of all atoms are independent of the positions of the others, an assumption that is not completely correct. The higher thermal parameters for water, observed both in the x-ray and neutron studies, may indeed be a consequence of a small variation in oxygen position depending on the particular orientation of the water molecule. There are five O-O distances of about 2.68. Contacts of this magnitude are generally hydrogen bonds in hydrated crystals. The proposed disorder permits all of these contacts to be hydrogen bonded all of the time. Somewhat similar disorder is, in fact, found in ice. ---Page Break--- The class 48 $NaAl(SO4)2\cdot12H2O$. The alum forms of the cation are large and the alum, which is by far the most common type, occurs if the cation is of intermediate size. In all the alums there are two crystallographically different water molecules, each associated exclusively with either the monovalent or trivalent cation. The trivalent cation is always surrounded by six water molecules in a nearly regular octahedron, but the orientation of the octahedron with respect to the cell axes is different in each of the three types. The monovalent cation in the A and C alums also has six waters in a nearly regular octahedron. The large cation in the K alum can accommodate 12 oxygen neighbors. To attain this large coordination number, the water octahedron is compressed along the threefold axis and stretched out normal to the axis until it is nearly planar. The two ends of the resulting trigonal antiprism are separated by only about 0.068. The sulfate groups at each end of this antiprism are then moved along the threefold axis toward the central cation until six sulfate oxygens are about the same distance from the cation as are the water molecules. A slightly distorted cubic close-packed array of oxygens thus surrounds the cation. In the structure, six water molecules approach the small.

sodium cation ‘much more closely than in the structure. This motion cannot take place unless ‘the hydrogen bonding system changes. The most striking result is that the ‘sulfate groups become oppositely oriented along the threefold axis. Discussions of the relations among the three structures have been given by Lipson (9) and by Gona and Srirane [°), one of the alums has been investigated by modern counting techniques although Okaya, Ahmed, Pepinsky ---Page Break--- and Vand on have studied monomethyl ammonium aluminum sulfate dodecahydrate (sp) by photographic methods and refined the structure by least squares. Rave et al. (7) do not classify miso in a particular structure type because “the difference between a and palun types is not adequately defined structurally.” On the other hand, we believe that the three structure types may be clearly distinguished and that MASD is a member of the palims. The characteristic that distinguishes the alums from the g and a alums is the orientation of the sulfate group. In the alums this group is oriented opposite to its orientation in the q and a alums. The alums have twelvefold and the other alums have sixfold coordination of oxygen about the central, monovalent cation. Okaya et al. probably overlooked this difference in coordination because the distances which they state are from the center of gravity of the CHi,* on are actually from the nitrogen or carbon atoms of the disordered ion. Several of the alums have been investigated using both X-ray and neutron diffraction methods. The X-ray data were taken at Los Alamos Scientific Laboratory and the neutron data at Puerto Rico Nuclear Center. Cesium Alum (Ce Al (50,)Q.22%,0) Experimental, ‘To grow the crystals needed for the study, fine wires were suspended in ‘a supersaturated solution of Cs alum and numerous small crystals formed on ‘these wires. Most of the crystals were scraped from the wires and the remainder were suspended in a saturated solution which was then allowed to evaporate slowly. An octahedron, mm on an edge, was

selected for study. ---Page Break--- ‘The crystal was briefly immersed in liquid nitrogen to increase its temperature and thus reduce the effects of extinction. The neutron diffraction intensities of the nO zone were measured. Using a wavelength of 1.068, none equivalent reflections within the range 2 ≤ 90° were measured; of these, 68 were observed according to the criterion (I-Background) ≥ 2.0 x (I+Background)'/2. Because of the large incoherent scattering of hydrogen, absorption corrections were applied. The linear absorption coefficient for Ce alum is 452 cm■^{1}. Calculated transmission factors were between 0.292 and 0.353. Refinement of the structure with X-ray data. The atomic positions given by Lipson (15) were used as starting values for a full matrix least squares refinement of all non-hydrogen parameters. Anisotropic thermal parameters were used in the form, B = [B■h^2 + B■k^2 + B■l^2 + B■h + B■k + B■l]. Two sets of X-ray data were taken; one with a fixed counter, fixed crystal technique, and the other using a "2θ scan" technique. The results are given in Table 5. In nearly all cases, the parameter differences are smaller than the standard deviation. The thermal parameters obtained from the fixed crystal data, however, are systematically slightly larger, probably because at higher angles, a portion of the intensity is lost because of 4θ separation. ---Page Break--- Refinement of the structure with neutron diffraction data. Structure factors were calculated by using the parameters obtained from the X-ray analysis but without any hydrogen contribution. The structure factors were initially scaled so that gF = ZF, and a difference Fourier projection was calculated. Approximate hydrogen positions were obtained and a least squares refinement minimizing $\Sigma w(F - x)^2$ was calculated where $w = 1/(F + 0.02)^2$. Parameters in this refinement were isotropic temperature factors for each crystallographically different atom, the scale factor, and coordinates of the hydrogen atoms. The sulfur and oxygen

Atons were not allowed to move. Table 6 gives the final parameter. Fig. 8 is a difference Fourier showing hydrogen atom only. Discussion: The interatomic distances and bond angles are given in Table 7. The errors were computed by using the entire variance-covariance matrix and include the trivial effect of lattice constant error. However, the errors in distances and angles involving hydrogen assume no error in the heavy atom positions. The anisotropic thermal parameters were transformed to obtain the thermal ellipsoid parameters which are given in Table 8. The isotropic thermal parameters computed from the neutron data, except those for cesium and aluminum, are in good agreement with the isotropic parameters (Table 6) equivalent to the anisotropic parameters obtained from the X-ray data (18). The reason for the two exceptions is that cesium and aluminum are distinguished in projection only by their different scattering lengths and their different thermal parameters. Therefore, the correlation between eq and Bay is large (-0.82) and is manifest in the relatively large standard deviations of these two parameters. The octahedron about aluminum is oriented almost exactly along the cell axes and is only very slightly distorted. The Cs(2) distances are a little longer than the Cs-O(1) distances, 3.454 Å vs. 3.367 Å. The analogous distances in MASD are 3.42 Å to O(2) and 3.618 Å to O(2). The sulfate group is an almost perfect tetrahedron. Rigid body analysis of the sulfate group was carried out by the method of Cruickshank using a code written by Trueblood. The 7 andy matrix are in Table 9. Corrections to the S-O distances were computed according to the in-phase assumption of busing and theory. The O-O distances before and after being corrected are given in Table 7. These distances agree well with other recent accurate determinations which have been tabulated by Larson (1965). The direction of maximum motion of O(2) is normal to the S-O bond. The largest axis of the O(2) thermal.

Ellipsoid makes an angle of 85.7° with the O-H bond and the smallest axis makes an angle of 9.1° with the bond. There is only one possible system of hydrogen bonding in this structure. All hydrogen atoms take part in hydrogen bonds and all oxygen atoms except (2) have at least one hydrogen bond. The hydrogen positions could be reasonably guessed from the heavy atoms' locations obtained by X-rays. Hydrogen atoms could be clearly observed in a three-dimensional difference Fourier computed with reflections having sin θ/λ (O.MR-1). The O-H bond lengths were corrected for thermal motion according to Busing and Levy by using the isotropic thermal parameters obtained from the neutron diffraction data. These distances, before and after being corrected, are given in Table 7 and agree well with other neutron diffraction analyses of hydrated crystals. H(1) on O(2) is bonded to O(1) and this oxygen, being on a threefold axis, is bonded to three (1) atoms. A somewhat elongated trigonal pyramid consisting of the three hydrogen atoms and the sulfur atom thus surrounds (2). H(2) on O(2) and (3) on O(2) are bonded to O(2). These hydrogen atoms and the sulfur atom are nearly co-planar with O(2). (4) on O(2) is bonded to O(1). The angles involving H(2), H(2), and H() about O(2) are nearly tetrahedral. Tiamitton has given an empirical relation between O-O hydrogen bond lengths and O-H bond lengths or O-H-O angles. His empirical functions and the present experimental values are plotted in Fig. 9. The present O-H distances are systematically smaller than predicted but the differences are within the standard deviation of the measurement and the standard deviation of the prediction of the empirical function. There is no systematic trend in the O-O angles, all of which are nonlinear, but again the differences between the present experimental values and the empirical curve are not significant. Although the present results are of considerably greater accuracy than those of Tipson, the maximum shift.

in atomic position in only 0.04R. Except as noted, all calculations on the alums were performed on a TIN 7094 at Los Alamos using codes written by Larson, Root, and Cromer (92). ---Page Break--- Other alums' neutron diffraction (and X-ray) data have been taken on sodium and deuterated ammonium alum. The data is now being analyzed. If these studies indicate, the structure of potassium alum will be examined to determine the role of hydrogen bonding in sulfate disorder, which is rather pronounced in the potassium alum, mr a-Tartaric Acid. The crystal structure of d-tartaric acid was determined some fifteen years ago by Stern and Beevers (2%) by an elegant deconvolution of the Patterson function. Although their results revealed an interesting network of O-H hydrogen bonds and the general shape of the molecule, no attempt was made to refine the structure enough so that the bond lengths and angles of this important organic acid can be discussed with confidence. The present report deals with the refinement of the structure based on three-dimensional X-ray intensity data obtained by counter measurement on COXD, a computer-controlled diffractometer (Cole, Okaya, and Chambers) (4), and on two projections of neutron diffraction data. The X-ray results were obtained by Okaya and Stemple of TRY Watson Laboratory. The neutron results were collected at P-RN.C., and the work reported jointly (25). The cell edges from the neutron X-ray work are a = 7.715R, b = 6.006, c = 6.251, 700K. J = 100.1 ± 0.29, the space group is 4a Pay. are ---Page Break--- (25) Starting from the atomic coordinates given by Stern and Beevers, the refinement of the structure was made from the X-ray data in the usual manner by using a full-matrix least-squares program on a TEM 709. Only isotropic temperature factors were used for the hydrogen atoms. The atomic coordinates, their standard deviations, and thermal parameters are shown in Table 10. As shown in Table 10, the isotropic temperature factors of two hydrogen atoms have become negative; although it is doubtful that

Any read significance can be attributed to such a result, one notices that these two hydrogen atoms are those bonded to the carbon atoms. To confirm and refine the hydrogen positions, two (hOg and hkO) zones of neutron diffraction data were taken. Because of an accident, the hOA data had to be collected on two different crystals. Refinement was carried out by means of least squares analysis, starting with the x-ray parameter set. The carbon and oxygen positional parameters (as given in Table 10) were held constant. Refinement was carried out on all the hydrogen parameters, the carbon and oxygen temperature parameters, and three scale factors. The refinement proceeded with isotropic temperature factors, followed by six rounds of least squares with anisotropic temperature factors. The weights are w= 1/(a(F) + .025F) where (P) is based on counting statistics. Non-observed reflections were given zero weight. The resultant parameters are given in Table 10. ---Page Break--- Discussion Bond distances and angles have been calculated from the x-ray atomic coordinates in Table 10 (a); they are shown in Figures 10 and 11, respectively. Around C(1) and O(2), only the average of the three angles involving the hydrogen atom is shown for each stem. The results of the hydrogen determination by neutron diffraction are given in Table 11 for comparison. The molecule consists of two -CH-OH-COOH parts, each part containing a planar carbonyl group and a tetrahedral -CH-OH configuration. In each hydroxycarboxyl group, the hydroxyl oxygen stays close to the carboxyl plane; it is interesting to note that a similar situation also exists in the mesotartaric ion (26). It may be seen from the figures that although these two parts are similar in overall shape, there exist slight differences. The carboxyl group of part 3, (2), (2), O(2), and O(5) is less planar than that of part II and the O(1) - O(5) distance is much shorter than the corresponding O(+) - O(6) distance in part II; this is mainly due to the large (4) ~ ¢(3) ~ O(4)

aneie. It is interesting to notice that such seemingly equivalent groups start to take slightly different configurations. It is difficult to decide whether this asymmetry of the molecule is due only to differences in the hydrogen-bond formation or is inherent in the tartrate ion itself. The question might be answered when accurate crystal structure analyses are made in various crystals with tartaric as well as mesotartaric ions. The planes of the two parts make an angle of 54.69. In these two carboxyl groups which retain their protons, there are two distinct C-C-O angles; narrow C-OH of around 120° and wide C=O of about 125°. This situation is found in many crystal structures of molecules with carboxyl groups; in case a carboxyl group loses its proton, the two C-C-O angles become almost equivalent and are about 118°. The change in the shape of carboxyl groups due to the state of protonation was exhibited in various acid salts of dicarboxylic acids, e.g., ammonium hydrogen D-tartrate (21), dipotassium ethylene-tetracarbonylate, potassium acid phthalate and others. The structure consists of a complicated network of O-H--O hydrogen bonds. The scheme is essentially the same as that given by Stern and Beevers; the fifth contact given in their paper is ruled out as a hydrogen bond. Donohue (29) discussed the hydrogen-bond system in the crystal and proposed two possible schemes; the difference between these two schemes is based on the position of the proton on carboxyl I, i.e., the choice between O(2) and O(5) for the hydroxyl oxygen of this group. The difference in the two C-C-O angles given by Stern and Beevers leads to the conclusive evidence on the position of the proton without even locating its position; therefore, the hydrogen-bond system could have uniquely been assigned (Scheme A by Donohue) if enough data on the shape of carboxyl groups had been accumulated. As is evident from the figures and Table 12, the two carboxyl groups do not have identical surroundings: possible implication of

the situation on the symmetry of the Jon has been discussed in the previous paragraphs. The neutron diffraction data confirm the hydrogen bonding scheme deduced from the x-ray data. As has been noted in previously determined compounds, the values of the O-H and C-H bond distances (see Table 11) from neutron data are about 158 longer than those determined from x-ray data. This discrepancy is due to an inadequate description of the x-ray scattering from a bound hydrogen. The bond distances derived from the neutron diffraction data are closer to accepted values. In addition, the two (H-O) hydrogen bond angles (see Table 12) which were found to be less than 160° by x-rays are shown to be closer to 170°. Although the accuracy of the determination is not really high enough to make the following statement with certainty, we note that the inverse relationship between O-H and O-O distance in hydrogen bonds seems to hold.

The Magnetic Structure of S-Pd(II) Introduction At room temperature, Pd(II) has a tetragonally distorted CsCl type crystal structure, with (0,0,0) positions in the unit cell occupied by Fe atoms, and (1/2,1/2,1/2) positions occupied by Mn (4/5) and Pd (1/5) atoms. The arrangement of the Yb and Pd atoms in the body center position is random in the S-phase and is possibly ordered in the g-phase. These differences give rise to different magnetic properties. Recently, a detailed investigation of the magnetic and thermodynamic properties for both phases was carried out by H. Yamauchi, who suggested that these properties could be explained using one of two possible antiferromagnetic lattices. These have unit cells defined by a1 = a, b1 = b, and c1 = 2c, respectively; where the unprimed quantities refer to the chemical cell. The purpose of this investigation, which deals with the g-phase only, was to ascertain, by means of a powder neutron diffraction experiment, if one of these two models is indeed correct. The temperature dependence

of magnetic peaks was examined as well. ‘The powder sample, obtained from the MRC Manufacturing Corporation, had been prepared by arc melting. After heat treatment of the sample above 500° and quenching in air to room temperature, the diffraction pattern was consistent with β-Pa,jing. The tetragonal lattice parameters, a = 2.67, and c = 3.618 as reported by Yanauchi (6) were confirmed. Neutron Diffraction Results Power neutron diffraction data were collected to an angle of 2θ = 45° (λ = 1.08Å) on the β-phase of Pagh, at room temperature. These data showed magnetic peaks that could be indexed on the basis of a cell with a = 4%a and b = c. All magnetic reflections conform to the condition h + k = 0. The new cell contains the disordered P,0.4 stone at the positions, 1/2, 0, 1/2 and 0, 2/2, 1/2 hereafter referred to as the Mn site. The Pa atoms are at 0,0,0 and 2/2,3/2,0. ‘The diffraction intensities are satisfied if only the Mn moments are considered to be aligned antiferromagnetically with the spin vectors perpendicular to the c axis. If Mn alone contains an ordered moment, only the angle from the c axis may be determined (6), a saturation moment of 4.16 μB was assigned to the Mn on the basis of the observed intensity data and its temperature dependence. The observed and calculated intensities for both the nuclear and magnetic peaks are given in Table 12. The experimental Mn form factor measured by Corliss and Hastings (717) was used. te ---Page Break--- Since some Pd moment has been observed in other Palin alloys, other possible uniaxial models were investigated with the object of determining the possible limits of Pd contribution. ‘The symmetry of the Pd site does not allow for an induced P moment and indeed no substantial improvement of the agreement is noted by assuming one. Nothing may be said about the Pd moment on the Mn site since the Mn and Pd moments for this site are extremely highly correlated. ‘The temperature dependence of magnetic intensities was examined from room temperature to the transition point.

using the magnetic (101) and the contiguous mclear (101) reflection. The behavior of the magnetic moment as a function of temperature is given in Fig. 12 and compared with the Brillouin function for $= 4/2. The agreement is quite good. From this curve, B.1. Jeg = 98 was deduced and used in all calculations. From the data, it was concluded that the magnetic intensity did not disappear completely until 380°C, which is somewhat higher than the Neel point of 350° reported by Yamauchi. This temperature difference is not surprising since Yamauchi reports that imperfect quenching or partial annealing may significantly alter the Neel temperature. Also noted was a decrease in intensity accompanied by an increase in temperature in agreement with Yamauchi et al. Magnetic Intensity Program A Fortran computer program has been written to compute magnetic neutron intensities. The input consists of the atomic positions of the atoms, associated spin vectors, form factors, and indices of desired reflections. The output is the magnetic structure factor squared of the specified reflections. It has been used to calculate the magnetic intensities of Pd, CoCr2, and FeSiO. This program is available as PRIC 78. Conclusions The knowledge gained from the previous studies will be briefly summarized. The disordered hydrogen positions in copper formate tetrahydrate at room temperature have been found and some of the properties of the antiferroelectric transition at -N0° determined. The study raises many questions. Particularly, how is the structure related to the electrical effects? Since there is very little change in intensity and no change in space group in passing through the transition, a change from dynamic to static atsonder may be postulated. We hope to initiate a study that will define the atomic shift caused by an electric field. The structure including hydrogens of the three Alun (AYB)(50)+32H2O types (4, 4,7) have been refined by means of both x-ray (Los Alamos

Scientific Laboratory and neutron extraction (Puerto Rico Nuclear Center) data, The Alun, Cs Al (80,),+224,0 is reported here. Analysis is nearing completion on sodium and deutero-ammonium elune. When complete, the structure should show the effect of +1 cation size and hydrogen bonding on the structural details of the series of compounds such as the shape of the oxygen octahedron around the #1 cation and the disorder of the sulfate group (found in some Alums). Neutron data has been combined with the x-ray data of Okaya and Stemple of IBM to give refinement of the structure of d-Tartaric Acid. The hydrogen bonding scheme has been unequivocally defined by the neutron data. In addition, it has been shown once again that use of the free stone form factor will shift the nitrogen position determined from x-ray data into the bond. That is, closer to the atom to which it is most tightly bound. The phase of Pain, is antiferrimagnetic. The magnetic cell is related to the tetragonal chemical cell by the transformation at = /2a and c! = c. The magnetic moment for Mn is 4.1 + .2A. The spins are aligned perpendicular to the axes and the magnetization closely follows a Brillouin dependence from room to the Heel point.

References S.A. Friedberg and R.B. Flippen, Proc. VII Int. Cont. Low Temp. Phys. 122 (1960). Je Itoh and Y. Kamiya, J. Phys. Soc. Japan 27, Suppl. B-1, 512 (1962). T. Haseda, R. Wedena, Y. Kobayashi and S. Kanda, J. Phys. Soc. Japan 22, Suppl. B1, 528 (1962). R.B. Flippen and S.A. Friedberg, J. Chem. Phys. 38, 2652 (1963). H. Kobayashi and T. Haseda, J. Phys. Soc. Japan 18, 542 (1963). S.C. Mathur and A. Mookergi, BULL, Am. Phys. Soc. 10, 254 (1965). R. Kirylayon, H. Toanoto and K. Matsuo, Acta Cryst. 7, 482 (1954). H. Kirtyama, Bull. Chem. Soc. Japan 35, 1199 (1962). K. Okada, Phys. Rev. Letters 15, 252 (1965). L. Martin and H. Waterman, J. Chem. Soc. 1559 (1959). A.G. Chynoweth, Phys. Rev. 113, 159 (1959). K. Okada, J. Phys. Soc. Japan 16, bik.

(1961). JA, Gonzato and R. Arndt, J. Mol. Cryst. 1, to be published. 4H. Kiriyana, Bull. Chem. Soc. Japan 35, 1205 (1962). 4H. Lipson, Proc. Roy. Soc. A, 152, 347 (1935). F. Jona and G. Shirane,

Ferroelectric Crystals, International Series of Monographs on Solid State Physics, Vol. I+ 395. Oxford Ferguson, Tres Y Okaya, M.S. Ahmed, R. Pepinsky and V. Vand, Z. Krist. 109, 367 (1952). W.C. Hamilton, Acta Cryst. 12, 609 (1959). 1, Toh (1956). K.K. Trueblood, I.U.Cr. World List of Computer Programs, ed. Groningen (1962). Deli J. Cruickshank, Acta Cryst. W.C. Hamilton, Annual Review of Physical Chemistry, 15, 28 (1962). = ---Page Break--- 5. 36. A. W.R. Busing and H.A. Levy, Acta Cryst. 17, 142 (1964). Y. Stern and C.A. Beevers, Acta Cryst. 3, 341 (1950). H. Cole, Y. Okaya and F.W. Chambers, Rev. Sci. Inst. 34, 872 (1963). I. Okaya, K.R. Stouple and M.I. Kay, The Crystal Structure of a-Tartaric Acid. Submitted to Acta Cryst. J. Kroon, A.P. Peerdeman and J.M. Vijvoet, Acta Cryst. 29, 295 (1965). A.J. Van Bonne and J.M. Vijvoet, Acta Cryst. 12, 61 (1958). Y. Okaya, Acta Cryst. 20, (to be published), (1966). J. Donohue, J. Chem. 56, 502 (1952). G. Grube, K. Bayer and H. Bim, Z. Electrochem. 42, 805 (1936). G. Grube and O. Winkler, Z. Electrochem. 42, 615 (1936). B. Raub and W. Mahler, Z. Metallkunde 45, 450 (1954). J.P. Burger, R. Wenling and J. Wucher, J. Phys. Radium 20, 427 (1959). M.A.R. Wendling, Compt. Rendus 252, 408 (1961). H. Yamauchi, J. Phys. Soc. Japan, 19, 652 (1964). G. Shirane, Acta Cryst. 32, 282 (1959). L.M. Corliss, T.Y. ELLMot and J.M. Tastings, Phys. Rev. 104, 924 (1956). Joe Cable, Z.O. Wollan, W.C. Koehler and H.R. Chia, Phys. Rev. 128, BLE (1956). ---Page Break--- One nko ho on AL date Table 1 Discrepancy Indices for Copper Formate Tetrahydrate Kiriyana et al. (7) R R 0.20 0.090 0.096 0.098 0.095 Least Squares Refinement of Today Date R 0.208 0.133 0.208 The Determination R 0.052 0.201 0.220 0.208 0.080 0.086 ---Page Break--- Table 2 Heavy Atom Parameters in Copper Formate

Tetrahydrate Least Squares Kirtyann et al. Refinement of X-ray Data Task Determination to ° ° ° ° ° ° 0.84 + 0.098? 2.02 + 0b RF cx 0.258 0.238 + 0.008 0.237 + 0.00 ¥ 270 0.268 + 0.002 0.269 ¥ 0.001 z 0.018 0.018 ¥ 0.002 0.024 ¥ 0.001 B35 67 3 0.25 ob F016 op(2) x 0.206 0.207 + 0.001 0.205 + 0.001 ¥ -0.092 -0.090 ¥ 0.001 -0.092 ¥ 0.001 2 -0.080 0.081 ¥ 0.002 -0.080 F 0.001 B35 Lat F018 127 $0.16 op(2) x 0.137 o.aah 0.106 + 0.00 % 0.210 0.212 0.213 = 0.00 % 0.086 0.092 0.088 F oLoor Buss x10 us Fo. yl) x 0.425, 0.425 + 0.002, 0.430 + 0.002 E 0.399 0.400 F 0.001 o.400 F 0.002 E 0.647 0.645 ¥ 0.000 0.641 ¥ 0.008 EBL LI F021 19h F 0.20 oyl2) x 0.086 2.086 + 0.002 0.089 + 0.008 X 0.549 0.555 ¥ 0.001 0.357 F 0.008 E onkgs 0.488 F 0.002 o.B2 ¥ 0.008 E35 210 ¥ 0.25 259 $0.22 “Be ---Page Break--- Hydrogen Parameters in Copper Formate Tetrahydrate Weg 1 0.207 + 0.005 BP 0.312 + 0.005 Bf 0.481 + 0.008 22 0.475 + 0.009 20.084 + 0.003, We 0.089 + 0.009 Yh 0.295 + 0.009 Yk 0.080 + 0.007 ‘Table 5 0.652 + 0.008 0.385 + 0.005 0.296 + 0.008 0.462 + 0.007 0.520 + 0.005 0.475 + 0.010 ots 0.269 + 0.007 oon O02 + 0.008 0.592 0.598 0.005 0.005 0.528 + 0.015 0.339 + 0.005 0.860 + 0.017 0.585 + 0.015, 0.533 + 0.009 te hes oak] 33406 3.6 5 06 3942.6 BT E05 tans bteat 29409 ---Page Break--- tape & Bond Distances and Angles in Copper Formate Tetrahydrate Within the formate group c-0(1) 1.26 + oak 0(2)-c-0(2) c-0(2) ‘1.23 ¥ 0.01 ‘H-C-O(1) es EgEg3 Ease sie started octahedron shout corner Cu-Op(1) hy 2 + 0.1 oak (1)-cu-Op(2) eke kr eeyieirets} Cund(2) Op(2)-cu-)(2) water (2 cay Sale gart ik O-n(3) 1.08 ¥ 0.08 87 + be water (2) (QxiyH[A) tates past ts 21 antes because 2 bas lt visit) O-H() 9.95 + 0.068 no + 6° O-H(5) 1.08 * 0.07 126 5 5° 0-u(6) L15 ¥ 0.09 99 FAP o-n(7) 0.91 ¥ 0.07 ~ nitrogen tte (2. (2) 2.83)=H(4) =< 66 + 3° wae fp eee G,(2)-H(4)-Op(2) 166 + 3 (2)-O4(2) 2.81 (1)-H(5)-O,(2) 166 + 7° 4S: aa ee Out Oy £ tey-a(2 ” 5) ses? aay iD 27 94(2)-H(5)-9,(2) 167 + 9 (ye 5)) 2.82 Qy(1)-H(1)-O4(2) 176 + 3° 1.84 (2) ia} (2) 152 ¥ 6° ie (6)

wa} 1.90 HIRO) 0 ~ (2)~9y(2) 2.76 + Oy(2)-H(3)-0,(2) 169 + 3° 3)=0,2) t (2) #7) =O (2) 176 ¥ 6° H(7)-Gy2.) z * nie) ~ ‘Oxygens related by centers of symmetry were ---Page Break--- ays SE sas: Oltse weet Ba By ag a es z a Ze ze gekos eprcot offest 695tt watce lores ay ote zt a ay zy a alg tq ty corn ore wre 6504 6059- olor 60ST oltent Leetye- gproze~ Tei09 aH66 opt HS Stir@- oTrea-

SHBs9¢ env 66¢ ogee 6et0y Legere HOS e Ty TM, bi Ue Ty ‘eqzgoe otra ofa¢e ONtO9E bd ug " @ wrt outs one saseo wi09 ur (2°120°0 + °a)/Sx = a veqep uwos 92 au waz saqumt JonoT ou put wasp TeAsh2 pews ouy wos ow Bioquna zoddn OGL seep uovaowssaTp Aor-x masz o%Ket “(*0S)tv80 203 sxanomesed sosnbe 42007 eckLat econ sciege omens eGren Smser ectrec e204 ane ele Stet stegte Lio gen woo § orarn 9SF9¢t00 ‘0- oret0000°0| 2eepave2 "0 on Snge"0 erat a96H'0 ontleont 0 3d 55 NK MH 0$760200‘0- 1666100 "0- ng6ers0°0 SrS9089°0 Se3960nC 0 BAGOTHE'O z ypoediag-t Sovran t wdtgest'o THIKSST“O LGLIEST‘O~ Sr 2650 0 <e9g1z°0 anteeale-o sisesse-o onresee"o etsoee6"0 stle2e'0 éé 3 (20 (ayo (2)%o (eo ---Page Break--- beast squares parameters for Cshi(S0, Equivalent isotropic thermal parameters Aten, HQ) H(2) 3) H(8) ce a 0,(2) 0,(2) oy) 0,(2) a 2.8 £07 224005 1.6 $0.4 2.74006 Sed 4 3a (2.6) 0.5 £13 (2.3) 25 +07 (1.3) 3.9 4007 (25) 2.2 40.3 (2.2) 2.8 + 0.3 (2.2) 19 £02 (1.9) Table 6 0.604 2 0.750 +2 0.696 42 ose £3 Be +12ii,0 from neutron diffraction data ‘from X-ray data are in parentheses x 0.219 +2 0.222 +2 0.064 +2 0.203 +8 0.28 +2 0.995 +5 o.5ib +2 0.555 +3 ---Page Break--- Table 7 Interatomic distances and angles in CaAL(30,),-22H,0 from fixed crystal and neutron diffraction data. Standard deviations in parentheses apply to the rightmost digit Distances corrected for thermal motion are in parentheses. A - 6 0,(2) 12.882(5)R cs - 6 O,(1) 3.361(5 26 at} 33 ‘The sulfate group 8 = 0,(2) 1.479(9) 04(1)-8405(2) 109..9(2)° (alge) 05(2)-8-04(2: 109.0(2) S - 3 0,(2) L.475(5) Sola} -O5(B)-oof2) 60.0 (2485) 05(2)-05(2)-08(2) 60.2(2) Og(1)-5 09(2) 2.41 7(8)

0,(2)-0,(1)-05(2. 59-5(3) seke-€ ale) 2.39916) Water molecules Oy(2)-HQ.) 0, 961(26) H(1)-0,(2)-H(2) 207.6(24) (0.955) 0,(2)-H(2) 0.965(29) (0.968) o(2)-H3) 0.974(26) H(3)-04(2)-K(4) 107.2(20) eat) (ails) 2) . wt (0.595) Hydrogen bonds 05(2)-3 Oy(2) 2.822(6) 0,(2)-H(L)-4(2) 165(2) 05(2)-3 #Q) 1.902(25) 05(2)- Oy(2) 2. 766(7) 04(2)-H(2)-0,(2) 1m) es(2)- ate) Leugs) 0(2)-04(2) 2.648(7) 0(2)-H(5)-04(2) 166(3) 05(2)-Ht3) 2.692(27) {2)-0,(2) 2.635(7) 9461) -HC4)-04(2) 365(5) ean Co 2.657(33) Miscellaneous angles 22(2)° (1)-0,(1)-H(1) r0afny° 130 e H(1)=09(1)-8 126(2} rome H(1)-0, 109(2) H(2)-0,(2)-H(5) 101(1) (2) -0%K 126(2) 8 = 0,f2)-H(2) 19(2 #(2)-04 20803) 8 = 05(2)-H(3) 33(2) ---Page Break--- table & ‘Thermal eLispsciae in CoAL(304),*12Hg0, fixed crystal date ters cs 0) 04(2) (2) 9,(2) RS Amplitude g Ges Gee SE SSE g ERG E pee pirection angles relative to crystel axes KER BEB GOBER MYR rrr 1.68 Lak wae ae 8 Ro LB Bie 2.6 a5 02 fret BER 35- Y a? ST MT 5h ¥ 7 Skt 5h.T Bu reise zen ane & evel Ono CRF ---Page Break--- rable 9 ‘translation and torsional vibration matrices for the sulfate group relative to the unit cell axes 0.0160 0.0015 9,0025 feg.2 8.8 8.8 0,060 0.0015 | R 2 #1 29.2 8.8 \ deg? 0.0160, 29.2 0.0020 9.007 9.007 SL 59 BD CH). (0.0020 0.0027 Rad 5.1 3.9) dee ® o.oo) * 52 360 ---Page Break--- ole a gee w obye st 096s * x 6 &t Ee wore surnsoy uoyaoesss70 worsen % zot'o- %6 2yG'0 % ste-0 é ee0 « zero % eo “ 61200 z $008°0 n oreo & y62"0 kz Lt20°0" ee S9L0"0~ eS $906"0 @ 909° B 62°90 % ecko % x sway Ot uF moTeTASP yyeuTpzo09 STuOWY “(8) OT STEVE ' ' t . e a ---Page Break--- es et vn 19 at ot (oH (St (Ht (ou (eye (oH FP 9 ~ OT uy CesgR waBorPAY soz sxogo8s oangusadon oydos.0eT ---Page Break--- able 11 (a) Bond distances involving hydrogen atoms from coordinates determined from the neutron study. (2) ~ HC) (2) = Ht) afk) = HGS) (5) = H(6) (2) - (2) (3) = (2) (>) Bond angles in degrees ‘around oxygens eq.) 18s (a: hg $3 (3) 243 oth) = 0f5) = a n5 Fh around ¢(1) HL) = of2) = 02) aah 3 H(1) - (2) ~ cf2) ‘107 $3

H(1) ~ e(2) - o(3) 0 F5 ‘round ¢(3) H(2) - c(3) - o(4) nrsh (2) = 6(3) = of iors wa) 2603 26th) dog Eh 39- ---Page Break--- TABLE 12 Hydrogen-bond system in the D-tartaric acid crystal. ‘The second values for H-0, H..0 and angles around hydrogens are those obtained by the neutron study. Bonds A 2 c > From (2) (4) (2) (5) te (6) (3) a) (5) of (my Bey de) Gey dey ae) Gx Beye) (lem ye) Hydrogen (3) H(5) (4) (6) irvoived Distances 2.839 2.909 2.653 2.707 (a) Ont 0.8, 0.98 0.8, 0.97 2.9, 1.00 0.9, 1.00 He--0 2.1, 1.86 21, 195 1.8, 1.64 Lg, LTD ingles sro 157°, 11° 112°, 1698 176°, 172° 152°, 168° hydrogens: Separations Listed by 0-0, 0, 05 0, -7 Os -0 Stern and Beevers ---Page Break--- TABLE 15 A comparison of the observed and calculated intensities (a) from Paling at T= 297K. no Ios (teate), (roade), ojtova (200) 26.2 0.05 oon. 28.7 a 0.05 100 332 3h9 o.0k cca) 26.0 2b. 0.05 ao. wA3 wa 2.07 ao 5.6 5d 0.35 (eno) 2h oe 3b an 0.09 an 21.0 (noe) Bat (212) aa 35 oe oe ant 0.07 200 a1 0.35 (a) both nuclear and magnetic intensities given are, per chemical unit Celie Mbgg © 0159 5 10" cay yy = 0436 x 207 ess 5 2B = 1G ---Page Break--- ---Page Break--- ---Page Break--- ---Page Break--- Fics 4b omubte nestereas oops of 108 ---Page Break--- ayazveroea, De JUNLVEIGN3L St- Ov- Sb- 0" Hp - *(000H) 99 NI NO! SIS3Y31SAH TWWY3HL ISNVYL 3HL 40 AINA AXVYLIGYY LNVLSNOO 9141937310 ~ ---Page Break--- oayoaTaoIp FAUT O43 uo De JUNLVHIdWIL Se- Ov- Sb- O'Hb (OODH) 99 NI NOILISNVEL 3HL NO 493443 SVI8 30 LIND ASVELIBYY LNVLSNOD 9141937310 ~ ---Page Break--- ---Page Break--- ---Page Break--- ---Page Break--- H(4) jos O12) O13) 13Ig An. 120 C12) 2 1.52. “TET 0.95 H(N-C(1) 140g 0.84 (5) O14) 1.545 OW) —H(3° 140 C13) 0% oN 8 | oft) 25 1Sly C(4) Wl I3lg Lig 5) Olé) 8 ot 0.87 H(6) Fig. 10 Bond distances of d-Tartaric Acid from X-ray diffraction ---Page Break--- Figs 2 125.9 Bond angles of d-Tartaric Acid from X-ray diffraction ---Page Break--- (22fea w22) £303 9 roxnqeisdiog, paowar Bh oyyeaTae" BL seT (u1/4) 3unavaaam31 039NG3e NOLLVZILINOWW

391LLv7ENS --- Page Break ---