

# PRNC084

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PUERTO RICO NUCLEAR CENTER

NEUTRON DIFFRACTION PROGRAM

PROGRESS SUMMARY REPORT NO. 4

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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

it 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

atoms with unpaired electrons. Since the magnetic properties of substance

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).

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## Copper Formate Tetrahydrate

### Introduction

The physical properties of copper formate tetrahydrate have been extensively

(2,5,4,5,6)

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 Kiriyama,

Toanoto, and Vateuo (7), who found the crystal to be monoclinic, space group

$P2_1/a$  with

$a = 8.25$ ,  $b = 0.28$ , and  $c = 6.35$  Å,  $\beta = 101^\circ 5'$  and with two formula

units per unit cell. A dielectric anomaly at  $-38.9^\circ\text{C}$  has been reported by

Kiriyama (8) and independently by this laboratory, (9). 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 anomaly.

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  $z = 1/2$ ,

where Fig. 2 it has been proposed (10) that the magnetic ordering arises from

exchange through the formate groups. The Cu-Cu distance within the copper formate layers is 5.77%. The shortest Cu-Cu distance between layers is 6.35%, 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.

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#### Preparation of Specimens

Saturated solutions of copper formate were prepared by dissolving  $\text{CuO}$  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 cut along each of the three crystallographic axes. These crystals were sealed

in thin glass tube

A drawing showing the crystal habit is given in Fig.3.

The Phase Transition

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As noted in a preliminary report by Chakraborty et al., an antiferroelectric transition

occurs in copper formate tetrahydrate at  $-30.9^{\circ}\text{C}$ . 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 Chakraborty et al. 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.

versus polarization, within a small temperature range.

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Figure 1a 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% and a large discontinuous decrease occurs at this temperature. Above this transition point,  $T_c$ , the Curie-Weiss law,  $\epsilon = C/(T - T_c)$ , is satisfied, and a plot of the reciprocal dielectric constant versus temperature is a straight line, as seen in the figure with  $T_c = -58^\circ\text{C}$  and  $C = 3.2 \times 10^4 \text{ }^\circ\text{C}$ . The (00L) 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 shows a small discontinuity

at  $T_c$  as shown in Fig. 1a. 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 (00), "

crystal plate. This high anisotropy can be expected from the predominant 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. 1b).

On passing through the transition point, the loop disappears. The double hysteresis loop was observed only in a narrow temperature region from  $-42.6^{\circ}\text{C}$  to the transition point. This range seemed to depend upon the applied ac amplitude.

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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  $19\text{ KV/cm}$ , 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 jerky. In short 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  $0.07^\circ\text{C}/\text{min}$ . and the accuracy of temperature measurement was  $\pm 0.05\%$ , The temperature was first lowered from room temperature to  $-63^\circ\text{C}$  and then raised. A thermal hysteresis of  $0.3^\circ\text{C}$  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. 64

Superimposing a DC field on the 1000 cycle AC field of equal 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.

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X-ray photographs, using precession camera and CuK $\alpha$  radiation, were

taken at various temperatures from room temperature, about  $20^\circ\text{C}$ , to  $-50^\circ\text{C}$ .

The photographs were recorded on the same film by moving the cassette a small

four 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

$P2_1$  (8,18)

results are in agreement with Kiriyama and indicate that

the transition probably results from hydrogen motion. Thermal expansion

coefficients are  $5 \times 10^{-6}$ ,  $-2 \times 10^{-7}$  and  $8 \times 10^{-6}/^\circ\text{C}$  along a, b, and c respec-

tively.

Some hko neutron reflections were measured below the Curie point. No

reflections which should be absent in space group  $P2_1/a$  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 axes of copper formate tetrahydrate at room temperature,

Torentz corrections, and in the final stages of the analysis, emprtical extine-  
?tion corrections were applied, Full matrix Least aquares refinements using  
Asotropic temperature factors and with separate scale factors for each zone  
minimized  $\chi^2$  (984 where  $w = 1/(6P + 0.005F)$  and  $sP$  was based on counting  
statiaticn For unobserved reflections  $w = 0$ .

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The OO reflections from the Oke and nO zones also had  $v = 0$  because they  
vere so strongly influenced by extinction. Discrepancy indices quoted are  
 $R_{int} = \sum |F_o| / \sum |F_c|$  and  $R_y = \sum |F_o|$  with unobserved reflections  
omitted. these values are listed in Table 1.

The xeray data of Kiriyan et al. ( ) vere refined by least aquares using  
?eotropic temperature factors and with weights  $w = 1/(P, + 0.027.2)$ , The orte-  
inal paraneters, the Le

t squares parancters and our final heavy toa pareneters  
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 nonhydrogen atoms found by Kiriya 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 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<sup>-</sup> in one position and H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> 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.

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We were then led, partly by small features in the difference Fourier and partly by the known geometry of water, to a picture of statistically disordered water molecules. It was

the disordered water molecules, it was this

order 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)-O-H(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(4) has unit weight, H(5) has weight  $1/2$  and H(6) and H(7) have weight  $W_i$ . In half of the unit cells the orientation is H(4)-O-H(5), in one fourth

St A<sub>e</sub> 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  $R_w = 0.066$ . The resulting hydrogen parameters are given in Table 5.

From PMR measurements Kiriyana (?) 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  $R_w = 0.356$ . The agreement is clearly less satisfactory than for our disordered model. One might argue that the positions of H(5), H(6) and (7) are approximations to a free rotation of minima in a hindered rotation. However, the presence of curvature H(5), omitted in Kiriyana's model, does seem to be necessary for good refinement of the

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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 result

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  $Y$  odd, are sensitive to the  $z$  parameters. Finally,

we have postulated that the positions of all atoms are independent of the positions of all other 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

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 hydrogen-bonded crystals. The proposed disorder

permits all of these contacts to be hydrogen bonded all of the time. Somewhat

similar Gitter order is, in fact, found in ice.

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?The class  $48 \text{ NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . The alum forms. If the cation is 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  $\text{KAl}(\text{SO}_4)_2$  and  $\text{NaAl}(\text{SO}_4)_2$  alums also has six waters in a nearly regular octahedron.

The large cation in  $\text{Al}_2\text{O}_3$  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 this axis until the four equatorial oxygens are nearly planar. The two ends of the resulting trigonal antiprism are separated by only about

0.068 Å. 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  $\gamma$  structure six water molecules approach the small sodium cation much more closely than in the  $\alpha$  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 Shirane (10). One of the alums has been investigated by modern counting techniques although Okaya, Ahmed, Pepinsky

ar

and Vand on have studied monomethyl ammonium aluminum sulfate dodecahydrate

(sp) ty photographic methods and refined the structure by least squares.

rave et ats 7) ao not ctassity 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 my be clearly

distinguished and that MASD is a meaber of the palims. The characteristic

that distinguishes the 7 aluns tron theg and aaluns is the orientation of

the sulfate group. In the 7 aluns this group is oriented opposite to its

orientation in theqand@alums, The saluns have twelvefold and thew alums

have sixfold coordination of cxygen about the central, monovalent cation.

an

Okaya et al. yrobably overlooked this difference in coordination because

the distances which they state are from the center of gravity of the CHI,\*

on are actually frem the nitrogen or carbon atous of the disordered ion.

Several of the aluas have been investigated using both X-ray and neutron

Diffraction methods. The x-ray data was taken at Los Alamos Scientific

laboratory and the Neutron Data at Puerto Rico Nuclear Center.

cesium Alum (Ce AL (50,0)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 remain-

der were suspended in a saturated solution which was then allowed to evapor-

ate slowly. An octahedron, mm on an edge, was selected for study.

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The crystal was briefly immersed in Liquid nitrogen to increase its moisture

and thus reduce the effects of extinction. The neutron diffraction

intensities of the  $h0l$  zone were measured. Using a wavelength of 1.068, none

equivalent reflections within the range  $2 \leq \theta \leq 90^\circ$  were measured, of these, 6

were observed according to the criterion  $(I - \text{Background}) \geq 2.0 \times (\sigma + \text{Background})^{1/2}$ ,

Because of the large incoherent scattering of hydrogen, absorption corrections

were applied, The Linear absorption coefficient for Ce alum is 452 cm<sup>-1</sup>.

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,

$U_{ij} = [U_{11} \quad U_{12} \quad U_{13} \quad U_{21} \quad U_{22} \quad U_{23} \quad U_{31} \quad U_{32} \quad U_{33}]$

Two sets of X-ray data were taken; one with a fixed counter, fixed crystal technique, and the other using a  $\theta$ - $2\theta$  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

scattering angles a small portion of the intensity is lost because of  $2\theta$  separation.

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## 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  $|F_o| = |F_c|$ , and a difference Fourier projection was calculated. Approximate hydrogen positions were obtained and a least squares refinement minimizing  $\sum w(F_o - F_c)^2$  was calculated where  $w = 1/(F_o + 0.02)^2$ . 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 atoms were not allowed to move, Table 6 gives the final parameters. Fig. 8 is a difference Fourier showing hydrogen atoms 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

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and their different thermal parameters. Therefore, the correlation between  $r_{eq}$  and  $B_{eq}$  is large (-0.82) and is manifested 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 (9) using

(20)

2 code written by Trueblood, the 7 angle matrix

are in Table 9. Corrections

to the S-O distances were computed according to the in phase assumption of Busing and Levy (1962), 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  $85.7^\circ$  with the S-O bond and the smallest axis makes an angle of  $9.1^\circ$  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 O(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  $\sin^2 \theta / \lambda > 0.1$  (O.M.R.-1, The O-H bond lengths were corrected

for thermal motion according to Busing and Levy (1962) by using the isotropic

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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 analysis of hydrated crystals. H(1) on O<sub>1</sub>(2) is bonded to O<sub>1</sub>(1) and this oxygen, being on a threefold axis, is bonded to three hydrogen atoms. A somewhat elongated trigonal pyramid consisting of the three hydrogen atoms and the sulfur atom thus surrounds O<sub>1</sub>(2). H(2) on O<sub>1</sub>(2) and H(3) on O<sub>2</sub>(2) are bonded to O<sub>2</sub>(2). These hydrogen atoms and the sulfur atom are nearly co-planar with O<sub>2</sub>(2). H(4) on O<sub>3</sub>(2) is bonded to O<sub>3</sub>(1). The angles involving H(2), H(3) and H(4) about O<sub>2</sub>(2) are nearly tetrahedral.

Stammiton (22) 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

O angles, all of which are nonlinear, but again the differences between the present experimental values and the empirical curve are not significant.

patnough the present results are of considerably greater accuracy than  
those of (Tompson 9), the minimum shift in atomic position is only 0.04 Å.  
Except as noted, all calculations on the alum were performed on an

TIN 7094 at Los Alamos using codes written by Larson, Root and Cromer (92),

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other Alums

Neutron diffraction (and X-ray data have been taken on scandia 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,

or tartaric acid.

The crystal structure of d-tartaric acid was determined some fifteen  
years ago by Stern and Beevers (2%) by 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 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 TRW 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  $a = 7.715 \text{ \AA}$ ,  $b = 6.006$ ,

$c = 6.251 \text{ \AA}$ ,  $\beta = 100.1^\circ$ , the space group  $C_{2h}^2$ .

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(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 an IBM 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 real 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 (h0g and hk0) zones of neutron diffraction data were taken. Because of an accident, the h0a 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  $w = 1/(\sigma(F) + 0.025F)$  where  $\sigma(F)$  is based on counting statistics, Non-observed reflections were given zero weight. The resultant

Parameters are given in Table 10.

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## 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 carboxyl

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

I, C(1), O(1), 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 11; this is mainly due to the large (4) ~  $\phi$ (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 analysis are made in various crystals with tartaric as well as mesotartaric ions. The planes of the two parts make a dihedral angle of 54.69°, In these two carboxyl groups which retain their protons,

there are two distinct C-C-O angles; narrow C~

O-H of around 120° and wide

-19-

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C-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-O angles become almost equivalent and are about 118°. The change in the shape of carboxyl groups due to the state of ionization was exhibited in various acid salts of tetracarboxylic acids, e.g., ammonium hydrogen D-tartrate

(21), dipotassium ethylene-tetracarboxylate, 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 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 (2) and (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 ion 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

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are, about 15% 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 (see Table 12)

angles which were found to be less than  $160^\circ$  by x-rays are shown to be closer

to  $170^\circ$ . 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  $\text{SrPd}_2\text{Si}_2$

Introduction

At room temperature  $\text{SrPd}_2\text{Si}_2$  has a tetragonally distorted CsCl type crystal

structure, with (0,0,0) positions in the unit cell occupied by Fe atoms, and

(1/2,1/2,2/2) positions occupied by Mn (4/5) and Fe (1/5) atoms. The arrangement

of the Yb and Pd atoms in the body center position is random in the

β-phase and is possibly ordered in the α-phase. These differences give

rise to different magnetic properties (5°), recently, « 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

lattices have unit cells defined by  $a' = J$

$a' = a$  and  $c' = 2c$ , respectively;

where the unprimed quantities refer to the chemical cell. The purpose of

this investigation, which deals with the β-phase only, was to be ascertain,

---Page Break---

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  $\text{Fe}_2\text{P}$ . The tetragonal lattice parameters,  $a = 2.67$ , and  $c = 3.618$

as reported by Yanaguchi (6) were confirmed.

#### Neutron Diffraction Results

Power neutron diffraction data were collected to an angle of  $2\theta = 45^\circ$  ( $\lambda = 1.08 \text{ \AA}$ ) on the  $\beta$ -phase of  $\text{Fe}_2\text{P}$ , at room temperature. These data showed magnetic peaks that could be indexed on the basis of a cell with  $a = 4a$  and

$c = c$ . All magnetic reflections conform to the condition  $h + k$

aaa.

the new cell contains the disordered  $\text{P}_{0.4}$  ions at the positions,  $1/2$ ,

0, 1/2 and 0, 2/2, 1/2 hereafter referred to as the Mn site, The Pa tons 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  $\phi$  axis, If Mn alone contains an ordered moment, only the angle from the  $\phi$  axis may be determined. The saturation moment of 4.16. 2M

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?

Gn

form factor measured by Corliss and Hastings [7] was used.

te

---Page Break---

Since some Pd moment has been observed in other Pd alloys, other possible uniaxial models were investigated with the object of determining

?the possible Limits of Pa contribution.

?The symmetry of 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 Fd moment on the Mn site since the 1 and Pa 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  $S = 4/2$ , ?The agreement is quite good. From this curve  $B.1. J_{eff} = 98$  was deduced and used in all calculations.

From the data, it was concluded that the magnetic intensity did not disappear completely until 380° which is somewhat higher than the Neel point of 350° reported by Yamauchi (99), this temperature difference is not

surprising since Yamauchi reports that imperfect quenching or partial anneal-

ing may significantly alter the Neel temperature. Also noted was a decrease

in  $\chi$  accompanied by an increase in  $\chi$  with increasing temperature in agreement

2)

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### 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.

23.

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?The output is the magnetic structure factor squared of the specified reflections.

It has been used to calculate the magnetic intensities of PA,)ing, Ci Cr 2 and Fe,SiO,

?The program is available as PRIC 78.

we 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 antiferro-  
electric transition at  $-N0^\circ$  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 disorder

may be postulated. We hope to initiate a study that will define the atomic

disorder caused by an electric field.

?The structure including hydrogens of the three Alun (AYB) (50, ) $+32H_2O$

types (4, 4,7) have been refined by means of both x-ray (Los Alamos

Scientific Laboratory) and neutron diffraction (Puerto Rico Nuclear Center)

data, ?Thep Alun, Cs Al (80, ) $+224H_2O$  is reported here. Analysis is nearing

completion on sodium and deuterio-ammonium chloride. When complete, the structure

should show the effect of  $+1$  cation size and hydrogen bonding on the struc

?tural details of the series of compounds such as the shape of the oxygen

---Page Break---

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 dTartaric 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 ion 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  $\beta$ -phase of  $\text{PbCl}_2$  is antiferromagnetic. The magnetic cell is related to the tetragonal chemical cell by the transformation  $a' = a/2$  and  $c' = c$ . The magnetic moment for Mn is  $4.1 \pm 0.2 \text{ \AA}$ , The spins are aligned perpendicular to the  $c$  axis and the magnetization closely follows a Brillouin dependence from room to the Néel point.

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Table 1

Discrepancy Indices for Copper Formate Tetrahydrate

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0.20 0.090

oz 0.096

onan 0.098

0.095

Least Squares

nefindment oF Tofay Date

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0.208

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Table 2

Heavy Atom Parameters in Copper Formate Tetrahydrate

Least Squares

Kiriyann et al Refinement of x-ray Data

CO ° °

° °

° °

0.84 + 0.098? 2.02 + Ob 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

¥ -c.092 -0.090 ¥ 0001 -0.092 ¥ 0.001

2 -0.080 0081 ¥ 0-002 -0.080 F 0-001

B35 Lat F018 127 \$0.16

op(2) x 0.137 o.aah 0.106 + o.oo

% 0.210 0.212 0.213 = o.oo

% 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.4on 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 0,0b0 + 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

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33406

3.6 5 06

3942.6

BT E05

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## Bond Distances and Angles in Copper Formate Tetrahydrate

Within the formate groups

C-O(1) 1.26 ± 0.01 Å

C-O(2) 1.23 ± 0.01 Å

H-C-O(1)

Octahedral geometry

Cu-Op(1) 2.01 ± 0.01 Å

Cu-Op(2)

Cu-Op(3)

Water (2)

Water (2)

O-H(3) 1.08 ± 0.01 Å

Water (2) (QxyH[A] tates past ts 21 antes because 2 bas It visit)

O-H(4) 1.05 ± 0.01 Å

O-H(5) 1.08 ± 0.01 Å

O-H(6) 1.05 ± 0.01 Å

o-n(7) 0.91 ¥ 0.07 ~

syrogen tte

(2. (2) 2.83 )=H( 4 ) =< 66 + 3°

wae fp eee G,(2)-H(4)-Op(2) 166 + 3

(2)-04(2) 2.81 (1)-H(5)-0,(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)-04(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

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beast squares parameters for Cshi(S0,

Equivalent isotropic thermal parameters

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3)

H(8)

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224005

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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 dat

?from X-ray data are in parenthesisii

x

0.219 +2

0.222 +2

0.064 +2

0.203 +8

0.28 +2

0.995 +5

0.51b +2

0.555 +3

---Page Break---

Table 7

Interatomic distances and angles in CaAl<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O

from fixed crystal and neutron diffraction data.

Standard deviations in parentheses, apply to the right most digit

Distances corrected for thermal motion are in parentheses.

A - 6 O, (2) 12.882(5) Å

Ca - 6 O, (1) 3.361(5) Å

26 at} 33

?The sulfate group

8 = O, (2) 1.479(9) Å 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 eLispaciae 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

direction angles relative to crystal axes

KER BEB

GOBER MYR

rrr

1.68

Lak

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ae 8

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a5

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ST MT 5h

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7 Skt 5h.T

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Ono CRF

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table 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

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kz Lt20°0"

ee S9L0"0~

eS \$906"0

@ 909°

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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

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Table 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  $\phi(1)$

HL) = of2) = 02) aah 3

H(1) - (2) ~ cf2) ?107 \$3

H(1) ~ e(2) - o(3) 0 F5

?round  $\phi(3)$

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-O, H..O 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)

involved

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

angles

src 157°, 11° 112°, 1698 176°, 172° 152°, 168°

hydrogens:

Separations

Listed by 0-0, 0, 05 0, -7 Os -0

Stern and

Beavers

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TABLE 15 A comparison of the observed and calculated intensities (a)

from Paling at T= 297K.

no los (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

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ayazveroea,

De JUNLVEIGN3L

St- Ov- Sb-

0" Hp - \*(000H) 99

NI NO!

SIS3Y31SAH TWWY3HL

ISNVYL 3HL 40

AINA AXVYLIGYY LNVLSNOO 9141937310

~

---Page Break---

oayoaTaolp FAUT O43 uo

De JUNLVHIdWIL

Se- Ov- Sb-

O'Hb (OODH) 99 NI

NOILISNVEL 3HL NO

493443 SVI8 30

LIND ASVELIBYY LNVLSNOD 9141937310

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H(4)

jos

O12) O13)

13lg 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)

WI I3lg

Lig 5)

Olé) 8 ot

0.87

H(6)

Fig. 10 Bond distances of d-Tartaric Acid from X-ray diffraction

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Figs 2

125.9

Bond angles of dTartaric Acid from X-ray diffraction

---Page Break---

(22feaw22) £303 9

roxnqeisdiog, paowar Bh oyyeaTae" BL seT

(u1/4) 3unavaaam31 039NG3e

NOLLVZILINOWW 391LLv7ENS

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