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PUERTO RICO NUCLEAR CENTER

NEUTRON DIFFRACTION PROGRAM

PROGRESS SUMMARY REPORT NO. 5

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?The neutren diffraction group at the Puerto Rico Mucleer Center hes

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 atom is very weak

and its position can be determined only with great difficulty. If neutrons

are used, however, they are scattered by the nuclei of the atoms, and at

a certain extent, diffraction of neutrons by light elements compares favorably

with that from heavier elements,

There is also a neutron-nucleus spin interaction in compounds which

possess atoms with unpaired electrons. Since the magnetic properties of

substances are related to the way the electron spins are arranged within

the crystal, neutron diffraction provides an accurate method for deter-

mining such spin arrangements (magnetic structures).

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Yanganese Formate Dityarate

1. Introduction

In two papers by Okada (1965) and Okada, Kay, Crouer, and Almodovar (1965) the crystal structure and some of the electrical properties of copper formate tetrahydrate were described.

The more common and more stable form of the plus two formates of transition metal size similar to copper or manganese is a monoclinic dihydrate phase. Of known similar structure are the cerium and manganese (Osaki, Takai and Watanabe) (1954), hereafter referred to as (1), iron (2963), copper (4 puxowska-strayzevsia (1965), hereafter referred as (38), and nickel (Krogunn and Mattes (1963). The present study defines the hydrogen positions in at least one of these compounds (manganese) which should be typical of the group. As might be expected from the greater stability of the dihydrates, the manganous formate shows a stable hydrogen bonding scheme with no disorder.

The crystal structure of Mn formate dihydrate has been determined by W (2964) and by Mascarenhas (1954). The cell parameters ($a=0.6$, $b=7.29$, $c=9.60$, $\beta=97.7^\circ$) determined by the former authors were used in the present study. The space group is $F2s/e$.

The structure consists of Mn atoms at cell corners related by symmetry to Mn atoms at face centers. A second set of Mn positions is found in the face centers. In other words set one is in the plane at $x=0$ and set

Two at $X=1/2$, The Manganese atoms near $X=0$ are linked together by formates in the manner of copper formate (Okada, Kay, Cromer, and Almodovar).

To complete the octahedron around Mn_1 atoms, the second formate group links Mn to the plane approximately perpendicular to (100). The structure is shown in the stereogram in Fig. 1.

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a

The octahedron around Mn_2 is completed by water oxygens. The environments around the two types of manganese are thus radically different from each other; one is octahedrally coordinated to six formate oxygens and

the other to two formate oxygens and four water oxygens. This structure probably accounts for the two magnetic transitions (Abe, Vorigait, Matsumura, Torii and Yeemngta (1961)) found in Mn formate at 5.7K and 1.7%. According to Abe et. al. (1964), cations on the first site, only, probably order, first at 5.7 and then totally at 1.7%

TE, Bagerizental,

Three zones of neutron diffraction data were taken on $(Mn(HCO_2)_2 \cdot 2H_2O)$ crystals grown from water solution to find the hydrogen positions. A set of approximate parameters were found using (Fylke ~ Fyn,c,o) Fourier projections and refined by means of least squares (Roof, Craner, and Larson (1965)) to an R of 0.12.

The final parameters are given in Table T and compared with the results of Gi. xcept for the y coordinate of C2, all coordinates agree within 2c. This ecrepancy seems to effect only the 05-C2-0h angle as seen in Table Tia.

MIT Conclusions

The hydrogen bonding schene indicated by OHW is correct. It might be noted that there are water-cxygen to oxygen approaches that could be conceivably hydrogen bended of the order of 3.18 The hydrogen positions do not, however, ndait of such Linkages and difference maps show no significant extra hydrogen density net ascribable to anisotropic vibrations.

It will be noted that the formate hydrogens have enormous temperature factors which are equivalent to root mean square amplitudes of vibration

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a
about .38, the stereo projection presented in Fig. 1 shows the formate

hydrogens surroundings are such as to permit a good deal of flapping; i.e. the tgeto other atom distances are elt creater than 2.58

We may then conclude that the Gitydrates unique tydrogen bonding scheme

?and three dimensional formate bridging array may be correlated with the

greater stability of these compounds as compared to copper formate tetrahydrat

Copper Formate Dihydrate

Introduction

During the early phases of the manganese formate work, Bukawski-Strayzevake published a refinement of copper formate dihydrate from three zones of x-ray data. The refinement consisted of Fourier projections with the Co abstracted. No attempt was noted in the paper to either do complete difference maps or to even compute 1 Fe map to eliminate series termination errors. The low R of ≈ 1 was probably due to the effect of the heavy copper scattering.

Noted was the greater distortion of the octahedron of oxygens about

copper in comparison to nickel (Kiroman and Matt

(1965)) by elongation of

?two of the six Cu-O bonds (see Table I). BS correlated the elongation of

the Cu-O with the elongation of C-O in the formate group. The extent of the elongation noted amounted to -0.02 and 0.058 differences in the carbon-oxygen approaches in the two formate groups (Table I). Such differences imply a fair degree of difference of bond character between the two C-O bonds in a formate ion. The effect is somewhat larger than might be expected from the differences

between the oxygen linkages to different types of copper orbitals.

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oS

TL, results of Cu Formate Refinement

For these reasons we re-refined the x-ray data by means of Least Squares using the program of Roof, Cromer and Larson (195) using a weighting scheme of $W = (F_o + \text{zero})^2$ with correction for anomalous dispersion for the copper, the results are given in Table II together with the results of BS.

?The coordinates

ace translated to the origin used by GH and the atoms
relabeled for easy comparison with the Hn formate work.

se 6-0 distances in the copper formate Dihydrate now agree quite well
with the 0-0 distances in other formates, including copper formate «Mi,0,
within the standard deviations of the standard,

5S reported a O2-O3 hydrogen bond of 2.99 Å the OF related to the
© at 2.998 from Oye by the screw axis transformation 18 choten, © 2-03
distance of 2.76 Å found. This is the hydrogen bonded approach found in
sanganese formate.

ssynarous Copper Formate

Ts Introduction

1h three Generalized Least squares refinement of the anhydrous copper

formate x-ray data of Barclay, and

ymnaré (1961) was used using the Roof,

Croner, and Larson (1965) program. Anisotropic temperature factors and an
empirical extinction correction were included. The results were in very

good agreement with the Barclay and Kennard Fourier results. There was,

however, just enough change to bring all C-O distances within 2 standard deviations of the average, confining our results on Copper formate dihydrate.

The new distances and angles are given in Table IIb and the positions) end

thermal parameters in IIIb.

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TZ, Conclusions

The general molecular geometry of the various transition metal formate inorganic isomorphous with Mn has been determined by the various authors quoted. The study reported here defined the hydrogen bonding scheme, There are clearly some distortions, as expected in the octahedral surroundings of the metal ions.

Fine details (i.e., of less than $\approx 0.05\text{\AA}$) are not established in any of these compounds except possibly the i, It is clear that three dimensional, x-ray counter work and neutron diffraction on a deuterated compound are needed.

ums

1. Introduction

In our 1966 Annual Report (FRICOH) and in Cromer, Kay, and Larson (1966) the structure of the alum, $(\text{C}\&\text{AL}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O})$ was described. The structures as exemplified by $\text{M}_2\text{Al}_2(\text{SO}_4)_6 \cdot 12\text{H}_2\text{O}$ respectively, have now been completed. The x-ray work was done by Cromer and Larson at Los Alamos Scientific Laboratory. Neutron diffraction data was taken at PERMCs to determine the hydrogen positions.

The Alums are a large class of double salts having the general formula $\text{M}_2\text{B}_2(\text{RO})_6 \cdot 12\text{H}_2\text{O}$ where A can be $\text{W}, \text{V}, \text{Cr}, \text{Mn}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Co}, \text{Fe}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{Bi}, \text{Sb}, \text{As}, \text{Sn}, \text{Pb}, \text{Bi}, \text{Sb}, \text{As}, \text{Sn}, \text{Pb}, \text{Bi}, \text{Sb}, \text{As}, \text{Sn}$; B can be $\text{Al}, \text{Fe}, \text{Mg}, \text{Zn}, \text{Ni}, \text{Co}, \text{Cu}, \text{Mn}, \text{Cr}$; R can be $\text{H}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{Ga}, \text{Ce}, \text{Pr}, \text{V}; \text{R}$ can be $\text{H}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{Ga}, \text{Ce}, \text{Pr}, \text{V}$.

The compounds are cubic with space group $\text{Pa}\bar{3}$ (240 Table IV). The gross structures were originally determined by Lipscomb (1935) and refined in the present work.

The type of alum formed depends on the size of the trivalent cation.

When the cation is small the 7 alum forms, the only known representative of this class is $\text{NeAl}_2(\text{SO}_4)_6 \cdot 12\text{H}_2\text{O}$, the 4 alum forms if the cation is large and

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ot

the g_1 alun, 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 grand alun also has six waters in a nearly regular octahedron.

The large cation in Falun 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 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 γ structure six water molecules approach the small sodium cation much more closely than in the α structure. This notion 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.

From Table IV, it may be noted that 640 on the threefold (XXX) axis

(vetonging to the sulfate group) is pointed towards the AT position $\{a/2, 2/2, 1/2\}$ in the 7 alums, but towards the AL[?]® et the cell origin in oh and Pato.

IT Y-Kum: WakL(50,)9°22H,0

The atom positions found (Table IV) do not differ by more than about

0.058 from those reported by Lipson (1956). The hydrogen parameters are

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4.

tabulated in Table V. The interatomic distances and bond angles are given in Table VI. The standard deviations were calculated using the entire variance-covariance matrix and include the lattice parameter error. However, the values involving hydrogen atom positional parameters from the neutron data refinement assume no error in heavy atom positions.

The water molecules about the aluminum atom form a perfect octahedron although this is not required by the crystal symmetry. Whereas the principal orthogonal axes of this octahedron coincide almost exactly with the cell axes, and within a few degrees in alum, the octahedron at the origin in 7 alum is rotated by 39.4° about the threefold axis of the body

Along the diagonal of the unit cell, The Al-O distance to the sites in both Cs alum and Na alum, The octahedron of water about the sodium atom is somewhat distorted by being stretched out along the threefold axis of the cell.

The angles in the sulfate group depart from those of a regular tetrahedron by a small but apparently significant amount, The differences, for equivalent angles, are in the same direction as those in Cs alum although the departure from tetrahedral symmetry of the sulfate group in Cs alum were not significant. The rigid body motion, discussed below, might well account for the apparent deviation from tetrahedral symmetry, The anisotropic thermal parameters for both neutron and x-rays work are given in Table VI a and b

The anisotropic thermal parameters of the sulfate group do not seem to be consistent with the rigid body analysis given by Cruickshank (1956).

We might expect a torsional oscillation of the group about the threefold axis. However, the major axis of the $O(2)$ thermal ellipsoid, instead of being normal to the threefold axis is at an angle of 65.5° , I believe that this is a case in which the translational and the rotational motions are coupled.

Thus the Cruickshank analysis does not apply. The $O(2)-O(2)$ hydrogen bond

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is fairly short, 2.62 Å, and the $O(2)-H$ distance is 1.64 Å, The principal axis of the $O(2)$ thermal ellipsoid makes an angle of 44.5° with the S-O bond and an angle of 79.9° with the $O-ti(4)$ bond, Thus a motion of 0.367%

(the rime, amplitude along this axis) changes the O---i(!) Aatance from OAR to 1.628, a small amount. However, if this 0.368 motion were to be ddrected along a Line normal to both the §-0 bond and the threefold axis, the O--st(h) atatance would be reduced to 2.538 This sulfate group Mes on & threefold axis so that a simple rotation about this axis will reduce three Onnaif Alstances and ve reason that the whole group therefore is forced to translate along the threefold axis vnevenver it rotates about this axa.

Figure 2 Sa a stereo view of a portion of the structure, A sulfate group {2 at the center of the figure and the direction of view is normal to ?the threefold axis and in « plane containing the \$-0,(1) and \$-0,(2) bonds. The ellipsoids have been derived from the neutron diffraction date and are scaled so that their axes are tvo tines the rime, amplitude, The alunioun ?ston and ite water neighbors 4s at the top center and the sodium atou with its neighbors 1s at the left, The notion of 0,(2), 20 as to avoid the kydrogen neighbor

can be clearly seen, This figure was produced by the 80-020 aiorofilm plotter using a code recently developed by Larson (1966).

?Toe fact that the thermal motion of O4(2) was fount to be essentially ?the sane from both the x-ray and neutron diffraction measurmentis is strong evidence that the apparent notion is not an artifact remiting fron systematic error in the date,

corrections to the O-H bond lengths were computed according to the in phase or "riding motion" assumption of Busing and Levy (1964). The O-H bond lengths appear to be about 0.015% shorter than those found in Cs alum (CKL)

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10.

Due to the uncertainty in the thermal motion correction the difference is probably not significant, further analysis is planned,

The O-H distances, except for O(2)-H(4), show the usual feature that bonds determined from x-ray data are shorter than those determined by neutron diffraction. The O-H bonds in this structure are all nearly the same and do not show any particular correlation of long O-H bonds and short, O-H hydrogen bonds. As in alum, water (1), which is associated with the monovalent cation

forms hydrogen bonds that link O(2) of one sulfate group with O(2) of another.

Again, as in alum, water (2) forms hydrogen bonds with O(2) and water (1).

In the present case there is a strong indication that shorter hydrogen bonds

tend to be more nearly linear.

TIT qh, -Abuns ND,AL(S04)p*22020

Deuterated ammonium alum was selected as and alu: to study by neutron

?The hydrogen atoms in the water molecules

diffraction for several reasons

could be located accurately, In addition the nature of the disorder of the ammonium ion, which must exist if the space group is to remain Pa, could also vary average centric

?ve determined. ?The ammonium ion can attain the nei

asymmetry by rotating freely or by randomly assuming either of two orientations.

It was also of interest to verify the sulfate group disorder found by Larson

?and Cromer (1966) by means of x-ray diffraction and to determine whether any

water molecule disorder is coupled with the sulfate disorder.

Refinement of the structure

A full matrix least squares refinement including anisotropic temperature

factors was carried out, This refinement led to $R = 9.2\%$ in the case

of the x-ray refinement, the thermal parameters for the sulfate oxygens were

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quite large and quite anisotropic. Other thermal parameters behaved normally.

The ellipsoids are somewhat smaller than those obtained from the analogous

x-ray refinement of ordered Mii , alun but the directions of the axes are in

good agreement for the two cases

A difference Fourier clearly revealed small peaks from disordered sulfate

oxygen atoms. A model with a fraction, k , of reversed sulfate oxygen atoms

was then refined as in the x-ray refinement of K alun (Larson, and Croser, (1966)).

However, no attempt was made to displace $1/2$ ND, groups along the threefold

axis as was done for the potassium atom in K alun. This additional disorder

would have introduced too many highly correlated parameters. Anisotropic

thermal parameters for the reversed oxygen, $Og(2)$, did not remain real 20

finer refinement was made with the reversed oxygen atoms isotropic and all

other atoms anisotropic. The final R index was 8.4%. The final parameters

are given in Table VIII. The disorder parameter is 0.116 Å² in good agreement with the value indicated by the x-ray data for My alum. In the

Tables V, and following, the symbols O_g(2)' and O₉(2)' are used for the

reversed sulfate oxygen atoms and D' is used for the half deuterium atoms

in the disordered ND₂ group.

The various interatomic distances and bond angles and their standard deviation are given in Table IX. The anisotropic thermal parameters were transformed to obtain the thermal ellipsoid parameters, which are given in Table X. The O-D bond lengths have been corrected assuming that D rides on O (Busing and Levy, 1964). No such corrections were made to O-H and N-D ends because of uncertainties introduced by the disorder,

Agreement of these distances with those from the x-ray study of the
tums (Larson and Croner, 1966) is reasonable except for three striking

exceptions. The O_g(2)-O₄(2) and O₉(2) hydrogen bond distances are both

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about 0.05R longer than in WII, alum. The Al-O₂(2) distance found here is 1.065

0.008R. If these differences are real, they must arise from an isotope

0.005R whereas the analogous distance found by x-rays in Ni, NiSe

effect. To settle the question, an x-ray study was made of deuterated ammonium

nitrate and a refinement was made exactly as had been made for Ni, NiSe

19 were no significant differences between these

(Warren and Cromer, (1966))- The x-ray studies of Ni, and NiSe, alums,

As another check to determine if we had systematic errors in either our x-ray or neutron work, the neutron data for Ni alum (Crozier, Key, and Larson, (1966)) were refined while letting all parameters vary. (In the original work heavy atoms had been held in fixed positions for the neutron refinement).

Unfortunately only limited three-dimensional data were available and there were only 144 observations to determine 7h parameters, Nevertheless the refinement converged satisfactorily and the parameters did not change very much. The

refined Al-O₂(2) distance was 1.679 ± 0.014, A good agreement with the x-ray

value, In this case no systematic difference existed in the two techniques.

We believe that the most likely reason for the difference between the

present neutron results and the x-ray results is that the model used for refinement does not properly account for the disorder. Thus, the systematic error exists in the least-squares model and not in either of the experimental methods. No provision for positional disorder of the nitrogen atom in the ammonium ion was made in either refinement. In the refinement of K alum the potassium disorder was coupled with sulfate group disorder. Neglect of this disorder would have a much greater effect on the neutron because the deuterium contributes a large amount to the scattering whereas the hydrogen atoms are practically negligible in x-ray results. We therefore reason that the x-ray results are probably correct and the neutron results are in error.

scattering. We therefore reason that the x-ray

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difference. Fouriers revealed no significant features and there is no

evidence for water disorder coupled with sulfate group disorder. Further, there

0 no marked anisotropy in the thermal motion of the deuterium atoms which might suggest positional disorder. As noted by Croner and Larson (1966) the sulfate oxygen atom can form hydrogen bond with the same hydrogen atoms whether the oxygen atom is in position 0,(2) or 0,(2)'.

The two bond distances in the ND₂ group differ by 0.0868 but this difference is probably not real. The longer distance has a large standard deviation and further there is the possibility for some positional disorder of the ND₂ group coupled with the sulfate group disorder. Although the thermal ellipsoid of the nitrogen atom suggests this possibility, the ellipsoids of the deuterium do not. The ND₂ group perhaps has to move very little to

accommodate the reversed 0,(1) atom because either an O-

D...H hydrogen bond

?can form (the O...H distance is 2.648) or the Van der Waals radius of the nitrogen atom is smaller along a symmetry axis of the ND₂ group than in other directions.

?The O-D bonds of water (1) are significantly shorter than those of water (2).

?The difference is related to the strength of the hydrogen bonds, the shorter O-D bonds being associated with longer hydrogen bonds, The shorter hydrogen bonds also tend to be closer to linearity.

A stereo drawing of a portion of the structure is shown in Fig. 3. The aluminum ion at $1/2, 1/2, 1/2$, (4n Sts two orientations) is shown with its six water neighbors in the lower right front. The octahedron about the aluminum at $2/2, 0, 1/2$ is shown at the lower left front. The sulfate group (in the normal orientation only) is in the middle. All water molecules hydrogen bonded to the sulfate group are shown.

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Except as noted below, all calculations were performed with $TE\approx 709\%$ using codes written by Larson, Roof, and Cromer (1963, 1964, 1965).

Magnetic Structures

I Introduction

Recent nuclear magnetic resonance measurements by Pence, Médents, Mi Saffar, and Kleinberg (1964) have confirmed that $CoCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ are antiferromagnetic of point group C_{2h} at liquid helium temperatures, and that each salt has one of three possible magnetic structures

In order,

to uniquely determine the correct structures a neutron diffraction study was

required, The results of such a study are described in the present report.

Crystals of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are monoclinic, and according

to Mizuno (1960, 1962) belong to the space group $C2/m$. There are two molecules

in the unit cell, For the nickel salt $a=20.25\text{\AA}$, $b=7.05\text{\AA}$, $c=6.57\text{\AA}$ and

$\beta=122.91^\circ$. For the Co salt $a=10.34$, $b=7.405$, $c=6.67$, and $\beta=122.20^\circ$.

The metal ions are situated on inversion centers at the cell corners, and

at the centers of the $a:b$ faces, They are octahedrally coordinated to four water molecules and two chlorine atoms as shown in Fig. 4, These oxygens form a slightly distorted square, with the cations at the center, while chlorines are located on the two normals to the oxygen plane. The remaining two water molecules of the formula unit are located in the mirror plane and are relatively free, but do take part in the hydrogen bonding scheme.

The local magnetic fields at the proton positions have been measured by applied and zero field magnetic resonance methods at 1.1% by Spence, Mudders, El Saffar, and Kleinberg (1964). By applying magnetic symmetry theory to these data, it was found that the possible magnetic space groups which describe the magnetic ordering are $P2_1/c$, $C2/c$ and $T2/c$. Clearly, $P2_1/c$ and $T2/c$ are

equivalent, but generate different structures when applied to an axial vector

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-5-

in a centrosymmetric cell. Conditions for magnetic Bragg scattering from the (102) zone, for the three different structures that are generated by applying each of these methods to the usual monoclinic cell, are that β be even-even, even-odd, and odd-odd respectively.

Examples 60

single crystals of FeCl_2 grown from aqueous solution at about 30°C had the habit described by Groth (1906). An approximately cylindrical crystal was suspended from a quartz crystal mount that was attached to the tail of a glass fiber. At 4.2% the crystals were aligned, and measurements were made on the (102) zone to give a set of approximate unit cell parameters.

The subsequent search for magnetic reflections showed that the space group is $P2_1/m'$, with the magnetic structure as given in Fig. 5. This structure

consists of antiferromagnetic (001) planes with an antiferromagnetic coupling between planes, to give a magnetic cell that is twice the size of the chemical cell, along the c axis.

the angle between the spin direction and the a' axis was determined as that angle which produced a minimum value for the function $BEIF$, - Fel
It was found to be $22,5^\circ$ from the a' axis towards the a axis, with a standard

deviation of about 1.0° , the observed magnetic form factor values of HfE''
are shown in Fig. 6. The solid line shows the spherical part of the magnetic form factor, calculated by Watson and Freeman (1961), and is seen to give a good fit with the data.

This result differs from having a spin direction along the a' axis as has been proposed from susceptibility measurements by Reseda, Kobayashi, and Date (1959) and, Flippin and Friedberg (1960). On the other hand $\chi^* 1\#$

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-16e

is in good agreement with the results of the antiferromagnetic resonance and magnetic susceptibility measurements of Date (1965), who has found the spin axis to be $25^\circ 45'$ from the

HE Coty: Sti0

Neutron diffraction data have been taken at 4.2%, and 25%, on the

ext

(oR) tone. only reflections of the type $o\bar{s}d$ -odd, were observed therefore,
?the space group $4s\ I,0/e$ and the structure, except for spin direction, $1s$ as
shown in Figs 5.

?Thin magnetic astructure consists of antiferroaagnetic (OOL) planes, with
an antiferromagnetic coupling between the planes, to give a magnetic cell
that is double the chemical cell, in the ϕ direction,

As the miclear intensity data have not yet been refined, the set of
experizental structure factors was scaled by dividing each mumbor of the
set by the sun of the set. Tho observed structure factors vere then compared
to acts of calculated astructure factors, watch were sealed in the gane way.
Tre angle between the spin direction and the c axis, is defined to be thet
angle at which JiP . - Fel te minimus, This angle ves found to be about
 25° . there say be quite & large standard deviation on this angle, as it
was quite difficult to determine the beckground scattering at 4.2% The
form factor curve for this angle {a shom in Fig, 7. We note that the path
engin for (202) was quite iarge because of the crystal ehepe, thus giving
?the lov observed value, The reflections (105) and (305) which have such
large error flags cleo have intensities that are only about 3%, of the
largest observed intensity.

IV Conclust

?There are four possible intraplanar superexchange paths in the cobalt chloride hexahydrate. ?They are shown in Fig. 1b, The paths 1-5, are

initially the same as in cobalt chloride dihydrate, where they serve to

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-r-

interlin: the strongly coupled ferromagnetic chain

In that case they have

?the smaller exchange energy. Short range order is attributed to the strong Co-Cl-Co intrachain coupling. ?The magnetic structure does not stabilize until the energies of the paths 1-5 predominate over the thermal energy. This occurs at about 17.5%

In the case of the cobalt chloride hexahydrate, there is no strong

Co-Co coupling along the axis. Instead, there is the very weak: $J_{0-0;-0;-C0}$, ?coupling along path 5 in Fig. . Thus in the hexahydrate we expect antiferromagnetic

netic sheets to be formed in the (001) plane, at about 17%, as a consequence of the paths 14%. As the temperature is decreased there is increasing short range order until about 2,25°K, where the goal: in interplaner forces bring 3-dimensional stability to the structures

This conclusion is illustrated in the specific heat data of cobalt chloride hexahydrate, as measured by Robinson and Friedberg (1960). They found in these that approximately 52% of the entropy of the transition was obtained above the Neel temperature, and it is seen that the limiting entropy $R \ln 2$ is reached in the vicinity of the hydrate's Neel temperature,

except for the difference in spin direction, the magnetic ordering in

MgCl₂·6H₂O is the same as for the CoCl₂·6H₂O. The spin direction for the former

is at 197.59 from the a₁ axis, and for the latter salt is approximately along the c axis. This, changing the cation in these two isostructural salts does not change the magnetic ordering.

It is of interest now to study the antiferromagnetism in HBr·6H₂O, CuCl₂·6H₂O and NiCl₂·2H₂O, and it is planned to do 40, 000 copies available.

See also the crystals

ote: ?The experinental data for the Yagnetic studies on Co and 11iCip+6H,0 vere taken
fat the U.S. Haval Research Reactor and anelyzed and interpreted at PRIC.

---Page Break---

Ferroelectrics

In an effort to provide the solid state physiciat

st PARNC, (and

other Laboratories) with the etonic gecustrical knowledge with which to
Anterpret their electrical measureuents, the crystel structure determinations
of several ferroelectric compounds of interest have been undertaken.

I Wad,

Data has been taken on NeliQ, about 15°C below the transition texperature.

While a rigorous analysis awaits further data correction, preliminary results do not seem to indicate any strongly preferred vibrational mode that would account for the phase transition. Such motions may show up after an extinction correction is made or at higher temperatures. Data will be taken at higher temperatures

TE thesis (se05)2

The room temperature structure of HfSi_2 , has almost been completed. Preliminary results show that the heavy atom positions determined by Untermyer (1966) are correct and those by Chou and Chotang (1957) contain errors. Hydrogen positions will be available shortly.

HfSi₂ (8005)2

Preliminary measurements

how HfSi_2 space group $P6_3/m$ with $a=6.32$, $b=6.11$, $c=6.24$, Z=4 molecules/unit cell.

Liquid structures

It was hoped to determine the structure (coordination) of molten SiO_2 .

If different isotopes of Sn with substantially different scattering lengths

may be used, then the neutron diffraction patterns may be combined to yield separate parts of the radial distribution function.

---Page Break---

age

Measurements have been made of the scattering lengths of all available

isotopes of Sn These are: $b_{\text{Sn}} = 4.5002$, $b_{\text{DT}} = 4.6402$, $b_{\text{De}} = 5.0$

$b_{\text{VO}} = 6.50$, $b_{\text{De}} = 6.0400$, $b_{\text{DO}} = 6.4$, $b_{\text{Dee}} = 15.5$

$b_{\text{Sn}} = 4.5902$, the above isotopes account for 96% of the scattering length of natural tin, If only isotopic incoherence is included the total scattering

cross section is 4.62×10^{-28} cm² and the coherent cross section 4.61×10^{-28} cm²,

Measurements given in Bacon (1962, Neutron Diffraction) indicate 4.9 and 4.6

for the above cross sections, respectively, While the former figure may be

due to experimental error, there is also a possibility of nuclear spin

incoherence, If this is the case

the effect should be fairly substantial

Because odd muon account for only about 15% of the total natural isotopic abundance,

Because of the closeness of the scattering lengths of the Sn isotopes to each other it was decided to pursue the work with ^{119}Sn using ^{119}Sn , ^{117}Sn , ^{115}Sn , ^{113}Sn which have scattering lengths of 79, -67, 14, -18 fm, respectively.

---Page Break---

ECEESE RE RE RERPREG

-20-

feble-l

Structural Parameters for Vin Formate «

?are given first, followe

Parameters from neutron data

Sckay parameters (Oi) in parentheses.

Gy, and Hi, are vater oxygens and hydrogens, respectively

x

o

6

+ 0564, 0015 (038)

-3265t. 0012(.325)

09854, oo12(..096)

+0868, oon2(..084)

sWshat, 0012(.439)

+2035%, 0016(.213)

«2700, oon (.267)

4az0t, 0015(.420)

x

o

3

«P23ut. o019(-220)

61344, 0017(.622)

+2067t, 0020(-102)

+2682, 0021(..266)

Text. 0021(. 723)

-6565t, 0019(..656)

+8262, 0020(.485)

2

o

o

-27agt. oon5(-274)

hszet, o0n2(.435)

-2035%.0013(.204)

hoot, 0012(.398)

-ke0bt, o0n2(.420)

926 0028(.49%)

+0656, 00n5(..066)

+2958. 0015 (.296)

+227, 006

+3958. 008

+051, 05

0091. 008

-2614. 005

ake, 002

Ja by standard deviations followed by

B

a.283(2.2)

2.42.5(2.2)

2.78.3(2-2)

2.2%.2(2.8)

2.1t.2(1.8)

2.2t.2(2.7)

2,54.2(2.3)

(1.5)

Pat

2.24.3(1.8)

3.08, 3(2.4)

ete

6.38.9

3.945

3.98.6

3.285

---Page Break---

a

Bond Distances and Angles in Manganese and Copper Formate Dihydrates with Standard Deviations. X-Ray results for $\text{M}(\text{O}(\text{H}))_2$ and previous X-ray refinements of the copper compound are given in parentheses. Corrections to bond distances involving hydrogens due to the H "riding" on the Oxygen are given in brackets.

MANGANESE COPPER

I Metal-Oxygen Octahedra

Mn-O (2.15) 2.30. Cu-O (2.26)

Mn-O (2.135) (2.25) 2.982, 2.026 (2.02)

Mn-O (2.22) 2.015. Cu-O (2.01)

Mn-O (7) 2.087 (90)

Mn-O (80.2) 2.056

Mn-O (03) 2.827)

Mn-O (2.22) 2.364.019 (2.35)

Mn-O (2,24) 2.087, 2.017 (2.02)

Mn-O (2.36) 2.975. 5 91)

Mn-O (1.0) 2.66 ()

Mn-O (2.8) 2.96

Mn-O (09.8) 2.05 (69)

IX FORMATE GROUPS

co 1,264.02 (22) 1,261.05 (2.29)

c1-ce Leite (2.25) 2.30808 (39)

ca-ca-ce qak.5t.2 (226) 2 (2)

tpl 1.054, 052.20)

OL-ch-Hpl 126. 545.8

cencheFpl 126,.983.8

---Page Break---

te.

Table Tia Contd.

2-03 azstce (1425) 1.26405 (uz)

C2=04 1.26.02 (u21) 128, 05 (2)

2tig2 05 (2.06)

05=C2=04 123.0814 (123) azote (aah)

052g mister

ObacBatig2 1ag.5t2.2

TXT HYDROGEN BONDS AND WATER MOLECULES

ota Loot ob [2402

a2 934.08 nay

HOH aoste

ano aphce (213) 2.7oh02 (2.85)

Hal-ob Lptos

a,a-i-08 asots

aoe 2.19.08 (2.81) 2.tat.oe (2.62)

y2-0e 2.008.053

oa-ii2-02 arrts

Opts 1954.05 (961

othe 098.05 (-09)

wpa 07 582.3

ozo (2.61) aris (2.79)

OL 1.864.05

O2-HyS-O1, viet

02-05 2.75t.02 (27) 2.67802 (2.76)

ORE 1.86%.05

OyarHy05 arete

---Page Break---

3.

?Table IIe

Bond Distances and Angles with Standard Deviations in Anhydrous Copper Formate

?Old Keray refinement results are in parentheses

TONS DISTANCES STANDARD

DEVIATIONS

cu - 1 Lesh (2.985) +009

cu - 2.939 (2.982) +008

ca LgvL (1.986) +007

cu = L952 (2.98) +009

ou - 2.415 (2.391) +008

cu - cu 3.432 (3.035) +005;

a-o 2.2k3 (2.255) Os

ao 2.269 (1.295) +03,

2 - 02 1.250 (1.270) +035,

ca = ob 267 (2.208) ok

a1 - cu - ce B34 (U9) 35

= ca - 98.9 (95) BD

ceca oh 9 (69) oT

> = cu ob 81.8 (66) 235

a-a-o 320.9 ze Lo

= co- h 323.6 ze ua

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the

?Bebble IIT

Refined Parameters and Standard Deviations from X-Ray Data of

Original Parameters are in Parentheses

Atoms x y z B

ou, ° ° ° hia

owe 3 6 ° uta

a -0.22, 0.05(.055) zat. 0.00(.027) ?? «2964.003(.302) EES.

ce w322t, 0.05(.303) «6064, 0.04(.600) «Wast.00R(.422) 2a

a +0p't.00e(.098) teat. 0.00(.096) «zat. 0.00(.223) 205

oe 20U5%, 0.00(.007) 264. 0.03(.267) sant ove(sbai) 93

3 s430%.002(.425) « 7058.005(.705) «HOR#, 0.00.405) 2.683

oF +20KE, 0.02(.204) «35%, 0.03(.356) saKE.00n(.495) Leeks

oa .2.5t, 0.02(.209) hgh 0.02fshub) 0754. 0.02(.075) 2.383

oe wast ov{4ia} Bow 0.0a205) ssa5 one 3.36) 2h

---Page Break---

?Table 111

Refined Parameters and Standard Deviation from X-Ray data of Barclay and Kennard

Original Parameters are in Parentheses

x y z

oo +2150 (.1252). 0002 +0587 (-0506), 0008 +0062 (0065). 0005

a +0292, (-02u%)..000 13254 (.3226). O25 4.2614 (.2625). 00

cy +2172 (.2710).000 -1540 (.1595)- 0015 +2549 (-2536).0082

a +0096 (095). 0005 +2433 (.2427).0009 +2605 (.2622). 0008

ce +2225 (2285). 0006 10215 (.0262).00L0 -195. (.1950)-003

° +0070 (0061), 0005 +0(U4 (.07U2)..0009 ago (.2902). 0012

oe HUB (,2493). 0005, e121 (-12207).0009 +- 1869 (~+1459). 0025,

?Thermal Parameters

po fa po fa Bs fe

ca oon 00h. 207 0002 =, 0005 +0006

ot +0028 00K +0066 =.0007 +0021 ~-00s

2 0005 +008 +0103, 001g. =, 0008 +0085

a 001g +0043 039 00a =, 0015 -.0029

cy +0021 008g +0105 0002 =, 00K 0024

3 +0004 +005 +0083, 10051 =. 0024 -.0002

ob + 00n4 +0087 +0196 +0002 +002 +0005

---Page Break---

Table 1V

cent Date and Heavy Atom Parameters for the Alums Studied by
Neutron Diffraction (in order of +1 cation size)

Sample 0AN(SO₄)₂·12H₂O ??ND4AL(SO₄)₂·21240 CAAL(SO₄)₂ pr 120

Space Op.

® was 32.352

GLE) ? (65, 05, -3) ?_?

(4,752) ?_ (©, 0, 0) ?

3(4,%,%) 2652 +5090 327

C2) (sie) BAS 2408 2596

og(2)X 295% opae +2009

y 2105 260% whan

2 saubt ans 36

aytayx +0167 +0456 --1595

x + oho; 305 +9507

2 518 2510 28h

ofa)x ?Ba sone 3s

Y +9596 -- 0069 -.0080

Zz +9573 156 +0000

---Page Break---

2

rey

Hydrogen parameters in Hak1(50)p.12%²⁰ from Least squares

toa

QQ)

Ht)

(3)

(4)

refinement of neutron diffraction data,

0.5958(21)

0.4 709(22)

0.5504(25)

0.5926(21)

Zz

0.5272(20)

0.3225(21)

0.2031(15)

0.3822(15)

0.3665(21)

0.3808(20)

0.4999(2)

0.2204(25)

---Page Break---

28.

?Table VI

interatomic distances and angles in Å (50,)g- 121.0

standard deviation, in parentheses, apply to the first digit

Distances corrected for thermal motion are in parentheses

Distances and angles from neutron data are underlined.

12-65, (2) 1.881(2)8

Yan604(2) 2.455(2)

?The sulfate group

8-09(1) 46a (4)

(aks)

'8-30,(2) ash (2)

(48)

4(2)-30(2) 2.589(4)

04(2)-20,(2) 2,366(4)

eter molecules

(2-02) 0.184)

2.915(24)

Gov)

o(2)-H(2) 0.05(4)

0,991(24)

G54)

4f2)-H03) 0.924)

0.916(27)

(009)

ay(2)-t4) a.01(s)

0.991(20)

1.006

{2)-A1-04(2)

O42) -Ad-04(2)

y(2)-He-0,(2.)

4 (2)-ta=0y(2)

05(2)=8-04(2)

0¢(2)-8-09(2)

9(2)=04(2)-04(2)

04(2)=04(2)-04(2)

Og(2)-09(2)-04(2)

H(2)-04(2)-H(2)

u(3)-0,(2)-1H(4)

90, 0(2)°

90, 0(2)

85.0(2)

95-02)

aa0.a(2)

108.9(2)

60.0

60.3(2)

59.42)

20302)

---Page Break---

Hydrogen bonds

a(2)-30 (2)

0,(2)--3 H(2)

Og(2) -0,(2)

(2) -2(2)

og(2) -04(0)

(2) -H(4)

(2) -04(2)

(2) -H(3)

29.

?Table VI Conta.

2. TH7(4) g(2)-#(2) -04(2)

2.703(25)

2,822(3) (2) -H(2) -94(2)

2.901125)

2.605(5) og(2) -1(4) -04(2)

1.655(20)

2.64903) (2) 83) -04(2)

2.613037)

16005)

3563)

aik(2)

376(2)

---Page Break---

Atos

Ha,

09(2)

0,2)

(2)

a,(2)

?30

Teble THe

?Toermal elipeotds in Tak2(50y Jp 2250 from X-ray data

Standard deviations, in parentheses, apply to rightmost digit

Direction angles relative to crystal axes

ne

dap Tate & « a x

0.270(5)R 2, 26(23)R? shee he? shi?

0,160(3) 2.55(8)

0,160(3) 2.55(8)

oat} Re 5he7 he She

0, 1404 3} 1.54(5)

0,140(3) 1.54(6)

cable) 265) oe

a 3} ei ais ?

le

113(7) 2. 36(393 Sh ST shy

2a BB)

0: or 2ehh} 10.62(21) 2a} 115(1) h(a

orients) 200} ua 88) tt

+h, 76(26) 43) 133(2) 98(5)

2.63(12) 53(6) ato ag 3

0.27a(4) 2. 34(12) au(u) 12e(10) ?ho(6 |

T 6) 61

SH ERR I a} Sif}

0, 206(5 | 3.35(10) 95(4) 568 Bath)

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ae

able VITO

?Thermal ellipsoids in MeAl(SO₄)₂·p- 12120 from neutron diffraction data

Standard deviations, in paréntheret, apply to the rightmost digit

Direction angles relative to crystal axes

2S

Aton pplitede BL L a 2

Ma 0. 05(24)R 0.5025)R* shi? she hie

o.20(6) 3.3(20)

0.2016) 3:3(20)

a 0.4;(20) 2.3(20) she hi she

0,0:20) 2.5033

@.05(40) 0n5(a5,

8 22M} 1.529) sh het sh

ol20(h) 3.502)

0.204) 5.5002)

1 0.2065; 5-2(36 Shed MT SAT

oat) oo} a3

onan(5: w50a)

o,(2 0.36(2 n.6(35 21a 234) 76(5)

fe) 355} 2.3 3 a} 30(20) 204(24)

. 0-10(8 0.816) silt) a3) 20(20)

o.20(2 3.010 aué7) (aT) 86(59)

iil aaa} 3h} Sie} ?Bae owe}

Ona L6(6 913) 0047) 2209:

2 0.123 1.216) 364) aaah) 306 (24)

owe) oH Sun 36033 ae) (55)

orb: 2M) we 105036) xe)

#Q) 0.324) 8.3(20) 23(20) 9n(26) 61(20)

ovzats) 3.0035, 901238) 2(5310) 8o{539)

212500) Bots: 1i(20) athe) 23656)

#2 0.35(4) 9.4(22) mwas) 0035 1)

oz tisha

0.1465) 1.6(32) aah) a1) tea)

6) 0.20(3) 3.3(33) elee) ?ate0} 201139)

508) an9) S345) pha 3109

0.2163 5.834) 65a 6o(a5 ie2(a2)

0. 22(3; 3.9(20) 29(299) 5705) a(S)

i) ova 3 3.5(02) 37488) 551 3} 89(87)

o.22(h 119) 65(29) 39(a7 46(a7)

---Page Break---

(oLyre- (ga)ozt ? (6a)egt- ae)nee ?Cn)96S (BE)LOH

(966 (LYS ?(EnJens (YAS (ED LOE

(g6)e08- 3 (?s)ocL ?(Ano6n??(esoeL

(lero ? (@a)6i2- (96)CET- ?(6S)9L (659669 (an)ets

(esr (syn get (East (96602 (ETEK

(cunt (6LJowe(ULYEHT (Seen (BEEK Cone

(onort

(Fours (seple (oor)90ç ?(en)see = (9LYELB? (Gn)

' (eed

ba ty (eorex % (es)t99

my ye eotst sy (endone

(6669 (962)k2 (6te)Nee ?(noa)OGeT (Late ?_?(28T)96

ety ay (oscjese- Ts (eer eset

ty sy (Gor)obt wy Ts (cages

my ey (ootdoct- % (ondont

gry ex rx ote ore (new

exe

(siK6r6"0

(6) 00

(9)erge"0

(5166270

(ge)enée"0

(yxét9ro

(e2yatsro

an

o

(S)p2n0°o

(ge)sticro

(e)6192"0

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a19Tp eomUsya 91 04 Arde ?cosayyuared uF ?suoTINTASD BIVENS

o%aat-?("os)tv"an 105 sxeyoeured sarenbs 3009]

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(ez)gtt"o =

(s)gsetro

(n)lz02"0

(g)tx00"o-

(9)<gttt'o,

(s)oLto°0

(a)igror0

(ec pntero

(o)eere-0

(ogyasiero

Oa

(g)rore"o

(6r)S084"0

(rayeuryro

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e

?Tabte Tx

Intevetcnic distances and bond angles tn 10,40(59,);

standard deviations, in perertheses, appay to the righthaoet eight

Distances corrected Fer thermal ceviow are in parentheses

a6 0,(2) 1.065(5)8 0,(2)-41-0,(2) 90.6(2)°

,(2)-A1-0,(2) 03.2(2)

6 Oh) 3-057) (2-8-0, (2) Toe2(1)

0, (2)-1-0,0) 204.00)

¥.04(2)! 2.64(13)

§D, croup

m-2D(1)* 1,204(45) D(1)*=H=D(2) 102.8 (4),

w~60(2)" 1,016(16) ?D(2)*=t-D(2)* 15.99

80, group

8+05(2) 2-49(2) 04(2)=8+05(2) 109.4(6)

8-0,(1)' 21439(23) 0,(2)=8-0,(2) 1109.6(3)

8-0,(2) 16443(9) 0g(2)"=8+0,(2)* oe(2)

8+0,(2)" sba(4) 0,(2)'-8-04(2) a6(2)

Water molecules

Q(2)-0(1) 0.934(9)8 (2)+0,(1)-D(2) 106.19"

(0.965)

0,,(2)-D(2) 0.954(9)8

(0.97%)

0,(2)-D(5) 0.993(7) (3)=0,(2)=D(4) 12106.2(7)

(2.008)

04(2)-0(4) 0.908(7)

(2.005)

---Page Break---

og(2)93 0,02)

9,(2)-°D()

05(2)=04(2)

0,(2)-0(2)

09(2)-0,(2)

o(2)-0(4)

0,(2)"=04(2)

0,(2)'-D(2)

0(2)"-04(2)

0,(2)'-D(4)

9,(2)-9,(2)

0,(2)-008)

he

?Table 1X contimed

2.T1e(a2) 9g(2)-23)-0,02)

2.06321)

2.7119) 0,(2)-D(2)-0,(2)

2.652(20)

2.6178) 04(2)-D(4)-0,(2)

1.643(9)

2,05(4) og(2)*-D(2)-0,(2)

1.99(4)

2.714) 0,(2)"=D(4)-0(2)

cat)

2.652(9) 9,(2)-D(3)-0,(2)

1.662(9)

163.6(9)

168.219)

269.17)

3512)

62(2)

1ihe(6)

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?35+

rabie x

Thermal ellipsoids in ND,A2(S0,),°220,0

Standard deviations, in parentheses, apply to the rightmost digit

rea. 0. Direction angles relative to cell axes

Aton haplitle y a ® 7

¥ wex(2)AM2T)AP hee oh mT

8) 2.703) : - -

80) 2.703) : : -

Da)! 285) 6.0023) ST ht oht

223) 8.3027) - - -

+32(5) 8.327) * - -

D(2)*se7te) 5.79) 2825) rar) 222)

wee) -3.6(8)? 20719) 37(20)?90(a7)

s(2) 7.812) 6920) x(a) 2222)

a 0x(28)?0.(6) SHAT 7 ut

22) 1.24) - - :

22) 1.204) - : :

s 0.183) 2.58) ST MT SMT

one) 1.004) - - :

o.1(2) 1.04) : - -

002) nse) .6) OT ot MT

0.25() 5.05) : - -

0.25(1) 5.065) : - -

o,(2) oar) 2.203) 336) 303(6) 287)

22) 5.706) 6(4) "6(3) 624)

0.09(2) o.(2), (7) 1224) 316)

(2) ovena)?5.6(3) 308) 726) 218)

0.2K) 1.62) ?_98(28) zo(12)T2(20)

0.16(2)2.(3) 4820) sete) 34)

oy@) ora) eee) 337) 9x27) 029)

os) 1.8(2) 8927) 30(24)?200(23)

0.10(2) 0.8(2) mn x(a) 26(8)

---Page Break---

om

pa)

(2)

(3)

D(a)

Jeph tate

0.1802)

0,22(2)

0.26(2)

0.2202)

0.2702)

0.2703)

0.15(2)

0,20(2)

0.22)

0.16()

0.20)

0.18(2)

Table x continued

2.43)

4.063)

5.5(8)

3-9(4)

2.63)

5.108)

1.12)

3.1(5)

346)

2.0(2)

3.66)

2.6(2)

3360

Direction angles relative to cell axes

@ B

holo)

e9(9)

(6)

4x9)

#300)

232(8)

ar(s)

207(8)

75)

o(an)

16(8)

59(26)

63(8)

4e(a0)

aer(9)

asco)

20(6)

207(6)

7318)

alto)

sia)

?itao)

29(20)

65(a2)

7

62(6)

67(a1)

(6)

sx(9)

(6)

r(7)

0e(7)

325(li2)

36(40)

329(27)

yo1(20)

na(a7)

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20.

37-

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Figures

Stereoscopic Figures (1,2,3) should be viewed with one's eyes decoupled

Lie, The right side of the figure should be view by the right eye and the

Left side by the left eye, A piece of paper extending from the nose to the

figure with an edge between the halves of the figure and one eye on each side

of the paper, or a comercial viewer, ts of ald.

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Figs 1 Stereocran of Manganous Poraate Dihydrate,

View is slightly off (100) direction.

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Fig. 2 Stereogram of Sodium Alum Ellipsoids are scaled to twice the RMS. amplitude of vibration.

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are scaled to twice the RMS. amplitude of vibration

Fig. 3 Stereogram of Dodecahedral Ammonia Alum, Ellipsoids

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Figs b Sketch of Color X-ray diffraction patterns showing metal ion and possible exchange sites.

endings of the

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VV V

derangement of magnetic moments in $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ for the magnetic space group C_{2h}^2 . The angle between the magnetic moment and the a axis is approximately 10° ,

Fig. 5

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5.

Form factor for Ni^{2+} in $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, from data taken at 1.5°K , Solid line is the theoretical curve for the spherical part. All indices are based on the magnetic unit cell.

Fig. 6

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Magnetic form factor
of

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