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INTRODUCTION

The neutron diffraction group at the Puerto Rico Nuclear Center has worked on essentially two types of problems. The first is concerned with the chemical binding of atoms in crystals and molecules, and the second with the nature of ferromagnetism.

Both problems are related to the spatial arrangement of atoms in molecules. If either x-rays or neutrons are scattered from crystals, patterns can sometimes be analyzed which show the arrangement of atoms in the crystal. The amplitude of x-rays diffracted from atoms is proportional to the atomic number of scattering atoms. Thus, if there are light and heavy atoms in the same compound, the contribution of the light atoms is very weak and its position can be determined only with great difficulty. If neutrons are used, however, they are scattered by the nuclei of the atoms, and as a result, diffraction of neutrons by light elements compares favorably with that from heavier elements.

There is also a neutron-electron spin interaction in compounds which possess atoms with unpaired electrons. Since the magnetic properties of substances are related to the way the electron spins are arranged within the crystal, neutron diffraction provides an accurate method for determining such spin arrangements (magnetic structures).

Manganese Formate Dihydrate

I. Introduction

In two papers by Okada (1965) and Okada, Kay, Cromer, and Almodovar (1966) 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 ionic size similar to copper or manganese is a monoclinic dihydrate phase. Of known similar structure are the magnesium and manganese (Osaki, Nakai and Watanabe) (1964), hereafter referred to as ONW), zinc (ONW (1963)), copper (M. Bukowaka-Strzyzewska (1965), hereafter referred as BS) and nickel (Krogmann 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 bending scheme with no disorder.

The crystal structure of Mn formate dihydrate has been determined by ONW (1964) and by Mascarenhas (1964). The cell parameters ($a=8.86$, $b=7.29$, $c=9.60$, $\beta=97.7^\circ$) determined by the former authors were used in the present study. The space group is $P2_1/c$.

The structure consists of Mn1 atoms at cell corners related by symmetry to Mn atoms at a face centers. A second set of Mn2 positions is found in b and c 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 $.4H_2O$ (Okada, Kay, Cromer, and Almodovar). To complete the octahedron around Mn1 atoms, the second formate group links Mn1 to Mn2 in a plane approximately perpendicular to (100). The structure is shown in the stereogram in Fig. 1.

The octahedron around Mn2 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, Morigaki, Matsuura, Torii and Yamagata (1964)) found in Mn formate at 3.7°K and 1.7°K. According to Abe et. al. (1964), cations on the first site, only, probably order, first two dimensionally at 3.7° and then totally at 1.7°.

II. Experimental

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 $(F_{obs} - F_{Mn,C,O})$ Fourier projections and refined by means of least squares (Roof, Cromer, and Larson (1965)) to an R of 0.11.

The final parameters are given in Table I and compared with the results of ONW. Except for the y coordinate of C2, all coordinates agree within 2σ. This discrepancy seems to effect only the O3-C2-O4 angle as seen in Table IIa.

III Conclusions

The hydrogen bonding scheme indicated by ONW is correct. It might be noted that there are water-oxygen to oxygen approaches that could be conceivably hydrogen bonded of the order of 3.1Å. The hydrogen positions do not, however, admit of such linkages and difference maps show no significant extra hydrogen density not 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 about .3Å. 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 H_F-to other atom distances are all greater than 2.5Å.

We may then conclude that the dihydrates unique hydrogen bonding scheme and three dimensional formate bridging array may be correlated with the greater stability of these compounds as compared to copper formate tetrahydrate.

Copper Formate Dihydrate

I. Introduction

During the early phases of the manganese formate work M. Bukawska-Strzyzewska published a refinement of copper formate dihydrate from three zones of x-ray data. The refinement consisted of Fourier projections with the Cu substracted. No attempt was noted in the paper to either do a complete difference map or to even compute a Fc map to estimate 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 (Krogman and Mattes (1963))by elongation of two of the six Cu-O bonds (see table IIa). BS correlated the elongation of Cu-O with the elongation of C-O in the formate group. The extent of the elongation noted amounted to .1 and .06Å differences in the carbon-oxygen approaches in the two formate groups (table IIa). 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.

II. Results of Cu Formate Refinement

For these reasons we rerefined the x-ray data by means of least squares using the program of Roof, Cromer and Larson (1965) using a weighting scheme of $W=1/(Fo + .02Fo^2)^{1/2}$ with correction for anamolous dispersion for the copper. The results are given in Table IIIa together with the results of BS. The coordinates are translated to the origin used by ONW and the atoms relabled for easy comparison with the Mn formate work.

The C-O distances in the copper formate dihydrate now agree quite well with the C-O distances in other formates, including copper formate $.4H_2O$, within the standard deviations of the results.

BS reported a O_w2-O3 hydrogen bond of 2.99Å. If the O3 related to the O3 at 2.99Å from O_w2 by the screw axis transformation is chosen, a O_w2-O3 distance of 2.76Å found. This is the hydrogen bonded approach found in manganese formate.

Anhydrous Copper Formate

I. Introduction

A three dimensional least squares refinement of the anhydrous copper formate x-ray data of Barclay, and Kennard (1961) was run using the Roof, Cromer, 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, confirming our results on Copper formate dihydrate. The new distances and angles are given in Table IIb and the positional and thermal parameters in IIIb.

II. Conclusions

The general molecular geometry of the various transition metal formate dihydrates 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 Ca. 0.05Å) are not established in any of these compounds except possibly the Ni. It is clear that three dimensional x-ray counter work and neutron data on a deuterated compound are needed.

Alums

I. Introduction

In our 1966 Annual Report (PRNC-84) and in Cromer, Kay, and Larson (1966) the structure of the β Alum, ($CsAl(SO_4)_2 \cdot 12H_2O$) was described. The α and γ alum structures as exemplified by ND_4 and Na,$Al(SO_4)_2 \cdot 12H_2O$ 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 P.R.N.C. to determine the hydrogen positions.

The Alums are a large class of double salts having the general formula $A^{+1}\ B^{+3}(RO_4) \cdot 12H_2O$ where A can be NH_4, CH_3NH_3, Na, K, Rb, Cs; B can be Al, Ga, Cr, Fe, V; R can be S, Se or Te.

The compounds are cubic with space group Pa_3 (see Table IV). The gross structures were originally determined by Lipson (1935) and refined in the present work.

The type of alum formed depends on the size of the monovalent cation. If the cation is small the γ alum forms. The only known representative of this class is $NaAl(SO_4)_2 \cdot 12H_2O$. The β alum forms if the cation is large and the α 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 α and γ alums also has six waters in a nearly regular octahedron.

The large cation in β alum can accommodate 12 oxygen neighbors. To attain this large coordination number the water octahedron is compressed along the threefold axis and stretched out normal to this axis until it is nearly planar. The two ends of the resulting trigonal antiprism are separated by only about 0.06Å. 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 surround the cation.

In the γ structure six water molecules approach the small sodium cation much more closely than in the α 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.

From Table IV, it may be noted that S-O on the three fold (X,X,X) axis (belonging to the sulfate group) is pointed towards the A^+ position at (1/2,1/2,1/2) in the γ alums, but towards the Al^{+3} at the cell origin in α and β alum.

II γ-Alum: $NaAl(SO_4)_2 \cdot 12H_2O$

The atom positions found (Table IV) do not differ by more than about 0.05Å from those reported by Lipson (1936). The hydrogen parameters are 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 in β alum, and withing a few degrees in α alum, the octahedron at the origin in γ alum is rotated by 39.4° about the threefold axis of the body diagonal of the unit cell. The Al-O distance is the same 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 departures 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 VII 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 $O_s(2)$ thermal ellipsoid, instead of being normal to the threefold axis is at an angle of 65.5°. We believe that this is a case in which the translational and the rotational motions are coupled. Thus the Cruickshank analysis does not apply. The $O_s(2)$-$O_w(2)$ hydrogen bond is fairly short, 2.62Å, and the $O_s(2)$-H(4) distance is 1.64Å. The principal axis of the $O_s(2)$ thermal ellipsoid makes an angle of 84.5° with the S-O bond and an angle of 79.9° with the O---H(4) bond. Thus a motion of 0.367Å (the r.m.s. amplitude along this axis) changes the O---H(4) distance from 1.64Å to 1.61Å, a small amount. However, if this 0.36Å motion were to be directed along a line normal to both the S-O bond and the threefold axis, the O---H(4) distance would be reduced to 1.51Å. This sulfate group lies on a threefold axis so that a simple rotation about this axis will reduce three O---H distances and we reason that the whole group therefore is forced to translate along the threefold axis whenever it rotates about this axis.

Figure 2 is a stereo view of a portion of the structure. A sulfate group is at the center of the figure and the direction of view is normal to the threefold axis and in a plane containing the S-$O_s(1)$ and S-$O_s(2)$ bonds. The ellipsoids have been derived from the neutron diffraction data and are scaled so that their axes are two times the r.m.s. amplitude. The aluminum atom and its water neighbors is at the top center and the sodium atom with its neighbors is at the left. The motion of $O_s(2)$, so as to avoid the hydrogen neighbors, can be clearly seen. This figure was produced by the SC-4020 microfilm plotter using a code recently developed by Larson (1966).

The fact that the thermal motion of $O_s(2)$ was found to be essentially the same from both the x-ray and neutron diffraction measurements is strong evidence that the apparent motion is not an artifact resulting from systematic error in the data.

Corrections to the S-O bond lengths were computed according to the in phase or "riding motion" assumption of Busing and Levy (1964). The S-O bond lengths appear to be about 0.015Å shorter than those found in Cs alum (CKL) but because of the uncertainty in the thermal motion correction the difference is probably not significant. Further analysis is planned.

The O-H distances, except for $O_w(2)$-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-O hydrogen bonds. As in alum, water (1), which is associated with the monovalent cation forms hydrogen bonds that link $O_s(1)$ of one sulfate group with $O_s(2)$ of another. Again, as in alum, water (2) forms hydrogen bonds with $O_s(2)$ and water (1). In the present case there is a strong indication that shorter hydrogen bonds tend to be more nearly linear.

III α -Alum: $ND_4Al(SO_4)_2 \cdot 12D_2O$

Deuterated ammonium alum was selected as an α alum to study by neutron diffraction for several reasons. The hydrogen atoms in the water molecules 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_3 could also be determined. The ammonium ion can attain the necessary average centric symmetry 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 $R=9.2^{o}/_{o}$. As in the case of the x-ray refinement, the thermal parameters for the sulfate oxygens were [illegible] 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 NH_4 alum 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 alum (Larson, and Cromer, (1966)). However, no attempt was made to displace k/2 ND_4 groups along the threefold axis as was done for the potassium atom in K alum. This additional disorder would have introduced too many highly correlated parameters. Anisotropic thermal parameters for the reversed oxygen, $O_s(2)'$, did not remain real so final refinement was made with the reversed oxygen atoms isotropic and all other atoms anisotropic. The final R index was $8.4^o/_o$. The final parameters are given in Table VIII. The disorder parameter is 0.116 ± 0.022 in good agreement with the value indicated by the x-ray data for NH_4 alum. In the Tables V, and following, the symbols $O_s(1)'$ and $O_s(2)'$ are used for the reversed sulfate oxygen atoms and D' is used for the half deuterium atoms in the disordered ND_4 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 S-O and N-D bonds because of uncertainties introduced by the disorder.

Agreement of these distances with those from the x-ray study of the alums (Larson and Cromer, (1966)) is reasonable except for three striking exceptions. The $O_s(2)$-$O_w(2)$ and $O_w(2)$ hydrogen bond distances are both about 0.05Å longer than in NH_4 alum. The Al-O_W(2) distance found here is 1.865 ± 0.005Å whereas the analogous distance found by x-rays in NH_4 alum is 1.916 ± 0.008Å. If these differences are real, they must arise from an isotope effect. To settle the question, an x-ray study was made of deuterated ammonium alum and a refinement was made exactly as had been made for NH_4 alum (Larson and Cromer, (1966)). There were no significant differences between these x-ray studies of NH_4 and ND_4 alums.

As another check to determine if we had systematic errors in either our x-ray work or neutron work, the neutron data for Na alum (Cromer, Kay, 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 74 parameters. Nevertheless the refinement converged satisfactorily and the parameters did not change very much. The resulting Al-O_W(2) distance was 1.879 ± 0.014, in 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 scattering. We therefore reason that the x-ray results are probably correct and the neutron results are in error.

Difference Fouriers revealed no significant features and there is no evidence for water disorder coupled with sulfate group disorder. Further, there is no marked anisotropy in the thermal motion of the deuterium atoms which might suggest positional disorder. As noted by Cromer and Larson (1966) the sulfate oxygen atom can form hydrogen bonds with the same hydrogen atoms whether the oxygen atom is in position $O_s(2)$ or $O_s(2)'$.

The two N-D distances in the ND_4 group differ by 0.086Å 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 ND_4 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 ND_4 group perhaps has to move very little to accommodate the reversed $O_s(1)$ atom because either an O---D-N hydrogen bond can form (the O---N distance is 2.64Å) or the Van der Waals radius of the nitrogen atom is smaller along a symmetry axis of the ND_4 group than in other directions.

The O-D bonds of water (1) are significantly shorter than those of water (2). This 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 ammonium ion at 1/2,1/2,1/2, (in its two orientations) is shown with its six water neighbors in the lower right front. The octahedron about the aluminum at 1/2,0,1/2 is shown at the lower left front. The sulfate group (in its normal orientation only) is in the middle. All water molecules hydrogen bonded to the sulfate group are shown.

Except as noted below, all calculations were performed with an IBM-7094 using codes written by Larson, Roof, and Cromer (1963, 1964, 1965).

Magnetic Structures

I Introduction

Recent nuclear magnetic resonance measurements by Spence, Middents, El Saffar, and, Kleinberg (1964) have confirmed that $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ are antiferromagnetic of point group 2/m1' 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 $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ are monoclinic, and according to Mizuno (1960, 1961) belong to the space C2/m. There are two molecules in the unit cell. For the nickel salt $\underline{a}$=10.23A, $\underline{b}$=7.05A, $\underline{c}$=6.57A, and β =122°10'. For the Co salt $\underline{a}$=10.34, $\underline{b}$=7.06, $\underline{c}$=6.67, and β =122°20'. 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 oxygen 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 nmr methods at 1.1°K by Spence, Middents, El Saffar, and Kleinberg (1964). By applying magnetic symmetry theory to these data, it is found that the possible magnetic space group symbols which describe the magnetic ordering are P_C2_1/a, C_c2/c and I_c2/c. Clearly, C_c2/c and I_c2/c are equivalent, but generate different structures when applied to an axial vector in a given monoclinic cell. Conditions for magnetic Bragg scattering from the $(h0\ell)$ zone, for the three different structures that are generated by applying each of these symbols to the usual monoclinic cell, are that h, ℓ be odd-even, even-odd, and odd-odd respectively.

II $NiCl_2 \cdot 6H_2O$

Single crystals of $NiCl_2 \cdot 6H_2O$ grown from aqueous solution at about 30°C had the habit described by Groth (1906). An approximately cylindrical crystal was suspended from a titanium-zirconium crystal mount that was attached to the tail of a Hofman dewar. At 4.2°K the crystals was aligned, and nuclear peaks were measured on the $(h0\ell)$ zone to give a set of approximate unit cell dimensions.

A subsequent search for magnetic reflections showed that the space group is I_c2/c, 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 $a'=c\perp$ axis was determined as that angle which produced a minimum value for the function $R=\Sigma|F_o - F_c|$. It was found to be 22.5° from the a' axis towards the a axis, with a standard deviation of about 1.0°. The observed magnetic form factor values of Ni^{2+} are shown in Fig. 6. The solid line is the spherical part of the Ni^{2+} 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 proppsed from susceptibility, measurements by Haseda, Kobayashi, and, Date (1959) and, Flippen and Friedberg (1960). On the other hand it is in good agreement with the results of the antiferromagnetic resonance and magnetic torque measurements of Date (1966), who has found the spin easy axis to be 25° ± 3 from the a' axis.

III $CoCl_2 \cdot 6H_2O$

Neutron diffraction data have been taken at 4.2°K, and 1.5°K, on the (h0ℓ) zone. Only reflections of the type odd-odd, were observed. Therefore, the space group is I_c2/c and the structure, except for spin direction, is as shown in Fig. 5.

This magnetic structure consists of antiferromagnetic (001) planes, with an antiferromagnetic coupling between the planes, to give a magnetic cell that is double the chemical cell, in the c direction.

As the nuclear intensity data have not yet been refined, the set of experimental structure factors was scaled by dividing each number of the set by the sum of the set. The observed structure factors were then compared to sets of calculated structure factors, which were scaled in the same way. The angle between the spin direction and the c axis, is defined to be that angle at which $\sum|F_o - F_c|$ is a minimum. This angle was found to be about 2.5°. There may be quite a large standard deviation on this angle, as it was quite difficult to determine the background scattering at 4.2°K. The form factor curve for this angle is shown in Fig. 7. We note that the path length for (101) was quite large because of the crystal shape, thus giving the low observed value. The reflections $(10\bar{5})$ and $(30\bar{5})$ which have such large error flags also have intensities that are only about 3°/₀ of the largest observed intensity.

IV Conclusions

There are four possible intraplaner superexchange paths in the cobalt chloride hexahydrate. They are shown in Fig. 4. The paths 1-3, are essentially the same as in cobalt chloride dihydrate, where they serve to interlink the strongly coupled ferromagnetic chains. 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 1-3 predominate over the thermal energy. This occurs at about 17.3°K.

In the case of the cobalt chloride hexahydrate, there is no strong Co-Cl-Co coupling along the c axis. Instead, there is the very weak $\mathrm{CO}\text{-}\mathrm{O}_I\text{-}\mathrm{O}_I\text{-}\mathrm{Co}$, coupling along path 5 in Fig. 4. Thus in the hexahydrate we expect antiferromagnetic sheets to be formed in the (001) plane, at about 17°K, as a consequence of the paths 1-4. As the temperature is decreased there is increasing short range order until about 2.25°K, where the weak in interplaner forces bring three dimensional stability to the structure.

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°/o 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 dihydrate's Neel temperature.

Except for the difference in spin direction, the magnetic ordering in $NiCl_2 \cdot 6H_2O$ is the same as for the $CoCl_2 \cdot 6H_2O$. The spin direction for the former salt is 22.5° from the a' axis, and for the latter salt is approximately along the c axis. Thus, changing the cation is these two isostructural salts does not change the magnetic ordering.

It is of interest now to study the antiferromagnetism in $NiBr_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$ and $NiCl_2 \cdot 2H_2O$, and it is planned to do so, as soon as the crystals become available.

Note: The experimental data for the Magnetic studies on Co and $NiCl_2 \cdot 6H_2O$ were taken at the U.S. Naval Research Reactor and analyzed and interpreted at PRNC.

Ferroelectrics

In an effort to provide the solid state physicists at P.R.N.C. (and other laboratories) with the atomic geometrical knowledge with which to interpret their electrical measurements, the crystal structure determinations of several ferroelectric compounds of interest have been undertaken.

I $NaNO_2$

Data has been taken on $NaNO_2$ about 15°C below the transition temperature. 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.

II $NaH_3(SeO_3)_2$

The room temperature structure of $NaH_3(SeO_3)_2$ has almost been completed. Preliminary results show that the heavy atom positions determined by Unterlitner (1966) are correct and those by Chou and Chotang (1957) contain errors. Hydrogen positions will be available shortly.

III $KH_3(SeO_3)_2$

Preliminary measurements show $KH_3(SeO_3)_2$ space group Pbc with $\underline{a}$=6.32, $\underline{b}$=16.11, $\underline{c}$=6.24, Z=4 molecules/unit cell.

Liquid Structures

It was hoped to determine the structure (coordination) of molten $SnCl_2$. 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.

Measurements have been made of the scattering lengths of all available isotopes of Sn. These are: $b^{116} = .58 \pm .01$, $b^{117} = .64 \pm .02$, $b^{118} = .58 \pm .01$, $b^{119} = .58 \pm .01$, $b^{119} = .60 \pm .02$, $b^{120} = .64 \pm .01$, $b^{122} = .55 \pm .03$, $b^{124} = .59 \pm .02$. The above isotopes account for $98^{o}/_{o}$ of the isotopic content of natural tin. If only isotopic incoherence is included the total scattering cross section is 4.62×10^{-24}cm and the coherent cross section 4.61×10^{-24}cm. 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 nuclei account for only about $15^{o}/_{o}$ 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 liquid work with Cu Cl using Cu, Cu^{63}, Cu^{65}, Cl, Cl^{35}, Cl^{37} which have scattering lengths of .79, .67, 1.11, .96, 1.18, $.26 \times 10^{-12}$cm, respectively.

Table I

Structural Parameters for Mn Formate $\cdot 2H_2O$ Parameters from neutron data are given first, followed by standard deviations followed by X-Ray parameters (ONW) in parentheses.
O_w and H_w are water oxygens and hydrogens, respectively

Atom	X	Y	Z	B
Mn1	0	0	0	1.2±.3(1.1)
Mn2	.5	.5	0	2.4±.5(1.1)
C1	.0364±.0015(.038)	.2231±.0019(.220)	.2749±.0015(.274)	2.7±.3(2.1)
C2	.3265±.0012(.328)	.6134±.0017(.621)	.4322±.0012(.433)	2.1±.2(1.8)
O1	.0983±.0012(.096)	.1067±.0020(.102)	.2033±.0013(.204)	2.1±.2(1.8)
O2	.0868±.0012(.084)	.2682±.0027(.266)	.4004±.0012(.398)	2.2±.2(1.7)
O3	.4341±.0012(.439)	.7217±.0021(.723)	.4204±.0012(.420)	2.3±.2(2.3)
O4	.2135±.0016(.213)	.6565±.0019(.656)	.4926±.0018(.494)	2.1±.2(1.5)
O_w1	.2700±.0014(.267)	.4826±.0020(.485)	.0656±.0015(.066)	2.2±.3(1.8)
O_w2	.4120±.0015(.410)	.1113±.0026(.107)	.2958±.0015(.296)	3.0±.3(2.4)
H_1	-.065±.004	.283±.008	.227±.006	7.8±1.2
H_2	.335±.004	.482±.006	.395±.004	6.3±.9
H_w1	.227±.003	.609±.004	.051±.003	3.9±.5
H_w2	.203±.003	.394±.004	.009±.004	3.9±.6
H_w3	.307±.003	.099±.005	.261±.003	4.0±.5
H_w4	.460±.002	.146±.004	.224±.002	3.2±.5

Table IIa

Bond Distances and Angles in Manganese and Copper Formate Dihydrates with Standard Deviations. X-Ray results for Mn (ONW) and previous X-ray refinement 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				
M1-01	2.172±.012	(2.15)	2.304±.018	(2.28)
M1-02	2.135±.017	(2.15)	1.988±.016	(2.02)
M1-04	2.218±.014	(2.21)	2.019±.017	(2.01)
01-M1-02	89.7±.5	(88.7)	89.2±.7	(90)
01-M1-04	88.4±.5	(88.2)	88.5±.6	(87)
02-M1-04	88.1±.5	(87.3)	86.8±.7	(89)
M2-03	2.219±0.15	(2.21)	2.368±.019	(2.35)
M2-O_w1	2.216±.013	(2.24)	2.044±.017	(2.02)
M2-O_w2	2.168±.015	(2.16)	1.974±.015	(1.97)
O_3-M_2-O_w1	86.6±.5	(87.0)	87.6±.6	(88)
O_3-M_2-O_w2	89.1±.6	(88.4)	86.9±.6	(87)
O_w1-M_2-O_w2	89.8±.5	(89.8)	87.5±.7	(89)
II FORMATE GROUPS				
C1-01	1.26±.02	(1.28)	1.26±.03	(1.29)
C1-02	1.27±.02	(1.26)	1.30±.02	(1.19)
01-C1-02	124.5±1.2	(126)	121±2	(124)
C1-H_F1	1.05±.05[1.11]			
01-C1-H_F1	116.5±3.8			
02-C1-H_F1	118.9±3.8			

Table IIa Contd.

C2-O3	1.25±.02	(1.25)	1.26±.03	(1.27)
C2-O4	1.26±.02	(1.27)	1.24±.03	(1.21)
$C2-H_F2$	1.03±.05	[1.08]		
O3-C2-O4	123.0±1.4	(128)	130±2	(124)
$O3-C2-H_F2$	117.5±2.1			
$O4-C2-H_F2$	119.5±2.2			
III HYDROGEN BONDS AND WATER MOLECULES				
O_w1-H_w1	1.00±.04	[1.02]		
O_w1-H_w2	.99±.04	[1.01]		
$H1-O_w1-H_2$	109±2			
O_w1-O4	2.75±.02	(2.73)	2.78±.02	(2.85)
H_w1-O4	1.79±.04			
O_w1-H_w1-O4	158±3			
O_w1-O2	2.79±.02	(2.81)	2.82±.02	(2.82)
H_w2-O2	1.80±.03			
O_w1-H_w2-O2	177±3			
O_w2-H_w3	.95±.03	[.96]		
O_w2-H_w4	.89±.03	[.89]		
$H_w3-O_w2-H_w4$	107.5±2.3			
O_w2-O1	2.80±.02	(2.81)	2.77±.03	(2.79)
$O1-H_w3$	1.86±.03			
O_w2-H_w3-O1	172±3			
O_w2-O3	2.75±.02	(2.75)	2.67±.02	(2.76)
$O3-H_w4$	1.86±.03			
O_w2-H_w4-O3	178±2			

Table IIb

Bond Distances and Angles with Standard Deviations in Anydrous Copper Formate
Old X-ray refinement results are in parentheses

ATOMS	DISTANCES	STANDARD DEVIATIONS
Cu - O1	1.944 (1.945)	.009
Cu - O2	1.939 (1.942)	.008
Cu - O3	1.971 (1.986)	.007
Cu - O4	1.931 (1.928)	.009
Cu - O3	2.415 (2.397)	.008
Cu - Cu	3.432 (3.435)	.003
C1 - O1	1.243 (1.235)	.013
C1 - O3	1.269 (1.295)	.013
C2 - O2	1.258 (1.278)	.015
C2 - O4	1.287 (1.284)	.014
O1 - Cu - O2	88.4 (89)	.35
O1 - Cu - O3	94.9 (95)	.33
O2 - Cu - O4	88.9 (89)	.37
O3 - Cu - O4	87.8 (88)	.35
O1 - C1 - O3	120.9 122	1.0
O2 - C2 - O4	123.6 122	1.1

Table IIIa

Rerefined Parameters and Standard deviations from X-ray Data of
. M. Bukowska-Strzyzewska
Original parameters in parentheses

Atom	X	Y	Z	B
Cu1	0	0	0	1.4±.1
Cu2	.5	.5	0	1.7±.1
C1	.022±.003(.033)	.214±.004(.217)	.296±.003(.302)	2.6±.5
C2	.312±.003(.308)	.606±.004(.600)	.423±.002(.422)	2.1±.4
O1	.094±.002(.094)	.101±.002(.096)	.224±.002(.223)	2.0±.3
O2	.065±.002(.067)	.266±.003(.267)	.421±.002(.417)	1.9±.3
O3	.430±.002(.425)	.703±.003(.705)	.401±.002(.406)	2.6±.3
O4	.204±.002(.204)	.358±.003(.356)	.494±.001(.493)	1.8±.3
O_w1	.265±.002(.269)	.494±.002(.464)	.073±.002(.075)	2.3±.3
O_w2	.415±.002(.411)	.107±.002(.103)	.315±.002(3.16)	2.2±.3

Table IIIb

Refined Parameters and Standard Deviation from X-Ray data of Barclay and Kennard
Original Parameters are in Parentheses

	X	Y	Z
Cu	.1150 (.1152).0001	.0587 (.0588).0002	.0062 (.0065).0003
Cl	.0191 (.0164).0008	.3254 (.3226).0013	.1614 (.1613).0016
C2	.2772 (.2778).0006	.1340 (.1353).0015	.2349 (.2336).0021
01	.0896 (.0893).0005	.2433 (.2427).0009	.1605 (.1621).0014
02	.2223 (.2223).0006	.0275 (.0262).0010	.1936 (.1950).0013
03	.0070 (.0067).0005	.0787 (.0781).0009	-.1910 (.1902).0012
04	.1488 (.1493).0005	-.1211 (-.1207).0009	-.1469 (-.1459).0015

Thermal Parameters

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	.0014	.0041	.0107	.0002	-.0005	-.0006
Cl	.0024	.0042	.0066	-.0007	.0021	-.0013
C2	.0025	.0044	.0103	.0019	-.0006	.0083
01	.0012	.0043	.0139	.0026	-.0015	-.0029
02	.0021	.0049	.0105	-.0002	-.0048	-.0024
03	.0014	.0043	.0093	-.0031	-.0024	-.0002
04	.0014	.0047	.0196	.0001	.0024	-.0025

Table IV

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

Sample	$NaAl(SO_4)_2 \cdot 12H_2O$	$ND_4Al(SO_4)_2 \cdot 12H_2O$	$CsAl(SO_4)_2 \cdot 12H_2O$
Space Gp.	———	$Pa\bar{3}$	———
a	12.213	12.234	12.352
$A^+(X,Y,Z,)$	———	(.5, .5, .5)	———
$Al^{+3}(X,Y,Z)$	———	(0, 0, 0)	———
S(X,X,X)	.2652	.3090	.3287
$O_s(1)$ (X,X,X)	.3343	.2408	.2596
$O_s(2)$X	.2957	.3142	.2789
Y	.2783	.2607	.3411
Z	.1417	.4173	.4364
$O_w(1)$X	.0767	.0456	-.1593
Y	.0403	.1383	.0507
Z	.3188	.2977	.2847
$O_w(2)$X	.1371	.0184	.1524
Y	.9596	-.0169	-.0020
Z	.0573	.1546	.0000

Table V

Hydrogen parameters in $NaAl(SO_4)_2.12H_2O$ from least squares refinement of neutron diffraction data

Atom	x	Y	z
H(1)	0.5958(21)	0.3172(20)	0.3663(21)
H(2)	0.4709(22)	0.3123(21)	0.3808(20)
H(3)	0.5504(18)	0.2031(15)	0.4958(17)
H(4)	0.5926(17)	0.3422(16)	0.1104(18)

Table VI

Interatomic distances and angles in $NaAl(SO_4)_2 \cdot 12H_2O$
Standard deviations, in parentheses, apply to the rightmost digit
Distances corrected for thermal motion are in parentheses
Distances and angles from neutron data are in underlined.

Al-6O_w(2)	1.881(2)Å	O_w(2)-Al-O_w(2)	90.0(1)°
		O_w(2)-Al-O_w(2)	90.0(1)
Na-6O_w(1)	2.453(2)	O_w(1)-Na-O_w(1)	85.0(1)
		O_w(1)-Na-O_w(1)	95.0(1)
The sulfate group			
S-O_s(1)	1.461(4)	O_s(1)-S-O_s(2)	110.1(1)
	(1.476)	O_s(2)-S-O_s(2)	108.9(1)
S-3O_s(2)	1.454(2)	O_s(2)-O_s(2)-O_s(2)	60.0
	(1.478)	O_s(2)-O_s(2)-O_s(1)	60.3(1)
O_s(1)-3O_s(2)	2.389(4)	O_s(2)-O_s(1)-O_s(2)	59.4(1)
O_s(2)-2O_s(2)	2.366(4)		
Water molecules			
O_w(1)-H(1)	0.78(4)	H(1)-O_w(1)-H(2)	$\underline{103(2)}$
	$\underline{0.973(24)}$		
	$\underline{(1.017)}$		
O_w(1)-H(2)	0.83(4)		
	0.997(24)		
	$\underline{(1.054)}$		
O_w(2)-H(3)	0.92(4)	H(3)-O_w(2)-H(4)	$\underline{108(2)}$
	0.976(17)		
	$\underline{(1.009)}$		
O_w(2)-H(4)	1.01(3)		
	0.991(20)		
	1.006		

Table VI Contd.

Hydrogen bonds

$O_s(1)$-3$O_w(1)$	2.747(4)	$O_s(1)$-H(2) -$O_w(1)$	162(3)
$O_s(1)$--3 H(2)	1.783(25)		
$O_s(2)$ -$O_w(1)$	2.822(3)	$O_s(2)$ -H(1) -$O_w(1)$	156(3)
$O_s(2)$ -H(1)	1.907(23)		
$O_s(2)$ -$O_w(2)$	2.623(3)	$O_s(2)$ -H(4) -$O_w(2)$	174(2)
$O_s(2)$ -H(4)	1.635(20)		
$O_w(1)$ -$O_w(2)$	2.649(3)	$O_w(1)$ -H(3) -$O_w(2)$	178(2)
$O_w(1)$ -H(3)	1.673(17)		

Table VIIa

Thermal ellipsoids in $NaAl(SO_4)_2 \cdot 12H_2O$ from X-ray data
Standard deviations, in parentheses, apply to rightmost digit

			Direction angles relative to crystal axes		
Atom	RMS Amplitude	B_i	α	β	γ
Na	0.170(5)Å	2.28(13)Å^2	54.7°	54.7°	54.7°
	0.180(3)	2.55(8)			
	0.180(3)	2.55(8)			
Al	0.159(4)	1.99(10)	54.7	54.7	54.7
	0.140(3)	1.54(6)			
	0.140(3)	1.54(6)			
S	0.183(2)	2.63(7)	54.7	54.7	54.7
	0.168(2)	2.24(4)			
	0.168(2)	2.24(4)			
$O_s(1)$	0.173(7)	2.36(19)	54.7	54.7	54.7
	0.251(4)	4.97(15)			
	0.251(4)	4.97(15)			
$O_s(2)$	0.367(4)	10.62(21)	31(1)	115(1)	74(1)
	0.202(4)	3.22(12)	79(2)	39(3)	53(4)
	0.164(4)	2.12(11)	118(1)	118(4)	42(4)
$O_w(1)$	0.245(4)	4.76(16)	44(3)	133(2)	98(3)
	0.182(4)	2.63(12)	53(8)	60(11)	51(16)
	0.172(4)	2.34(12)	111(11)	122(10)	40(16)
$O_w(2)$	0.149(4)	1.75(10)	36(6)	117(5)	67(4)
	0.178(4)	2.50(11)	54(6)	46(6)	114(6)
	0.206(3)	3.35(10)	95(4)	56(5)	34(4)

Table VIIb

Thermal ellipsoids in $NaAl(SO_4)_2 \cdot 12H_2O$ from neutron diffraction data
Standard deviations, in parentheses, apply to the rightmost digit

			Direction angles relative to crystal axes		
Atom	RMS Amplitude	B_i	α	β	γ
Na	0.06(27)Å	0.3(25)Å^2	54.7°	54.7°	54.7°
	0.20(6)	3.3(20)			
	0.20(6)	3.3(20)			
Al	0.17(10)	2.3(28)	54.7	54.7	54.7
	0.08(10)	0.5(13)			
	0.08(10)	0.5(13)			
S	0.14(9)	1.5(19)	54.7	54.7	54.7
	0.20(4)	3.3(12)			
	0.20(4)	3.3(12)			
$O_s(1)$	0.20(5)	3.2(16)	54.7	54.7	54.7
	0.24(3)	4.5(11)			
	0.24(3)	4.5(11)			
$O_s(2)$	0.38(2)	11.6(13)	27(4)	113(4)	76(3)
	0.19(3)	2.8(9)	64(5)	30(10)	104(14)
	0.10(4)	0.8(6)	97(7)	71(13)	20(10)
$O_w(1)$	0.20(2)	3.0(8)	24(167)	114(174)	86(39)
	0.20(2)	3.3(8)	67(174)	25(167)	80(21)
	0.14(3)	1.6(6)	97(23)	98(17)	11(19)
$O_w(2)$	0.12(3)	1.2(6)	36(14)	121(14)	106(24)
	0.21(2)	3.4(7)	56(15)	34(18)	85(35)
	0.18(2)	2.4(6)	79(25)	103(36)	17(27)
H(1)	0.32(4)	8.3(20)	23(20)	91(16)	67(20)
	0.22(4)	3.8(13)	90(134)	2(310)	88(315)
	0.23(4)	4.0(15)	113(20)	92(342)	23(36)
H(2)	0.35(4)	9.4(22)	44(15)	110(13)	127(11)
	0.24(4)	4.5(15)	53(16)	43(17)	72(18)
	0.14(5)	1.6(12)	71(14)	126(17)	42(11)
H(3)	0.21(3)	3.3(11)	28(22)	112(20)	107(19)
	0.10(6)	0.7(9)	83(18)	38(11)	127(10)
	0.27(3)	5.8(14)	63(21)	60(13)	42(12)
H(4)	0.21(3)	3.5(11)	37(88)	53(85)	89(87)
	0.22(3)	3.9(10)	115(109)	57(85)	44(18)
	0.12(4)	1.1(9)	65(19)	19(17)	46(17)

Table VIII

Least squares parameters for $ND_4Al(SO_4)_2 \cdot 12D_2O$

Standard deviations, in parentheses, apply to the rightmost digit

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\beta_{11} \times 10^5$ or B ($\mathring{A}^2$)	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^5$
Al	0	0	0	140(46)	β_{11}	β_{11}	-130(100)	β_{12}	β_{12}
N	1/2	1/2	1/2	538(33)	β_{11}	β_{11}	170(109)	β_{12}	β_{12}
D(1)'	0.4479(21)	$\underline{x}$	$\underline{x}$	1253(128)	β_{11}	β_{11}	-253(390)	β_{12}	β_{12}
D(2)'	0.4505(19)	0.5655(16)	0.5134(29)	963(152)	637(147)	1250(204)	224(219)	234(296)	69(339)
S	0.3101(8)	$\underline{x}$	$\underline{x}$	249(42)	β_{11}	β_{11}	161(108)	β_{12}	β_{12}
$O_s(1)$	0.2397(6)	$\underline{x}$	$\underline{x}$	651(53)	β_{11}	β_{11}	-362(100)	β_{12}	β_{12}
$O_s(1)$'	0.3757(60)	$\underline{x}$	$\underline{x}$	4.4(28)					
$O_s(2)$	0.3139(6)	0.2649(8)	0.4194(7)	467(49)	673(76)	285(48)	506(100)	87(85)	561(103)
$O_s(2)$'	0.2177(38)	0.3775(38)	0.2942(36)	1.0(10)					
$O_w(1)$	0.0467(6)	0.1374(5)	0.2993(5)	484(48)	303(38)	432(45)	141(77)	-220(79)	-144(73)
$O_w(2)$	0.0170(5)	-0.0171(5)	0.1505(4)	351(38)	289(36)	156(31)	-18(67)	-94(57)	-4(58)
D(1)	0.1163(6)	0.1681(6)	0.2926(6)	518(48)	699(59)	762(59)	-133(96)	-239(88)	-346(87)
D(2)	-0.0041(6)	0.1952(5)	0.2848(6)	780(58)	490(47)	730(53)	65(102)	-302(98)	-331(78)
D(3)	0.2027(4)	0.0273(5)	0.0441(5)	307(33)	527(43)	542(43)	- 93(71)	99(67)	65(79)
D(4)	0.1856(5)	0.0428(5)	0.9153(5)	407(38)	556(43)	394(38)	-168(69)	120(68)	-31(70)

k = 0.116(22)

Table IX

Interatomic distances and bond angles in $ND_4Al(SO_4)_2 \cdot 12D_2O$
Standard deviations, in parentheses, apply to the rightmost digit
Distances corrected for thermal motion are in parentheses

Al-6 $O_w(2)$	1.865(5)Å	$O_w(2)$-Al-$O_w(2)$	90.8(2)°
		$O_w(2)$-Al-$O_w(2)$	89.2(2)
N-6 $O_w(1)$	3.031(7)	$O_w(1)$-N-$O_w(1)$	75.2(1)
		$O_w(1)$-N-$O_w(1)$	104.8(1)
N-$O_s(1)'$	2.64(13)		
ND_4 group			
N-2D(1)'	1.104(45)	D(1)'-N-D(2)	101.8(4)
N-6D(2)'	1.018(16)	D(2)'-N-D(2)'	115.9(9)
SO_4 group			
S-$O_s(1)$	1.49(2)	$O_s(1)$-S-$O_s(2)$	109.4(8)
S-$O_s(1)'$	1.39(13)	$O_s(2)$-S-$O_s(2)$	109.6(8)
S-$O_s(2)$	1.448(9)	$O_s(1)'$-S-$O_s(2)'$	102(2)
S-$O_s(2)'$	1.41(4)	$O_s(2)'$-S-$O_s(2)$	116(2)
Water molecules			
$O_w(1)$-D(1)	0.934(9)Å	D(1)-$O_w(1)$-D(2)	106.1(9)°
	(0.965)		
$O_w(1)$-D(2)	0.958(9)Å		
	(0.978)		
$O_w(2)$-D(3)	0.993(7)	D(3)-$O_w(2)$-D(4)	108.2(7)
	(1.008)		
$O_w(2)$-D(4)	0.984(7)		
	(1.005)		

Table IX continued

$O_s(1)$-3 $O_w(1)$	2.772(11)	$O_s(1)$-D(1)-$O_w(1)$	163.6(9)
$O_s(1)$-^{3}D(1)	1.863(11)		
$O_s(2)$-$O_w(1)$	2.777(9)	$O_s(2)$-D(2)-$O_w(1)$	168.1(9)
$O_s(2)$-D(2)	1.832(10)		
$O_s(2)$-$O_w(2)$	2.617(8)	$O_s(2)$-D(4)-$O_w(2)$	169.7(7)
$O_s(2)$-D(4)	1.643(9)		
$O_s(2)'$-$O_w(1)$	2.83(4)	$O_s(2)'$-D(2)-$O_w(1)$	167(2)
$O_s(2)'$-D(2)	1.89(4)		
$O_s(2)'$-$O_w(2)$	2.77(4)	$O_s(2)'$-D(4)-$O_w(2)$	162(2)
$O_s(2)'$-D(4)	1.82(4)		
$O_w(1)$-$O_w(2)$	2.652(9)	$O_w(1)$-D(3)-$O_w(2)$	174.4(6)
$O_w(1)$-D(3)	1.662(9)		

Table X

Thermal ellipsoids in $ND_4Al(SO_4)_2\cdot 12D_2O$

Standard deviations, in parentheses, apply to the rightmost digit

Atom	r. m. s. Amplitude	B_i	Direction angles relative to cell axes		
			α	β	γ
N	.23(2)Å	4.2(7)Å^2	54.7°	54.7°	54.7°
	.18(1)	2.7(3)	-	-	-
	.18(1)	2.7(3)	-	-	-
D(1)'	.28(5)	6.0(23)	54.7	54.7	54.7
	.32(3)	8.3(17)	-	-	-
	.32(3)	8.3(17)	-	-	-
D(2)'	.27(2)	5.7(9)	28(25)	74(21)	112(22)
	.21(2)	3.6(8)	107(19)	17(20)	90(17)
	.31(2)	7.8(12)	69(22)	84(14)	22(22)
Al	.03(14)	0.1(6)	54.7	54.7	54.7
	.12(2)	1.2(4)	-	-	-
	.12(2)	1.2(4)	-	-	-
S	0.18(3)	2.5(8)	54.7	54.7	54.7
	0.11(2)	1.0(4)	-	-	-
	0.11(2)	1.0(4)	-	-	-
$O_s(1)$	0.15(2)	1.7(6)	54.7	54.7	54.7
	0.25(1)	5.0(5)	-	-	-
	0.25(1)	5.0(5)	-	-	-
$O_s(2)$	0.17(1)	2.2(3)	33(6)	105(6)	118(7)
	0.27(1)	5.7(6)	63(4)	76(3)	68(4)
	0.09(2)	0.7(2)	74(7)	122(4)	37(6)
$O_w(1)$	0.21(1)	3.6(3)	43(8)	72(6)	127(8)
	0.14(1)	1.6(2)	98(18)	20(12)	72(20)
	0.16(1)	2.1(3)	48(10)	98(24)	43(14)
$O_w(2)$	0.17(1)	2.2(2)	13(7)	93(27)	102(9)
	0.15(1)	1.8(2)	89(27)	10(14)	100(13)
	0.10(1)	0.8(2)	77(7)	81(11)	16(8)

Table X continued

Atom	r. m. s. Amplitude	B_i	Direction angles relative to cell axes		
			α	β	γ
D(1)	0.18(1)	2.4(3)	40(9)	63(8)	62(6)
	0.22(1)	4.0(3)	129(9)	48(10)	67(11)
	0.26(1)	5.5(4)	98(8)	127(9)	38(8)
D(2)	0.22(1)	3.9(4)	43(9)	114(9)	57(9)
	0.17(1)	2.4(3)	83(8)	30(8)	61(6)
	0.27(1)	5.7(4)	132(8)	107(6)	47(7)
D(3)	0.15(1)	1.7(2)	17(8)	78(8)	102(7)
	0.20(1)	3.1(3)	107(8)	38(40)	123(42)
	0.21(1)	3.4(3)	87(15)	54(42)	36(40)
D(4)	0.16(1)	2.0(2)	42(14)	77(10)	129(17)
	0.21(1)	3.6(3)	116(8)	29(10)	101(10)
	0.18(1)	2.6(2)	59(16)	65(12)	42(17)

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Figures

Stereoscopic figures (1,2,3) should be viewed with one's eyes decoupled i.e. The right side of the figure should be viewed 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 commercial viewer, is of aid.

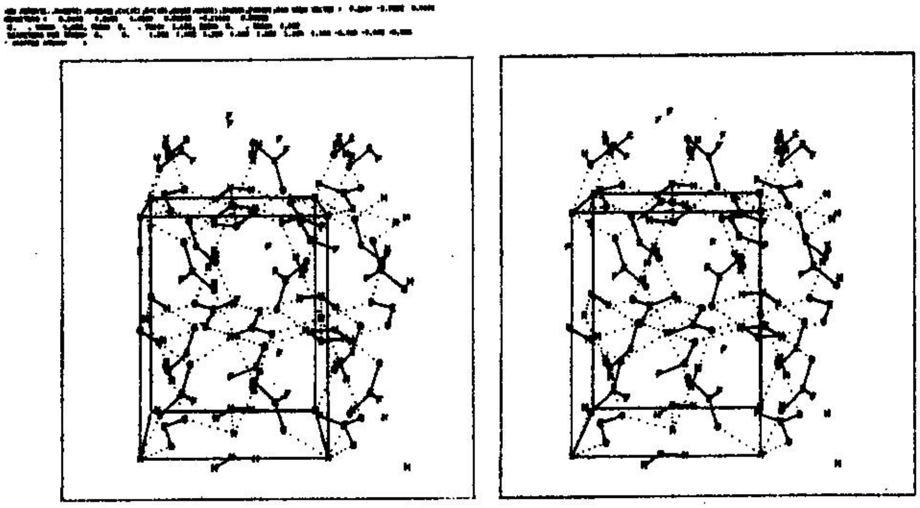


Fig. 1 Stereogram of Manganous Formate Dihydrate.
View is slightly off (100) direction.

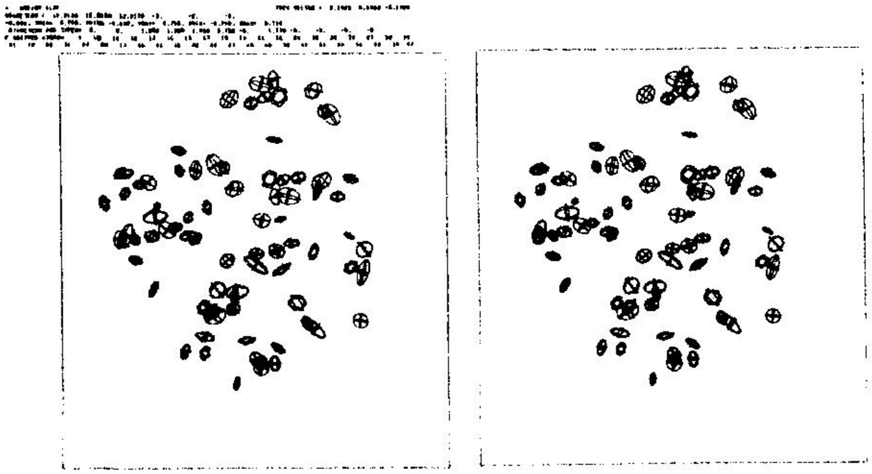


Fig. 2 Stereogram of Sodium Alum. Ellipsoids are scaled to twice the R.M.S. amplitude of vibration.

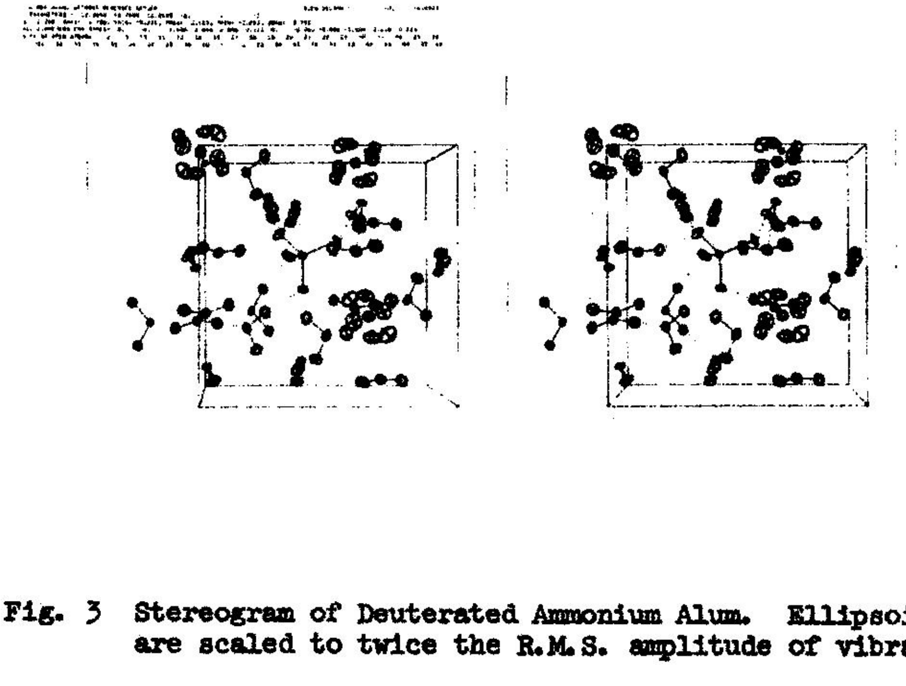


Fig. 3 Stereogram of Deuterated Ammonium Alum. Ellipsoids are scaled to twice the R.M.S. amplitude of vibration

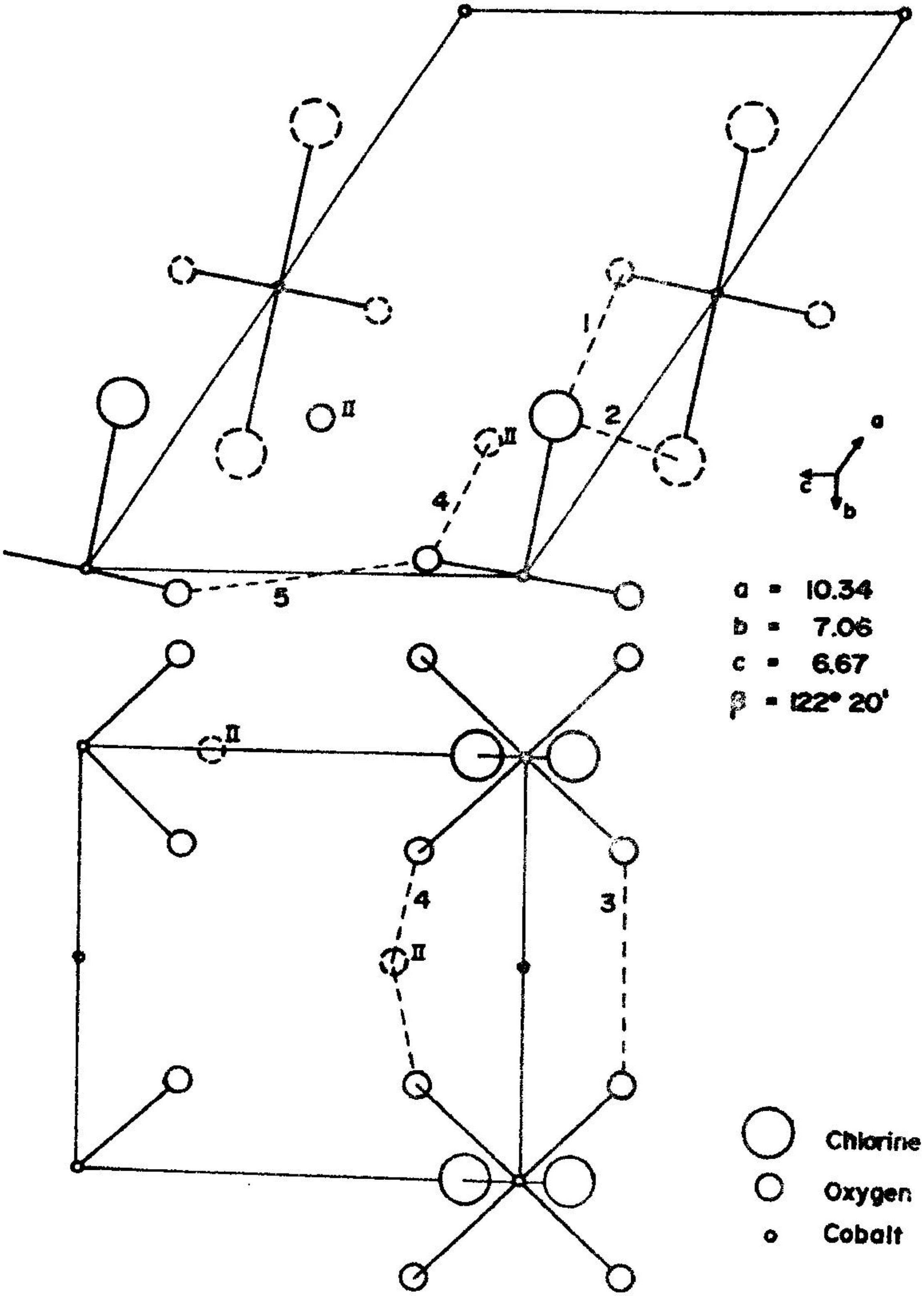
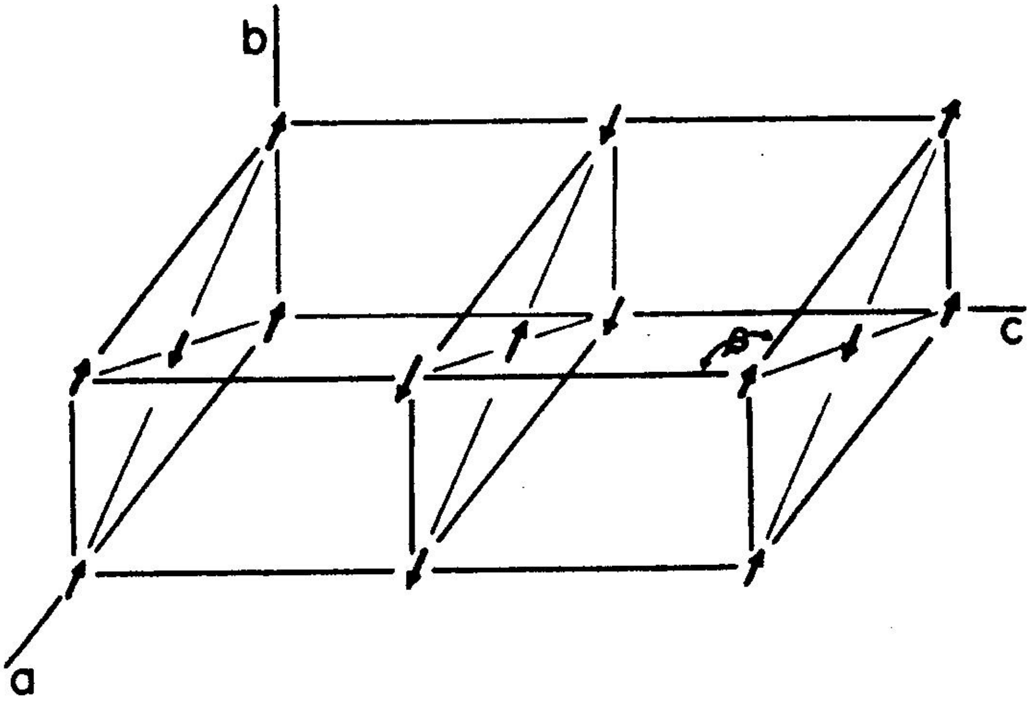
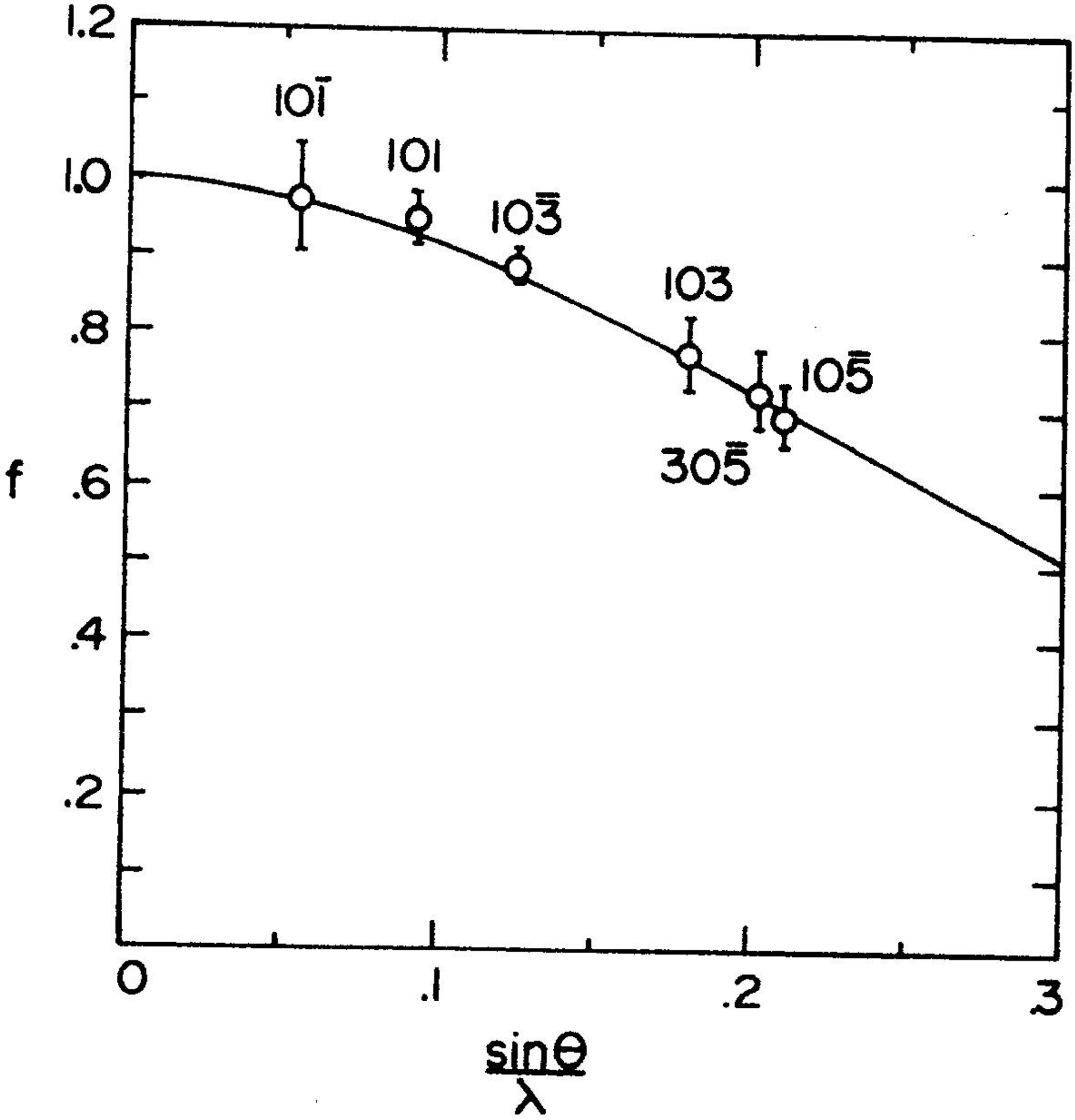


Fig. 4 Sketch of Co(or Ni)Cl$_2$·6H$_2$O showing surroundings of the metal ion and possible exchange paths.



Arrangement of magnetic moments in $NiCl_2 \cdot 6H_2O$ for the magnetic space group I_c2/c. The angle between the magnetic moment and the a axis is approximately 10°.

Fig. 5



Form factor for Ni^{2+} in $NiCl_2 \cdot 6H_2O$, 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

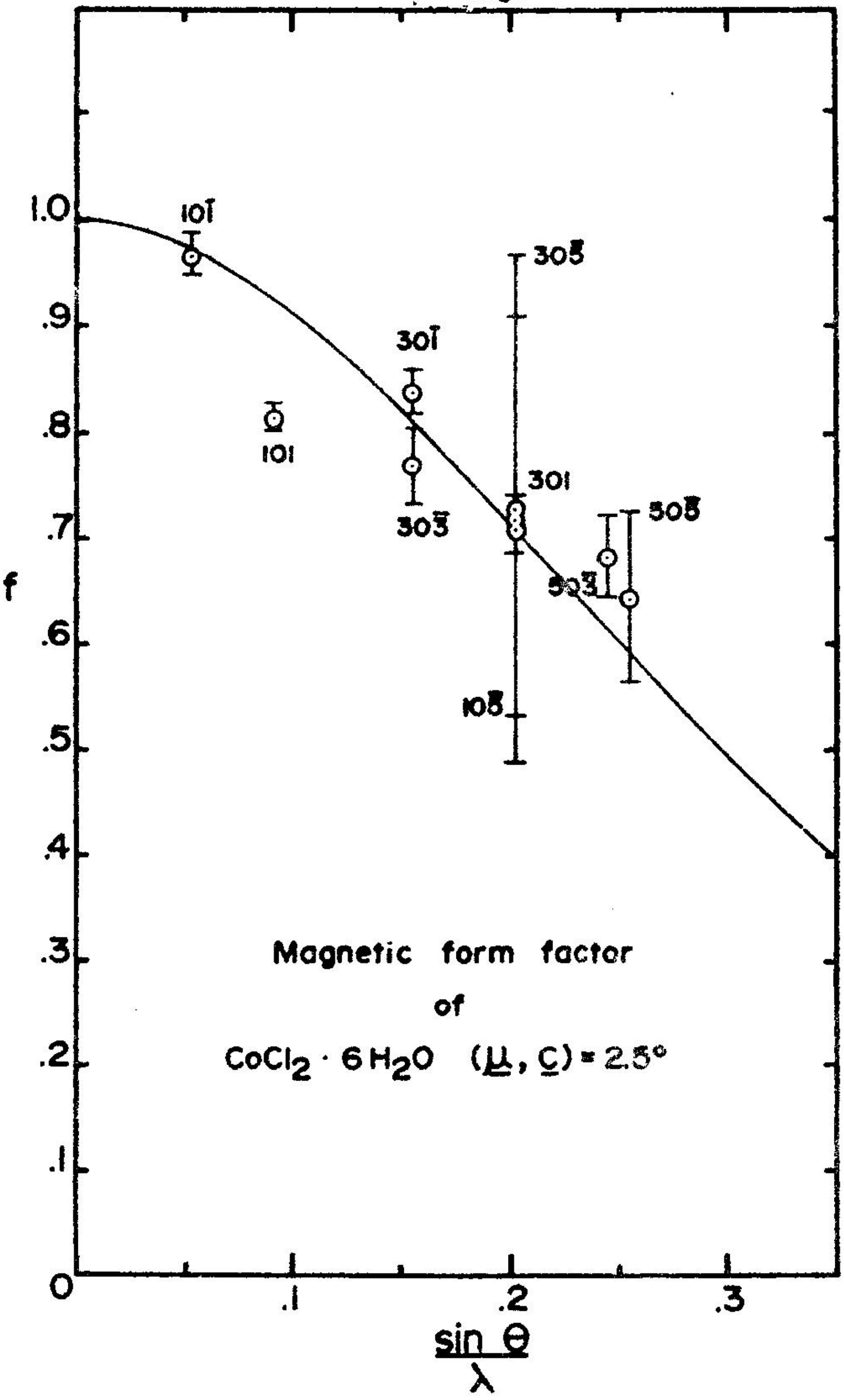

1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
.1
.2
.3
f
sin Θ / λ
101̄
301̄
101
303̄
305̄
301
508̄
503̄
108̄
Magnetic form factor
of
CoCl$_2$ · 6 H$_2$O (μ, c) = 2.5°

Fig. 7

Publication List

Dates and Titles of Publications

1. Crystal Structure by Neutron Diffraction and the Antiferroelectric Phase Transition in Copper Formate Tetrahydrate, K. Okada, M.I. Kay, D.T. Cromer, I. Almodovar, J. Chem. Phys. 44, 1648 (1966).

2. Magnetic Structure of the Zeta Phase of Pd_3Mn_2 Alloy, J.A. Gonzalo and M.I. Kay, J. Phys. Soc. Japan 21, 1626 (1966).

3. Refinement of the Structure of D-Tartaric Acid by X-Ray and Neutron Diffraction, Y. Okaya, N.R. Stemple, and M.I. Kay, Acta Cryst 21, 237 (1966).

4. Refinement of the Alum Structure
   1 X-Ray and Neutron Diffraction Study of $CsAl(SO_4)_2 \cdot 12H_2O$, a β Alum, D.T. Cromer, M.I. Kay, A.C. Larson 21, 383 (1966).

5. Refinement of the Alum Structures
   II X-Ray and Neutron Diffraction of $NaAl(SO_4)_2 \cdot 12H_2O$, γ Alum, D.T. Cromer, M.I. Kay, and A.C. Larson, Acta Cryst, in press.

6. Refinement of the Alum Structures,
   IV Neutron Diffraction Study of Deuterated Ammonium Alum $ND_4Al(SO_4) \cdot 12D_2O$ and α Alum, D.T. Cromer, and M.I. Kay, Acta Cryst, in press.

7. Magnetic Structure of $NiCl_2 \cdot 6H_2O$, R. Kleinberg, J. Appl. Phys. To be published March, 1967.

Papers presented at meetings

1. Crystal Structure by Neutron Diffraction and Antiferroelectric properties of Copper Formate Tetrahydrate, K. Okada, M.I. Kay, D.T. Cromer, I. Almodovar, American Crystallographic Assn. Meeting, Austin, Texas, Feb., 1966.

2. Refinement of Alum Structures, D.T. Cromer, M.I. Kay, A.C. Larson American Crystallographic Assn. Meeting, Austin, Texas, Feb., 1966.

3. Magnetic Structure of Zeta Pd_3Mn_2, J.A. Gonzalo and M.I. Kay, International Union of Crystallography, International Congress, Moscow, U.S.S.R., July, 1966.

4. Magnetic Structure of $CoCl_2 \cdot 6H_2O$, R. Kleinberg, presented at American Physical Soc. Meeting, Mexico City, Aug., 1966.

5. Magnetic Structure of $NiCl_2 \cdot 6H_2O$, R. Kleinberg, 12th Annual Conference of Magnetism and Magnetic Materials, Washington, D.C., Nov., 1966.

6. The Hydrogen Positions in Mn Formate $\cdot 2H_2O$, M.I. Kay, I. Almodovar, and S.F. Kaplan, American Crystallographic Assn. Meeting, Atlanta, Georgia Jan., 1967.