# Crystal structure of magnesium potassium sulfate hexahydrate $MgK_2(SO_4)_2 \cdot 6H_2O$

By K. K. KANNAN and M. A. VISWAMITRA

Department of Physics, Indian Institute of Science, Bangalore, India

## Auszug

Die Kristallstruktur des mit $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ isomorphen $MgK_2(SO_4)_2 \cdot 6H_2O$ wurde aus dreidimensionalen Interferenzdaten mittels Fourier- und Ausgleichsmethoden verfeinert. Raumgruppe ist $P2_1/a$; die Gitterkonstanten sind: $a = 9{,}072$, $b = 12{,}212$, $c = 6{,}113$ Å, $\beta = 104°50'$; $Z = 2$. Mg ist von sechs $H_2O$-Sauerstoffatomen oktaedrisch umgeben. Jedes dieser Atome ist mit zwei $SO_4$-Sauerstoffatomen durch Wasserstoffbindung gekoppelt. Das Mg-Atom hat somit zwölf O-Atome als zweitnächste Nachbarn, welche die Ecken eines abgeplatteten Ikosaeders bilden. Die S-Atome sind nahezu tetraedrisch von O-Atomen umgeben. Ein $H_2O$- und fünf $SO_4$-Sauerstoffatome bilden die nächste Umgebung der K-Atome. Die Polyeder und die K-Atome sind durch die Gleitrichtung und durch gemeinsame Ecken zu Ketten parallel $a$ angeordnet. Die Struktur ist aus diesen parallelen Ketten aufgebaut; die Polyeder um die S- und die Mg-Atome sind dazwischen eingelagert.

## Abstract

The crystal structure of $MgK_2(SO_4)_2 \cdot 6H_2O$, isomorphous with $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$, has been refined from three-dimensional x-ray data using Fourier and least-square methods. The space group is $P2_1/a$, with $a = 9.072$, $b = 12.212$, $c = 6.113$ Å, $\beta = 104°50'$ and $Z = 2$. The magnesium atom has octahedral coordination of six water oxygens (Mg—O $= 2.056$ to $2.188$ Å, O—Mg—O angle $= 89°34'$ to $90°32'$) each of which is hydrogen-bonded to two sulfate-oxygen atoms ($\sim 2.75$ Å). Thus there are twelve second-nearest neighbours to the magnesium atom and they occupy the corners of a flattened icosahedron. The bond lengths and angles in the sulfate group are close to the tetrahedral values (S—O $= 1.442$ to $1.507$ Å and O—S—O angle $= 107°$ to $112°$). One water and five sulfate-oxygen atoms form the nearest neighbours of the potassium atom (K—O $\sim 2.9$ Å). The potassium polyhedra related by $a$ glide share a corner oxygen and run as a chain parallel to the $a$ axis. The structure is built of these parallel chains, the space in between them being filled by $SO_4$ and $Mg^{++}$ polyhedra.

## Introduction

Tutton's salts form one of the best known series of isomorphous compounds. They are double sulfates with the general formula $M'_2M''(SO_4)_2 \cdot 6H_2O$ where $M'$ is a monovalent positive ion like K, $NH_4$, Rb, Cs or Tl, and $M''$ is a divalent ion like Mg, Ca, Zn, V, Cd, Co, Fe or Ni. The sulfate groups in these compounds can be easily substituted by selenates. They crystallize in the space group $P2_1/a$ with two molecules in the unit cell. X-ray structure analysis of these salts [$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$] was first reported by HOFMANN[1]; WYCKOFF[2] pointed out this structure could only be approximately correct as some of the O—O distances were far too short. Proton magnetic resonance of the Tutton's salts $K_2Zn(SO_4)_2 \cdot 6H_2O$ $K_2Mg(SO_4)_2 \cdot 6H_2O$, $K_2Ni(SO_4)_2 \cdot 6H_2O$, $K_2Cu(SO_4)_2 \cdot 6H_2O$ and $K_2Co(SO_4)_2 \cdot 6H_2O$ was recently studied in this laboratory by CHIDAM-BARAM[3,4] and RAGHAVENDRA RAO[5] who also found that the Hofmann structure could not accommodate the hydrogen-bond scheme obtained from resonance study without large shifts in oxygen positions. This made us re-examine the structure of $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$. The $x, y$ coordinates of the atoms were first obtained from a $hk0$ $M_4$ minimum-funtion map. When we had proceeded to determine the "$z$" coordinates, after first refining the $x, y$ parameters from difference Fourier maps, MARGULIS and TEMPLETON[6] reported a complete and accurate structure analysis of the same salt. The $x, y$ coordinates we had obtained were in very good agreement with their values. The coordinates obtained by HOFMANN for Mg, N and S atoms were found to be essentially correct while there were serious errors in the oxygen parameters given by HOFMANN. The hydrogen positions obtained from the x-ray study of MARGULIS and TEMPLETON were consist-

[1] W. HOFMANN, Die Struktur der Tuttonschen Salze. Z. Kristallogr. 78 (1931) 279—333.

[2] R. W. G. WYCKOFF, Crystal structures. Interscience Inc., New York, 1957, Vol. II.

[3] R. CHIDAMBARAM, Ph. D. thesis, 1961, Indian Institute of Science, Bangalore.

[4] R. CHIDAMBARAM and C. RAGHAVENDRA RAO, Proton magnetic resonance study of the structure of two Tutton's salts. Jour. Chem. Physics 38 (1963) 210—213.

[5] Private communication.

[6] T. N. MARGULIS and DAVID TEMPLETON, Crystal structure and hydrogen bonding of magnesium ammonium sulphate hexahydrate. Z. Kristallogr. 117 (1962) 344—357.

ent[7] with the orientations of the $p$—$p$ vector of the water protons reported by CHIDAMBARAM and RAO. The crystal structures of $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ have also been recently solved by GRIMES *et. al.*[8] and MONTGOMERY and LINGA-FELTER[9] respectively. We have now determined the structure of $K_2Mg(SO_4)_2 \cdot 6H_2O$ (mineral name: Schönite) using three-dimensional x-ray data.

## Experimental

The specimens used in this investigation were cut from single crystals of $K_2Mg(SO_4)_2 \cdot 6H_2O$ grown by slow evaporation of a saturated aquous solution. Equi-inclination $hk0$, $hk1$, $hk2$, $hk3$ and $h0l$ intensity data were collected with $CuK\alpha$ radiation on multiple films using a Weissenberg camera[10] having a $3''$ diameter cassette. The intensities of the spots were estimated by visual comparison with a suitable intensity scale and Lorentz-polarization, and absorption corrections ($\mu = 108.23$ cm$^{-1}$; $\mu r = 1.4$) were applied. In the case of higher-level photographs, the Phillips spot-size correction[11] was applied to the elongated spots.

## Unit cell and space group

The unit-cell dimensions obtained at $30\,^\circ C$ for $K_2Mg(SO_4)_2 \cdot 6H_2O$ are compared with those obtained for other isomorphous crystals in Table 1. The monoclinic angle $\beta$ was first obtained from $hk1$ and $hk2$ photographs by BUERGER's offset method[12], and then from measurement on the zero-level $h0l$ picture.

It is seen from Table 1 that our values are in close agreement with those reported by HOFMANN. There is, however, as much

[7] D. H. TEMPLETON, ALLAN ZALKIN and T. N. MARGULIS, Comments on the orientation of the proton-proton vectors of water in Tutton's salts. Jour. Chem. Physics **39** (1963) 3155.

[8] N. W. GRIMES, H. F. KAY and M. W. WEBB, The crystal structure of ammonium nickel sulphate hexahydrate. Acta Crystallogr. **16** (1963) 823—829.

[9] H. MONTGOMERY and E. C. LINGAFELTER, The crystal structure of Tutton's salts. I. Zinc ammonium sulfate hexahydrate. Acta Crystallogr. **17** (1964) 1295—1299.

[10] M. A. VISWAMITRA, A low temperature Weissenberg camera. Jour. Sci. Inst. **39** (1962) 381—383.

[11] D. C. PHILLIPS, On the visual estimation of x-ray reflexion intensities from upper-Level Weissenberg photographs. Acta Crystallogr. **7** (1954) 746—751.

[12] M. J. BUERGER, X-ray crystallography, p. 375—380, John Wiley and Sons Inc., New York, 1942.

Table 1

| Substance | $a$ | $b$ | $c$ | $\beta$ | Reference |
|---|---|---|---|---|---|
| $K_2Mg(SO_4)_2 \cdot 6H_2O$ | 9.072 Å | 12.212 Å | 6.113 Å | 104°50' | Present |
|  | 9.058 | 12.265 | 6.107 | 104°48' | HOFMANN[1] |
| $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ | 9.324 | 12.597 | 6.211 | 107°14' | MARGULIS and TEMPLETON[6] |
| $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ | 9.181 | 12.459 | 6.239 | 106°57' | GRIMES et al.[8] |
| $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ | 9.28 | 12.57 | 6.25 | 106°48' | MONTGOMERY and LINGAFELTER[9] |

(±.015)

as $7\%$ difference in the cell volumes of the potassium and the corresponding ammonium compounds. This might, perhaps, be one of the reasons for the coordinate differences of 0.01 (in fractions of cell edges) that we find for some of the atoms in $K_2Mg(SO_4)_2 \cdot 6H_2O$ and $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$.

The extinction conditions observed are

$hkl$: No condition

$h0l$: $h = 2n$ present

$0k0$: $k = 2n$ present.

The space group is therefore $P2_1/a$.

$$d_{meas} = 2.034 \ g/cm^3, \qquad d_{cal} = 2.043 \ g/cm^3,$$

$$Z = 2.$$

## Structure determination

As mentioned earlier we proceeded to determine first the structure of the isomorphous $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ by making use
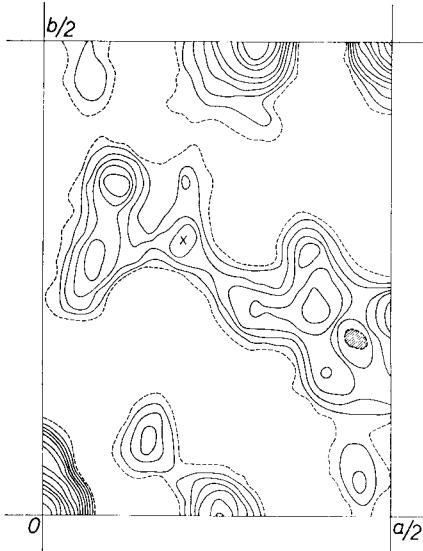


Fig. 1 a. Patterson projection $P(xy)$
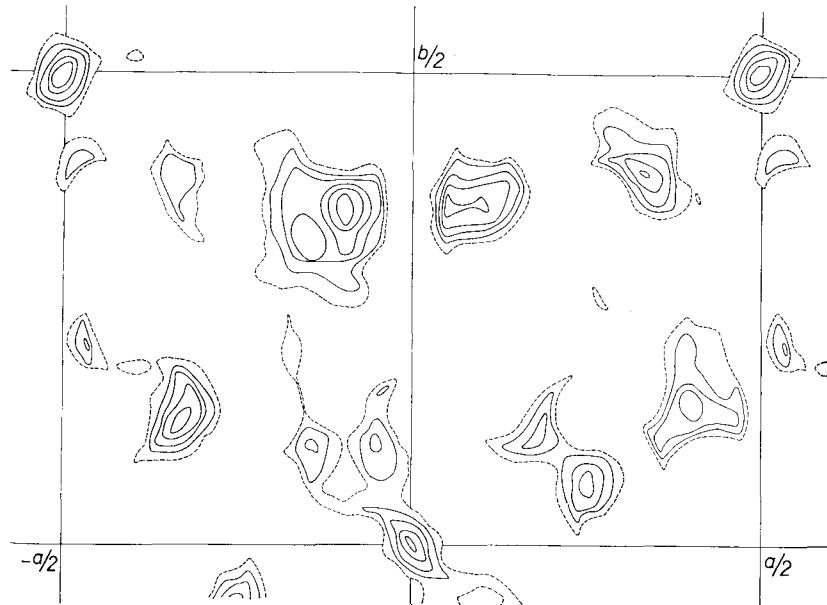
Fig. 1 b. Minimum-function map, $M_2(xy)$, based on the sulfur rotation peak marked $\times$ in 1 a

of BUERGER's image-seeking procedures[13]. Although this structure has now been solved by MARGULIS and TEMPLETON we give below the Patterson and the minimum-function maps just to illustrate how the whole structure was practically obtained in one straightforward computation of $M_4$ minimum function (Fig. 1).

The $x$, $y$ coordinates obtained for the $NH_4$ compound were used to calculate the first set of $hk0$ structure factors of $K_2Mg(SO_4)_2 \cdot 6H_2O$

[13] M. J. BUERGER, Vector space and its applications in crystal structure investigation, John Wiley and Sons Inc., New York, 1959.
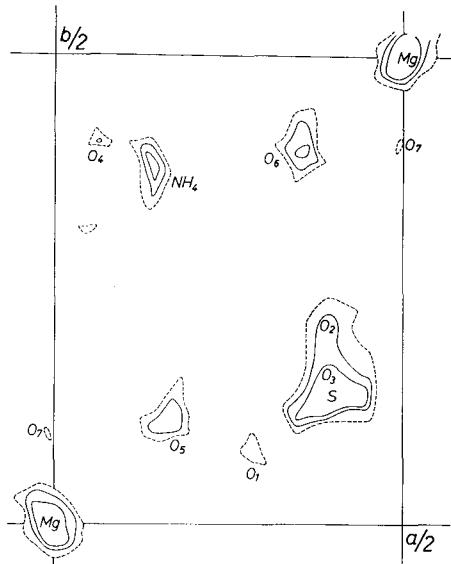


Fig. 1 c. Minimum-function map, $M_4(xy)$, formed from the $M_2(xy)$ map by utilizing the vertical glide in the structure

($R$ value $= 42^0/_0$). Refinement of these by three successive difference syntheses brought the $R$ value to $18^0/_0$. The "$z$" coordinates given by MARGULIS and TEMPLETON were then used to compute the $h0l$ structure factors. Refinement of these $x,y,z$ coordinates by $hk0$ and $h0l$ difference-Fourier maps reduced $R$ to $16^0/_0$ with a common isotropic temperature factor $B = 1$.

The structure was then refined by least-squares calculations on the National Elliot 803 B computer at Hindustan Aeronautics Ltd., Bangalore, using $hk0$, $h0l$, $hk1$, $hk2$ and $hk3$ three-dimensional data. The program was written to include diagonal terms only. Two cycles of refinement of the $x,y,z$ coordinates and individual isotropic temperature factors for the different species of atoms improved the $R$ factor for the three-dimensional data from $21^0/_0$ to $14.6^0/_0$. Scattering factors used were those given by FORSYTH and WELLS[14]. At this stage a three-dimensional model of the structure was made and the bond lengths and angles were calculated. The coordinates of the six water-hydrogens were also fixed so that the orientations of the $p$—$p$ vectors were consistent with the results of proton magnetic resonance obtained by CHIDAMBARAM and RAO[4] for $K_2Mg(SO_4)_2 \cdot 6H_2O$. A structure-factor calculation with hydrogens included (with $B = 1.51$) improved

Table 2. *Final atomic parameters*

| Atom | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| Mg | 0 | 0 | 0 | 0.96 |
| K | .131 | .346 | .345 | 1.29 |
| S | .410 | .137 | —.271 | 0.78 |
| $O_1$ | .285 | .060 | —.379 | 1.46 |
| $O_2$ | .403 | .232 | —.431 | 1.46 |
| $O_3$ | .388 | .173 | —.055 | 1.46 |
| $O_4$ | .553 | .080 | —.242 | 1.46 |
| $O_5(H_2O^1)$ | .172 | .111 | .169 | 1.46 |
| $O_6(H_2O^2)$ | —.169 | .113 | .026 | 1.46 |
| $O_7(H_2O^3)$ | .004 | .066 | —.307 | 1.46 |
| $H_1$ | .243 | .127 | .102 | 1.51 |
| $H_2$ | .214 | .095 | .327 | 1.51 |
| $H_3$ | .139 | —.176 | —.020 | 1.51 |
| $H_4$ | .270 | —.094 | .063 | 1.51 |
| $H_5$ | .013 | —.150 | .321 | 1.51 |
| $H_6$ | .104 | .060 | —.335 | 1.51 |

[14] J. B. FORSYTH and M. WELLS, On an analytic approximation to the atomic scattering factor. Acta Crystallogr. 12 (1959) 412—415.

Table 3. *Observed and calculated structure factors*

Calculations are for the coordinates given in Table 2 and are for the asymmetric part of the cell. The threshold for the unobservables * is taken equal to or less than half the minimum observed

| h | k | l | $F_o$ | $F_c$ |
|---|---|---|-------|-------|
| 0 | 2 | 0 | 2.93 | 2.60 |
| 4 |  |  | 23.66 | -29.33 |
| 6 |  |  | 2.75 | 3.60 |
| 8 |  |  | 7.72 | 6.64 |
| 10 |  |  | 6.57 | -7.07 |
| 12 |  |  | 2.15 | 1.74 |
| 14 |  |  | 4.17 | 5.20 |
| 0 | 0 | 1 | 1.31 | -1.89 |
| 2 |  |  | 11.00 | -10.94 |
| 3 |  |  | 18.36 | 23.65 |
| 4 |  |  | 3.79 | 4.42 |
| 5 |  |  | 0.23 | * 0.23 |
| 6 |  |  | 1.40 | 1.28 |
| 7 |  |  | 2.15 | 1.94 |
| 1 | 1 | 0 | 6.51 | -7.21 |
| 2 |  |  | 3.84 | -4.34 |
| 3 |  |  | 21.68 | 26.99 |
| 4 |  |  | 6.04 | -4.87 |
| 5 |  |  | 2.79 | -0.40 |
| 6 |  |  | 5.10 | -3.95 |
| 7 |  |  | 6.49 | -6.12 |
| 8 |  |  | 3.40 | 2.67 |
| 9 |  |  | 6.06 | 5.53 |
| 10 |  |  | 2.39 | *-2.39 |
| 11 |  |  | 6.82 | 6.49 |
| 12 |  |  | 0.66 | * 0.66 |
| 13 |  |  | 2.53 | -3.03 |
| 14 |  |  | 2.41 | 2.74 |
| 15 |  |  | 0.38 | * 0.38 |
| 2 | 0 | 0 | 9.05 | 10.01 |
| 1 |  |  | 7.56 | 7.59 |
| 2 |  |  | 2.11 | 2.58 |
| 3 |  |  | 5.96 | -5.88 |
| 4 |  |  | 4.64 | 4.97 |
| 5 |  |  | 2.75 | 2.32 |
| 6 |  |  | 3.25 | 2.49 |
| 7 |  |  | 3.53 | -3.19 |
| 8 |  |  | 2.59 | 1.68 |
| 9 |  |  | 3.46 | 3.03 |
| 10 |  |  | 0.10 | *-0.10 |
| 11 |  |  | 3.49 | 3.03 |
| 12 |  |  | 2.36 | 1.98 |
| 13 |  |  | 2.93 | -3.06 |
| 14 |  |  | 4.82 | 3.24 |
| 15 |  |  | 2.41 | -1.89 |
| 3 | 1 | 0 | 8.14 | 9.48 |
| 2 |  |  | 0.79 | *-0.79 |
| 3 |  |  | 1.61 | *-1.61 |
| 4 |  |  | 8.78 | 9.04 |
| 5 |  |  | 10.85 | 11.32 |
| 6 |  |  | 3.19 | 3.62 |
| 7 |  |  | 4.94 | 5.18 |
| 8 |  |  |  | *-0.22 |
| 9 |  |  | 7.79 | -6.96 |
| 10 |  |  | 5.75 | -6.04 |
| 11 |  |  |  | *-1.24 |
| 12 |  |  |  | * 1.16 |
| 13 |  |  | 5.71 | 5.10 |
| 14 |  |  | 2.07 | 2.11 |
| 15 |  |  | 1.69 | 1.30 |
| 4 | 0 | 0 | 13.64 | -15.65 |
| 1 |  |  | 6.84 | 7.71 |
| 2 |  |  | 15.60 | 17.85 |
| 3 |  |  | 5.16 | -4.64 |
| 4 |  |  | 15.30 | 15.29 |
| 5 |  |  | 9.56 | -9.67 |
| 6 |  |  | 9.38 | -9.05 |
| 7 |  |  | 2.14 | -1.64 |
| 8 |  |  | 5.55 | -5.28 |
| 9 |  |  | 6.35 | 6.51 |
| 11 |  |  |  | * 0.48 |
| 12 |  |  |  | * 0.93 |
| 13 |  |  |  | *-1.91 |
| 5 | 1 | 0 | 15.37 | 16.14 |
| 2 |  |  | 8.00 | -7.10 |
| 3 |  |  | 14.23 | -13.13 |
| 5 |  |  |  | *-0.25 |
| 6 |  |  | 3.75 | 3.87 |
| 7 |  |  | 10.25 | 9.36 |
| 8 |  |  | 6.02 | -5.73 |
| 9 |  |  | 2.50 | 2.03 |
| 10 |  |  |  | *-1.60 |
| 11 |  |  | 2.50 | -2.90 |
| 12 |  |  | 2.54 | 3.12 |
| 13 |  |  | 3.47 | 2.91 |
| 14 |  |  |  | *-0.19 |
| 6 | 0 | 0 |  | *-0.09 |
| 1 |  |  |  | * 0.72 |
| 2 |  |  | 6.66 | 6.65 |
| 3 |  |  |  | * 1.27 |
| 4 |  |  | 2.66 | 2.30 |
| 5 |  |  | 3.49 | -3.14 |
| 6 |  |  |  | *-0.19 |
| 7 |  |  | 2.96 | 2.91 |
| 8 |  |  |  | *-1.12 |

| h | k | l | $F_o$ | $F_c$ |
|---|---|---|-------|-------|
| 6 | 9 | 0 | 2.57 | 2.19 |
| 10 |  |  | 4.56 | 4.18 |
| 11 |  |  |  | *-2.13 |
| 12 |  |  | 2.82 | 2.27 |
| 13 |  |  |  | *-0.35 |
| 7 | 1 | 0 | 8.27 | 7.27 |
| 2 |  |  | 3.68 | 4.19 |
| 3 |  |  | 3.16 | 3.91 |
| 4 |  |  |  | *-0.81 |
| 5 |  |  | 3.57 | -2.66 |
| 6 |  |  |  | *-1.25 |
| 7 |  |  |  | *-1.32 |
| 8 |  |  |  | *-0.35 |
| 9 |  |  | 3.10 | -2.73 |
| 10 |  |  |  | * 1.83 |
| 11 |  |  |  | *-0.98 |
| 12 |  |  |  | *-1.11 |
| 8 | 0 | 0 | 3.69 | 4.50 |
| 1 |  |  | 6.69 | -7.34 |
| 2 |  |  |  | *-0.60 |
| 3 |  |  | 3.80 | -3.29 |
| 4 |  |  |  | * 0.98 |
| 5 |  |  | 3.33 | 3.20 |
| 6 |  |  | 5.08 | 5.14 |
| 7 |  |  |  | * 0.38 |
| 8 |  |  |  | *-0.38 |
| 9 |  |  | 3.65 | -3.49 |
| 10 |  |  | 2.01 | -1.74 |
| 11 |  |  | 2.14 | 1.55 |
| 9 | 1 | 0 | 2.34 | -1.53 |
| 2 |  |  | 6.15 | 7.17 |
| 3 |  |  | 5.66 | 5.66 |
| 4 |  |  | 2.84 | -2.83 |
| 5 |  |  |  | * 1.38 |
| 6 |  |  | 2.88 | -3.86 |
| 7 |  |  |  | *-1.89 |
| 8 |  |  | 3.77 | 3.32 |
| 9 |  |  |  | * 0.47 |
| 10 | 0 | 0 | 4.21 | 4.00 |
| 1 |  |  | 3.37 | -3.20 |
| 2 |  |  |  | * 0.40 |
| 3 |  |  |  | *-1.19 |
| 4 |  |  |  | * 0.01 |
| 5 |  |  | 3.76 | 3.91 |
| 6 |  |  | 1.74 | 1.13 |
| 7 |  |  |  | * 0.14 |
| 11 | 1 | 0 | 1.90 | 1.52 |
| 2 |  |  |  | *-0.15 |
| 3 |  |  |  | * 1.57 |
| 4 |  |  |  | *-0.69 |
| 2 | 0 | 1 | 22.53 | -28.08 |
| -2 |  |  | 19.43 | 29.56 |
| 4 |  |  | 5.16 | 5.43 |
| -4 |  |  |  | * 1.16 |
| 6 |  |  | 11.98 | 13.58 |
| -6 |  |  | 3.10 | -2.48 |
| 8 |  |  | 4.68 | 4.10 |
| -8 |  |  | 7.23 | -7.01 |
| 10 |  |  |  | * 0.30 |
| -10 |  |  |  | * 0.14 |
| 2 | 0 | 2 | 6.78 | 6.31 |
| -2 |  |  | 21.06 | -23.16 |
| 4 |  |  | 4.27 | 3.64 |
| -4 |  |  | 3.35 | 2.59 |
| 6 |  |  | 2.77 | 2.21 |
| -6 |  |  | 9.48 | 10.25 |
| 8 |  |  |  | *-0.23 |
| -8 |  |  | 4.12 | 4.62 |
| 10 |  |  |  | * 1.05 |
| -10 |  |  | 3.15 | -2.81 |
| 2 | 0 | 3 | 3.02 | 1.88 |
| -2 |  |  | 9.54 | 9.42 |
| 4 |  |  | 2.64 | -2.09 |
| -4 |  |  | 3.91 | -3.94 |
| 6 |  |  |  | * 0.87 |
| -6 |  |  | 4.38 | 3.68 |
| 8 |  |  | 1.96 | 2.35 |
| -8 |  |  | 8.37 | 9.18 |
| -10 |  |  | 5.75 | 5.72 |
| 2 | 0 | 4 | 3.96 | 3.47 |
| 5 |  |  |  | *-0.78 |
| 6 |  |  |  | * 0.06 |
| 7 |  |  | 1.90 | 2.38 |
| -2 | 0 | 4 | 14.15 | 15.20 |
| 5 |  |  | 5.21 | -4.39 |
| 6 |  |  | 2.47 | -2.74 |
| 7 |  |  | 3.66 | 2.90 |
| 4 | 0 | 4 | 2.21 | -2.32 |
| 5 |  |  | 1.99 | 2.73 |
| 6 |  |  | 7.27 | 6.83 |
| -4 | 0 | 4 | 9.05 | 9.53 |
| 5 |  |  | 2.29 | -2.13 |
| 6 |  |  |  | * 0.50 |
| 7 |  |  |  | * 0.84 |
| 6 | 0 | 4 |  |  |

| h | k | l | $F_o$ | $F_c$ |
|---|---|---|-------|-------|
| 6 | 0 | 5 | 2.77 | 2.51 |
| -6 | 0 | 4 | 7.92 | -7.91 |
| 5 |  |  | 3.71 | 3.32 |
| 6 |  |  | 5.77 | 6.87 |
| 7 |  |  | 2.77 | -2.52 |
| 8 | 0 | 4 |  | *-0.03 |
| -8 | 0 | 4 | 4.72 | -4.67 |
| 5 |  |  | 5.81 | -6.22 |
| 6 |  |  | 4.64 | 5.17 |
| -10 | 0 | 4 | 4.67 | 4.70 |
| 5 |  |  | 3.08 | -3.37 |
| 0 | 1 | 1 | 5.41 | 8.21 |
| 2 |  |  | 5.64 | 6.40 |
| 3 |  |  | 8.32 | 10.76 |
| 4 |  |  | 3.92 | -3.14 |
| 5 |  |  | 10.52 | 11.73 |
| 6 |  |  | 4.25 | 4.37 |
| 7 |  |  |  | *-1.14 |
| 8 |  |  | 4.72 | 3.77 |
| 9 |  |  |  | *-0.34 |
| 10 |  |  | 8.64 | 8.70 |
| 11 |  |  |  | *-1.25 |
| 12 |  |  |  | * 0.56 |
| 13 |  |  | 5.38 | -4.74 |
| 14 |  |  | 3.02 | -2.05 |
| 15 |  |  |  | *-0.17 |
| 1 | 1 | 1 | 11.65 | 18.45 |
| 4 |  |  | 7.56 | 7.81 |
| 5 |  |  | 4.46 | 4.59 |
| 6 |  |  | 7.81 | 8.15 |
| 7 |  |  | 10.92 | 12.41 |
| 8 |  |  |  | *-1.70 |
| 9 |  |  |  | * 0.10 |
| 10 |  |  | 3.51 | -2.20 |
| 11 |  |  | 6.55 | -5.66 |
| 12 |  |  |  | * 0.22 |
| 13 |  |  | 5.66 | 4.89 |
| 14 |  |  |  | * 0.55 |
| 15 |  |  | 2.09 | 1.84 |
| -1 | 1 | 1 |  | *-0.26 |
| 3 |  |  | 8.04 | 9.57 |
| 4 |  |  | 8.37 | -10.98 |
| 5 |  |  |  | *-1.60 |
| 6 |  |  | 2.84 | -2.93 |
| 7 |  |  |  | *-0.97 |
| 8 |  |  | 7.55 | 8.32 |
| 9 |  |  | 10.05 | 9.73 |
| 10 |  |  | 8.12 | -6.85 |
| 11 |  |  | 3.60 | 3.61 |
| 12 |  |  |  | * 0.51 |
| 13 |  |  |  | *-0.42 |
| 14 |  |  | 4.25 | 3.37 |
| 15 |  |  | 1.26 | -0.78 |
| 2 | 1 | 1 | 13.83 | 18.17 |
| 2 |  |  | 11.58 | 14.97 |
| 3 |  |  | 10.67 | 15.00 |
| 4 |  |  | 15.89 | 21.92 |
| 5 |  |  | 12.11 | -13.85 |
| 6 |  |  | 4.85 | -4.77 |
| 7 |  |  |  | * 1.55 |
| 8 |  |  | 7.67 | -7.41 |
| 9 |  |  |  | * 1.19 |
| 10 |  |  | 7.51 | 7.80 |
| 11 |  |  | 2.42 | -2.42 |
| 12 |  |  | 3.30 | 3.23 |
| 13 |  |  |  | *-0.08 |
| 14 |  |  |  | *-1.80 |
| 15 |  |  |  | * 1.30 |
| -2 | 1 | 1 | 5.54 | 5.63 |
| 2 |  |  | 3.65 | -3.34 |
| 3 |  |  | 6.05 | 6.15 |
| 4 |  |  | 7.56 | -9.54 |
| 5 |  |  | 9.90 | 10.35 |
| 6 |  |  | 13.05 | 16.06 |
| 7 |  |  | 8.67 | -8.75 |
| 8 |  |  | 6.14 | 6.52 |
| 9 |  |  |  | * 0.43 |
| 10 |  |  | 6.78 | -6.54 |
| 11 |  |  |  | * 0.81 |
| 12 |  |  |  | * 0.52 |
| 13 |  |  | 1.93 | -2.66 |
| 14 |  |  | 4.79 | 4.28 |
| 15 |  |  |  | * 0.25 |
| 3 | 1 | 1 | 2.15 | -0.81 |
| 2 |  |  | 2.89 | -3.50 |
| 3 |  |  | 6.22 | -6.90 |
| 4 |  |  | 8.28 | 8.63 |
| 5 |  |  | 8.71 | 9.22 |
| 6 |  |  |  | * 1.74 |
| 7 |  |  | 10.37 | 12.60 |
| 8 |  |  | 9.28 | -7.99 |
| 9 |  |  |  | * 1.60 |
| 10 |  |  | 4.77 | 4.31 |
| 11 |  |  | 2.50 | -2.66 |
| 12 |  |  |  | * 1.02 |

| h | k | l | $F_o$ | $F_c$ |
|---|---|---|-------|-------|
| 3 | 13 | 1 | 2.71 | 1.99 |
| 14 |  |  | 2.71 | -2.39 |
| 15 |  |  | 2.50 | 2.54 |
| -3 | 1 | 1 | 12.71 | -15.34 |
| 2 |  |  | 10.11 | 9.68 |
| 4 |  |  | 7.78 | 7.13 |
| 5 |  |  | 8.30 | 8.63 |
| 6 |  |  |  | * 1.31 |
| 7 |  |  | 9.43 | -10.89 |
| 8 |  |  |  | *-0.02 |
| 9 |  |  |  | * 1.51 |
| 10 |  |  | 3.04 | -2.21 |
| 11 |  |  | 8.61 | 8.99 |
| 12 |  |  | 2.23 | 1.28 |
| 13 |  |  |  | *-1.18 |
| 14 |  |  | 2.44 | -1.82 |
| 15 |  |  |  | *-0.91 |
| 4 | 1 | 1 |  | * 0.57 |
| 2 |  |  | 5.46 | 4.39 |
| 3 |  |  | 7.97 | 7.69 |
| 4 |  |  | 5.22 | 4.55 |
| 5 |  |  | 2.84 | 2.40 |
| 6 |  |  |  | *-0.49 |
| 7 |  |  | 5.22 | 5.50 |
| 8 |  |  |  | * 0.15 |
| 9 |  |  | 4.08 | -3.49 |
| 10 |  |  | 2.39 | 1.49 |
| 11 |  |  | 4.40 | -3.73 |
| 12 |  |  | 5.59 | 3.95 |
| 13 |  |  |  | * 1.41 |
| 14 |  |  |  | * 0.55 |
| -4 | 1 | 1 | 7.58 | 7.64 |
| 2 |  |  | 8.08 | -8.24 |
| 3 |  |  | 6.30 | 5.30 |
| 4 |  |  | 3.59 | 3.05 |
| 5 |  |  |  | *-0.61 |
| 6 |  |  | 10.58 | 10.66 |
| 7 |  |  | 2.42 | 0.34 |
| 8 |  |  | 10.66 | 10.83 |
| 9 |  |  |  | *-0.18 |
| 10 |  |  | 3.88 | -3.48 |
| 11 |  |  | 2.33 | -2.90 |
| 12 |  |  |  | *-0.84 |
| 13 |  |  |  | * 1.16 |
| 14 |  |  | 4.47 | 3.78 |
| 5 | 1 | 1 | 3.02 | 2.19 |
| 2 |  |  | 7.45 | 7.42 |
| 3 |  |  | 6.05 | 6.66 |
| 4 |  |  | 2.40 | -2.70 |
| 5 |  |  |  | * 0.03 |
| 6 |  |  | 2.07 | -2.07 |
| 7 |  |  |  | * 0.52 |
| 8 |  |  | 2.50 | 3.14 |
| 9 |  |  | 4.73 | 3.86 |
| 10 |  |  |  | * 1.47 |
| 11 |  |  | 2.20 | 1.84 |
| 12 |  |  | 4.12 | -3.57 |
| 13 |  |  | 3.59 | -2.87 |
| 14 |  |  | 8.60 | 7.60 |
| -5 | 1 | 1 |  | *-0.90 |
| 2 |  |  |  | * 0.46 |
| 3 |  |  | 2.27 | 1.66 |
| 4 |  |  | 3.34 | 2.20 |
| 6 |  |  | 2.99 | -2.18 |
| 7 |  |  | 2.45 | 2.09 |
| 8 |  |  | 2.48 | -2.30 |
| 9 |  |  | 2.46 | -1.76 |
| 10 |  |  | 3.94 | 3.92 |
| 11 |  |  | 4.39 | 4.49 |
| 12 |  |  |  | *-0.72 |
| 13 |  |  |  | * 1.26 |
| 14 |  |  | 2.64 | -2.57 |
| 6 | 1 | 1 | 11.98 | -11.50 |
| 2 |  |  |  | *-0.88 |
| 3 |  |  | 7.09 | -6.24 |
| 4 |  |  | 4.31 | -3.70 |
| 5 |  |  | 10.01 | 8.37 |
| 6 |  |  | 2.77 | 2.81 |
| 7 |  |  |  | *-0.25 |
| 8 |  |  | 5.85 | 5.08 |
| 9 |  |  | 4.58 | -5.00 |
| 10 |  |  |  | *-0.77 |
| 11 |  |  |  | * 1.56 |
| 12 |  |  |  | * 1.03 |
| 13 |  |  |  | * 2.00 |
| -6 | 1 | 1 | 4.90 | -4.09 |
| 2 |  |  | 6.02 | 4.91 |
| 3 |  |  |  | *-1.24 |
| 4 |  |  | 7.05 | 7.10 |
| 5 |  |  | 4.65 | 3.56 |
| 6 |  |  | 5.05 | -4.41 |
| 7 |  |  | 6.59 | 6.25 |
| 8 |  |  | 4.23 | 3.58 |
| 9 |  |  | 4.53 | -4.47 |
| 10 |  |  | 6.05 | 4.77 |

## Table 3. (Continued)

| h | k | l | $F_o$ | $F_c$ |
|---|---|---|---|---|
| -6 | 11 | 1 | 2.49 | - 2.49 |
|  | 12 |  | 2.27 | - 1.64 |
| 7 | 1 | 1 | 3.18 | - 3.46 |
|  | 2 |  | 10.66 | 11.20 |
|  | 3 |  | 5.28 | 5.49 |
|  | 4 |  |  | *- 1.47 |
|  | 5 |  | 3.77 | 3.48 |
|  | 6 |  | 2.65 | - 3.35 |
|  | 7 |  |  | * 0.06 |
|  | 8 |  | 5.49 | 4.72 |
|  | 9 |  |  | * 1.02 |
|  | 10 |  |  | *- 0.93 |
|  | 11 |  | 4.08 | 3.30 |
| -7 | 1 | 1 | 9.11 | 8.77 |
|  | 2 |  | 8.95 | 7.75 |
|  | 3 |  | 8.03 | - 7.58 |
|  | 4 |  |  | * 1.14 |
|  | 5 |  |  | *- 0.76 |
|  | 6 |  |  | *- 1.65 |
|  | 7 |  | 9.70 | 8.20 |
|  | 8 |  |  | * 1.87 |
|  | 9 |  |  | * 1.17 |
|  | 10 |  |  | * 1.51 |
|  | 11 |  |  | *- 1.16 |
|  | 12 |  | 5.64 | - 4.41 |
| 8 | 1 | 1 |  | *- 0.37 |
|  | 2 |  |  | * 1.52 |
|  | 3 |  |  | *- 0.03 |
|  | 4 |  |  | * 0.41 |
|  | 5 |  | 3.49 | 3.53 |
|  | 6 |  |  | * 1.17 |
|  | 7 |  |  | *- 1.59 |
|  | 8 |  |  | * 2.00 |
|  | 9 |  |  | *- 0.67 |
|  | 10 |  |  | *- 0.42 |
| -8 | 1 | 1 | 6.08 | - 5.38 |
|  | 2 |  |  | * 1.79 |
|  | 3 |  |  | *- 1.74 |
|  | 4 |  | 7.50 | 6.54 |
|  | 5 |  | 3.78 | 2.99 |
|  | 6 |  | * 1.13 |  |
|  | 7 |  |  | *- 0.01 |
|  | 8 |  |  | *- 1.83 |
|  | 9 |  | 3.97 | - 3.05 |
|  | 10 |  | 4.70 | 3.79 |
|  | 11 |  | 1.87 | 2.08 |
| 9 | 1 | 1 |  | *- 0.31 |
|  | 2 |  |  | * 1.22 |
|  | 3 |  | 3.31 | 2.32 |
|  | 4 |  | 2.33 | 2.27 |
|  | 5 |  | 3.35 | 3.06 |
|  | 6 |  |  | * 0.74 |
|  | 7 |  |  | *- 0.29 |
|  | 8 |  | 2.38 | - 1.52 |
| -9 | 1 | 1 | 2.37 | 2.09 |
|  | 2 |  | 4.77 | 3.91 |
|  | 3 |  |  | * 1.20 |
|  | 4 |  |  | *- 0.01 |
|  | 5 |  |  | * 0.47 |
|  | 6 |  |  | *- 0.66 |
|  | 7 |  | 2.00 | 2.02 |
|  | 8 |  |  | * 0.49 |
|  | 9 |  | 1.28 | 1.82 |
|  | 10 |  |  | *- 0.93 |
| 10 | 1 | 1 | 5.02 | 4.50 |
|  | 2 |  |  | * 0.95 |
|  | 3 |  |  | * 1.43 |
|  | 4 |  |  | *- 0.21 |
|  | 5 |  | 4.45 | - 4.07 |
|  | 6 |  | 1.22 | 1.19 |
| -10 | 1 | 1 | 1.95 | 1.96 |
|  | 2 |  |  | * 0.50 |
|  | 3 |  | 2.02 | 2.02 |
|  | 4 |  |  | * 1.36 |
|  | 5 |  |  | *- 0.93 |
|  | 6 |  | 4.63 | 3.26 |
|  | 7 |  |  | *- 0.98 |
|  | 8 |  | 1.49 | - 1.49 |
| -11 | 1 | 1 | 1.38 | - 0.60 |
|  | 2 |  | 2.31 | - 3.39 |
|  | 3 |  | 3.06 | 1.58 |
|  | 4 |  |  | 1.99 |
| 0 | 1 | 2 | 2.20 | - 0.79 |
|  | 2 |  | 4.65 | - 0.17 |
|  | 3 |  | 6.91 | - 7.36 |
|  | 4 |  | 12.21 | 16.23 |
|  | 5 |  | 11.49 | -14.64 |
|  | 6 |  | 2.02 | 2.62 |
|  | 7 |  | 7.97 | 7.56 |
|  | 8 |  |  | * 0.25 |
|  | 9 |  |  | * 1.46 |
|  | 10 |  | 6.36 | 6.69 |
|  | 11 |  | 2.33 | - 3.21 |
|  | 12 |  | 2.15 | 2.53 |
|  | 13 |  | 2.12 | 2.21 |
|  | 14 |  | 4.39 | - 3.66 |
|  | 15 |  | 1.97 | 2.15 |
| 1 | 1 | 2 | 1.64 | - 1.69 |
|  | 2 |  | 4.80 | - 6.55 |
|  | 3 |  | 3.07 | 3.41 |
| 1 | 4 | 2 | 4.86 | 4.96 |
|  | 5 |  |  | *- 0.47 |
|  | 6 |  | 3.57 | - 4.31 |
|  | 7 |  | 8.62 | 7.69 |
|  | 8 |  | 5.48 | - 4.64 |
|  | 9 |  | 4.81 | 5.00 |
|  | 10 |  | 6.75 | 7.06 |
|  | 11 |  |  | * 1.13 |
|  | 12 |  |  | * 0.60 |
|  | 13 |  |  | *- 0.18 |
|  | 14 |  | 3.73 | - 3.32 |
|  | 15 |  | 2.70 | 2.79 |
| -1 | 1 | 2 | 15.13 | 24.68 |
|  | 3 |  | 8.13 | -10.26 |
|  | 4 |  | 2.65 | - 2.27 |
|  | 5 |  | 5.50 | - 6.25 |
|  | 6 |  | 8.97 | 9.84 |
|  | 7 |  | 11.30 | 12.41 |
|  | 8 |  | 2.50 | - 2.53 |
|  | 9 |  |  | * 0.84 |
|  | 10 |  |  | *- 0.92 |
|  | 11 |  | 5.70 | - 4.73 |
|  | 12 |  |  | *- 0.05 |
|  | 13 |  | 3.95 | 4.19 |
|  | 14 |  |  | * 0.98 |
|  | 15 |  | 3.00 | 3.10 |
| 2 | 1 | 2 | 6.89 | 8.12 |
|  | 2 |  | 5.34 | - 5.46 |
|  | 3 |  | 4.67 | 4.28 |
|  | 4 |  | 4.83 | 5.09 |
|  | 5 |  | 2.90 | 3.15 |
|  | 6 |  | 8.32 | 8.76 |
|  | 7 |  |  | * 0.23 |
|  | 8 |  | 4.08 | 4.45 |
|  | 9 |  | 4.16 | - 5.04 |
|  | 10 |  | 3.69 | - 2.78 |
|  | 11 |  |  | *- 0.32 |
|  | 12 |  | 2.49 | 2.49 |
|  | 13 |  | 4.58 | 4.03 |
|  | 14 |  | 2.06 | 2.61 |
| -2 | 1 | 2 | 9.23 | -10.78 |
|  | 2 |  | 2.99 | 3.16 |
|  | 3 |  | 2.25 | 1.87 |
|  | 4 |  | 11.61 | 14.23 |
|  | 5 |  |  | *- 1.66 |
|  | 6 |  | 2.51 | 2.31 |
|  | 7 |  |  | *- 0.42 |
|  | 8 |  |  | *- 0.08 |
|  | 9 |  | 2.38 | 3.52 |
|  | 10 |  | 9.22 | 9.16 |
|  | 11 |  | 2.06 | 2.06 |
|  | 12 |  |  | * 1.04 |
|  | 13 |  | 4.05 | - 3.67 |
|  | 14 |  | 3.79 | - 3.55 |
|  | 15 |  |  | *- 0.31 |
| 3 | 1 | 2 |  | *- 1.35 |
|  | 2 |  | 7.36 | 7.82 |
|  | 3 |  | 9.67 | 11.46 |
|  | 4 |  | 5.58 | - 7.11 |
|  | 5 |  | 3.78 | 3.86 |
|  | 6 |  | 10.18 | -11.96 |
|  | 7 |  | 3.71 | - 4.08 |
|  | 8 |  | 4.83 | 5.99 |
|  | 9 |  |  | * 1.85 |
|  | 10 |  | 4.79 | 4.87 |
|  | 11 |  | 4.79 | 5.13 |
|  | 12 |  |  | *- 1.06 |
|  | 13 |  |  | *- 1.46 |
|  | 14 |  |  | *- 1.16 |
| -3 | 1 | 2 |  | *- 1.31 |
|  | 2 |  | 8.22 | 9.35 |
|  | 3 |  |  | *- 1.17 |
|  | 4 |  | 7.87 | - 8.27 |
|  | 5 |  | 6.00 | 5.62 |
|  | 6 |  |  | * 1.02 |
|  | 7 |  | 5.76 | - 4.61 |
|  | 8 |  |  | *- 0.05 |
|  | 9 |  | 3.39 | 3.49 |
|  | 10 |  | 3.37 | - 4.03 |
|  | 11 |  |  | * 0.47 |
|  | 12 |  | 2.34 | 2.34 |
|  | 13 |  | 2.61 | 2.84 |
|  | 14 |  | 4.97 | 4.38 |
| 4 | 1 | 2 | 8.08 | - 9.15 |
|  | 2 |  |  | *- 0.03 |
|  | 3 |  | 6.91 | - 8.06 |
|  | 4 |  | 3.54 | - 3.11 |
|  | 5 |  | 9.40 | 11.27 |
|  | 6 |  | 5.76 | 5.42 |
|  | 7 |  | 2.50 | - 2.99 |
|  | 8 |  | 7.80 | 8.56 |
|  | 9 |  | 3.67 | - 5.20 |
|  | 10 |  |  | *- 0.37 |
|  | 11 |  | 2.31 | 2.31 |
|  | 12 |  |  | *- 1.19 |
|  | 13 |  | 1.79 | 2.22 |
| -4 | 1 | 2 | 2.52 | - 2.96 |
|  | 2 |  | 4.90 | 5.80 |
|  | 3 |  |  | *- 0.24 |
|  | 4 |  | 2.01 | - 2.29 |
| -4 | 5 | 2 | 3.70 | - 3.52 |
|  | 6 |  | 9.15 | 8.60 |
|  | 7 |  | 9.69 | - 9.42 |
|  | 8 |  | 3.36 | 3.20 |
|  | 9 |  | 4.78 | 4.59 |
|  | 10 |  | 2.33 | - 2.17 |
|  | 11 |  | 6.63 | 6.57 |
|  | 12 |  |  | * 0.18 |
|  | 13 |  | 2.76 | - 2.56 |
|  | 14 |  | 2.83 | 2.76 |
| 5 | 1 | 2 |  | *- 1.14 |
|  | 2 |  |  | * 0.97 |
|  | 3 |  |  | * 1.47 |
|  | 4 |  | 4.46 | - 5.75 |
|  | 5 |  | 5.90 | 5.94 |
|  | 6 |  |  | * 0.13 |
|  | 7 |  |  | * 0.66 |
|  | 8 |  | 5.63 | 6.81 |
|  | 9 |  |  | * 0.98 |
|  | 10 |  |  | *- 1.98 |
|  | 11 |  | 4.35 | 3.93 |
|  | 12 |  | 2.37 | - 1.90 |
|  | 13 |  |  | * 1.02 |
| -5 | 1 | 2 | 6.26 | - 5.27 |
|  | 2 |  | 2.05 | 2.03 |
|  | 3 |  | 11.03 | 12.09 |
|  | 4 |  | 3.45 | 3.17 |
|  | 5 |  | 7.81 | 7.12 |
|  | 6 |  |  | * 1.80 |
|  | 7 |  | 6.78 | - 6.91 |
|  | 8 |  |  | *- 0.58 |
|  | 9 |  | 4.08 | 3.69 |
|  | 10 |  | 3.18 | - 3.40 |
|  | 11 |  | 4.95 | 5.34 |
|  | 12 |  |  | * 1.51 |
|  | 13 |  |  | *- 1.52 |
|  | 14 |  |  | * 0.82 |
| 6 | 1 | 2 |  | * 0.05 |
|  | 2 |  | 4.61 | 4.84 |
|  | 3 |  |  | * 0.58 |
|  | 4 |  |  | *- 0.86 |
|  | 5 |  |  | * 0.58 |
|  | 6 |  |  | * 0.26 |
|  | 7 |  |  | *- 1.35 |
|  | 8 |  | 2.96 | 2.94 |
|  | 9 |  |  | * 1.46 |
|  | 10 |  |  | * 1.70 |
|  | 11 |  |  | *- 0.17 |
|  | 12 |  | 2.42 | - 1.98 |
| -6 | 1 | 2 | 2.97 | 3.03 |
|  | 2 |  |  | *- 0.82 |
|  | 3 |  | 6.77 | - 6.71 |
|  | 4 |  | 8.13 | - 8.08 |
|  | 5 |  | 4.09 | - 3.41 |
|  | 6 |  | 7.58 | 7.78 |
|  | 7 |  | 3.39 | 2.97 |
|  | 8 |  | 8.92 | 8.88 |
|  | 9 |  | 3.17 | 3.21 |
|  | 10 |  | 2.07 | - 2.45 |
|  | 11 |  | 2.21 | - 1.93 |
| 7 | 1 | 2 |  | *- 0.17 |
|  | 2 |  | 6.03 | - 6.67 |
|  | 3 |  |  | * 0.70 |
|  | 4 |  |  | * 0.05 |
|  | 5 |  | 3.82 | 3.69 |
|  | 6 |  | 2.50 | 2.67 |
|  | 7 |  | 2.38 | 1.95 |
|  | 8 |  | 3.22 | - 3.30 |
|  | 9 |  |  | * 0.43 |
|  | 10 |  |  | *- 0.62 |
| -7 | 1 | 2 | 2.28 | - 2.27 |
|  | 2 |  | 8.33 | - 7.84 |
|  | 3 |  | 5.18 | 5.34 |
|  | 4 |  |  | * 1.89 |
|  | 5 |  | 4.84 | 3.88 |
|  | 6 |  |  | *- 0.71 |
|  | 7 |  |  | *- 0.92 |
|  | 8 |  |  | *- 1.69 |
|  | 9 |  |  | * 1.52 |
|  | 10 |  |  | * 1.50 |
|  | 11 |  | 5.01 | 4.08 |
|  | 12 |  |  | * 0.89 |
| 8 | 1 | 2 | 5.86 | 6.31 |
|  | 2 |  |  | * 0.63 |
|  | 3 |  | 3.79 | 4.83 |
|  | 4 |  |  | * 0.89 |
|  | 5 |  | 6.75 | - 7.18 |
|  | 6 |  | 2.20 | 2.19 |
|  | 7 |  |  | *- 0.66 |
|  | 8 |  |  | * 0.44 |
|  | 9 |  | 3.63 | 3.83 |
|  | 10 |  |  | * 0.24 |
| -8 | 1 | 2 | 2.68 | 2.20 |
|  | 2 |  | 3.36 | - 4.05 |
|  | 3 |  |  | * 1.84 |
|  | 4 |  |  | *- 0.17 |
|  | 5 |  |  | *- 1.35 |
|  | 7 |  | 2.96 | 3.03 |
| -8 | 8 | 2 | 1.91 | 1.86 |
|  | 9 |  |  | *- 1.15 |
|  | 10 |  |  | * 1.18 |
|  | 11 |  |  | *- 1.49 |
| 9 | 1 | 2 |  | * 0.01 |
|  | 2 |  | 3.04 | - 3.99 |
|  | 3 |  |  | * 1.39 |
|  | 4 |  | 2.82 | 2.42 |
|  | 5 |  |  | * 0.46 |
|  | 6 |  | 2.86 | 2.91 |
|  | 7 |  | 1.59 | 1.56 |
| -9 | 1 | 2 |  | * 0.93 |
|  | 2 |  | 5.32 | 5.17 |
|  | 3 |  |  | *- 1.37 |
|  | 4 |  |  | * 0.09 |
|  | 5 |  | 2.26 | 1.96 |
|  | 6 |  | 3.27 | - 4.09 |
|  | 7 |  | 5.13 | 5.17 |
|  | 8 |  |  | * 0.88 |
|  | 9 |  |  | *- 0.52 |
|  | 10 |  | 2.16 | 2.72 |
| 10 | 1 | 2 |  | * 0.15 |
|  | 2 |  |  | * 0.45 |
|  | 3 |  |  | *- 0.13 |
| -10 | 1 | 2 | 3.30 | - 3.98 |
|  | 2 |  |  | * 0.73 |
|  | 3 |  |  | *- 1.41 |
|  | 4 |  | 5.71 | 5.00 |
|  | 5 |  | 2.50 | 2.62 |
|  | 6 |  |  | *- 0.99 |
|  | 7 |  | 1.78 | - 1.02 |
|  | 8 |  |  | *- 0.92 |
| -11 | 1 | 2 | 3.22 | 2.13 |
|  | 2 |  | 2.50 | 2.91 |
|  | 3 |  | 4.01 | - 0.97 |
|  | 4 |  | 2.50 | - 3.10 |
|  | 5 |  |  | * 0.21 |
| 0 | 1 | 3 | 1.90 | - 3.42 |
|  | 2 |  | 2.19 | 3.02 |
|  | 3 |  | 9.79 | -11.35 |
|  | 4 |  | 6.19 | - 6.96 |
|  | 5 |  | 5.98 | 7.73 |
|  | 6 |  | 8.18 | 9.06 |
|  | 7 |  | 3.92 | 3.28 |
|  | 8 |  |  | * 1.24 |
|  | 9 |  | 2.98 | - 3.78 |
|  | 10 |  | 4.40 | - 4.78 |
|  | 11 |  |  | * 0.04 |
|  | 12 |  | 2.34 | 2.00 |
|  | 13 |  | 3.02 | 3.18 |
|  | 14 |  | 3.41 | 3.31 |
| 1 | 1 | 3 | 2.82 | 4.22 |
|  | 3 |  | 8.63 | 11.93 |
|  | 4 |  | 2.10 | - 2.55 |
|  | 5 |  | 2.21 | 2.71 |
|  | 6 |  | 9.61 | -11.49 |
|  | 7 |  | 7.96 | - 8.81 |
|  | 8 |  | 2.97 | 3.34 |
|  | 9 |  | 2.39 | 1.63 |
|  | 10 |  | 2.82 | 2.66 |
|  | 11 |  | 3.96 | 4.51 |
|  | 12 |  | 1.82 | - 1.82 |
|  | 13 |  |  | * 0.16 |
|  | 14 |  |  | * 0.49 |
| -1 | 1 | 3 | 3.41 | - 3.56 |
|  | 2 |  | 4.25 | - 3.00 |
|  | 3 |  | 10.85 | 13.27 |
|  | 4 |  | 3.63 | 4.58 |
|  | 5 |  |  | * 0.55 |
|  | 6 |  |  | *- 1.15 |
|  | 7 |  |  | *- 1.06 |
|  | 8 |  |  | * 1.72 |
|  | 9 |  | 4.54 | 5.04 |
|  | 10 |  |  | * 0.96 |
|  | 11 |  |  | * 1.41 |
|  | 12 |  | 2.22 | - 2.22 |
|  | 13 |  |  | *- 0.79 |
|  | 14 |  | 3.40 | - 2.43 |
| 2 | 1 | 3 | 2.65 | - 3.23 |
|  | 2 |  | 5.40 | 5.59 |
|  | 3 |  | 2.14 | - 2.61 |
|  | 4 |  | 4.48 | - 4.50 |
|  | 5 |  |  | * 1.08 |
|  | 6 |  | 3.77 | 4.00 |
|  | 7 |  | 4.20 | - 4.17 |
|  | 8 |  | 6.41 | 7.17 |
|  | 9 |  |  | *- 1.57 |
|  | 10 |  |  | * 0.49 |
|  | 11 |  | 5.76 | 4.95 |
|  | 12 |  | 2.54 | - 2.60 |
|  | 13 |  |  | * 1.13 |
|  | 14 |  | 2.50 | 2.59 |
| -2 | 1 | 3 | 3.47 | - 2.68 |
|  | 2 |  |  | * 1.02 |
|  | 3 |  | 11.19 | -13.57 |
|  | 4 |  | 7.38 | 8.15 |
|  | 5 |  | 4.30 | - 3.98 |
|  | 6 |  |  | * 0.27 |
|  | 7 |  | 4.42 | 4.44 |
|  | 8 |  | 3.42 | - 3.36 |

Table 3. *(Continued)*

| h | k | l | $F_o$ | $F_c$ | h | k | l | $F_o$ | $F_c$ | h | k | l | $F_o$ | $F_c$ | h | k | l | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| -2 | 9 | 3 | | * 1.63 | 4 | 11 | 3 | | * 0.98 | 6 | 4 | 3 | 3.59 | 3.40 | 8 | 4 | 3 | 2.51 | 2.50 |
| | | 10 | 2.35 | 2.12 | | | 12 | 1.45 | - 1.88 | | | 5 | 4.42 | - 5.85 | | | 5 | | * 0.98 |
| | | 11 | 2.18 | - 2.63 | -4 | 1 | 3 | | * 1.29 | | | 6 | 2.22 | * 2.22 | | | 6 | | * 0.80 |
| | | 12 | 4.28 | 4.54 | | | 2 | 7.49 | 8.00 | | | 7 | | * 0.18 | | | 7 | 1.97 | - 1.44 |
| | | 13 | 2.72 | 2.57 | | | 3 | 7.75 | 7.69 | | | 8 | | *- 0.09 | -8 | 1 | 3 | 3.04 | 2.92 |
| | | 14 | | *- 0.73 | | | 4 | 11.30 | 13.80 | | | 9 | 4.00 | 3.74 | | | 2 | | * 1.17 |
| 3 | 1 | 3 | 6.66 | 7.53 | | | 5 | | *- 1.95 | | | 10 | | * 0.80 | | | 3 | | * 1.41 |
| | | 2 | 2.39 | 1.93 | | | 6 | 9.98 | -10.43 | -6 | 1 | 3 | 4.42 | - 3.66 | | | 4 | 4.42 | - 6.02 |
| | | 3 | | *- 0.91 | | | 7 | 4.39 | - 3.30 | | | 2 | 6.95 | 6.80 | | | 5 | 2.73 | - 2.28 |
| | | 4 | | * 0.40 | | | 8 | 3.20 | - 3.33 | | | 3 | | * 0.94 | | | 6 | 5.25 | 5.51 |
| | | 5 | 4.22 | 4.59 | | | 9 | 2.02 | * 2.02 | | | 4 | 3.41 | 2.55 | | | 7 | | * 1.20 |
| | | 6 | | * 2.24 | | | 10 | 6.81 | 7.62 | | | 5 | 2.31 | *- 2.30 | | | 8 | 2.50 | 2.93 |
| | | 7 | | *- 1.42 | | | 11 | 2.85 | 1.82 | | | 6 | 2.93 | *- 2.03 | | | 9 | | * 1.25 |
| | | 8 | | *- 0.27 | | | 12 | 2.36 | * 2.36 | | | 7 | 2.38 | - 2.23 | | | 10 | 2.35 | - 2.51 |
| | | 9 | 2.28 | - 2.28 | | | 13 | 1.99 | - 1.56 | | | 8 | | *- 0.73 | | | 11 | 1.23 | - 1.25 |
| | | 10 | | *- 1.64 | | | 14 | 1.22 | - 2.04 | | | 9 | | * 1.29 | 9 | 1 | 3 | 1.60 | 1.69 |
| | | 11 | 4.18 | 3.82 | 5 | 1 | 3 | 4.92 | 4.70 | | | 10 | | * 0.91 | | | 2 | 2.55 | 2.60 |
| | | 12 | | *- 0.11 | | | 2 | 9.87 | -12.50 | | | 11 | 3.43 | 2.61 | | | 3 | | *- 0.28 |
| | | 13 | 3.44 | 3.36 | | | 3 | | * 0.35 | | | 12 | 1.24 | 1.17 | | | 4 | 2.14 | * 2.14 |
| -3 | 1 | 3 | 12.04 | 14.58 | | | 4 | | *- 0.64 | 7 | 1 | 3 | 3.56 | 3.52 | -9 | 1 | 3 | 2.22 | - 2.22 |
| | | 2 | | * 0.72 | | | 5 | | * 0.98 | | | 2 | | *- 1.18 | | | 2 | 4.55 | - 4.28 |
| | | 3 | 3.57 | - 3.83 | | | 6 | 5.86 | 7.13 | | | 3 | 2.28 | 2.28 | | | 3 | 6.16 | 6.88 |
| | | 4 | 2.27 | 2.26 | | | 7 | 2.21 | 1.47 | | | 4 | | * 0.64 | | | 4 | | * 0.96 |
| | | 5 | 3.47 | - 2.13 | | | 8 | 3.54 | - 4.13 | | | 5 | 2.50 | - 2.61 | | | 5 | 2.34 | 2.22 |
| | | 6 | | *- 0.27 | | | 9 | | *- 0.71 | | | 6 | | * 0.76 | | | 6 | | *- 0.40 |
| | | 7 | 8.84 | 10.06 | | | 10 | 1.93 | *- 1.93 | | | 7 | | * 1.01 | | | 7 | 4.56 | - 4.39 |
| | | 8 | 2.50 | - 3.27 | | | 11 | | * 0.74 | | | 8 | | *- 1.25 | | | 8 | 2.89 | - 1.87 |
| | | 9 | 2.03 | *- 2.03 | -5 | 1 | 3 | 8.18 | 7.95 | | | 9 | 1.54 | 2.11 | | | 9 | 1.76 | 1.78 |
| | | 10 | | * 0.86 | | | 2 | 4.15 | 3.01 | -7 | 1 | 3 | | *- 0.26 | -10 | 1 | 3 | 3.13 | 2.85 |
| | | 11 | 3.36 | - 3.89 | | | 3 | 8.13 | - 8.22 | | | 2 | 6.31 | - 5.74 | | | 2 | | * 1.68 |
| | | 12 | 1.84 | 1.81 | | | 4 | 5.91 | - 4.18 | | | 3 | 6.64 | 6.75 | | | 3 | | * 0.74 |
| | | 13 | 3.14 | 2.32 | | | 5 | 2.22 | * 2.22 | | | 4 | | *- 1.15 | | | 4 | 1.78 | - 2.17 |
| | | 14 | 1.69 | - 1.35 | | | 6 | | * 0.72 | | | 5 | 3.78 | 3.75 | | | 5 | | *- 0.77 |
| 4 | 1 | 3 | | * 0.52 | | | 7 | 10.42 | 10.31 | | | 6 | 5.49 | 5.11 | | | 6 | | * 1.44 |
| | | 2 | 6.13 | 5.62 | | | 8 | | *- 0.48 | | | 7 | 4.19 | - 3.78 | | | 7 | | *- 0.06 |
| | | 3 | | * 1.56 | | | 9 | | *- 0.52 | | | 8 | | * 0.78 | -11 | 1 | 3 | | * 1.40 |
| | | 4 | 4.01 | 4.38 | | | 10 | | *- 1.41 | | | 9 | | * 1.15 | | | 2 | 2.30 | 1.99 |
| | | 5 | 6.19 | - 6.46 | | | 11 | 1.08 | *- 1.68 | | | 10 | 2.55 | - 2.44 | | | 3 | | * 0.73 |
| | | 6 | | * 1.62 | | | 12 | | * 1.14 | | | 11 | 2.48 | 1.93 | | | 4 | | * 0.19 |
| | | 7 | | * 1.04 | | | 13 | 2.10 | 1.97 | | | 12 | 0.85 | - 0.47 | | | 5 | | * 0.67 |
| | | 8 | | * 1.41 | 6 | 1 | 3 | 3.36 | 4.23 | 8 | 1 | 3 | | *- 0.45 | | | | | |
| | | 9 | 3.32 | 4.40 | | | 2 | | *- 0.52 | | | 2 | | * 0.35 | | | | | |
| | | 10 | | * 1.42 | | | 3 | 3.29 | 3.91 | | | 3 | | *- 0.24 | | | | | |

$R$ to 11.5°/₀. The final $R$ factor after two more cycles of least-squares refinement was 10.2°/₀. In this calculation, the threshold for the unobservables is taken less than or equal to half the minimum observed,
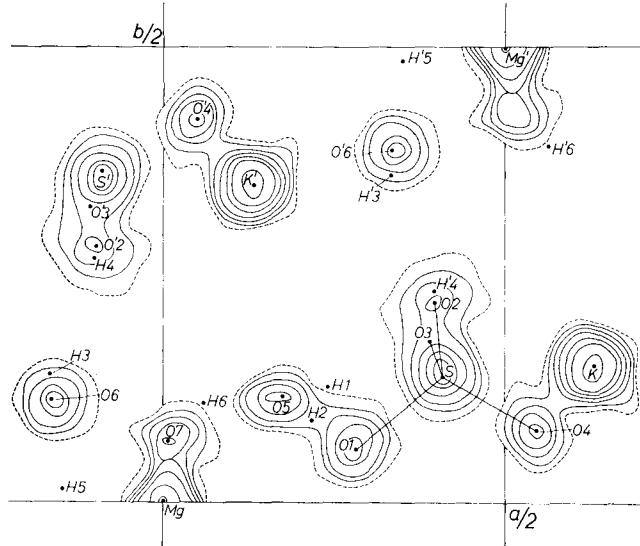


Fig. 2. Final electron-density projection $\varrho\,(xy)$

and reflections affected by extinctions have been omitted (if included $R = 12.6\%$). The final atomic parameters are given in Table 2. Table 3 gives the $F_0$ and $F_c$ values. Fig. 2 shows the electron-density projection $\varrho$ $(xy)$.

## Description of the structure

*The coordination polyhedron of the $Mg^{++}$* is close to a regular octahedron with the six water oxygens as nearest neigbours (Mg—O $= 2.056$ to 2.118 Å, and O—Mg—O angle $= 89°34'$ to $90°32'$ (Table 4). Each
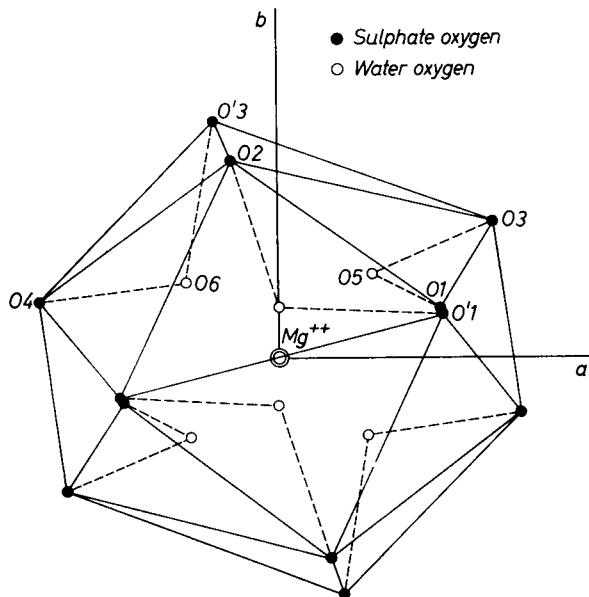


Fig. 3. Coordination of the $Mg^{++}$ ion. Black circles indicate the 12 sulfate-oxygen atoms forming the second-nearest neighbour polyhedron. They are all hydrogen-bonded (dotted lines) to water-oxygen atoms (open circles) forming the first-neighbour octahedral coordination of the $Mg^{++}$ ion.

of these six water oxygens is hydrogen-bonded to two sulfate-oxygen atoms at an average distance of 2.75 Å. Thus there are twelve second-nearest neighbours to $Mg^{++}$, all hydrogen-bonded to the first-nearest neighbours. An interesting feature about these twelve atoms is that they enclose a symmetric figure, six occupying the corners of a slightly distorted octahedron, and the remaining six extending beyond the centres of the octahedral faces. This polyhedron can also, perhaps, be described as a flattened icosahedron (Fig. 3).

Regarding the paramagnetic-resonance data of the isomorphous $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$, GRIFFITHS and OWEN[15] observed a strong rhombic component to the cubic field although in the crystal structure of the salt the water octahedron around the $Ni^{++}$ is almost a regular octahedron. GRIMES, KAY and WEBB[8] try to explain this on the basis of hydrogen bonds from the water oxygens. They suggest that the H-bond system, which indicates the electron-density distribution directions in the water molecules, may have a symmetry less than that of the water complex, so that the crystal field due to the water molecules at the $Ni^{++}$ ion has a symmetry lower than that of
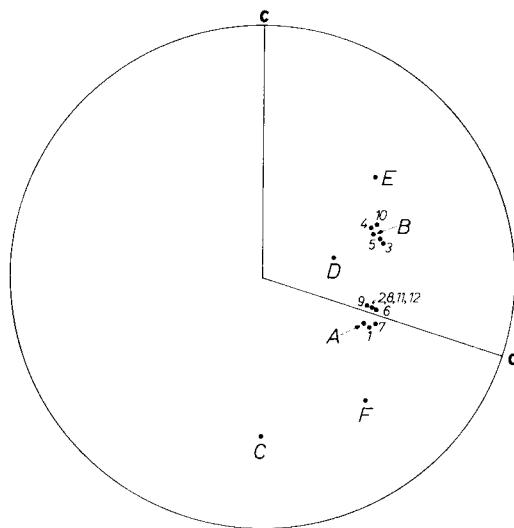


Fig. 4. Stereographic projection of the Mg—O vectors ($A$ to $F$) and the tetragonal axes (1—12) of the $g$ tensors in various TUTTON's salts.

$A$, $B$ and $C$ represent Mg—O vectors obtained in the present structure. $D$, $E$ and $F$ represent Mg—O vectors given by HOFMANN. 1 to 7 are for undiluted copper salts $M_2Cu(SO_4)_2 \cdot 6\ H_2O$ and $M_2Cu(SeO_4)_2 \cdot 6\ H_2O$, where M represents Cs, K, $NH_4$, Rb and Tl. 8 to 12 are for $M_2Zn(SO_4)_2 \cdot 6\ H_2O$ diluted with Cu, where M represents K, $NH_4$ and Rb

the water octahedron although the octahedron itself is a regular one. The distorted icosahedron of the second-nearest neighbours whose arrangement depends upon this hydrogen-bonding system, supports this view.

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[15] J. H. E. GRIFFITHS and J. OWEN, Paramagnetic resonance in nickel Tutton salts. Proc. Roy. Soc. [London] A **213** (1952) 459—473.

Table 4. *Interatomic distances and angles*

| Mg—O octahedron | | Hydrogen bonds | | SO$_4$ tetrahedron | | K$^+$ coordination | |
|---|---|---|---|---|---|---|---|
| Mg—O$_5$ (H$_2$O$^1$) | 2.118 Å | O$_5$—O$_1$ | 2.746 Å | S—O$_1$ | 1.490 Å | K—O$_1$ | 2.715 Å |
| —O$_6$ (H$_2$O$^2$) | 2.103 | O$_5$—O$_3$ | 2.746 | —O$_2$ | 1.507 | —O$_2$ | 2.899 |
| —O$_7$ (H$_2$O$^3$) | 2.056 | O$_6$—O$_3'$ | 2.663 | —O$_3$ | 1.459 | —O$_2'$ | 2.902 |
| O$_5$—O$_6$ | 2.986 | O$_6$—O$_4$ | 2.672 | —O$_4$ | 1.442 | —O$_3$ | 2.888 |
| —O$_7$ | 2.966 | O$_7$—O$_1$ | 2.748 | O$_1$—O$_2$ | 2.419 | —O$_4$ | 2.932 |
| O$_6$—O$_7$ | 2.931 | O$_7$—O$_2$ | 2.646 | —O$_3$ | 2.402 | —O$_5$ | 3.186 (H$_2$O$^1$) |
| O$_5$—Mg—O$_6$ | 90°05′ | O$_1$—O$_5$—O$_3$ | 114°46′ | —O$_4$ | 2.375 | —O$_6$ | 3.027 (H$_2$O$^2$) |
| O$_5$—Mg—O$_7$ | 90°32′ | O$_3'$—O$_6$—O$_4$ | 102°23′ | O$_2$—O$_3$ | 2.414 | | |
| O$_6$—Mg—O$_7$ | 89°34′ | O$_1'$—O$_7$—O$_2$ | 103°52′ | —O$_4$ | 2.414 | | |
| | | | | O$_3$—O$_4$ | 2.398 | | |
| | | | | O$_1$—S—O$_2$ | 107°39′ | | |
| | | | | O$_1$—S—O$_3$ | 109°01′ | | |
| | | | | O$_1$—S—O$_4$ | 108°14′ | | |
| | | | | O$_2$—S—O$_3$ | 108°59′ | | |
| | | | | O$_2$—S—O$_4$ | 109°58′ | | |
| | | | | O$_3$—S—O$_4$ | 111°33′ | | |

The stereographic plot (Fig. 4) of the $g_{\parallel}$ data on various Tutton's salts (taken mostly from the paper by BOWERS and OWEN[16]) match the Mg—O vectors ($A$ or $B$) obtained in the present structure and show no correlation with Mg—O vectors ($D$ or $F$) of HOFMANN.

*The sulfate ion* is only slightly distorted from a regular tetrahedron with O—S—O angles varying from 107 to 112° and the S—O bond distances ranging from 1.442 to 1.507 Å (Table 4). The sulphate-oxygen atoms form the second coordination sphere of the Mg$^{++}$ ion (Mg—O $\sim 4.5$ Å) and are linked to the first neighbours by H bonds as mentioned earlier.



● Sulphate oxygen    o Water oxygen    ⊛ Sulphur    ⊚ K$^+$    ⊚ Mg$^{++}$
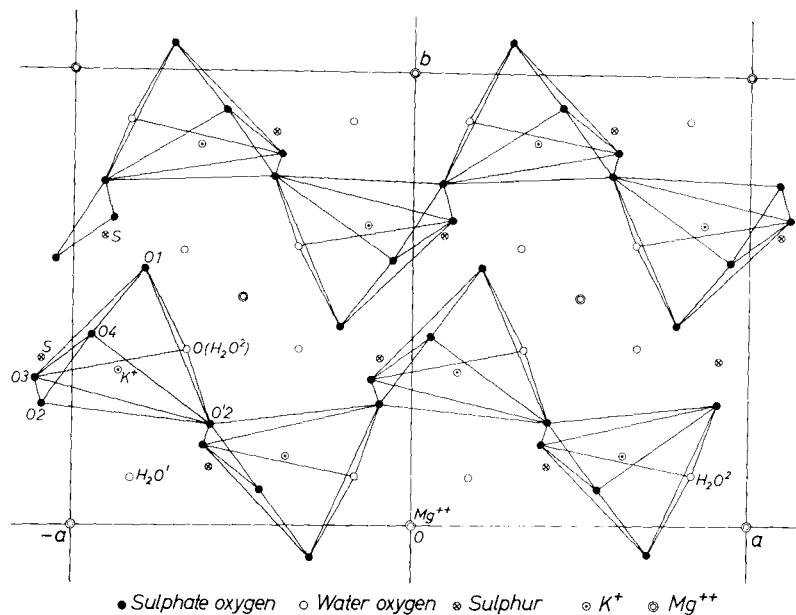
Fig. 5. Coordination of K$^+$

Coordination of K$^+$: One water (H$_2$O$^2$ in Fig. 5) and five SO$_4$ oxygens form the nearest neighbours of the K$^+$ ion at an average K—O distance of 2.94 Å (Table 4). Of the latter five, two of the oxygens (O$_1$ and O$_4$) belong to the same sulfate group. The water oxygen H$_2$O$^1$ extends beyond the centre of the triangle O$_3$O$_2'$O$_2$ (K—H$_2$O$^1$ = 3.19 Å) and, with its inclusion the potassium ion, becomes seven coordinated.

[16] K. D. BOWERS and J. OWEN, Paramagnetic resonance. II, Reports on Progr. in Physics 18 (1955) 304—373.

The coordination polyhedra of potassium atoms related by the *a* glide share a corner atom ($O_2$) and run as a chain parallel to the *a* axis. The structure can be described as a packing of these parallel chains, with the sulfate and the magnesium coordination polyhedra filling the space in between them.

## Acknowledgement