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The high-temperature modification of magnesium sulfate (β-$MgSO_4$) from single-crystal data

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Mg–O) = 0.001 Å; R factor = 0.017; wR factor = 0.046; data-to-parameter ratio = 19.5.

Single crystals of the high-temperature modification of magnesium sulfate, β-$MgSO_4$, were obtained from chemical transport reactions with Cl_2 as transport agent. The redetermination of the crystal structure confirms the previous powder study [Coing-Boyat (1962). *C. R. Acad. Sci.* **258**, 1962–1964], but with higher precision and more reliable interatomic distances. The title compound crystallizes in the $CuSO_4$ structure type (space group *Pnma*) and is isotypic with other first-row metal sulfates of the type $M^{II}SO_4$ (M = Mn, Fe, Co, Zn). The Mg^{2+} cation is surrounded by six O atoms in a distorted octahedral [2+2+2] coordination ($\overline{1}$ symmetry). By edge-sharing, $[MgO_{4/2}O_{2/1}]_\infty$ chains are established parallel to [010] which are linked into a framework by corner sharing with slightly distorted SO_4 tetrahedra (m symmetry).

Related literature

For standardization of structure data, see Gelato & Parthé (1987). The structure of the first polymorph of $MgSO_4$ was described by Rentzeperis & Soldatos (1958). Very recently, redeterminations of the structures of both α- and β-$MgSO_4$ by neutron powder diffraction were published by Fortes *et al.* (2007). For a review of chemical transport reactions for preparative purposes, including metal sulfates, see Gruehn & Glaum (2000). An overview of isotypic sulfates of the $CuSO_4$ and the $CrVO_4$ structure types was given by Wildner & Giester (1988). For the bond-valence model, see Brown (2002) and Brese & O'Keeffe (1991). Average S—O distances were calculated by Baur (1981) and ionic radii were taken from Shannon (1976).

Experimental

Crystal data

$MgSO_4$	a = 8.5787 (8) Å
M_r = 120.37	b = 6.6953 (6) Å
Orthorhombic, *Pnma*	c = 4.7438 (5) Å
V = 272.47 (5) Å^3	μ = 1.21 mm^{-1}
Z = 4	T = 293 (2) K
Mo $K\alpha$ radiation	0.18 × 0.14 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	683 independent reflections
Absorption correction: ψ scan (*PLATON*; Spek, 2003)	598 reflections with $I > 2\sigma(I)$
T_{min} = 0.780, T_{max} = 0.864	R_{int} = 0.032
4736 measured reflections	3 standard reflections frequency: 120 min intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.017	35 parameters
$wR(F^2)$ = 0.046	$\Delta\rho_{max}$ = 0.48 e Å^{-3}
S = 1.13	$\Delta\rho_{min}$ = −0.41 e Å^{-3}
683 reflections	

Table 1
Selected bond lengths (Å).

Mg—O1^{i}	1.9743 (6)	S—O1	1.4558 (6)
Mg—O2	2.1012 (5)	S—O3^{iii}	1.4803 (9)
Mg—O3^{ii}	2.2670 (6)	S—O2	1.4936 (9)

Symmetry codes: (i) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$; (iii) $x, y, z-1$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* implemented in *PLATON* (Spek, 2003); method used to solve structure: coordinates taken from an isotypic structure (Wildner & Giester, 1988); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2051).

References

Baur, W. H. (1981). *Structure and Bonding in Crystals*, edited by M. O'Keeffe & M. Navrotsky, pp. 31–52. New York: Academic Press.
Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. Oxford University Press.
Coing-Boyat, J. (1962). *C. R. Acad. Sci.* **258**, 1962–1964.
Dowty, E. (2000). *ATOMS for Windows*. Version 5.1. Shape Software, Kingsport, Tennessee, USA.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fortes, A. D., Wood, I. G., Vočadlo, L., Brand, H. E. A. & Knight, K. S. (2007). *J. Appl. Cryst.* **40**, 761–770.
Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.
Gruehn, R. & Glaum, R. (2000). *Angew. Chem. Int. Ed.* **39**, 692–716.
Rentzeperis, P. J. & Soldatos, C. T. (1958). *Acta Cryst.* **11**, 686–688.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Wildner, M. & Giester, G. (1988). *Mineral. Petrol.* **39**, 201–209.

supplementary materials

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The high-temperature modification of magnesium sulfate (β-$MgSO_4$) from single-crystal data

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Comment

Magnesium sulfate is dimorphic and crystallizes in a low-temperature modification (α-$MgSO_4$; space group *Cmcm*, $CrVO_4$ structure type) and a high-temperature modification (β-$MgSO_4$, space group *Pnma*, $CuSO_4$ structure type). The corresponding crystal structures have already been determined from intensity data using the Debye–Scherrer method (α-$MgSO_4$: Rentzeperis & Soldatos, 1958; β-$MgSO_4$: Coing-Boyat, 1962). The previous structure refinement of β-$MgSO_4$ converged at a reliability factor R[F] = 0.144 without inclusion of temperature factors and indication of standard uncertainties. In order to obtain more precise results for comparative studies with other $M^{II}SO_4$ phases, where M is a first row transition metal, the crystal structure of β-$MgSO_4$ was re-determined by means of single-crystal data.

The crystal structure of β-$MgSO_4$ contains one Mg, one S and three O atoms in the asymmetric unit. The basic structural features are $[MgO_{4/2}O_{2/1}]_\infty$ chains made up of edge-sharing [MgO_6] octahedra and SO_4 tetrahedra. The chains run parallel to [010] and are interconnected by corner-sharing with the SO_4 tetrahedra into a framework structure (Fig. 1, 2).

The [MgO_6] octahedron ($\overline{1}$ point symmetry) is considerably distorted and shows a [2 + 2+2] coordination, with two short Mg—O distances to the terminal O atoms and two medium and two long distances to the bridging O atoms of the $[MgO_{4/2}O_{2/1}]_\infty$ chains. However, the average Mg—O distance of 2.114 Å is in good agreement with the sum of the ionic radii (2.08 Å; Shannon, 1976).

The SO_4 tetrahedron (*m* point symmetry) is slightly distorted, with an average S—O bond length of 1.471 Å which is likewise in very good agreement with the value of 1.473 Å given by Baur (1981) for more than 100 S—O bonds in various sulfates(VI).

The O atoms have coordination numbers of 2 (O1) and 3 (O2, O3). O1 has one Mg and one S as neighbours, both with the shortest observed Mg– and S—O distances. O2 and O3 act as the bridging atoms in the $[MgO_{4/2}O_{2/1}]_\infty$ chains and thus have two Mg and one S as coordination partner.

Results from the bond valence sum (BVS) calculations (Brown, 2002), using the parameters of Brese & O'Keeffe (1991), are in accordance with the expected values (in valence units) of 2 for Mg, 6 for S and 2 for O: Mg 2.02, S 6.05, O1 2.04, O2 2.09, O3 1.90.

During the submission process of the present article the author was informed that the crystal structures of α- and β-$MgSO_4$ have also been re-determined on the basis of neutron powder diffraction data. The results (lattice parameters, atomic coordinates, standard uncertainties, distances) published very recently (Fortes *et al.*, 2007), are very similar to those of the single-crystal study of β-$MgSO_4$ presented here. However, in contrast to the neutron powder study of β-$MgSO_4$ at 300 K (Fortes *et al.*, 2007), no constraints had to be applied during refinement. Therefore the present study is considered as an accurate supplement of the neutron powder study of β-$MgSO_4$ at room temperature.

Experimental

$MgSO_4{\cdot}7H_2O$ (Merck, p·A.) was dehydrated at 973 K for 12 h in an open porcelain crucible. X-ray powder diffraction (XRPD) showed a single phase product. 0.5 g of the polycrystalline material was mixed with 50 mg $PtCl_2$ and heated in sealed and evacuated silica ampoules in a temperature gradient 1173 → 1073 K for one week. Under these conditions $PtCl_2$ is decomposed and the released Cl_2 acts as the transport agent. After the reaction time, the ampoule was taken out of the two-zone furnace and was quenched in a cold water bath. Only few single crystals of β-$MgSO_4$ with an unspecific habit and maximal edge lengths up to 0.4 mm were obtained in the colder zone of the ampoule, indicating rather small transport rates which has also been observed in previous studies (Gruehn & Glaum, 2000).

Refinement

In contrast to the previous refinement from powder data (Coing-Boyat, 1962) where the non-standard setting *Pbnm* of space group No 64 was used, the structure was refined in the standard setting *Pnma*. Atomic coordinates were taken from the isotypic compound $ZnSO_4$ (Wildner & Giester, 1988) as starting parameters and finally standardized with the program *STRUCTURETIDY* (Gelato & Parthé, 1987). The present study confirms the basic structural features determined from the previous investigation by Coing-Boyat (1962), but with a much higher precesion and more reliable interatomic distances.

Figures

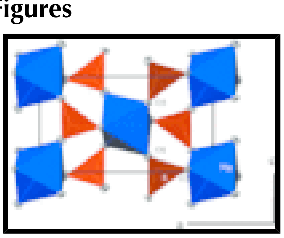

Fig. 1. The crystal structure of β-$MgSO_4$ in polyhedral representation projected along [001]. Displacement ellipsoids are given at the 74% probability level.

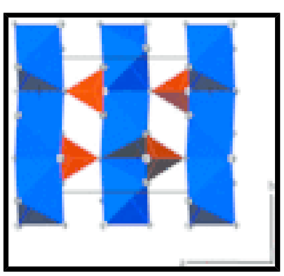

Fig. 2. The crystal structure of β-$MgSO_4$ in a projection along [010]. Colour code and probability level of the displacement ellipsoids as in Fig. 1.

Magnesium sulfate(VI)

Crystal data

$MgSO_4$	F_{000} = 240
M_r = 120.37	D_x = 2.934 Mg m^{-3}
Orthorhombic, *Pnma*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2n	Cell parameters from 25 reflections
a = 8.5787 (8) Å	θ = 11.3–17.4°

b = 6.6953 (6) Å	μ = 1.21 mm^{-1}
c = 4.7438 (5) Å	T = 293 (2) K
V = 272.47 (5) Å^3	Plate, colourless
Z = 4	0.18 × 0.14 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.032
Radiation source: fine-focus sealed tube	θ_{max} = 36.0°
Monochromator: graphite	θ_{min} = 4.8°
T = 293(2) K	h = −14→14
ω/2θ scans	k = −11→11
Absorption correction: ψ scan (PLATON; Spek, 2003)	l = −7→7
T_{min} = 0.780, T_{max} = 0.864	3 standard reflections
4736 measured reflections	every 120 min
683 independent reflections	intensity decay: none
598 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Primary atom site location: isomorphous structure methods
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2 + 0.0698P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.017	$(\Delta/\sigma)_{max}$ < 0.001
$wR(F^2)$ = 0.046	$\Delta\rho_{max}$ = 0.48 e Å^{-3}
S = 1.13	$\Delta\rho_{min}$ = −0.41 e Å^{-3}
683 reflections	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
35 parameters	Extinction coefficient: 0.144 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$

Mg	0.0000	0.0000	0.0000	0.01046 (10)
S	0.32046 (3)	0.2500	0.02598 (5)	0.00547 (8)
O1	0.37429 (7)	0.06895 (9)	0.16526 (13)	0.01011 (12)
O2	0.14650 (10)	0.2500	0.03881 (18)	0.00824 (14)
O3	0.37517 (10)	0.2500	0.73002 (17)	0.00961 (15)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg	0.01031 (18)	0.00964 (18)	0.01143 (19)	−0.00266 (14)	0.00449 (13)	−0.00363 (13)
S	0.00485 (11)	0.00647 (11)	0.00508 (11)	0.000	−0.00029 (7)	0.000
O1	0.0113 (3)	0.0090 (2)	0.0101 (2)	0.00216 (19)	−0.00221 (19)	0.00243 (18)
O2	0.0047 (3)	0.0088 (3)	0.0112 (3)	0.000	0.0004 (2)	0.000
O3	0.0108 (4)	0.0121 (3)	0.0059 (3)	0.000	0.0020 (3)	0.000

Geometric parameters (Å, °)

Mg—O1^{i}	1.9743 (6)	Mg—Mg^{iv}	3.3477 (3)
Mg—O1^{ii}	1.9743 (6)	Mg—Mg^{v}	3.3477 (3)
Mg—O2^{iii}	2.1012 (5)	S—O1^{vi}	1.4558 (6)
Mg—O2	2.1012 (5)	S—O1	1.4558 (6)
Mg—O3^{ii}	2.2670 (6)	S—O3^{vii}	1.4803 (9)
Mg—O3^{i}	2.2670 (6)	S—O2	1.4936 (9)
O1^{i}—Mg—O1^{ii}	180.00 (5)	O3^{ii}—Mg—O3^{i}	180.00 (4)
O1^{i}—Mg—O2^{iii}	94.01 (3)	O1^{vi}—S—O1	112.75 (5)
O1^{ii}—Mg—O2^{iii}	85.99 (3)	O1^{vi}—S—O3^{vii}	109.26 (3)
O1^{i}—Mg—O2	85.99 (3)	O1—S—O3^{vii}	109.26 (3)
O1^{ii}—Mg—O2	94.01 (3)	O1^{vi}—S—O2	107.37 (3)
O2^{iii}—Mg—O2	180.00 (4)	O1—S—O2	107.37 (3)
O1^{i}—Mg—O3^{ii}	92.50 (3)	O3^{vii}—S—O2	110.82 (5)
O1^{ii}—Mg—O3^{ii}	87.50 (3)	S—O1—Mg^{viii}	137.14 (4)
O2^{iii}—Mg—O3^{ii}	105.28 (3)	S—O2—Mg	126.44 (2)
O2—Mg—O3^{ii}	74.72 (3)	S—O2—Mg^{v}	126.44 (2)
O1^{i}—Mg—O3^{i}	87.50 (3)	Mg—O2—Mg^{v}	105.61 (4)
O1^{ii}—Mg—O3^{i}	92.50 (3)	S^{ix}—O3—Mg^{viii}	127.32 (2)
O2^{iii}—Mg—O3^{i}	74.72 (3)	S^{ix}—O3—Mg^{x}	127.32 (2)
O2—Mg—O3^{i}	105.28 (3)	Mg^{viii}—O3—Mg^{x}	95.18 (3)

Symmetry codes: (i) −*x*+1/2, −*y*, *z*−1/2; (ii) *x*−1/2, *y*, −*z*+1/2; (iii) −*x*, −*y*, −*z*; (iv) −*x*, *y*−1/2, −*z*; (v) −*x*, *y*+1/2, −*z*; (vi) *x*, −*y*+1/2, *z*; (vii) *x*, *y*, *z*−1; (viii) −*x*+1/2, −*y*, *z*+1/2; (ix) *x*, *y*, *z*+1; (x) *x*+1/2, −*y*+1/2, −*z*+1/2.

Fig. 1

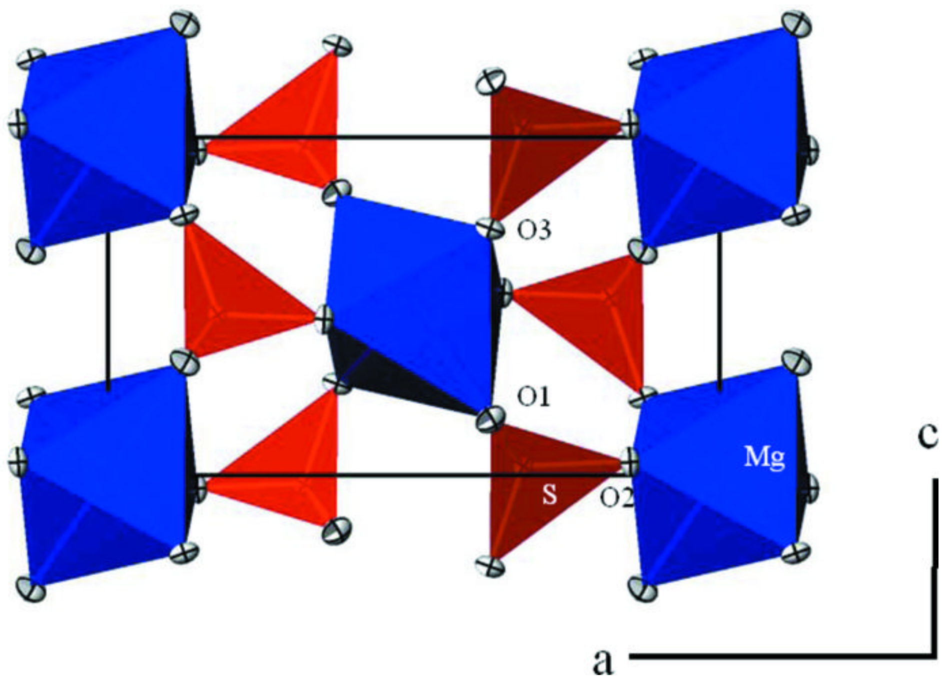

Fig. 2