Rietveld refinement of the crystal structure of α-$CoSO_4$

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The crystal structure of α-$CoSO_4$ has been refined by the Rietveld method from X-ray powder diffraction data. The structure is orthorhombic, space group Pnma, $a=8.6127(4)$, $b=6.7058(3)$, $c=4.7399(2)$ Å, $V=273.75(3)$ Å^3. Final $R_B=2.41\%$, $R_P=5.24\%$, $R_{WP}=6.66\%$, R_{WP} (expected) $=5.74\%$ (WP=weighted profile). The structure consists of edge-sharing octahedral chains parallel to [010] interconnected by SO_4 tetrahedra.

I. INTRODUCTION

The compounds $Me^{2+}XO_4$ (Me^{2+} = Mg, Mn, Fe, Co, Ni, Cu, Zn; X=S, Se) occur in two different structure types, with space groups Cmcm and Pnma (Wildner and Giester, 1988). At low temperatures, $CoSO_4$ (β-form) crystallizes in the space group Cmcm, and above 432 °C at atmospheric pressure, α-$CoSO_4$ is the stable phase in the space group Pnma (Pistorius, 1961). The crystal structure of α-$CoSO_4$ was determined by Coing-Boyat (1959) and refined by Dunitz and Pauling (1965).

The high temperature quenchable phase α-$CoSO_4$ is isostructural with chalcocyanite ($CuSO_4$) and zincosite ($ZnSO_4$). We are currently studying Jahn–Teller driven phase transitions in mixed crystals, and as part of the study of the $CuSO_4$–$CoSO_4$ system, we have refined the structure of $CoSO_4$ to provide precise data for the end-member structures.

II. EXPERIMENT

The low temperature form of $CoSO_4$ (β-$CoSO_4$) was obtained by heating $CoSO_4 \cdot 7H_2O$ at 250 °C for 3 h followed by 300 °C for 2 h. The resulting purple powder was then heated in a platinum foil basket for 15 min at 660 °C. The run product was quenched using compressed air, and was a light red powder, which X-ray examination showed to be α-$CoSO_4$.

The powder was ground for 15 min in an automatic grinder and was then gently back pressed into an aluminum holder. The upper surface of the sample was serrated with a razor blade to minimize any preferred orientation during data collection. The diffraction data for Rietveld refinement were collected at 25 °C with a Philips PW1710 X-ray powder diffractometer with Bragg–Brentano geometry using Cu$K\alpha$ X radiation (40 mA, 40 kV), fixed 1° slits and a diffracted-beam monochromator. Data for the Rietveld refinement were collected over the range 20°–135°2θ with a step interval of 0.05°2θ and a count time of 5 s per step. The sample was then mixed with a silicon standard (SRM 640*b*, $a=5.430940\pm0.000035$ Å) and a continuous scan was done over the 2θ range 10°–145°. The scan speed was set at 0.3°2θ/min. with an integration time of 8 s; all other experimental conditions were as above. The observed powder pattern for α-$CoSO_4$, obtained using the continuous scan, is given in Table I.

The Rietveld structure refinement was done using the program LHMP1 (Hill and Howard, 1986; a modified version of the program by Wiles and Young, 1981). The refinement was done in the space group Pnma with the structural parameters reported by Dunitz and Pauling (1965) as the starting model. Scattering factors for Co, S, and O were taken from the *International Tables for X-Ray Crystallography* (1974). Peaks were modeled using the pseudo-Voigt profile function which was corrected for peak asymmetry to 30°2θ. The background was modeled using a refinable fourth-order polynomial. The isotropic temperature factors were unstable towards refinement and were fixed at accepted single-crystal values, with an overall temperature factor refined. The refined structure parameters, *R* values and bond distances are reported in Table II.

III. DISCUSSION

The crystal structure of α-$CoSO_4$ is characterized by edge-sharing octahedral chains running parallel to [010] and interconnected by SO_4 tetrahedra. The coordination of the octahedral cation in α-$CoSO_4$ is distorted into a (2+2+2) configuration (Table II). The same octahedral distortion is observed in $ZnSO_4$, whereas a (4+2) octahedral distortion is observed in $CuSO_4$ (Wildner and Giester, 1988). The (4+2) distortion around the copper site in $CuSO_4$ is attributed to the Jahn–Teller effect with Cu^{2+} in octahedral coordination. However, the (2+2+2) distorted octahedral geometries observed in $ZnSO_4$ and α-$CoSO_4$ cannot be attributed to the Jahn–Teller effect, and must result from structural connectivity requirements. The SO_4 tetrahedron in α-$CoSO_4$ is also strongly distorted (Table II).

Comparison of the relative distortions in this structure type are best made using the bond-valence distributions (Table III). All three structures have the similar M^{2+}–O bond-valence patterns: M–O(1) < M–O(2) < M–O(3). The major control on these values is the coordination number of the specific anion: The strongest bond always involves the O(3) anion that is the only [2]-coordinate anion in the structure. Similarly, in the Zn and Co structures, the S–O(3) bond is the strongest of the S–O bonds, again dictated by coordination number. For the Cu^{2+} structure, the issue of anion coordination number is complicated by the well-known Jahn–Teller instability of regular ($Cu^{2+}\phi_6$) octahedra (ϕ=unspecified ligand) which induces a spontaneous (4+2) distortion of the octahedron coordinating the Cu^{2+}. The $ZnSO_4$ structure has no intrinsic electronic

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TABLE I. Observed powder pattern for α-$CoSO_4$ ($\lambda = 1.54060$ Å). Observed compared to the pattern calculated[a] using the structure parameters obtained through Rietveld refinement (Table II) and the program LHMPI (Hill and Howard, 1986).

$2\theta^b$	d_{obs}	I_{obs}	$I_{(PK,calc)}$	*h k l*
20.59	4.310	16	15	2 0 0
21.35	4.159	49	53	1 0 1
22.96	3.871	1	1	0 1 1
24.62	3.627	42	42	2 1 0
25.18	3.534	100	100	1 1 1
26.55	3.354	4	1	0 2 0
27.96	3.188	4	2	2 0 1
33.86	2.645	58	65	2 2 0
34.36	2.608	42	49	1 2 1
36.57	2.455	52	58	3 0 1
37.94	2.370	18	18	0 0 2
38.97	2.309	18	17	2 2 1
39.41	2.284	12	11	1 0 2
41.92	2.153	3	1	4 0 0
43.54	2.077	7	6	2 0 2
44.14	2.050	4	2	4 1 0
44.81	2.021	6	3	0 3 1
45.77	1.9810	17	19	3 2 1
46.09	1.9678	8	8	1 3 1
46.91	1.9353	3	1	0 2 2
49.85	1.8277	4	1	3 0 2
50.30	1.8124	14	14	4 2 0
51.74	1.7653	27	34	2 2 2
51.81				3 1 2
54.70	1.6766	13	15	0 4 0
55.59	1.6519	1	1	3 3 1
56.81	1.6192	4	2	5 0 1
57.82	1.5934	8	8	4 0 2
58.61	1.5737	6	5	5 1 1
59.11	1.5617	2	1	2 4 0
59.41	1.5544	14	16	1 4 1
59.43				1 0 3
60.13	1.5376	4	3	0 1 3
61.18	1.5136	4	3	1 1 3
63.03	1.4737	5	3	4 3 1
63.78	1.4580	17	16	5 2 1
64.72	1.4391	11	12	4 2 2
64.91	1.4354	11	12	6 0 0
66.23	1.4099	10	14	1 2 3
67.15	1.3929	1	1	5 0 2
67.63	1.3842	13	15	3 4 1
67.64				3 0 3
68.52	1.3683	7	7	0 4 2
71.98	1.3109	<1	1	5 3 1
72.42	1.3040	<1	1	2 4 2
74.01	1.2798	3	2	2 5 0
74.05				3 2 3
74.28	1.2758	8	9	1 5 1
74.29				1 3 3
77.74	1.2275	6	5	6 0 2
79.28	1.2074	4	3	6 3 0
79.27				6 1 2
80.62	1.1907	3	1	7 0 1
80.63				4 2 3
82.17	1.1721	2	1	7 1 1
86.70	1.1221	<1	1	7 2 1
88.91	1.0999	4	3	5 2 3
89.94	1.0899	5	3	6 4 0
90.88	1.0811	7	7	2 2 4
90.86				2 6 0
91.43	1.0760	4	3	8 0 0
96.54	1.0322	3	1	5 1 1
96.51				5 3 3
97.48	1.0247	4	2	8 2 0
97.83	1.0220	1	1	0 5 3
98.53	1.0166	1	1	3 6 1
103.14	0.9833	1	1	3 3 4
103.51	0.9808	1	1	7 3 2
105.52	0.9676	1	1	0 4 4

[a] The calculation used atomic scattering factors for Co, S, and O (corrected for anomalous dispersion).

[b] Includes $2\theta_{obs}$ plus 2θ positions of additional calculated reflections.

TABLE II. Refined structure parameters and *R*-Values for $CoSO_4$.

Space group Pnma			
Cell parameters (Rietveld)		Cell parameters[a] (Least squares)	
a,Å	8.6127(4)	*a*,Å	8.6112(5)
b,Å	6.7058(3)	*b*,Å	6.7025(5)
c,Å	4.7399(2)	*c*,Å	4.7396(3)
V,Å^3	273.75(3)	*V*,Å^3	273.55(5)
Z	4		
Refinement *R* values[b]			
R_B	2.41	R_P	5.24
R_{WP}	6.66	R_{WP}(exp.)	5.74
$D-W$	1.34	$N-P$	2273
Atomic parameters[c]			
	x	*y*	*z*
Co	0	0	0
S	0.1795(4)	1/4	0.4740(11)
O1	0.1267(12)	1/4	0.7729(19)
O2	0.3547(10)	1/4	0.4506(19)
O3	0.1287(7)	0.0648(10)	0.3413(12)
Bond distances (Å)			
Co–O1×2	2.272(5)	S–O1	1.488(9)
Co–O2×2	2.105(6)	S–O2	1.51(1)
Co–O3×2	2.01(1)	S–O3×2	1.46(1)
⟨Co–O⟩	2.129	⟨S–O⟩	1.480

[a] Cell parameters refined from powder data (corrected using internal standard; Table I) using the program Celref (Appleman and Evans, 1973).

[b] R_B=Rietveld Bragg agreement index; R_P=Rietveld profile agreement index; R_{WP}=Rietveld weighted profile agreement index; *D–W* =Durbin–Watson *d*-staticstic; *N–P*=Number of data.

[c] B_{iso} fixed at 0.77, 0.56, and 0.85 for Co, S, and O, respectively.

stabilizations due to *d*-electron effects, and can be thought of as the prototype arrangement on which *d*-electron effects act as a perturbation. The M–O(1) bonds are in a *trans* arrangement, and the weakest bonds in the structure; this is due to the intrinsic connectivity of the structural

TABLE III. Bond-valence[a] analyses for α-$CoSO_4$, $CuSO_4$, and $ZnSO_4$.

		α-$CoSO_4$	
	Co	S	Σ
$^{[3]}$O(1)	0.215×2	1.448	1.878
$^{[3]}$O(2)	0.330×2	1.348	2.008
$^{[2]}$O(3)	0.428×2	1.575×2	2.003
Σ	1.946	5.946	
		$CuSO_4$	
	Cu	S	Σ
$^{[3]}$O(1)	0.144×2	1.603	1.891
$^{[3]}$O(2)	0.347×2	1.310	2.004
$^{[2]}$O(3)	0.520×2	1.539×2	2.059
Σ	2.022	5.991	
		$ZnSO_4$	
	Zn	S	Σ
$^{[3]}$O(1)	0.183×2	1.473	1.839
$^{[3]}$O(2)	0.315×2	1.395	2.025
$^{[2]}$O(3)	0.482×2	1.566×2	2.048
Σ	1.960	6.000	

[a] Bond-valence parameters from Brown (1981).

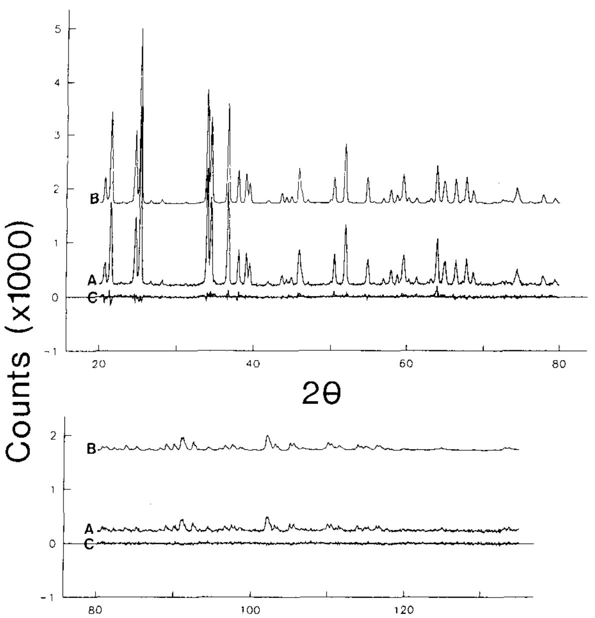

FIG. 1. (a) Observed X-ray powder pattern for α-$CoSO_4$; (b) Pattern calculated from refined parameters (plus 1500 counts); (c) Residual: $I(\mathrm{obs}) - I(\mathrm{calc})$.

arrangement, as the polyhedra cannot link in this fashion unless they are extremely distorted (this may be easily shown to be the case using distance-least-squares refinement). Thus the structure has an intrinsic (4+2) distortion of the octahedron that is exploited by the Jahn–Teller relaxation that is associated with occurrence of Cu^{2+} at the octahedrally coordinated site. However, the additional octahedral elongation produced by the Jahn–Teller distortion in $CuSO_4$ changes the pattern of S–O bond valences. Despite the differences in octahedral distortions in α-$CoSO_4$ and $ZnSO_4$, both these structures show the bond-valence pattern $S–O(3) > S–O(1) > S–O(2)$. On the other hand, $CuSO_4$ shows the pattern $S–O(1) > S–O(3) > S–O(2)$, reflecting the increased elongation of the octahedron along the O(1)–Cu–O(1) axis. Presumably the differences between the Co and Zn members are a reflection of the *d*-electronic structure of Co^{2+}, but the character of the distortions induced by electronic instabilities in 3*d* transition metals is, except for Cu^{2+}, not well characterized. A thorough and systematic examination of this feature in isostructural series would be of interest.

The *Powder Diffraction file* includes a pattern for α-$CoSO_4$ (11-125). The intensities of the PDF file are in poor agreement with those observed in the present study. There is also poor agreement between this study and the unit cell parameters and the interplanar spacings reported in PDF 11-125. The data reported here also include a number of weak lines that are not listed in PDF 11-125.

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