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Lattice constants and space groups of the low and high temperature polymorphic forms of anhydrous cobaltous sulfate.

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Introduction

In the course of an investigation of the magnetic properties of anhydrous cobaltous sulfate, Hocart & Serres (1931) found that $CoSO_4$, which has been formed by the dehydration of $CoSO_4.7\,H_2O$ at 400 °C., possessed a magnetic moment of 25 magnetons/molecule, while the same substance, dehydrated at 700 °C., possessed a magnetic moment of 26 magnetons/molecule. They determined the unit cell of the form which had been dehydrated at 700 °C., and concluded that it was orthorhombic with

$$a_0 = 4{\cdot}66,\ b_0 = 6{\cdot}72,\ c_0 = 8{\cdot}47\ \text{Å}\ .$$

They further claimed, without giving the powder pattern of the form dehydrated at 400 °C., that its pattern differed only with regard to peak intensity.

Recently Dimaras (1957) succeeded in growing single crystals of anhydrous nickelous sulfate which possessed a sufficient size to enable him to determine the unit cell and space group. The present investigation was undertaken in the expectation that one of the forms of $CoSO_4$ would be isostructural with $NiSO_4$, and that an unambiguous assignment of the powder pattern of that form of $CoSO_4$ could be made in analogy to the known pattern of $NiSO_4$.

Experimental

Baker analyzed reagent grade $CoSO_4.7\,H_2O$ was used. The main impurities were 0·11% alkalies and earths, 0·001% copper, 0·0002% iron and 0·13% nickel.

A weighed quantity of $CoSO_4.7\,H_2O$ was heated to 300 °C. for a period of two hr. The weight loss agreed with the expected value. There was no further weight loss on heating to 700 °C.

The X-ray powder diffraction patterns of the $CoSO_4$ prepared at 300 °C., and at 700 °C., ground into a paste with petroleum jelly, were obtained at 25 °C. in a Norelco high angle recording diffractometer, using Fe $K\alpha$ radiation ($\lambda = 1{\cdot}9373$ Å) and a Mn filter. The scanning speed was $\frac{1}{8}°$ (2θ) per min. Pre-calibrated high-purity sodium chloride was used as an internal standard.

Results

The diffraction patterns for the two forms were completely different. This shows that the high and low phases are distinct polymorphis forms.

(*a*) All the observed diffraction peaks of the low-temperature modification could be satisfactorily assigned as being due to an orthorhombic lattice with the following unit-cell dimensions, as obtained by a least-squares treatment:

$$a_0 = 5{\cdot}191 \pm 0{\cdot}002,\ b_0 = 7{\cdot}864 \pm 0{\cdot}002,$$
$$c_0 = 6{\cdot}516 \pm 0{\cdot}002\ \text{Å}\ .$$

The selection rules appear to be:

$00l$: none present;
$h0l$: h even, l even;
hkl: $h+k$ even.

From this it follows that the possible space groups are: C_{2v}^{12}–$Cmc2_1$, C_{2v}^{16}–$C2cm$ and D_{2h}^{17}–$Cmcm$. The low-$CoSO_4$ pattern is very similar to that of $NiSO_4$. Dimaras (1957) concluded that $Cmcm$ is the most probable space group for $NiSO_4$, although the other two space groups are not definitely ruled out. Consequently, we can come to the same tentative conclusion in the present case.

Table 1. *Powder pattern of low-*$CoSO_4$

d_o	d_c	hkl	$100\ I/I_0$
4·333 Å	4·332 Å	110	85
3·931	3·932	020	70
3·607	3·608	111	100
3·367	3·367	021	30
2·601	2·604, 2·595	112, 200	92 broad
2·509	2·509	022	10
2·340	2·340	130	63
2·201	2·202	131	4
2·053	2·055	221	7
2·031	2·030	202	20
1·967	1·966	040	20
1·902	1·901, 1·901	023, 132	11
1·804	1·804	222	30
1·691	1·690	310	5
1·684	1·683	042	15
1·637	1·636	311	9
1·592	1·592	133	8
1·567	1·567	240	6
1·524	1·524, 1·525	241, 114	8
1·506	1·505, 1·505	150, 024	11
1·501	1·500	312	16
1·443	1·444	330	18
1·412	1·410, 1·412	331, 242	27
1·381	1·380	204	4
1·367	1·367	152	6
1·337	1·337	134	9
1·311	1·311	060	5
1·2978	1·2976	400	18
1·2369	1·2372, 1·2371	153, 025	4
1·1529	1·1526	422	4
1·1513	1·1516	261	6
1·0809	1·0806	334	9
1·0720	1·0718	423	4
1·0541	1·0535	116	4
1·0408	1·0406	172	10
1·0280	1·0277	442	10
1·0169	1·0166	511	5
1·0152	1·0150	404	8

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Table 2. *Powder pattern of high-*$CoSO_4$

d_o	d_c	hkl	100 I/I_0
4·301 Å	4·301 Å	020	28
4·147	4·149	110	81
3·620	3·619	021	43
3·528	3·528	111	83
2·643	2·643	022	65
2·606	2·606	112	50
2·453	2·453	130	100
2·369	2·369	200	21
2·309	2·303, 2·308	131, 122	15
2·283	2·284	210	14
2·075	2·075	220	7
2·049	2·048	041	5
2·021	2·020	103	6
1·979	1·982, 1·979, 1·982	221, 132, 023	16
1·966	1·966	113	6
1·935	1·934	202	2
1·885	1·887	212	2
1·828	1·828	123	3
1·810	1·810	042	12
1·764	1·764, 1·762	222, 231	26
1·675	1·675	004	13
1·651	1·651	133	1
1·618	1·617	150	4
1·604	1·603	232	2
1·593	1·592	240	11
1·573	1·572	151	5
1·553	1·553, 1·553	114, 310	17
1·550	1·549, 1·549	241, 043	8
1·536	1·537	301	3
1·520	1·520	223	1
1·513	1·513	311	4
1·472	1·472	143	4
1·457	1·456	152	19
1·438	1·438	242	10
1·435	1·434	060	10
1·409	1·409	312	8
1·393	1·392	250	2
1·383	1·383, 1·383	330, 134	12
1·372	1·372	160	3
1·3677	1·3674	204	6
1·2751	1·2750, 1·2749	313, 115	7
1·2730	1·2728, 1·2727	340, 144	4
1·2505	1·2504	341	3
1·2267	1·2265	260	8
1·2064	1·2064, 1·2064	261, 063	4
1·1901	1·1898, 1·1895	342, 170	3
1·1846	1·1843	400	3
1·1732	1·1732	410	1
1·1712	1·1712	171	1
1·1692	1·1691	163	3
1·1554	1·1556, 1·1555	411, 215	2
1·1534	1·1539	244	3
1·1458	1·1462	351	2
1·1387	1·1387	314	3
1·1212	1·1209	172	2
1·0996	1·0989	352	5
1·0909	1·0908	270	2
1·0893	1·0891	064	3
1·0807	1·0803, 1·0803	431, 235	6
1·0788	1·0781	116	8
1·0770	1·0766	271	4
1·0668	1·0664	334	4
1·0506	1·0502	173	4
1·0322	1·0316, 1·0317	155, 353	3
1·0253	1·0251, 1·0252	245, 441	4
1·0246	1·0238	082	6

The above unit-cell dimensions may be compared with those of $NiSO_4$ (Dimaras, 1957), namely 5·155, 7·842 and 6·338 Å, respectively, or of $FeSO_4$ (Pistorius, 1959), namely 5·261, 8·013 and 6·454 Å, respectively.

The axial ratios are:

$$a_0:b_0:c_0 = 0{\cdot}6603:1:0{\cdot}8287 .$$

The calculated density of low-$CoSO_4$ at 25 °C., assuming 4 molecules per unit cell, is 3·870 g.cm.$^{-3}$. The pycnometric density is 3·791 g.cm.$^{-3}$ (Birk & Biltz, 1926).

The observed and calculated d-spacings, assigned indices and observed relative intensities for low-$CoSO_4$ are listed in Table 1.

(*b*) The diffraction pattern of the high-temperature polymorph of $CoSO_4$ could be explained on the basis of the earlier unit-cell dimensions (Hocart & Serres, 1931). However, it was necessary to carry out a least-squares treatment, since the earlier measurements were not sufficiently accurate. The present unit-cell constants for high-$CoSO_4$, oriented so as to show the relation to low-$CoSO_4$, are:

$$a_0 = 4{\cdot}738 \pm 0{\cdot}002,\ b_0 = 8{\cdot}603 \pm 0{\cdot}002,\ c_0 = 6{\cdot}699 \pm 0{\cdot}002\ \text{Å}.$$

The selection rules appear to be:

$hk0$: all allowed;
$h0l$: $h+l$ even;
$0kl$: $k = 2n$;
hkl: all allowed.

From this it follows that the possible space groups are D_{2h}^{16}–*Pbnm* and C_{2v}^{9}–*Pbn*2. The high-$CoSO_4$ pattern is very similar to those of $ZnSO_4$ and $CuSO_4$. Kokkoros & Rentzeperis (1958) concluded that $ZnSO_4$ and $CuSO_4$ are isomorphous, and probably belong to the space group D_{2h}^{16}–*Pbnm*. This conclusion was based on the holohedral appearance of their single crystals, and on the fact that they succeeded in working out a satisfactory structure based on this space group. Consequently, we may conclude that although *Pbnm* is the most probable space group for high-$CoSO_4$, the space group *Pbn*2 is not definitely excluded.

The axial ratios are:

$$a_0:b_0:c_0 = 0{\cdot}5508:1:0{\cdot}7787 .$$

The calculated density of high-$CoSO_4$ at 25 °C., assuming 4 molecules per unit cell, is 3·770 g.cm.$^{-3}$, representing an increase in volume of 2·58% over that of low-$CoSO_4$.

The powder data for high-$CoSO_4$ are listed in Table 2.

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