Acta Cryst. (1965). **18**, 737

Polymorphism in Anhydrous Cobalt Sulphate

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(*Received* 15 *June* 1964)

Three distinct crystal forms of cobalt sulphate, $CoSO_4$, have been found to exist. The structures of two of these forms have been independently published (Coing-Boyat, 1959) and the structure of the third is reported here. The relationships among the three structures are discussed in terms of the site symmetry of the sulphate ion.

Introduction

Hocart & Serres (1931) obtained anhydrous cobalt sulphate by heating the pentahydrate and reported two phases, *A* at 400 °C and *B* at 700 °C. On the basis of X-ray powder diffraction patterns they concluded that both phases were of the orthorhombic system. They also prepared crystals of anhydrous cobalt sulphate by crystallization from fused ammonium hydrogen sulphate and found the magnetic susceptibility and X-ray powder pattern of these crystals to be identical with those of phase *B*. More recently Coing-Boyat (1959*a*) reported, on the basis of powder diffraction photographs, that the two phases of cobalt sulphate of Hocart & Serres have the structures of vanadium chromate (Brandt, 1943) and zinc sulphate (Kokkoros & Rentzeperis, 1958) respectively. Cobalt sulphate *A* and vanadium chromate are also isostructural with nickel sulphate (Dimaras, 1957), magnesium sulphate (Rentzeperis & Soldatos, 1958), manganous sulphate (Coing-Boyat, 1959*a*), and ferrous sulphate (Coing-Boyat, 1959*b*). Cobalt sulphate *B* and anhydrous zinc sulphate are isostructural with anhydrous copper sulphate (Kokkoros & Rentzeperis, 1958).

We have carried out single-crystal studies on the *A* and *B* forms of cobalt sulphate that confirm Coing-Boyat's (1959*a*) powder diffraction results; and we have also discovered a third form *C*, which co-exists together with form *B*. In this paper, we present our results for all three forms and draw attention to the structural relationships among them.

Form A

Anhydrous cobalt sulphate form *A* was prepared by crystallization from fuming sulphuric acid (338 °C) (Étard, 1878). The purple single crystals were separated from the mother liquor, washed with acetone, mounted on glass fibres and protected from the atmosphere by coating with Formvar. From zero and upper layer Weissenberg photographs taken with unfiltered copper *K* radiation, the crystals are orthorhombic with

$$a=5\cdot19,\ b=7\cdot87,\ c=6\cdot51\ \text{Å}\ .$$

The space group *Cmcm* (D_{2h}^{17}) follows from the systematic absences and the holohedral appearance of the crystals. These results are in agreement with those of Coing-Boyat (1959*a*) who reported $a=5\cdot195$, $b=7\cdot872$, $c=6\cdot523$ Å and confirm that the *A* form has the vanadium chromate structure (Brandt, 1943). No further work was done on this form.

Form B

Anhydrous cobalt sulphate form *B* was prepared by mixing the hydrate with an excess of ammonium hydrogen sulphate and heating the mixture in a porcelain crucible. At a temperature of 500 °C, light red crystals of the *B* form separated from the melt. At lower temperatures (350 °C) violet crystals that proved to be isomorphous with langbeinite, $Mg_2K_2(SO_4)_3$, (Zemann & Zemann, 1957) were obtained. These are assumed to be the double salt $Co_2(NH_4)_2(SO_4)_3$, but no detailed analysis has been made.

After the melt had been cooled from 500 °C, well developed crystals of the *B* form were picked out and protected from the atmosphere by coating with Formvar. It was observed in all cases that rather more than a half of each crystal was transparent, whereas the remainder of what was apparently a single crystal appeared translucent, the two regions being sharply divided by a plane through the crystal.

From zero and upper layer line Weissenberg photographs taken about the three principal axes with unfiltered copper *K* radiation, the crystals are orthorhombic with

$$a=8\cdot62,\ b=6\cdot70,\ c=4\cdot75\ \text{Å}\ .$$

The systematic absences are compatible with the space group *Pnma* (D_{2h}^{16}). As reported by Coing-Boyat

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* This work was done in 1956–57 while the authors were at the Davy Faraday Laboratory of the Royal Institution of Great Britain, 21 Albermarle Street, London, W.1.

(1959*a*), who obtained cell constants $a = 8{\cdot}616$, $b = 6{\cdot}702$, $c = 4{\cdot}739$ Å, in close agreement with the above, the *B* form is isostructural with anhydrous zinc sulphate (Kokkoros & Rentzeperis, 1958).

The atomic positions in the *B* form were determined from electron-density projections on (010) and (001), and refined by least-squares analysis of partial three-dimensional data. Thermal motion was allowed for by inclusion of an overall isotropic temperature factor. The program employed was that of Milledge (1961). The final coordinates listed in Table 1 lead to an *R* index of 18·6% for the visually estimated reflexions observed on the photographs. Since the linear absorption coefficient of the crystals is 580 cm^{-1} for copper radiation and no correction for absorption was made, the absorption error is certainly the limiting factor of this refinement.

Table 1. *Atomic positions for cobalt sulphate form B referred to orthorhombic cell with* $a = 8{\cdot}61$ Å, $b = 6{\cdot}70$ Å, $c = 4{\cdot}75$ Å, *space group Pnma.*

Atom	*x*	*y*	*z*
Co	0	0	0
S	0·320	$\frac{1}{4}$	0·026
O(1)	0·367	$\frac{1}{4}$	−0·278
O(2)	0·146	$\frac{1}{4}$	0·026
O(3)	0·373	0·070	0·161

The coordinates of Table 1 lead to an approximately tetrahedral sulphate ion (S–O, 1·44 – 1·50 Å; O–S–O, 105·7 – 113·7°) and to a somewhat distorted octahedral arrangement of oxygen atoms about the cobalt ion (Co–O, 2 × 2·00 Å, 2 × 2·10 Å, 2 × 2·29 Å).

Form C

It has already been noted that crystals of form *B* did not appear to the optically homogeneous. Weissenberg photographs taken about the [010] axis show weak satellite reflexions that could be indexed as $h \pm l/5, k, l$, referred to the *B* cell. Only those reflexions with $h + l = 2n$ are accompained by such satellites (Fig. 1).

The satellites can clearly be indexed as reflexions with integral indices on the basis of a twinned pair of *B*-centred monoclinic cells with

$$a' = a_B \pm c_B/5,\ b' = b_B,\ c' = c_B\ .$$

The corresponding primitive cell that we assign to form *C* has

$$a = 4{\cdot}71,\ b = 6{\cdot}70,\ c = 4{\cdot}75\ \text{Å},\ \beta = 66{\cdot}2°$$

with $P2_1/m$ as probable space group.

The hypothesis that the satellite reflexions arise from a new phase of cobalt sulphate was tested by measuring the intensities of the satellite reflexions in the [010] zone and calculating the corresponding density projection. Intensities of reflexions common to both forms (those with $l = 5n$) were estimated by determining the fraction of the crystal in the *C* form from the ratio of the mean intensity of two satellite reflexions $h \pm l/5, 0, l$ to the intensity of the corresponding orthorhombic *h*0*l* reflexion. Since the two cobalt atoms in the unit cell of the *C* form could be placed at the special positions 0, 0, 0, and 0, $\frac{1}{2}$, 0, all reflexions were taken as having positive sign. The resulting electron density projection, shown in Fig. 2, provides very convincing proof that our assumptions concerning the origin of the satellite reflexions are correct. The sulphate ion is clearly recognizable with its mirror plane parallel to the plane of projection. In view of the roughness of the experimental data, no attempt has been made to determine the atomic positions accurately. Rough atomic positions for the *C* form are given in Table 2.

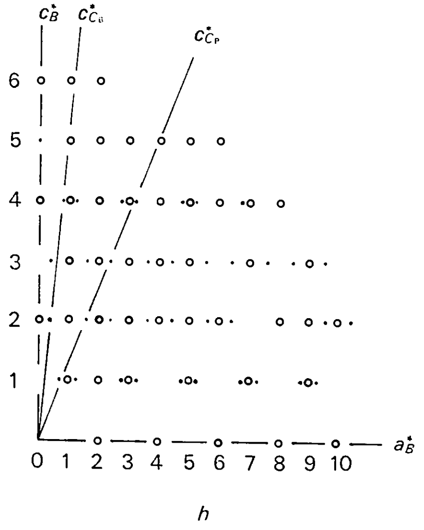

Fig. 1. Diagrammatic representation of the *h*0*l* reflexions from cobalt sulphate form *B*, showing satellite reflexions ascribed to form *C*.

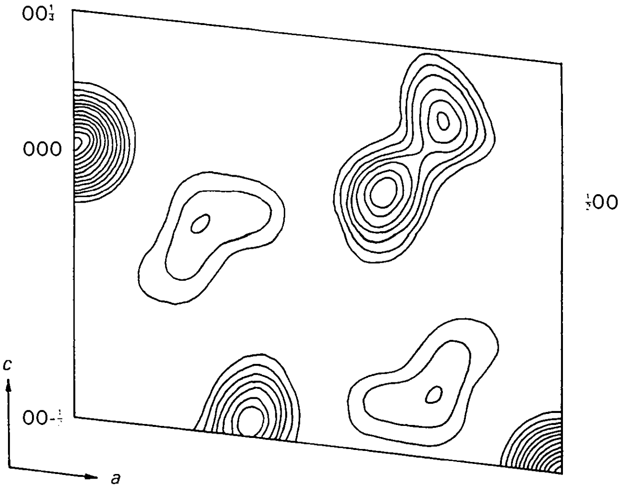

Fig. 2. (010) electron density projection of cobalt sulphate form *C*.

Table 2. *Rough atomic positions for cobalt sulphate form C, referred to the B-centred monoclinic cell with* $a'=8\cdot67$ Å, $b=6\cdot70$ Å, $c=4\cdot75$ Å, $\beta'=96\cdot4°$, *space group* $B2_1/m$.

Atom	x	y	z
Co	0	0	0
S	0·32	$\frac{1}{4}$	−0·02
O(1)	0·38	$\frac{1}{4}$	−0·29
O(2)	0·15	$\frac{1}{4}$	−0·08
O(3)	0·38	0·07	0·12

A number of attempts were made to prepare pure crystals of forms *B* and *C* by varying the conditions of crystallization, but without success. All crystals obtained were mostly form *B* with small portions of the two orientations of form *C*. The monoclinic crystals would seem to be associated with the translucent portions of the crystals, many of which appear morphologically to have less than *mmm* symmetry. The temperature range in which form *C* is stable is not known.

Relationship between the three forms

The three forms of cobalt sulphate are closely related to one another, as shown in Fig. 3. The comparison of the three structures is facilitated by changing the axial orientation of the *A* form to correspond to the setting *Bbmm*. In this setting $a'=7\cdot87$, $b'=6\cdot51$, $c=5\cdot19$ Å, and Fig. 3 shows the structures of all three forms projected on their (010) planes.

If we neglect the orientation of the sulphate tetrahedra it is seen that the arrangements of cobalt and sulphur atoms are very similar in all three forms. These arrangements can all be regarded as being based on a pseudohexagonal lattice with cobalt at $0,0,0$; $0,0,\frac{1}{2}$, and sulphur approximately at $\frac{1}{3},\frac{2}{3},\frac{1}{4}$; $\frac{2}{3},\frac{1}{3},\frac{3}{4}$. To this extent, all three forms are based on the nickel arsenide structure.

A second point of similarity is that in all three forms, the sulphur atom two oxygen atoms of the sulphate group lie on the mirror plane $y=\frac{1}{4}$. The other two oxygen atoms lie on opposite sides of this mirror plane and are equivalent by it. The three forms correspond to three different ways of rotating the sulphate tetrahedra in the mirror plane under the condition that approximate octahedral coordination about the cobalt atoms be satisfied.

In the *A* form, the one of highest symmetry, the sulphate tetrahedron has a second mirror plane $z=0$, *i.e.* the two oxygen atoms in the mirror plane $y=\frac{1}{4}$ are equivalent by reflexion across $z=0$. In the other two forms, this second mirror plane is missing so that the tetrahedron is free to rotate about an axis parallel to b and to move out of the plane $z=0$. The movement from $z=0$ that occurs is small in both cases. To go from the *A* to the *B* form, half of the sulphate tetrahedra in a given mirror plane are rotated 120° clockwise and the other half of the sulphate tetrahedra 120° counterclockwise. To go from the *A* to the *C* form, all the sulphate tetrahedra in any one mirror plane are rotated about 120° in the same sense, those in the next mirror plane being rotated in the opposite sense. This brings with it a loss of orthorhombic

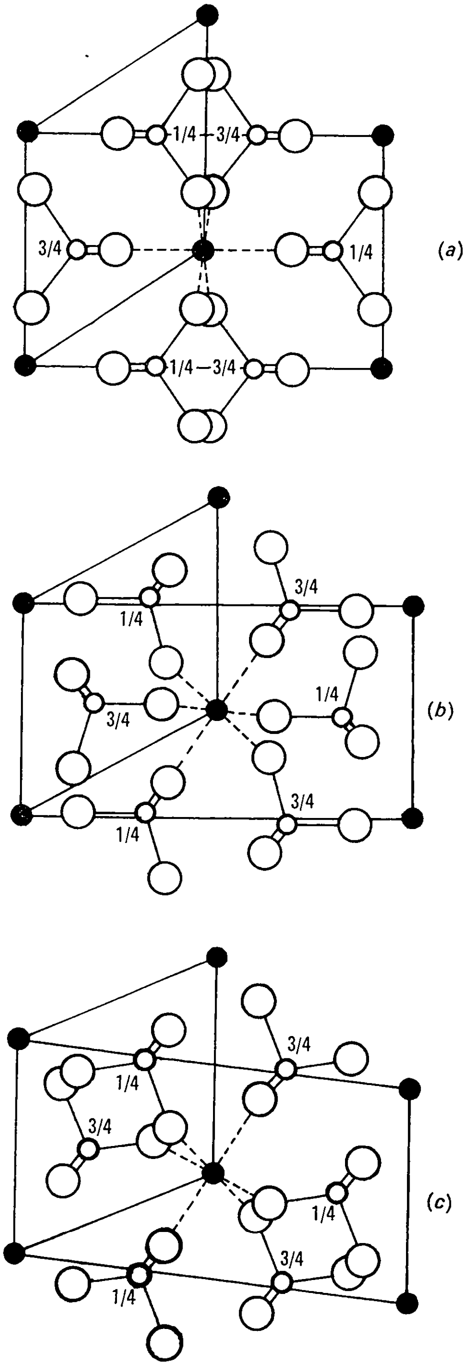

Fig. 3. Structures of anhydrous cobalt sulphate (*a*) form *A* (*b*) form *B* (*c*) form *C*, projected on (010). The cobalt atoms occur at $y=0$ and $y=\frac{1}{2}$. The pseudohexagonal 'nickel arsenide' cell is indicated in all three cases; for form *C* it corresponds to the conventional primitive cell.

symmetry, since sulphate tetrahedra in the same mirror plane are now related only by the translation $a/2+c/2$. The structure adjusts itself, accordingly, to the new degree of freedom by a slight departure of the lattice from orthogonality.

Up till now, the anhydrous sulphates of divalent magnesium, manganese, iron and nickel are only known to occur in the *A* form, those of copper and zinc only in the *B* form. Polymorphism has been reported only for anhydrous cobalt sulphate, but it is difficult to see why the divalent cobalt atom should be egregious in this respect. Further work may well reveal that the other anhydrous sulphates in this series exhibit the same or at least similar kinds of polymorphism.

We are grateful to Dr D. W. Green and to Dr. H. J. Milledge for help with computing. This work was done while the authors were at the Davy Faraday Laboratory of the Royal Institution of Great Britain and we are grateful to Sir Lawrence Bragg and the Managers for facilities.

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Acta Cryst. (1965). **18**, 740

The Structure of Ammonium Copper Sulphate $(NH_4)_2Cu(SO_4)_2 . 6H_2O$

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(*Received* 11 *May* 1964)

The structure of ammonium copper sulphate is shown to be very similiar to that of the nickel and magnesium ammonium sulphates except for the tetragonal distortion of the water molecule octahedra surrounding the copper ions. The orientation of the octahedron is in good agreement with paramagnetic resonance measurements and a reason for the poorer stability of the copper salt is suggested.

Introduction

Ammonium copper sulphate, a member of the isomorphous series known as Tutton salts, has a structure of particular interest because of the tetragonal distortion of the crystal field on the copper ion as revealed by paramagnetic resonance studies (Bleaney, Penrose & Plumpton, 1949). The structures of the corresponding nickel and magnesium salts of the series have already been described (Grimes, Kay & Webb, 1963; Margulis & Templeton, 1962), and as the procedure adopted to determine the structure of the copper salt was essentially the same as that used for the nickel salt, only the final results and conclusions are presented here.

Table 1. *Atomic coordinates and their standard deviations for ammonium copper sulphate*

	x/a	$\sigma x/a$	y/b	$\sigma y/b$	z/c	$\sigma z/c$
Ni	0	—	0	—	0	–
S	0·0878	±0·0013	0·6394	±0·00095	0·252	±0·0019
NH_4	0·1296	±0·0037	0·3498	±0·0028	0·3550	±0·006
O(1)	0·0857	±0·0037	0·7276	±0·0025	0·4030	±0·006
O(2)	0·1133	±0·0036	0·6753	±0·0026	0·0364	±0·007
O(3)	0·2217	±0·0037	0·5707	±0·0027	0·3687	±0·007
O(4)	−0·0520	±0·0036	0·5735	±0·0026	0·2135	±0·007
$H_2O(1)$	−0·1678	±0·0036	0·1070	±0·0025	0·0281	±0·007
$H_2O(2)$	0·1691	±0·0036	0·1189	±0·0026	0·1697	±0·007
$H_2O(3)$	0·0017	±0·0038	−0·0633	±0·0023	0·2987	±0·007

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