

## X-Ray and Magnetic Study of the System Cobalt Selenium

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X-ray studies of cobalt selenides have revealed three intermediate solid phases.

The  $\beta$ -phase, probably  $\text{Co}_3\text{Se}_3$ , has a cubic face-centered structure with lattice constant  $a = 10.431 \text{ \AA}$ . The phase is stable at  $400^\circ \text{C}$ , but not at  $600^\circ \text{C}$ . Its structure is closely related to that of  $\text{Co}_3\text{S}_3$  and pentlandite  $(\text{Fe}, \text{Ni})_3\text{S}_3$ .

The  $\gamma$ -phase has a range of homogeneity between  $\text{CoSe}_{1.03}$  and  $\text{CoSe}_{1.37}$  in samples quenched from  $600^\circ \text{C}$ . In the range up to  $\text{CoSe}_{1.18}$  the structure is hexagonal and of NiAs-like type, but from  $\text{CoSe}_{1.20}$  on the structure is monoclinic. The lattice constants vary continuously between these limits:

$$\begin{array}{ll} \text{CoSe} & a = 3.6294 \text{ \AA}, \quad c = 5.3006 \text{ \AA} \\ \text{CoSe}_{1.40} & a = 6.1372 \text{ \AA}, \quad c = 5.1976 \text{ \AA} \\ & b = 3.5673 \text{ \AA} \quad \beta = 91.22^\circ \end{array}$$

Density determinations show that the solid solution within the  $\gamma$ -phase takes place by subtraction of cobalt atoms as the selenium content increases from CoSe on.

At  $400^\circ \text{C}$  the  $\gamma$ -phase is split into two phases,  $\gamma_1$  with composition around  $\text{CoSe}_{1.03}$  and NiAs-like structure and  $\gamma_2$  with composition in the range  $\text{CoSe}_{1.20}$  to  $\text{CoSe}_{1.33}$  and monoclinic structure.

The  $\delta$ -phase has a composition close to  $\text{CoSe}_2$ . It is confirmed that the structure is of the pyrite type with lattice constant varying from  $a = 5.8611 \text{ \AA}$  for  $\text{CoSe}_{1.60}$  to  $a = 5.8588 \text{ \AA}$  for  $\text{CoSe}_2$ . A redetermination of the interatomic distances led to a selenium-selenium distance of  $2.43 \text{ \AA}$ , which is shorter than hitherto supposed.

Magnetic measurements have been carried out by the Gouy method in the temperature range  $-183^\circ$  to  $+450^\circ \text{C}$  for samples in the range CoSe to  $\text{CoSe}_2$ . Except for a slight ferromagnetism in the CoSe range, the susceptibilities are rather low and do not follow Curie's law. Magnetic moments calculated by the Curie-Weiss law are  $3.2 \text{ B.M.}$  for  $\text{CoSe}_{1.30}$  and  $2.56 \text{ B.M.}$  for  $\text{CoSe}_2$ , while the effective magnetic moments at  $450^\circ \text{C}$  are  $1.7 \text{ B.M.}$  and  $2.0 \text{ B.M.}$ , respectively.

A compound of cobalt and selenium was obtained for the first time by Berzelius<sup>1</sup> by heating a mixture of the elements. Later on, CoSe was prepared by Little<sup>2</sup> and Fabre<sup>3</sup>, who let selenium vapor react with cobalt in an atmosphere of hydrogen.

Fonzes-Diacon <sup>4</sup> prepared four more cobalt selenides. The  $\text{Co}_2\text{Se}_3$  and  $\text{CoSe}_2$  were formed by the action of hydrogen selenide on anhydrous cobaltous chloride, at and below dark red heat, respectively. If the hydrogen selenide was diluted with nitrogen and hydrogen chloride,  $\text{Co}_3\text{Se}_4$  was obtained at dark red heat. In addition,  $\text{Co}_2\text{Se}$  was obtained as a silver-white substance if any of the other cobalt selenides were heated in hydrogen at bright red heat.

The existence of a cobalt selenide  $3\text{CoSe}\cdot\text{Co}_2\text{Se}_3$ , or  $\text{Co}_5\text{Se}_6$ , was claimed by Meyer and Bratke <sup>5</sup>. They heated a mixture of cobalt and selenium with potassium carbonate at  $1\ 250^\circ\text{C}$  and got a product containing 61.7 % Co and 38.0 % Se.

The compound  $\text{CoSe}$  has also been obtained by precipitation from an aqueous cobaltous salt solution by Reeb <sup>6</sup> and from an alcoholic solution by Moser and Atynski <sup>7</sup>, who found the atomic ratio  $\text{Co}:\text{Se} = 1:1.032$ .

Of the six cobalt selenides ( $\text{Co}_2\text{Se}$ ,  $\text{CoSe}$ ,  $\text{Co}_5\text{Se}_6$ ,  $\text{Co}_3\text{Se}_4$ ,  $\text{Co}_2\text{Se}_3$  and  $\text{CoSe}_2$ ) described so far, only two have been verified by X-ray investigations. Goldschmidt <sup>8</sup> prepared  $\text{CoSe}$  by heating a mixture of the elements in hydrogen. The reaction product was examined with X-rays by Oftedal <sup>9</sup> who found that it had a structure of the *B8*-(NiAs-) type. The same conclusion regarding the structure of  $\text{CoSe}$  was reached by de Jong and Willems <sup>10</sup>. The lattice constants reported by Oftedal and de Jong and Willems are in good agreement.

Subsequently, de Jong and Willems <sup>11</sup> succeeded in preparing  $\text{CoSe}_2$  by heating a mixture of  $\text{CoSe}$  and Se for two days at about  $230^\circ\text{C}$ . X-ray studies of the heterogeneous product showed the presence of a phase with cubic structure of the *C2*-(pyrite-) type. The lattice constant of  $\text{CoSe}_2$  has been redetermined by Tengnér <sup>12</sup> and by Lewis and Elliott <sup>13</sup>. The latter authors also studied the interatomic distances in  $\text{CoSe}_2$ .

Cobalt monoselenide precipitates were studied by electron diffraction by Baroni <sup>14</sup> who recognized three different modifications. The amorphous  $\alpha$ - $\text{CoSe}$  was obtained by the action of ammonium selenide on a cobaltous salt solution. The  $\beta$ - $\text{CoSe}$  with *B8*-type structure was obtained in the same way from a solution containing cobaltous acetate and acetic acid. The  $\gamma$ - $\text{CoSe}$ , with a structure of the *B13*-(millerite-) type, was precipitated with hydrogen selenide from a cobaltous sulfate-sulfuric acid solution. The  $\gamma$ - $\text{CoSe}$  was found to change very rapidly into  $\beta$ - $\text{CoSe}$ .

The present study was undertaken as part of a series of investigations on the binary compounds of the iron group metals with sulfur, selenium and tellurium. It seemed especially interesting to determine the range of homogeneity of the  $\text{CoSe}$  phase, since a rather broad range might be expected, in analogy with the findings of Hägg and Kindström <sup>15</sup> for the  $\text{FeSe}$  phase. Magnetic measurements were also carried out to gain further insight in the interesting, but complicated magnetic behavior of these compounds.

## EXPERIMENTAL

Metallic cobalt was prepared by igniting "Cobaltum carbonicum puriss" from Th. Schuchardt to oxide at  $1\ 050^\circ\text{C}$  and then reducing the oxide by means of purified hydrogen gas at  $1\ 000^\circ\text{C}$ . A spectrographic search for impurities revealed only the presence of nickel in an amount of less than 0.01 %. The analysis was kindly carried out by sive.

ing. S. Rutlin, Statens Råstofflaboratorium, Oslo. Some cobalt prepared from "Baker's Analyzed" Cobaltous Nitrate was also used.

Highly refined selenium was placed at our disposal by Bolidens Gruvaktiebolag, Sweden. It carried the following analysis: copper 0.0002 %, iron 0.0007 %, tellurium 0.003 %, sulfur 0.01 %, non volatile matter 0.003 %.

The alloys were synthesized by heating appropriate amounts of the elements in evacuated, sealed silica tubes at temperatures ranging between 500° and 1 070° C. Considerable devitrification of the silica tubes took place during a 24-hour heating period at high temperatures. Most of the alloys were therefore prepared at 600° C. The desired composition was in many cases obtained by adding selenium to  $\text{Co}_2\text{Se}$  or  $\text{CoSe}$  samples. The composition of the samples ranged between  $\text{Co}_2\text{Se}$  and  $\text{CoSe}_2$  (33.33 and 66.67 atomic per cent selenium).

The light grey, sintered products were finely ground in an agate mortar and homogenized. One series of samples was kept at 600° C for 7 days and then quenched in ice water. Another series was kept at 400° C for 5 months and quenched from that temperature.

Some experiments were carried out to study the rate of formation of  $\text{CoSe}$  and  $\text{CoSe}_2$ . In one experiment, cobalt powder and selenium in atomic ratio 1:1 were heated at 350° C for 32 days. The X-ray photograph of the product showed the presence of large amounts of  $\text{CoSe}_2$ , indicating that equilibrium had not been attained. In another experiment, a mixture of  $\text{CoSe}$  and  $\text{Se}$  corresponding to the formula  $\text{CoSe}_2$  was ground in the mortar and then heated at 225° C for 21 days. Only small amounts of  $\text{CoSe}_2$  resulted from this treatment, and the heating was therefore continued at 300° C for 20 days. After this treatment more of the selenium had reacted with the  $\text{CoSe}$  phase to form  $\text{CoSe}_2$ , but unreacted selenium was still observed.

X-ray photographs were taken in 11.48 cm diameter powder cameras with asymmetric film mounting. Iron and copper radiation were used. The lattice constants are expressed in Ångström units on the basis of  $\lambda\text{FeK}\alpha_1 = 1.93597 \text{ \AA}$  and  $\lambda\text{CuK}\alpha_1 = 1.54051 \text{ \AA}$ . Lattice constant values from previous investigations, actually given in  $k\text{X}$ , are here expressed in Å by multiplication by the factor 1.00202. The mean error in the lattice constants is judged to be  $\pm 0.01 \%$  for the cubic structures,  $\pm 0.02 \%$  for the hexagonal structure and  $\pm 0.03 \%$  for the monoclinic structure.

## RESULTS AND DISCUSSION

As a result of the phase analysis, the existence of three intermediate phases,  $\beta$ ,  $\gamma$  and  $\delta$ , was established.

### 1. The $\beta$ -phase, $\text{Co}_2\text{Se}_3$ (?)

This phase was only present in the samples annealed at 400° C and has not been found by earlier investigators. It has a cubic structure with lattice constant:

$$a = 10.431 \text{ \AA}.$$

No significant variation in the lattice constant with composition was observed and the homogeneity range of the  $\beta$ -phase is consequently supposed to be very narrow. As far as it could be judged from the powder photographs, the structure of the  $\beta$ -phase is face-centered and related to that found by Lindqvist, Lundqvist and Westgren<sup>16</sup> for  $\text{Co}_2\text{S}_3$  and pentlandite  $(\text{Fe,Ni})_2\text{S}_3$ .

The composition of the  $\beta$ -phase was found to be in the range of  $\text{CoSe}_{0.80}$  or slightly below the  $\text{Me}_2\text{X}_3$  composition. No indications of the phase  $\text{Co}_2\text{Se}$  claimed by Fonzes-Diacon<sup>4</sup> were found. A density determination carried out on  $\text{CoSe}_{0.80}$  gave the result  $d = 7.05 \text{ g cm}^{-3}$ , but the sample contained some cobalt and  $\gamma$ -phase as well. The density of the  $\beta$ -phase is therefore lower than

7.05 g cm<sup>-3</sup> since the other phases present have higher densities. Assuming the formula Co<sub>9</sub>Se<sub>8</sub> for the β-phase and four formula units in the unit cell the calculated density is 6.799 g cm<sup>-3</sup>.

According to Lindqvist, Lundqvist and Westgren<sup>16</sup>, the atomic arrangement in Co<sub>9</sub>Se<sub>8</sub> is as follows, in terms of the space group *Fm3m* (*O<sub>h</sub><sup>5</sup>*):

32 Co in (f)  $x, x, x$ ; etc.                      24 S in (e)  $y, 0, 0$ ; etc.  
 4 Co in (b)  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ; etc.                8 S in (c)  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ ; etc.  
 with  $x = \frac{1}{8}$  and  $y = \frac{1}{4}$ .

A calculation of the intensities of Co<sub>9</sub>Se<sub>8</sub> was undertaken on the basis of these parameters, but the agreement between observed and calculated intensities was not very good. By increasing the  $y$  value to  $y = 0.265$  a much better agreement was obtained. The relative intensities calculated using this value are listed in Table 1 together with those observed from photometer recordings on basis of  $I_{\text{obs}}(440) = I_{\text{calc}}(440) = 100$ .

The structure consists of a slightly distorted cubic close-packing of selenium atoms with cobalt atoms in the interstices. Eight ninths of the cobalt atoms are surrounded tetrahedrally by selenium, the rest are surrounded

Table 1. Observed and calculated intensities for the β-phase, assuming isomorphism with Co<sub>9</sub>S<sub>8</sub>, FeKα radiation.

sin <sup>2</sup> θ × 10 <sup>4</sup>	hkl	I <sub>obs</sub>	I <sub>calc</sub>	sin <sup>2</sup> θ × 10 <sup>4</sup>	hkl	I <sub>obs</sub>	I <sub>calc</sub>
261	111	8	6.6	5 769	733	6	5.1
335	200	5	2.9	—	{820}	—	{0.4}
692	220	4	2.5	—	{644}	—	{0.2}
940	311	53	41	—	{822}	—	{0.1}
1 039	222	85	78	—	{660}	—	{0.3}
1 382	400	8	4.4	6 458	{751}	14	{5.1}
1 641	331	18	13	—	{555}	—	{3.4}
1 727	420	2	0.9	6 545	662	25	22
2 075	422	2	0.9	6 889	840	5	1.6
2 332	{511}	36	{23}	7 149	{911}	5	{0.1}
—	{333}	—	{0.1}	—	{753}	—	{3.5}
2 761	440	100	100	—	842	—	0.1
3 014	531	1	0.6	7 579	664	1	0.6
3 115	{600}	1	{0.2}	7 839	931	15	12
—	{442}	—	{0.2}	8 267	844	76	83
3 438	620	1	0.9	—	{933}	—	{0.5}
3 706	533	5	4.2	8 526	{771}	8	{5.9}
3 786	622	43	26	—	{755}	—	{0.3}
4 141	444	2	0.9	—	{10,0,0}	—	{0.3}
4 387	{711}	6	{2.2}	—	860	—	{0.2}
—	{551}	—	{0.2}	8 954	{10,2,0}	3	{1.3}
4 477	640	1	0.4	—	862	—	{0.5}
4 826	642	1	0.8	9 212	{951}	37	{38}
—	{731}	—	—	—	{773}	—	{0.0}
5 070	{553}	13	—	9 300	{10,2,2}	37	{28}
5 510	800	24	18	—	666	—	{9.4}

octahedrally. The octahedral Co-Se distances are 2.46 Å while the tetrahedral Co-Se distances range between 2.26 and 2.35 Å.

## 2. The $\gamma$ -phase, CoSe — Co<sub>3</sub>Se<sub>4</sub>

The cobalt-rich limit of the homogeneity range of the  $\gamma$ -phase is markedly different in the 600° and the 400° C series. X-ray powder photographs of these series show that CoSe is a two-phase preparation at 400° C, containing about equal amounts of the  $\beta$ - and  $\gamma$ -phases, while it only contains the  $\gamma$ -phase at 600°. The structure of the  $\gamma$ -phase is of the B8-(NiAs-) type and the lattice constants vary considerably with temperature and composition.

The results of the calculations for the 600° C samples are given in Fig. 1 and in Table 2. It appears from the figure that even at this temperature the  $\gamma$ -phase does not have the exact composition CoSe when it exists in equilibrium with the  $\alpha$ -phase (cobalt). The cobalt-rich composition limit for the  $\gamma$ -phase is probably close to CoSe<sub>1.02</sub> under the given conditions.

Table 2. Lattice constants of the  $\gamma$ -phase, 600° C series.

Composition	$a$ , ( $b\sqrt{3}$ ) in Å	$b$ in Å	$c$ in Å	$\beta$
CoSe <sub>0.80</sub>	(6.2841)	3.6281	5.3008	(90°)
CoSe <sub>1.00</sub>	(6.2864)	3.6294	5.3006	(90°)
CoSe <sub>1.05</sub>	(6.2745)	3.6226	5.2954	(90°)
CoSe <sub>1.10</sub>	(6.2545)	3.6111	5.2850	(90°)
CoSe <sub>1.15</sub>	(6.2297)	3.5967	5.2713	(90°)
CoSe <sub>1.20</sub>	6.2086	3.5846	5.2661	90.5°
CoSe <sub>1.25</sub>	6.1863	3.5805	5.2503	90.90°
CoSe <sub>1.30</sub>	6.1475	3.5766	5.2161	91.45°
CoSe <sub>1.35</sub>	6.1373	3.5695	5.2056	91.47°
CoSe <sub>1.40</sub>	6.1372	3.5673	5.1976	91.22°

The lattice constants found by Oftedal<sup>9</sup> for CoSe\* ( $a = 3.621 \pm 0.003$  Å,  $c = 5.289 \pm 0.004$  Å) and those found by de Jong and Willems<sup>10</sup> ( $a = 3.61$  Å,  $c = 5.28$  Å) agree fairly well with those reported here. The values determined by Baroni<sup>14</sup> ( $a = 3.51$  Å,  $c = 5.12$  Å) by means of electron diffraction are considerably lower.

With increasing selenium content the lattice constants of the  $\gamma$ -phase are found to decrease almost linearly to the composition CoSe<sub>1.15</sub>. At the composition CoSe<sub>1.20</sub> (54.55 atomic per cent Se) a lowering of the symmetry from hexagonal to monoclinic is observed. This change in symmetry is accompanied by a sharp bend in the curve for the  $b$ -axis. The angular deformation increases from  $\beta = 90.5^\circ$  at CoSe<sub>1.20</sub> to  $\beta = 91.47^\circ$  at CoSe<sub>1.35</sub>, and then decreases slightly until the composition limit of the  $\gamma$ -phase is reached. In the monoclinic range the  $c$ -axis decreases more rapidly with composition than it does in the hexago-

\* The preliminary values listed by Goldschmidt<sup>8</sup> ( $a = 3.594 \pm 0.003$  Å,  $c = 5.277 \pm 0.005$  Å) are somewhat lower than those later reported by Oftedal<sup>9</sup>.

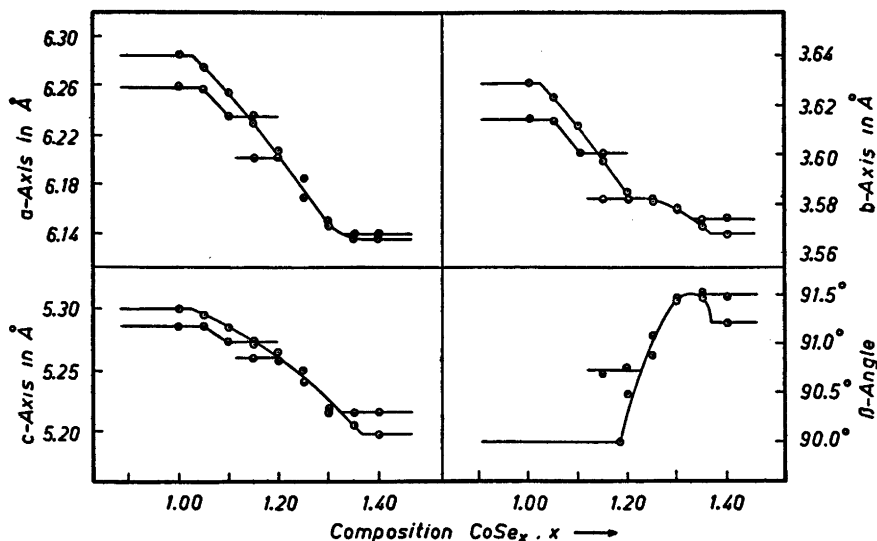


Fig. 1. Lattice constants of the  $\gamma$ -phase,  $\text{CoSe-Co}_3\text{Se}_4$ , after quenching from  $600^\circ\text{C}$   $\odot$  and  $400^\circ\text{C}$   $\bullet$ .

nal range, while the opposite is true for the  $b$ -axis. The decrease in the  $a$ -axis is almost linear within the whole homogeneity range.

As a result of the lattice constant determinations, the selenium-rich limit for the  $\gamma$ -phase in the  $600^\circ\text{C}$  series is found close to the composition  $\text{CoSe}_{1.37}$  (57.81 atomic per cent Se). On the X-ray photographs of  $\text{CoSe}_{1.40}$  lines from a new phase, the  $\delta$ -phase ( $\text{CoSe}_2$ ), are found. The compounds  $\text{Co}_3\text{Se}_4$  found by Fonzes-Diacon<sup>4</sup> and  $\text{Co}_5\text{Se}_6$  by Meyer and Bratke<sup>5</sup> both fall within the homogeneity range of the  $\gamma$  phase and need not be considered as separate phases. Neither the existence of the compound  $\text{Co}_2\text{Se}_3$ , claimed by Fonzes-Diacon<sup>4</sup>, nor the polymorphism of  $\text{CoSe}$  observed by Baroni<sup>14</sup> has been confirmed by the present authors.

The variation in density with composition for the  $\gamma$ -phase has been studied in some detail. The densities were determined at  $25^\circ\text{C}$  by the vacuum pycnometric method with kerosene as displacement liquid. There is an appreciable

Table 3. Observed and calculated densities in  $\text{g cm}^{-3}$  of the  $\gamma$ -phase.

Sample	$d_{\text{obs}}$	$d_{\text{calc}}$	Sample	$d_{\text{obs}}$	$d_{\text{calc}}$
$\text{CoSe}_{1.00}$	7.377	7.572	$\text{CoSe}_{1.20}$	7.232	7.257
$\text{CoSe}_{1.05}$	7.377	7.453	$\text{CoSe}_{1.25}$	7.196	7.200
$\text{CoSe}_{1.10}$	7.304	7.375	$\text{CoSe}_{1.30}$	7.135	7.183
$\text{CoSe}_{1.15}$	7.244	7.323	$\text{CoSe}_{1.35}$	7.071	7.142
			$\text{CoSe}_{1.40}$	7.072	—

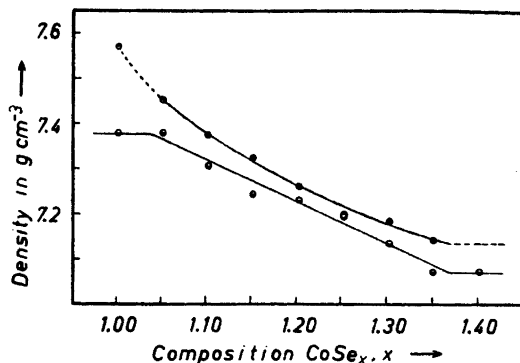


Fig. 2. Observed density  $\bullet$  and calculated density  $\circ$  of the  $\gamma$ -phase.

decrease in density with increasing selenium content, indicating that the solid solution is of the subtractive type. The observed density values and those calculated on the basis of subtraction of cobalt atoms from the CoSe structure when the selenium content increases are listed in Table 3.

From Fig. 2 it can be seen that the agreement between observed and calculated densities is very satisfactory in the region  $\text{CoSe}_{1.05}$  to  $\text{CoSe}_{1.35}$  and the hypothesis of a subtractive solid solution is therefore fully confirmed in this region. A discrepancy is, however, present for  $\text{CoSe}_{1.00}$ , but there is an obvious reason for this and that is the instability of  $\text{CoSe}_{1.00}$  with regard to the  $\beta$ -phase and the selenium richer  $\gamma$ -phase. Since both these phases have lower densities than stoichiometric CoSe, a partial decomposition of CoSe on quenching will lead to lower density values.\* Lines from the  $\beta$ -phase are not observed on the X-ray photographs of the quenched CoSe, but this may be due to the fine state of division of the  $\beta$ -phase in its early stage of formation.

Table 4. Lattice constants of the  $\gamma_1$ - and  $\gamma_2$ -phases, 400° C series.

Composition	$a$ , ( $b\sqrt{3}$ ) in Å	$b$ in Å	$c$ in Å	$\beta$
$\text{CoSe}_{1.00}$	(6.2597)	3.6141	5.2863	(90°)
$\text{CoSe}_{1.05}$	(6.2573)	3.6128	5.2861	(90°)
$\text{CoSe}_{1.10}$	(6.2366)	3.6006	5.2730	(90°)
$\text{CoSe}_{1.15}$	{ (6.237)	3.600	5.273	(90°)
	{ 6.200	3.580	5.256	90.7°
$\text{CoSe}_{1.20}$	6.2024	3.5813	$2 \times 5.2575$	90.76°
$\text{CoSe}_{1.25}$	6.1692	3.5809	$2 \times 5.2400$	91.09°
$\text{CoSe}_{1.30}$	6.1499	3.5773	$2 \times 5.2178$	91.47°
$\text{CoSe}_{1.35}$	6.1393	3.5732	$2 \times 5.2149$	91.56°
$\text{CoSe}_{1.40}$	6.1390	3.5736	$2 \times 5.2148$	91.48°

\* Experiments carried out by cand.real. J. Vihovde in this institute gave  $d = 7.333 \text{ g cm}^{-3}$  for a CoSe sample that had been quenched from 800° C and  $d = 7.165 \text{ g cm}^{-3}$  as mean value for four samples that had been cooled in the furnace.

The results of the lattice constant determinations for the samples annealed at 400° C are found in Table 4 and Fig. 1. In these samples the  $\beta$ - and  $\gamma$ -phases are coexistent up to the composition  $\text{CoSe}_{1.05}$ . At the composition  $\text{CoSe}_{1.10}$  only the  $\gamma$ -phase is observed on the X-ray photographs. When the composition is increased to  $\text{CoSe}_{1.15}$  two phases are present, while the preparations  $\text{CoSe}_{1.20}$  to  $\text{CoSe}_{1.35}$  contain only one phase, with lattice constants which seem to vary continuously with the composition.

The  $\gamma$ -phase, which exists in the range  $\text{CoSe}_{1.02}$  to  $\text{CoSe}_{1.37}$  in the 600° C series, is thus split into two phases,  $\gamma_1$  and  $\gamma_2$  at 400° C. The  $\gamma_1$ -phase is hexagonal and has a range of homogeneity around  $\text{CoSe}_{1.08}$ , while the monoclinic  $\gamma_2$ -phase has a range of homogeneity from  $\text{CoSe}_{1.20}$  to  $\text{CoSe}_{1.33}$ . Weak additional lines in the monoclinic range require a doubling of the  $c$ -axis for their explanation, and this is indicated in the table.

According to the present study, the homogeneity range of the  $\gamma$ -phase is rather susceptible to temperature changes. This reflects important variations in the entropy of the cobalt selenides with temperature and composition. It is also seen how the phases tend to accept more definite compositions as the temperature is lowered. Analogous observations have already been made by Grønvold and Haraldsen<sup>17</sup> for the  $B8$ -like phase in the system iron-sulfur and iron-selenium.

In the hexagonal  $\gamma$ -phase, each cobalt atom is surrounded by six selenium atoms at the corners of a right trigonal prism. The cobalt-selenium distances are 2.48 Å for  $\text{CoSe}$  and 2.46 Å for  $\text{CoSe}_{1.15}$ . These distances are much shorter than the sum of the ionic radii, but they compare very favorably with the sum of the metallic radii as given by Pauling<sup>18</sup>. If the radii of cobalt and selenium are corrected for eight and six coordination, respectively, while the normal valencies are maintained, the radius sum is 1.20 Å + 1.31 Å = 2.51 Å. This is only 0.03 Å higher than experimentally found for  $\text{CoSe}$ .

Each cobalt is further surrounded by two cobalt atoms at the distance  $c/2$ . This distance is rather short in the  $\gamma$ -phase, 2.65 Å for  $\text{CoSe}$  and 2.64 Å for  $\text{CoSe}_{1.15}$ , so that exchange interactions between the paramagnetic ions (leading to antiferromagnetism and ferromagnetism) might be expected.

The selenium atoms form an approximately hexagonal close-packing, the shortest distance (3.38 Å for  $\text{CoSe}$ ) between atoms in adjacent layers being smaller than between atoms in the layer (3.63 Å).

### 3. The $\delta$ -phase, $\text{CoSe}_2$

At the composition  $\text{CoSe}_{1.90}$ , the X-ray photographs show the  $\delta$ -phase as major constituent, but a few lines from the  $\gamma$ -phase are still visible. At the composition  $\text{CoSe}_{2.00}$  all lines from the  $\gamma$ -phase have disappeared and a slight shift in the positions of the back reflection lines of the  $\delta$ -phase is noted. Thus, the cobalt-rich limit of the homogeneity range of the  $\delta$ -phase lies slightly below the composition  $\text{CoSe}_2$ .

In agreement with earlier observations, the structure of  $\text{CoSe}_2$  is cubic of the  $C2$ - (pyrite-) type. The lattice constants are listed in Table 5. Tengnér's<sup>12</sup> result and that of Lewis and Elliott<sup>13</sup> are in good accord with ours for  $\text{CoSe}_{2.00}$ , while that of de Jong and Willems<sup>11</sup> is closer to our value for  $\text{CoSe}_{1.90}$ . The



Table 5. Lattice constants of the  $\delta$ -phase,  $\text{CoSe}_2$ .

Composition	$a$ in Å	Authors
$\text{CoSe}_{1.00}$	5.8611	Present
$\text{CoSe}_{2.00}$	5.8588	Present
Unknown	$5.866 \pm 0.003$	de Jong and Willems <sup>11</sup>
$\text{CoSe}_2$	5.857	Tengnér <sup>12</sup>
$\text{CoSe}_2$	$5.857 \pm 0.005$	Lewis and Elliott <sup>13</sup>

observed density of  $\text{CoSe}_{2.00}$  is  $7.087 \text{ g cm}^{-3}$  at  $25^\circ \text{C}$ , which compares favorably with the X-ray density  $7.160 \text{ g cm}^{-3}$ .

A redetermination of the parameter  $x$  was undertaken in order to establish the interatomic distances more accurately. Small changes in this parameter have a marked influence on the selenium-selenium distance, but rather little on the cobalt-selenium distance. The best agreement between observed and calculated intensities was obtained with  $x = 0.380$ . In Table 6 are listed

Table 6. Observed and calculated intensities for  $\text{CoSe}_2$  with  $x = 0.380$ , Cu radiation.

$\sin^2\Theta \times 10^4$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$	$\sin^2\Theta \times 10^4$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$
—	111	—	0.0	6 055	531	1	0.0
692	200	18	30	6 229	{ 600 }	5	{ 0.2 }
868	210	55	100		{ 442 }		{ 4.0 }
1 042	211	54	86	6 405	610	7	4.8
1 386	220	12	20	6 572	{ 611 }	20	{ 5.2 }
1 556	221	1	0.3		{ 532 }		{ 11 }
1 908	311	48	66	6 921	620	2	2.8
2 082	222	4	5.2		{ 621 }		{ 0.4 }
2 243	320	26	28	—	{ 540 }	—	{ 0.1 }
2 420	321	40	40		{ 443 }		{ 0.2 }
2 769	400	8	5.6	—	541	—	0.2
—	{ 410 }	—	{ 0.2 }	7 439	533	14	11
—	{ 322 }	—	{ 0.1 }	7 613	622	3	3.2
—	411	—	0.2	7 777	{ 630 }	19	{ 6.8 }
—	331	—	0.4		{ 542 }		{ 7.9 }
3 457	420	5	5.9	7 956	631	16	13
3 628	421	24	18	8 301	444	5	2.6
3 797	332	11	8.6	—	632	—	0.7
4 147	422	5	4.5	—	543	—	0.2
—	430	—	0.1		{ 711 }		{ 0.2 }
—	431	—	0.3	8 817	{ 551 }	2	{ 0.4 }
4 653	{ 511 }	—	{ 18 }	8 988	640	9	11
	{ 333 }	24	{ 3.6 }	9 160	{ 720 }	30	{ 14 }
5 005	{ 520 }	—	{ 4.4 }		{ 641 }		{ 17 }
	{ 432 }	24	{ 15 }		{ 721 }		{ 23 }
5 179	521	17	12	9 334	{ 633 }	40	{ 11 }
5 538	440	34	21		{ 552 }		{ 10 }
—	{ 522 }	—	{ 0.0 }	9 677	642	12	18
—	{ 441 }	—	{ 0.2 }	—	{ 722 }	—	{ 0.3 }
—	433	—	0.1	—	{ 544 }	—	{ 0.6 }

the results of the intensity measurements and calculations, together with the observed  $\sin^2\theta$  values of the  $\alpha_1$  reflections. The observed intensities are from photometric recordings of the film and the observed and calculated intensity of the 321 reflection have been set equal.

In the  $\text{CoSe}_2$  structure, each cobalt atom is surrounded octahedrally by six selenium atoms at the distance 2.42 Å. Each selenium atom is surrounded tetrahedrally by three cobalt atoms at the same distance and by one selenium atom at the distance 2.43 Å. These distances are explained satisfactorily by means of Pauling's<sup>18</sup> metallic radii. With the coordination number six for cobalt and four for selenium the radius sum is calculated to be  $1.16 \text{ \AA} + 1.26 \text{ \AA} = 2.42 \text{ \AA}$ , in perfect agreement with the observed value. The calculated selenium radius 1.26 Å is, however, somewhat high in comparison with the observed value 1.22 Å.

According to Pauling and Huggins<sup>19</sup>, the tetrahedral covalent radius of selenium is 1.14 Å, and a selenium-selenium distance of 2.28 Å is therefore expected if the chemical bonds in the  $\text{CoSe}_2$  structure were as proposed by these authors for pyrite. Their suggestion that the distance  $\text{Se-Se} = 2.54 \text{ \AA}$  found by de Jong and Willems<sup>11</sup> was too large has been confirmed by Lewis and Elliott<sup>13</sup>, who found  $\text{Se-Se} = 2.49 \pm 0.04 \text{ \AA}$ . Neither that value nor the one found by us (2.43 Å) is, however, equal to the tetrahedral covalent selenium distance (2.28 Å).

#### 4. Magnetic properties of the cobalt selenides

Samples in the range  $\text{CoSe}$  to  $\text{CoSe}_2$  were studied magnetically by the Gouy method at temperatures ranging from  $-183^\circ$  to  $+450^\circ\text{C}$ . The results of the measurements are found in Table 7. Field strength dependence of the susceptibility was noted in the range  $\text{CoSe}$  to  $\text{CoSe}_{1.20}$ . For  $\text{CoSe}$  the effect was rather large, but this is not surprising since the X-ray results indicated that  $\text{CoSe}$  was a two phase preparation in the  $600^\circ\text{C}$  series ( $\text{Co} + \text{CoSe}_{1.02}$ ). The ferromagnetism in  $\text{CoSe}$  disappeared at about  $770^\circ\text{C}$ , or far below the ferromagnetic Curie temperature of cobalt, which is  $1121^\circ\text{C}$  according to Myers and Sucksmith<sup>20</sup>. If, therefore, the ferromagnetism is due to cobalt, its disappearance might be interpreted to be the result of increased solubility of cobalt in the  $\gamma$ -phase at higher temperatures. The cobalt-rich limit for the  $\gamma$ -phase should thus be  $\text{CoSe}_{1.00}$  at about  $770^\circ\text{C}$ .

While the presence of metallic cobalt is probably the cause of the high magnetism of  $\text{CoSe}$ , the weak field strength dependence of the selenium-richer samples seems to be a property of the hexagonal  $\gamma$ -phase. Such a field strength dependent susceptibility has often been observed (see for example the results found by Haraldsen, Rosenqvist and Grønvold<sup>21</sup> for the chromium antimonides), and it may be due to what Néel<sup>22</sup> terms ferrimagnetism.

One can expect ferrimagnetism for substances where antiferromagnetic interactions are present and the sublattices are unequally populated with magnetic ions (*e.g.* because of non-stoichiometric composition of the phase in question). An unbalanced antiferromagnetism may very well be present in structures of *B8*-like type where metal ions are subtracted with increasing metalloid content, and this is a possible explanation for the field strength dependent susceptibility observed for samples in the region  $\text{CoSe}_{1.05}$  to  $\text{CoSe}_{1.20}$ .

Table 7. Magnetic susceptibility of the cobalt selenides,  $\chi_g \times 10^6$ .

Composition	Temperature in °C					
	- 183	-78	+20	+150	+ 300	+450
CoSe <sub>1.00</sub> *	810	810	812	932	1 049	1 021
CoSe <sub>1.05</sub> *	66	52	52	56	56	56
CoSe <sub>1.10</sub> *	28	29	30	33	35	34
CoSe <sub>1.15</sub> *	9.7	9.3	9.3	9.4	9.4	9.4
CoSe <sub>1.20</sub> *	5.6	5.5	5.2	5.6	5.5	5.5
CoSe <sub>1.25</sub>	3.88	3.53	3.33	3.10	2.99	2.97
CoSe <sub>1.30</sub>	3.96	3.86	3.54	3.25	3.05	2.87
CoSe <sub>1.35</sub>	4.11	3.59	3.21	2.82	2.66	2.50
CoSe <sub>1.40</sub>	4.06	3.60	3.18	2.72	2.51	2.46
CoSe <sub>1.50</sub>	4.72	4.04	3.55	3.08	2.78	2.54
CoSe <sub>1.70</sub>	5.93	4.63	4.00	3.38	2.85	2.60
CoSe <sub>1.80</sub>	6.21	4.95	4.21	3.62	3.15	2.69
CoSe <sub>1.90</sub>	6.83	5.36	4.66	3.98	3.23	2.73
CoSe <sub>2.00</sub>	6.73	5.42	4.60	4.01	3.33	2.68

\* These samples are ferromagnetic and the values refer to  $H_{\max} = 4\,117$  Ørsted.

The samples richer in selenium than CoSe<sub>1.20</sub> are completely paramagnetic at all temperatures used in this work. In Fig. 3 are found the molar susceptibilities of the paramagnetic samples as functions of the composition. The susceptibility varies in a non-linear way within the monoclinic range of the  $\gamma$ -phase and the selenium-rich composition limit of the  $\gamma$ -phase is seen to be close to CoSe<sub>1.37</sub> in perfect agreement with the X-ray result. The molar susceptibilities have been corrected for the diamagnetism of the cobalt and selenium ions with the values  $\chi_{\text{Co}^{++}} = -18.5 \times 10^{-6}$  per mole according to Klemm<sup>23</sup> and  $\chi_{\text{Se}^{--}} = -47.58 \times 10^{-6}$  per mole according to Angus<sup>24</sup>.

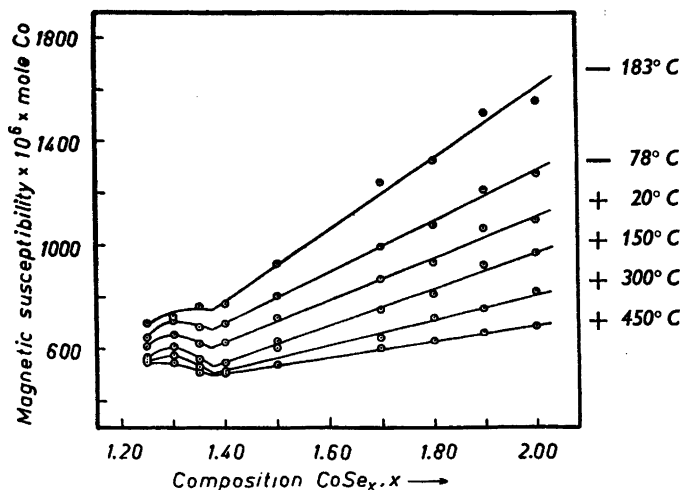


Fig. 3. Paramagnetic molar susceptibility of cobalt selenides in the range CoSe<sub>1.25</sub> to CoSe<sub>2.00</sub> after correction for induced diamagnetism.

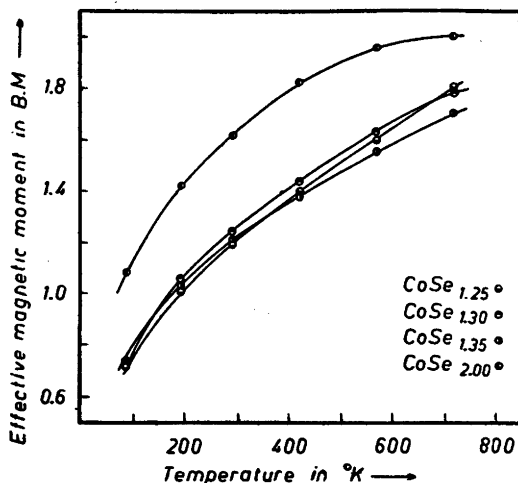


Fig. 4. Effective magnetic moments of the  $\gamma$ - and  $\delta$ -phases.

A strictly linear relationship between  $1/\chi_{\text{mole}}$  and  $T$  does not exist for the monoclinic  $\gamma$ -phase, but the approximate linearity can be described with a Weiss constant  $\Delta \approx 2100^\circ\text{K}$  for  $\text{CoSe}_{1.25}$ , which leads to a magnetic moment  $\mu = 3.4$  B.M. The corresponding values for  $\text{CoSe}_{1.30}$  are:  $\Delta \approx 1700^\circ\text{K}$  and  $\mu = 3.2$  B.M. and for  $\text{CoSe}_{1.35}$ :  $\Delta \approx 1100^\circ\text{K}$  and  $\mu = 2.7$  B.M. The physical significance of magnetic moments obtained by the Curie-Weiss law ( $\mu = 2.828 \sqrt{\chi_{\text{mole}}(T + \Delta)}$  Bohr magnetons) with large  $\Delta$  values is rather dubious, especially in cases like the present one, where the law fails to be valid in the high temperature region.

In such cases it is presumably more satisfactory to calculate the effective magnetic moment ( $\mu_{\text{eff}} = 2.828 \sqrt{\chi_{\text{mole}} T}$  B.M.) and study its variation with temperature. This has been done for the samples  $\text{CoSe}_{1.25}$ ,  $\text{CoSe}_{1.30}$  and  $\text{CoSe}_{1.35}$  and the results are given in Fig. 4. The effective magnetic moment shows the same temperature dependence for all three samples and raises from about 0.7 B.M. at  $90^\circ\text{K}$  to 1.7 B.M. at  $723^\circ\text{K}$ . The values level off to some extent above room temperature, but they do not become constant.

In magnetic respect the behavior of the  $\delta$ -phase,  $\text{CoSe}_2$ , is not much different from that of the monoclinic  $\gamma$ -phase. The magnetic susceptibility is wholly independent of the field strength and the Curie-Weiss law is fulfilled with  $\Delta = 440^\circ\text{K}$ . This gives a magnetic moment for the  $\delta$ -phase of  $\mu = 2.56$  B.M. From Fig. 4 it can be seen how the effective magnetic moment of  $\text{CoSe}_2$  varies with temperature and reaches the value 2.0 B.M. at  $723^\circ\text{K}$ .

According to the present results, the magnetic moments of the paramagnetic cobalt selenides are much lower than usually observed for ionic cobaltous compounds. In such cases a "spin only" value of 3.87 B.M. is expected, while the actual values lie in the range 4.3 to 5.6 B.M. (see Figgis and Nyholm<sup>25</sup>). Low magnetic moments (1.8 to 2.9 B.M.) are, however, observed for octahedral covalent complexes of divalent cobalt and a magnetic moment of 1.73

B.M. is expected both from the crystalline field theory according to Van Vleck<sup>26</sup> and from the valence bond theory by Pauling<sup>27</sup>. This is in reasonable agreement with the effective magnetic moment found both for the  $\gamma$ - and the  $\delta$ -phase above room temperature. Another possible way of explaining low magnetic moments is that there are interactions between the paramagnetic neighbors leading to antiferromagnetism. Such interactions are presumably more probable in the  $\gamma$ -phase where the nearest cobalt atoms are only 2.65 Å apart than in the  $\delta$ -phase where they are 4.14 Å apart.

According to the valence bond theory the magnetic moment of the  $\delta$ -phase is not expected to rise above 1.73 B.M. unless there is an orbital contribution to the magnetic moment of the unpaired electron. The magnetic moment found for CoSe<sub>2</sub> might thus be taken as an indication that orbital contributions are present and that the unpaired electron is in a 3d orbital instead of 5s as suggested by Figgis and Nyholm<sup>25</sup> for octahedral covalent compounds of divalent cobalt. The d<sup>2</sup>sp<sup>3</sup> bonds should then make use of one 3d and one 4d orbital of cobalt. A decrease in magnetic moment at low temperature is understandable in this picture as a result of increased 3d character of the d<sup>2</sup>sp<sup>3</sup> bonds and interaction between the cobalt atoms.

One of us (H.H.) wants to express his gratitude to *Norsk Hydros Fond* for financial support of this investigation. The authors are much indebted to Bolidens Gruvaktiebolag for generously supplying selenium.

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Received June 20, 1955.