The Structures of the Chromium Sulphides

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The system Cr–S has been studied at room temperature. In the range $CrS_{0.95}$–$CrS_{1.50}$—previously thought to be a berthollide range—six phases, each with a narrow homogeneity range, were established: namely, monoclinic CrS, trigonal 'Cr_7S_8', trigonal Cr_5S_6, monoclinic Cr_3S_4, trigonal Cr_2S_3 and rhombohedral Cr_2S_3. The structure of CrS is intermediate between the NiAs and PtS types. 'Cr_7S_8' probably has a partly disordered structure intermediate between the NiAs and $Cd(OH)_2$ types. The structures of the other chromium sulphides are also intermediate between those of NiAs and $Cd(OH)_2$, but the lattices are completely ordered. Cr_5S_6 is ferrimagnetic within a limited temperature range; at 5° C. the magnetic anisotropy is found to be of negative sign. The magnetic properties of structures related to the NiAs type are discussed in connection with geometrical aspects. It is suggested that in the chromium sulphides both ionic Cr–S bonds and metallic Cr–Cr bonds are present.

1. Introduction

Until not very long ago the system Cr–S was regarded as homogeneous in the range CrS–$CrS_{1.5}$. Haraldsen (1937) and Haraldsen & Mehmed (1938), who studied the system Cr–S by powder methods, divided the range CrS–$CrS_{1.5}$ into three—still broad—homogeneity

ranges. The magnetic properties of the Cr–S alloys were also investigated by Haraldsen and co-workers (Haraldsen & Neuber, 1937; Haraldsen & Mehmed, 1938); most interesting are the properties of alloys with compositions about $CrS_{1.18}$, which are ferrimagnetic in a limited temperature range. The concordance of the magnetic properties of the chromium sulphides with Haraldsen's tentative phase diagram, however, is far from perfect (compare Figs. 1(*a*) and 1(*b*)).

A recent re-investigation (Lotgering, 1956*b*) confirmed Haraldsen's magnetic measurements, indicating that the Cr–S bonds in chromium sulphides are ionic. The ionic picture is also in agreement with the electric conductivity of the alloys. Bertaut (1953), on the other hand, demonstrated that—at not too high a temperature—all ionic compounds should be ordered. This is in obvious disagreement with the berthollide conception of the Cr–S system. A re-investigation of the phase relations in this system therefore seemed worth while.

2. The system Cr–S at room temperature

The Cr–S alloys were prepared by heating weighted proportions of the elements *in vacuo* at 1000° C. for a day; after cooling they were powdered, once again heated at 1000° C. and slowly cooled to room temperature. In the case of preparations with a Cr content higher than $Cr_{0.88}S$, prolonged tempering at 300° C. was necessary to obtain reproducible results. No alloys with a sulphur content higher than $Cr_{0.67}S$ could be prepared in this way. The powdered chromium sulphides were investigated with a Philips diffractometer (Mo $K\alpha$ and Cu $K\alpha$ radiations).

At room temperature the following phases were found in the range Cr–$CrS_{1.5}$ (compare Fig. 1(*c*)):
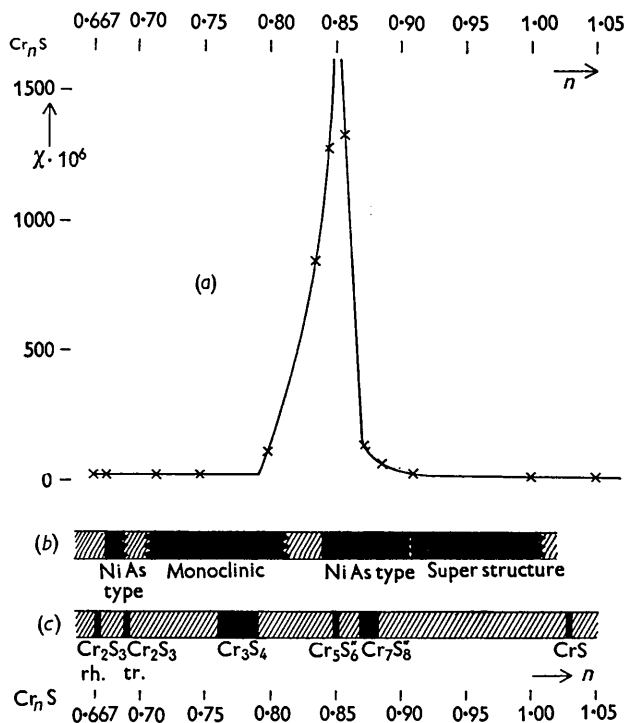
Fig. 1. (*a*) Magnetic susceptibilities (H = 2000 Oe.) of Cr_nS alloys at 293° K. (*b*) Phases in the system Cr–S at room temperature according to Haraldsen (1937). (*c*) Phases in the system Cr–S at room temperature according to this investigation.

Phase	Symmetry	Homogeneity range
α-Cr	Cubic b.c.	Very narrow
CrS	Monoclinic	Probably $\sim CrS_{0.97}$
'Cr_7S_8'	Trigonal	$Cr_{0.88}S$–$Cr_{0.87}S$
Cr_5S_6	Trigonal	$Cr_{0.85}S$
Cr_3S_4	Monoclinic	$Cr_{0.79}S$–$Cr_{0.76}S$
Cr_2S_3 tr.	Trigonal	$Cr_{0.69}S$
Cr_2S_3 rh.	Rhombohedral	$Cr_{0.67}S$

At intermediate compositions two-phase regions exist. CrS, Cr_5S_6, Cr_3S_4 and both forms of Cr_2S_3 have ordered structures, so these phases can be regarded as true compounds; for 'Cr_7S_8' a partly disordered structure is proposed. A survey of the alloys investigated is given in Table 1.

(Unfortunately all magnetic investigations of chromium sulphides were undertaken without a proper knowledge of the phase diagram, so most samples studied were mixtures of two phases. Nevertheless, it is evident that the ferrimagnetic properties shown by alloys in the range $Cr_{0.87}S$–$Cr_{0.80}S$ at temperatures between $\sim 300°$ K. and $\sim 175°$ K. are entirely due to Cr_5S_6. The Cr_2S_3 paradox—Haraldsen & Neuber (1937) and Lotgering (1956b) found that $Cr_{0.68}S$ becomes ferrimagnetic below $\sim 140°$ K., while Stegemann (1941) could not confirm this observation with $Cr_{0.67}S$—can probably be explained by the existence of two forms of Cr_2S_3 with different homogeneity ranges. CrS and 'Cr_7S_8' are probably antiferromagnetic with Néel temperatures of about $500°$ K., while Cr_3S_4 is paramagnetic down to $100°$ K.)

Table 1. *Composition, observed phases, unit-cell dimensions, and calculated and observed densities of the alloys investigated*

Composition	phase	a (Å)	b (Å)	$c.\sin\beta$ (Å)	β	U (Å³)	D_c (g.cm.⁻³)	D_0† (g.cm.⁻³)
Cr	C.b.c.	2·885	—	—	—	24·01	7·193	—
$CrS_{0.68}$	α-Cr	2·885	—	—	—	—	—	—
	CrS	3·82	$\sqrt3 \times 3·41$	5·97	101·5°	2×67·4	—	—
	'Cr_7S_8'	3·465	—	5·761	90°	59·92	—	—
$CrS_{0.83}$	α-Cr	2·885	—	—	—	—	—	—
	CrS	3·82	$\sqrt3 \times 3·41$	5·96	101·5°	2×67·3	—	—
	'Cr_7S_8'	3·465	—	5·757	90°	59·87	—	—
$CrS_{0.90}$	α-Cr	2·885	—	—	—	—	—	—
	CrS	3·832	$\sqrt3 \times 3·411$	5·958	101° 35′	2×67·43	—	—
	'Cr_7S_8'	3·464	—	5·762	90°	59·89	—	—
$CrS_{0.94}$	α-Cr	2·885	—	—	—	—	—	—
	CrS	3·835	$\sqrt3 \times 3·408$	5·963	101° 31′	2×67·47	—	—
	'Cr_7S_8'	3·465	—	5·763	90°	59·93	—	—
$Cr_{1.00}S$	α-Cr	2·885	—	—	—	—	—	—
	CrS	3·826	$\sqrt3 \times 3·414$	5·964	101° 36′	2×67·46	4·091?	4·241
	'Cr_7S_8'	3·464	—	5·763	90°	59·90	—	
$Cr_{0.91}S$	CrS	3·824	$\sqrt3 \times 3·421$	5·958	101° 30′	2×67·49	—	4·259
	'Cr_7S_8'	3·465	—	5·766	90°	59·94	—	
$Cr_{0.88}S$	'Cr_7S_8'	3·463	—	5·763	90°	59·86	4·303	4·260($Cr_{0.87}S$)
$Cr_{0.86}S$	'Cr_7S_8'	3·459	—	5·761	90°	59·68	—	—
	Cr_5S_6	$\sqrt3 \times 3·455$	—	2×5·756	90°	6×59·49	—	—
$Cr_{0.85}S$	Cr_5S_6	$\sqrt3 \times 3·454$	—	2×5·754	90°	6×59·45	4·261	4·239
$Cr_{0.84}S$	Cr_5S_6	$\sqrt3 \times 3·453$	—	2×5·754	90°	6×59·42	—	4·201($Cr_{0.83}S$)
	Cr_3S_4*	—	—	—	—	—	—	
$Cr_{0.82}S$	Cr_5S_6	$\sqrt3 \times 3·455$	—	2×5·758	90°	6×59·52	—	—
	Cr_3S_4	$\sqrt3 \times 3·449$	3·433	2×5·678	91° 4′	4×58·21	—	—
$Cr_{0.79}S$	Cr_5S_6*	—	—	—	—	—	—	4·167($Cr_{0.80}S$)
	Cr_3S_4	$\sqrt3 \times 3·448$	3·432	2×5·680	91° 12′	4×58·21	—	
$Cr_{0.77}S$	Cr_3S_4	$\sqrt3 \times 3·443$	3·428	2×5·634	91° 30′	4×57·59	4·158	—
$Cr_{0.75}S$	Cr_3S_4	$\sqrt3 \times 3·441$	3·427	2×5·624	91° 38′	4×57·43	—	4·079
	Cr_2S_3 tr.*	—	—	—	—	—	—	
$Cr_{0.71}S$	Cr_3S_4	$\sqrt3 \times 3·44$	3·43	2×5·61	91·5°	4×57·3	—	—
	Cr_2S_3 tr.	$\sqrt3 \times 3·429$	—	2×5·596	90°	6×56·98	—	—
$Cr_{0.69}S$	Cr_2S_3 tr.	$\sqrt3 \times 3·430$	—	2×5·594	90°	6×57·01	3·972	—
$Cr_{0.68}S$	Cr_2S_3 tr.	$\sqrt3 \times 3·431$	—	2×5·585	90°	6×56·95	—	3·946
	Cr_2S_3 rh.	$\sqrt3 \times 3·428$	—	3×5·566	90°	9×56·64	—	
$Cr_{0.67}S$	Cr_2S_3 tr.*	—	—	—	—	—	—	—
	Cr_2S_3 rh.	$\sqrt3 \times 3·429$	—	3×5·550	90°	9×56·51	3·922	—

* Trace.   † Haraldsen, 1937.

The powder diagrams proved sufficient for the determination of the crystal structures of the various phases, except in the case of CrS, where a complication presented itself. All preparations of CrS and alloys with a higher Cr content consisted of three phases—'Cr$_7$S$_8$', CrS and α-Cr—so they do not correspond to equilibrium conditions. Prolonged tempering reduces the proportions of 'Cr$_7$S$_8$' and α-Cr in the samples, but so far we have not succeeded in preparing the monoclinic phase entirely free from other phases.

3. The structure of the phase 'Cr$_7$S$_8$'

Haraldsen (1937) proposed for alloys with compositions Cr$_{0.88}$S–Cr$_{0.85}$S a NiAs-type structure with randomly distributed vacancies in the metal lattice. In diagrams of structures of this type no reflexions with $h-k = 3n$ and $l = 2m+1$ should be present. In our diagrams of the alloy Cr$_{0.88}$S, however, the reflexions (001) and (111) are observed, indicating that the vacancies in the metal lattice are confined to every second metal layer (layers perpendicular to the trigonal axis).

The structure derived—intermediate between the NiAs and Cd(OH)$_2$ types—is trigonal and can best be described in space group $P\bar{3}m1$:

1 Cr I   in 1(a): 0, 0, 0 .
$\frac{3}{4}$ Cr II in 1(b): 0, 0, $\frac{1}{2}$.
2 S   in 2(d): $\pm(\frac{1}{3}, \frac{2}{3}, z)$ with $z = \frac{1}{4}$.

Adopting this model, the agreement between observed and calculated intensities is satisfactory, except for the four observed (00l) reflexions, which were stronger than calculated (preferred orientation). For the other 35 observed reflexions the disagreement factor $\Sigma|pF_o^2-pF_c^2| \div \Sigma pF_o^2$ is 0·15 (p stands for the multiplicity factor). For a list of calculated and observed intensities see Table 3(a).

No super reflexions due to 'Cr$_7$S$_8$' were observed in the powder diagrams, nor in rotation and Weissenberg photographs about the c axis (see § 8). For several simple models with ordered metal vacancies the intensities of the super reflexions were calculated; these computations show that the super reflexions should have been clearly observable in our diagrams. Therefore it seems very probable that the vacancies in every second metal layer are distributed at random; a certain degree of short-range order, however, cannot be excluded.

The homogeneity range of the phase 'Cr$_7$S$_8$' is narrow: from Cr$_{0.88}$S ($a = 3.464 \pm 0.001$ Å, $c = 5.763$

± 0.002 Å) to Cr$_{0.87}$S ($a \doteq 3.459 \pm 0.002$ Å, $c = 5.761 \pm 0.003$ Å). The interatomic distances for Cr$_{0.88}$S are given in Table 2.

4. Structure and magnetic anisotropy of ferrimagnetic Cr$_5$S$_6$

In our diagrams of Cr$_{0.85}$S 41 reflexions were observed compatible with a partly disordered structure intermediate between the NiAs and Cd(OH)$_2$ types. However, 24 additional reflexions could not be indexed with a unit cell of this type. These reflexions could be interpreted as originating from a super cell with

$$a = a'.\sqrt{3} = 5.982 \pm 0.002 \text{ Å} \quad \text{and}$$
$$c = 2c' = 11.509 \pm 0.003 \text{ Å}$$

(cell edges with an accent refer to a unit cell of the NiAs type), indicating that the vacancies in every second Cr layer are ordered.

From the intensities of the super reflexions the following structure was derived:

Trigonal, space group $P\bar{3}1c$:

2 Cr I   in 2(a): $\pm(0, 0, \frac{1}{4})$.
2 Cr II in 2(c): $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$.
2 Cr III in 2(b): 0, 0, 0; 0, 0, $\frac{1}{2}$.
4 Cr IV in 4(f): $\pm(\frac{1}{3}, \frac{2}{3}, z; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z)$ with $z = 0$.
12 S   in 12(i): $\pm(x, y, z; -y, x-y, z; y-x, -x, z;$
                       $y, x, \frac{1}{2}+z; -x, y-x, \frac{1}{2}+z;$
                       $x-y, -y, \frac{1}{2}+z)$
                       with $x = \frac{1}{3}$, $y = 0$, $z = \frac{3}{8}$.

The intensity agreement (see Table 3(b)) is good, except for the four observed (00l) reflexions (preferred orientation); for the other 61 observed reflexions the disagreement factor is 0·08. The structure of Cr$_5$S$_6$ is schematically presented in Figs. 2(a) and 2(b). Interatomic distances are given in Table 2. The homogeneity range of Cr$_5$S$_6$ is very narrow.

The Cr ordering in Cr$_5$S$_6$ is the same both below and above the Néel temperature (about 30° C.), as is shown by comparison of diagrams recorded with the sample at 10° C. and 60° C. respectively. Ferrimagnetic Cr$_5$S$_6$ possesses pronounced magnetic anisotropy. When suspensions of the powdered alloy in an acetonic solution of cellulose acetate were allowed to dry in a magnetic field (at 5° C.), strong preferred orientation of the crystallites resulted*, showing that Cr$_5$S$_6$ pos-

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* I find that a very similar method for orientating ferrimagnetic material has been used by Jonker, Wijn & Braun (1956).

Table 2. *Interatomic distances in the trigonal chromium sulphides*

Phase	Composition	Cr–6 S	Cr–Cr($\parallel c$)	Cr–Cr($\perp c$)	S–S between layers	S–S($\perp c$)
'Cr$_7$S$_8$'	Cr$_{0.88}$S	2·464 Å	2·882 Å	3·463 Å	3·507 Å	3·463 Å
Cr$_5$S$_6$	Cr$_{0.85}$S	2·459	2·877	3·454	3·501	3·454
Cr$_2$S$_3$ tr.	Cr$_{0.69}$S	2·425	2·797	3·430	3·427	3·430
Cr$_2$S$_3$ rh.	Cr$_{0.67}$S	2·417	2·775	3·429	3·409	3·429

Table 3. Calculated and observed intensities

The reflexion intensities of Cr_3S_4 and CrS were measured with Cu $K\alpha$ radiation; for these compounds dispersion and anomalous scattering has been taken into account. The reflexion intensities of the other phases were measured with Mo $K\alpha$ radiation and the anomalous-scattering effect has been neglected.

(a) Intensities of 'Cr₇S₈'

hkl	$10^{-2}pF_c^2$	$10^{-2}pF_o^2$	hkl	$10^{-2}pF_c^2$	$10^{-2}pF_o^2$	hkl	$10^{-2}pF_c^2$	$10^{-2}pF_o^2$
000	54	-	213	17	20	216	27	35
001[x]	1	5	006	0	-	402	13	16
100	24	33	115	0	-	207	3	6
002[x]	1	4	302	1	-	008[x]	5 }	14
101	47	55	106	31	26	314	5 }	
102	151	150	205	7	-	108	2	-
003	0	-	214	12	13	403	3	-
110	94	89	303	0	-	306	0	-
111	1	4	220	21	15	225	0	-
103	25	22	221	0	-	320	2	-
200	10	14	116	1	-	321	5	-
112	3	-	310	5	-	315	4	-
201	20	22	222	1	-	322	18	21
004[x]	23	25	007	0	-	217	4	-
202	75	76	311	10	-	118	14 }	14
104	15	16	304	35	23	404	2 }	
113	1	-	206	21	17	410	13	14
203	14	16	215	10	-	411	0	-
005	0	-	312	39	22	208	2	-
210	12	16	107	4	12	323	4	-
211	24	20	223	0	-	226	0	-
114	84	82	313	8	7	009	0	-
105	11	10	305	0	-	412	0	-
212	93	72	400	2	-	307	0	-
204	9	11	117	0	-	316	14	13
300	33	33	401	3	-	405	2	-
301	0	-	224	23	21			

(b) Intensities of Cr₅S₆

h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$	h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$	h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$
0 0 0	182	-	3 1 2	2	-	4 0 6	1	-
0 0 2[x]	4	7	2 0 7	3	4	2 1 9	3	4
1 0 0	3	3	1 0 8	1	-	3 2 5	3	3
1 0 1	15	17	3 0 5	0	-	4 1 4	210	185
1 0 2	5	4	2 1 6	2	-	2 0 10	1	-
1 0 3	11	16	3 1 3	6	6	2 2 8[y]	19	20
1 1 0	69	73	2 2 4	198	196	3 3 0	72	74
0 0 4[x]	3	5	1 1 8	36	34	3 3 2	2	3
1 1 2	162	158	4 0 0	5	-	4 1 6	41	45
2 0 0	2	-	4 0 1	3	-	0 0 12	0	-
2 0 1	9	10	3 1 4	2 }	7	3 0 10	2	-
1 0 4	3	-	3 0 6	4 {		3 3 4	3	-
2 0 2	3	-	4 0 2	1	-	1 1 12	63	67
2 0 3	8	7	2 1 7	5 }	9	2 2 10	16	14
1 0 5	7	6	2 0 8	1 {		4 1 8	22	18
1 1 4	460	458	1 0 9	3	2	3 3 6	1	-
2 1 0	2	-	4 0 3	3	5	6 0 0	40	46
2 1 1	13	13	3 1 5	5	3	6 0 2	1	-
2 0 4	2	-	3 0 7	0	-	3 0 12	1	-
0 0 6	1	-	3 2 0	1	-	5 2 0	8	8
2 1 2	4	4	3 2 1	5	5	6 0 4	1	-
1 0 6	2	-	4 0 4	1	-	0 0 14	0	-
2 1 3	11	9	2 2 6	38	39	5 2 2	20	21
3 0 0	279	286	3 2 2	1	-	3 3 8	63	63
2 0 5	5	-	2 1 8	1	-	2 2 12	36 }	47
3 0 1	0	-	0 0 10	0	-	4 1 10	18 {	
3 0 2	7	6	3 1 6	1	-	5 2 4	67	75
2 1 4	3	-	2 0 9	2	-	1 1 14	8	9
1 1 6	77	72	3 2 3	4	8	6 0 6	1	-
3 0 3	0	-	4 1 0	25	28	5 2 6	13	19
1 0 7	4	7	4 0 5	2	-	3 3 10	1	-
2 0 6	1	-	4 1 1	0	-	4 4 0	2	-
2 2 0	25	25	1 0 10	1	-	3 0 14	0	-
2 1 5	8	7	4 1 2	64	53	4 4 2	6	10
3 0 4	6	7	3 0 8	202	161	6 0 8	36	45
2 2 2	62	56	3 2 4	1	-	4 1 12	41	51
0 0 8[x]	65 }	76	4 1 3	0	-	4 4 4	20	21
3 1 0	1 {		3 1 7	4	5	2 2 14	5 }	21
3 1 1	7	8	1 1 10	29	28	0 0 16[x]	5 {	
						5 2 8	7 }	

(c) Intensities of trigonal Cr₂S₃

h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$	h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$	h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$
0 0 0	144	-	2 2 2	71	61	1 1 10	30	27
0 0 2[x]	14	34	3 1 0	1	-	4 1 4	134	138
1 0 0	3	3	3 1 1	7	-	2 2 8	7	9
1 0 1	15	17	0 0 8[x]	45	39	3 3 0	49	38
1 0 2	4	2	3 1 2	2	-	3 3 2	6	-
1 0 3	11	15	3 0 5	0	-	4 1 6	43	40
1 1 0	31	33	2 0 7	3	-	3 0 10	5	-
0 0 4[x]	0	4	1 0 8	1	-	3 3 4	0	-
1 1 2	195	189	2 1 6	2	-	0 0 12	0	-
2 0 0	2	-	3 1 3	6	-	2 2 10	16	-
2 0 1	9	11	2 2 4	132	164	1 1 12	35	45
1 0 4	3	6	4 0 0	0	-	4 1 8	7	-
2 0 2	3	3	4 0 1	3	-	3 3 6	4	-
2 0 3	7	11	3 1 4	2	-	6 0 0	26	24
1 0 5	7	?	1 1 8	14 {	24	6 0 2	3	-
1 1 4	318	299	3 0 6	13 {		5 2 0	3	-
2 1 0	2	-	4 0 2	1	-	6 0 4	2	-
2 1 1	12	12	2 1 7	5	-	3 0 12	0	-
2 0 4	2	-	2 0 8	1	-	5 2 2	20	20
0 0 6[x]	5	9	4 0 3	2	-	3 3 8	39	46
2 1 2	4	4	1 0 9	3	-	0 0 14	0	-
1 0 6	2	5	3 1 5	4	-	4 1 10	17	-
2 1 3	10	?	3 2 0	1	-	5 2 4	39 }	69
3 0 0	208	187	3 2 1	4	-	2 2 12	19 {	
3 0 1	0	-	3 0 7	0	-	6 0 6	2	-
2 0 5	5	10	4 0 4	1	-	1 1 14	7	29
3 0 2	24	22	2 2 6	41	42	5 2 6	13	22
2 1 4	3	8	3 2 2	1	-	4 4 0	1	-
1 1 6	87	96	2 1 8	1	-	3 3 10	1	-
3 0 3	0	-	3 1 6	1	-	4 4 2	5	-
1 0 7	4	8	3 2 3	3	-	6 0 8	21	24
2 0 6	1	5	4 1 0[y]	10 }	16	3 0 14	1	-
2 2 0	10	8	0 0 10	2	-	4 4 4	10 }	49
2 1 5	7	9	4 1 2	70	58	4 1 12	21 {	
3 0 4	0	-	3 0 8	134	122	5 2 8	2	-

(d) Intensities of rhombohedral Cr₂S₃ (Hexagonal indices are given)

h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$	h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$	h k l	$10^{-3}pF_c^2$	$10^{-3}pF_o^2$
0 0 0	324	-	3 1 2	11	-	3 3 3	16	?
0 0 3[x]	32	353	2 0 10	5	-	4 1 9	116	116
1 0 1	23	24	0 0 12[x]	109	470	3 0 15	13	?
1 0 2	22	21	3 1 4	10	11	3 3 6	0	?
1 0 4	18	21	3 1 5	9	-	0 0 18	0	?
1 1 0	70	77	2 2 6	325	277	2 2 15	43	?
1 0 5	16	19	2 0 11	5	-	1 1 18	95	121
0 0 6	0	-	4 0 1	4	-	4 1 12	22	?
1 1 3	450	492	4 0 2	4	-	3 3 9	10	?
2 0 1	14	8	2 1 10	9	-	6 0 0	74	?
2 0 2	14	5	1 1 12	35 }	85	6 0 3	9	-
2 0 4	12	22	3 0 9	33 {		5 2 0	8	11
1 0 7	12	-	1 0 13	4	-	6 0 6	0	-
2 0 5	11	-	4 0 4	4	-	3 0 18	0 {	58
1 1 6	741	796	3 1 7	8	-	5 2 3	58 {	
1 0 8	10 {	14	4 0 5	4	-	3 3 12	111	105
2 1 1	20 {		2 1 11	7	-	0 0 21	11	-
2 1 2	19	7	3 1 8	7	-	4 1 15	49 {	170
0 0 9[x]	12	30	3 2 1	7	-	5 2 6	113 {	
2 1 4	17	16	3 2 2	7	-	2 2 18	55	61
2 0 7	8	8	1 0 14	3	-	6 0 9	6	-
3 0 0	497	461	4 1 0	26	28	1 1 21	21	38
2 1 5	15	17	3 2 5	6 {	14	5 2 9	38	40
3 0 3	58	61	0 0 15[x]	4 {		4 4 0	0	-
2 0 8	7	-	4 1 3[y]	182	160	3 3 15	4	7
1 0 10	7	-	3 0 12	345	329	4 4 3	17	27
1 1 9	208	276	1 1 15	76 }	426	6 0 12	65	70
2 1 7	13	-	4 1 6	350 {		3 0 21	4	-
2 2 0	25	20	2 2 12	19	?	4 4 6	33	43
3 0 6	0	-	3 3 0	130	110	4 1 18	65	58
1 0 11	6	-				5 2 12	7	-
2 2 3	173	103				2 2 21	12	-
2 1 8	11 {	21				0 0 24[x]	8	15
3 1 1	11 {					4 4 9[x]	11	15

(e) Intensities of Cr₃S₄

h k l	$10^{-2}pF_c^2$	$10^{-2}pF_o^2$	h k l	$10^{-2}pF_c^2$	$10^{-2}pF_o^2$	h k l	$10^{-2}pF_c^2$	$10^{-2}pF_o^2$
0 0 0	724	-	-3 1 2	18	21	-2 2 4	84 {	94
0 0 2	41	47	0 2 2	17	18	-2 1 7	19 {	
-1 0 1	19	16	3 1 2	12	-	2 2 4	112	137
1 0 1	43	42	-1 2 1	8	-	......		
0 1 1	37	35	1 2 1	18	-	-2 1 9	9	-
-1 0 3	24	26	-2 0 6	48 {	56	-3 1 8	50 {	68
1 0 3	39	37	-2 1 5	10 {		-1 3 2	26 {	
2 0 0	70	?	-1 1 6	16	-	1 3 2	1	-
1 1 0	116	128	1 1 6	119	123	5 1 2	29 {	30
0 0 4	5	7	2 1 5	3	-	4 2 2	3 {	
-2 0 2	33	46	2 0 6	8	-	0 3 3	8	-
-1 1 2	327	305	-1 0 7	58	59	0 2 8	65	73
1 1 2	12	-	1 0 7	17	-	2 1 9	0	-
2 0 2	179	200	2 2 0	34	29	3 1 8	72	90
0 1 3	96	69	-3 1 4	4	-	-5 0 5	2	-
-2 1 1	1	-	3 0 5	4	-	-2 0 10	4	-
2 1 1	27	30	0 2 4	4	-	-2 3 1	1	-
-1 0 5	0	-	0 1 7	26	34	2 3 1	2	-
1 0 5	4	-	3 1 4	5	-	-1 1 10	7	-
-2 0 4	158	160	-4 0 2	28	26	-5 1 4	22 {	52
-1 1 4	449	463	-2 2 2	16	30	-4 1 7	41 {	
1 1 4	369	350	2 2 2	87	-	-4 2 4	36	37
2 0 4	219	204	4 0 2	5 {	85	1 1 10	8	-
-3 0 1	14	13	0 0 8	99	83	3 0 9	0	-
3 0 1	7	?	-4 1 1	1	-	2 0 10	6	-
-2 1 3	93 {	102	4 1 1	41	34	-1 3 4	41 {	58
2 1 3	42	35	-1 2 5	0	-	5 0 5	1	-
0 1 5	1	-	-4 0 4	53	66	1 3 4	34	34
0 0 6	1	-	1 2 5	2	-	4 2 4	36 {	55
-3 0 3	55	58				-4 0 8	1 {	
3 0 3	3	-				5 1 4	36	-
3 1 0	433	320				4 1 7	6	-
0 2 0	231	237						

(f) Structure factors of CrS
(The signs given for F_C refer to the real parts of the structure factors)

h k l	F_C	F_O	h k l	F_C	F_O	h k l	F_C	F_O
0 0 0	+158.7	-	2 2 1	+21.6	20.5	1 1 2	+73.0	73.4
1 1 0	+52.1	50.6	0 4 1	-26.9	24.2	-2 0 2	+19.8	17.0
0 2 0	+41.6	42.6	-3 1 1	-21.4	21.7	-1 3 2	+18.9	-
2 0 0	+88.8	90.7	-2 4 1	-21.6	21.0	-2 2 2	+63.1	62.6
1 3 0	+82.8	82.0	3 1 1	-19.7	21.0	2 0 2	+17.0	-
2 2 0	+28.3	31.2	-1 5 1	+12.3	-	1 3 2	+17.7	-
0 4 0	+38.9	37.8	1 5 1	+12.0	-	0 4 2	+44.2	46.2
3 1 0	+26.8	26.1	-3 3 1	+4.9	-	2 2 2	+54.7	53.7
2 4 0	+30.2	28.7	3 3 1	+4.5	-	-3 1 2	+46.0	41.5
1 5 0	+16.8	14.5	0 6 1	+8.2	-	-2 4 2	+27.1	33.5
3 3 0	+48.7	48.5	-4 2 1	+11.7	14.1	-1 5 2	+47.0	54.6
0 6 0	+42.3	42.5	-2 6 1	+6.8	-	3 1 2	+38.7	33.6
4 0 0	+40.9	37.6	-3 5 1	+8.1	-	-3 3 2	+12.8	-
4 2 0	+14.3	14.9	4 2 1	+10.5	12.3	2 4 2	+33.1	29.0
2 6 0	+34.6	33.1	2 6 1	+6.4	-	1 5 2	+44.4	44.2
3 5 0	+11.3	11.0	3 5 1	+7.5	-	-4 0 2	+10.7	-
1 7 0	+20.4	23.2				3 3 2	+11.1	-
			1 7 1	-12.0	12.8	0 6 2	+12.2	-
-1 1 1	-41.1	38.5	-4 4 1	-11.6	12.0	-4 2 2	+33.2	35.7
0 2 1	+33.3	31.8				-2 6 2	+10.6	-
1 1 1	-38.9	39.0	0 0 2	+26.1	(33.5)[z]	-3 5 2	+32.2	37.4
-1 3 1	+8.1	-	-1 1 2	+81.2	82.9	4 0 2	+8.9	-
			0 2 2	+83.3	80.1	2 6 2	+9.6	10.5
						4 2 2	+26.8	24.5
						-1 7 2	+18.0	-

x Observed value too strong, probably because of preferred orientation. y From these reflexions onward only reflexions of the sub-cell (of pseudo NiAs type) are given. z From powder diagram; not included in R.

Fig. 2. (a) Schematic projection of the structures of Cr_5S_6, trigonal Cr_2S_3 and rhombohedral Cr_2S_3 on the c plane. The a axes of the hexagonal unit cell are indicated by full lines, the a' axes of the sub-cell of pseudo NiAs type by broken lines. (b) Schematic projection of the Cr layers in Cr_5S_6 on the (110) plane. The c axis is twice as long as the c' axis of the sub-cell of pseudo NiAs type. (c) Schematic projection of the Cr layers in trigonal Cr_2S_3 on (110). (d) Schematic projection of the Cr layers in rhombohedral Cr_2S_3 on the hexagonal (110) plane. Here the c axis is three times as long as the c' axis of the sub-cell.

sesses a plane of easy magnetization perpendicular to the trigonal axis (see Fig. 3).

5. The structure of trigonal Cr_2S_3

In our diagrams of $Cr_{0.69}S$ 32 reflexions were observed compatible with a partly disordered structure intermediate between the NiAs and $Cd(OH)_2$ types, and 18 super reflexions, which again could be indexed by means of a super cell with $a = a'.\sqrt{3}$ and $c = 2c'$. The structure derived is similar to that of Cr_5S_6, except for the (a) site now being unoccupied:

Trigonal, space group $P\bar{3}1c$:

2 Cr I   in 2(c): $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$.
2 Cr II in 2(b): $0, 0, 0$; $0, 0, \frac{1}{2}$.
4 Cr III in 4(f): $\pm(\frac{1}{3}, \frac{2}{3}, z$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z)$ with $z = 0$.
12 S in 12(i): $\pm(x, y, z$; $-y, x-y, z$; $y-x, -x, z$;
  $y, x, \frac{1}{2}+z$; $-x, y-x, \frac{1}{2}+z$;
  $x-y, -y, \frac{1}{2}+z)$
  with $x = \frac{1}{3}$, $y = 0$, $z = \frac{3}{8}$.

The intensity agreement (see Table 3(c)) is satisfactory, except for the four observed (00l) reflexions; for the other reflexions the disagreement factor is 0·14. The structure is schematically shown in Figs. 2(a) and 2(c); interatomic distances are given in Table 2. The homogeneity range of trigonal Cr_2S_3 is narrow:

at the limit with highest Cr content $a=5·939\pm0·002$ Å, $c = 11·192\pm0·003$ Å; at the lower limit $a = 5·943 \pm0·002$ Å, $c = 11·171\pm0·003$ Å.

6. The structure of rhombohedral Cr_2S_3

In the diagrams of $Cr_{0.67}S$ 36 reflexions were found, which are compatible with a partly disordered structure intermediate between NiAs and $Cd(OH)_2$ types—in agreement with a suggestion by Rüdorff & Stegemann (1943); moreover 14 super reflexions were observed indicating a super cell that is different from that of trigonal Cr_2S_3. These reflexions could be indexed by means of a unit cell with $a = a'.\sqrt{3}$ and $c = 3c'$. As only reflexions with $-h+k+l = 3n$ are observed, the lattice is rhombohedral and the distribution of the vacancies is evident at once.

The structure derived can best be described in space group $R\bar{3}$:

Rhombohedral description

1 Cr I   in 1(b): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.
1 Cr II in 1(a): $0, 0, 0$.
2 Cr III in 2(c): $\pm(x, x, x)$ with $x = \frac{1}{3}$.
6 S in 6(f): $\pm(x, y, z$; z, x, y; $y, z, x)$
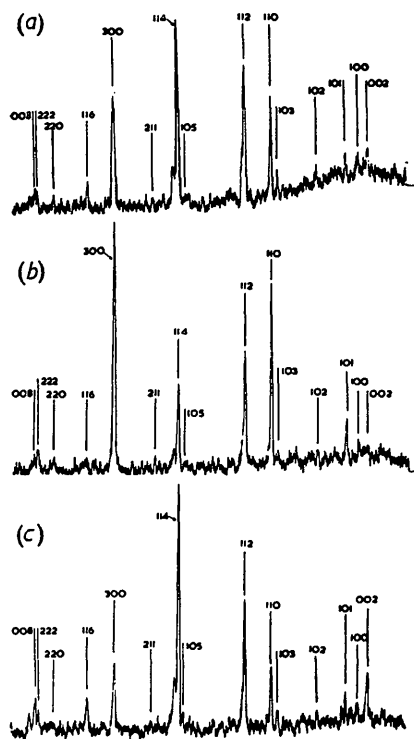 with $x = \frac{1}{4}$, $y = \frac{7}{12}$, $z = \frac{11}{12}$.

Fig. 3. The magnetic anisotropy of ferrimagnetic Cr_5S_6 at 5° C. (a) Diffractogram of unorientated sample. (b) Crystallites orientated by a magnetic field (H = 1100 Oe.) perpendicular to the flat sample; the prism reflexions are enhanced. (c) Crystallites orientated by a magnetic field (H=1100 Oe.) in the plane of the flat sample; now the basal reflexions are enhanced.

Fig. 4. (a) Schematic projection of the 'ideal' Cr_3S_4 structure on the c plane. The monoclinic unit cell is indicated by full lines, the sub-cell of pseudo NiAs type by broken lines. (b) Schematic projection of the 'ideal' Cr_3S_4 structure on the b plane. The arrows indicate directions and magnitudes (five times enlarged) of the observed deviations from the 'ideal' atomic positions.

Hexagonal description

$$(0, 0, 0; \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{2}{3}; \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{3}) +$$

3 Cr I in 3(b): 0, 0, $\tfrac{1}{2}$.
3 Cr II in 3(a): 0, 0, 0 .
6 Cr III in 6(c): $\pm(0, 0, z)$ with $z = \tfrac{1}{3}$.
18 S in 18(f): $\pm(x, y, z; \; -y, x-y, z; \; y-x, -x, z)$
        with $x = \tfrac{1}{3}$, $y = 0$, $z = \tfrac{1}{4}$.

The five observed (00l) reflexions are stronger than calculated (preferred orientation); for the other reflexions the disagreement factor is 0·12. For observed and calculated intensities see Table 3(d).) The structure is schematically presented in Figs. 2(a) and 2(d); interatomic distances for $Cr_{0.67}S$ are given in Table 2. At the homogeneity limit with the highest Cr content the unit-cell dimensions are: $a = 5·937\pm0·002$ Å, $c = 16·698\pm0·005$ Å; for $Cr_{0.67}S$ was found: $a = 5·939 \pm0·004$ Å, $c = 16·65\pm0·01$ Å.

7. The structure of Cr_3S_4

Our diagrams of $Cr_{0.77}S$ could be indexed by means of a monoclinic unit cell with

$$a=5·964\pm0·003 \text{ Å } (\sim a'.\sqrt3), \quad b=3·428\pm0·002 \text{ Å } (\sim a'),$$
$$c = 11·272\pm0·006 \text{ Å } (\sim 2c'); \quad \beta = 91° 30'\pm2'.$$

Only reflexions with $h+k+l = 2n$ are observed, so the lattice is body-centred. A plausible structure is the following*:

$$(0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})+$$

2 Cr I in 0, y, 0 with $y \sim 0$.
4 Cr II in $x, y, z; \; -x, y, -z$ with $x \sim 0$, $y \sim 0$, $z \sim \tfrac{1}{4}$.
4 S I in $x, y, z; \; -x, y, -z$ with $x \sim \tfrac{1}{3}$, $y \sim 0$, $z \sim \tfrac{3}{8}$.
4 S II in $x, y, z; \; -x, y, -z$ with $x \sim \tfrac{1}{3}$, $y \sim 0$, $z \sim \tfrac{7}{8}$.

The intensities calculated for this 'ideal structure' (see Fig. 4) gave a rough agreement with those observed, but it was evident that at least the x and z parameters must slightly deviate from their ideal values. If all y parameters are exactly zero, the structure is centrosymmetric and can be described in space group $I2/m$; if they are not the space group is $I2$.

The x and z parameters were refined—starting from the 'ideal positions'—by subsequent two-dimensional difference syntheses along the b axis. The parameters derived gave satisfactory intensity agreement for the (h0l) reflexions and also for the (hkl) reflexions, if all y parameters were put equal to zero. Therefore space group $I2/m$–C_{2h}^3 was adopted and the x and z para-

* The referee kindly pointed out to me that Okazaki & Hirakawa (1956) proposed this model for Fe_3Se_4.

meters were further refined by means of sections $y=0$ of three-dimensional difference syntheses. The final structure is the following*:

$$(0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})+$$

2 Cr I in 2(a): 0, 0, 0 .
4 Cr II in 4(i): $\pm(x, 0, z)$ with $x=-0.012$, $z=0.263$.
4 S I in 4(i): $\pm(x, 0, z)$ with $x=0.355$, $z=0.363^5$.
4 S II in 4(i): $\pm(x, 0, z)$ with $x=0.320$, $z=0.876$.

The deviations from the 'ideal structure' (indicated in Fig. 4) are such, that S I is approximately equidistant from its five Cr neighbours, S II from its four Cr neighbours, the distances S II–Cr being shorter than S I–Cr. The S atoms are pushed away from the vacancies present in every second metal layer. The interatomic distances are:

Cr I–2 S I'	2·45 Å	Cr II–1 S I	2·44 Å
–2 S I'''	2·45 Å	–2 S I'	2·43 Å
–1 S II	2·39 Å	–1 S II''	2·38 Å
–1 S II''	2·39 Å	–2 S II'''	2·37 Å
Cr I–2 Cr II	2·97 Å	S–12 S	3·26–3·63 Å

Cr –Cr (other distances) 3·32, 3·43, 3·58 Å

Special care was taken to avoid preferred orientation, and therefore all 47 measured reflexions (intensities see Table 3(e)) are included in the disagreement factor; for the final parameters the disagreement factor is 0·11. The homogeneity range of Cr_3S_4 extends from $Cr_{0.79}S$ ($a = 5.973\pm0.003$ Å, $b = 3.432\pm0.002$ Å, $c = 11.361\pm0.006$ Å; $\beta = 91°9'\pm4'$) to $Cr_{0.76}S$ ($a = 5.960\pm0.003$ Å, $b = 3.427\pm0.002$ Å, $c = 11.253\pm0.006$ Å; $\beta = 91°38'\pm2'$).

8. Epitaxy and structure of CrS

In his powder diagrams of CrS Haraldsen (1937) found a number of rather strong reflexions—additional to that of a NiAs-type lattice—which he assumed to originate from a super cell with $a = 2a'.\sqrt{3}$ and $c = 2c'$. Our diffractogram of CrS showed even more additional lines than Haraldsen had found, but they did not fit Haraldsen's super cell. Not being able to deduce a unit cell that fitted all powder lines, we tried to isolate crystallites large enough for single-crystal work. After several vain attempts a fragment was obtained that gave good rotation and Weissenberg photographs about one axis.

From these diagrams it was evident that the fragment consisted of two phases. One of the phases was identified as trigonal 'Cr_7S_8' (with c parallel to the rotation axis). The other phase has a C-centred monoclinic lattice with $c_{mon.}||c_{tr.}(c_{mon.}:c_{tr.} = 1.0565)$; $b_{mon.}$ is parallel to one of the three orthohexagonal b axes of 'Cr_7S_8' ($b_{mon.}:a_{tr.}.\sqrt{3} = 0.9855$). Therefore $b_{mon.}$ occurs in three orientations and $a_{mon.}$ in six orienta-

tions ($a_{mon.}\sin\beta:a_{tr.} = 1.0817$; $\beta = 101.6°$). This orientated intergrowth, together with the fact that in the powder diagrams lines due to α-Cr are present in addition to those of 'Cr_7S_8' and the monoclinic phase, leads to the conclusion that the latter phase is formed from Cr_7S_8+Cr by a solid-state reaction. This reaction involves diffusion of Cr into the 'Cr_7S_8' lattice and so the reaction rate will be rather low. For the unit-cell dimensions of α-Cr we found 2·885 Å, in close agreement with the value for pure Cr (2.88494 ± 0.00013 Å at 20° C.; Straumanis & Weng, 1955). Evidently α-Cr does not dissolve any appreciable amount of S in its lattice.

In the diagrams of the monoclinic phase reflexions (hkl) are extinguished for $h+k = 2n+1$ and furthermore $(h0l)$ reflexions are absent for $l = 2m+1$; so the space group is either Cc or $C2/c$. The reflexion intensities on the Weissenberg photographs of the zero, first and second layer lines about the c axis were measured with a photometer with small aperture. The intensities of reflexions on different layer lines were brought on a common scale by means of the 'Cr_7S_8' reflexions. A three-dimensional Patterson synthesis of the monoclinic phase showed that its composition is about CrS, while the symmetry is compatible with the centro-symmetric space group $C2/c$. The structure can be described in the following way:

$$(0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, 0)+$$

4 Cr in 4(a): 0, 0, 0; 0, 0, $\tfrac{1}{2}$.
4 S in 4(e): $\pm(0, y, \tfrac{1}{4})$.

From the Patterson synthesis the y parameter of S was deduced to be 0·317; refinement by an algebraic method yielded as final value $y_S = 0.320$. Calculated and observed structure factors are given in Table 3(f); the final value of the 'reliability index' R is 0·053.

The unit-cell dimensions found for CrS depend on the cooling rate; it appears that the homogeneity range of the phase CrS is narrow at room temperature, but rather extended at higher temperatures. Probably the best values at room temperature are: $a=3.826$ Å, $b = 5.913$ Å, $c = 6.089$ Å; $\beta = 101°36'$. The composition at which the phase CrS is homogeneous (when in equilibrium), however, cannot be determined from our data. The only investigator who has so far prepared pure CrS (free from other phases) is probably Mourlot (1899). He determined the density of his crystalline product as 4·08 g.cm.$^{-3}$, while from the analyses of his preparations a composition of $CrS_{0.97}$ is calculated. Assuming this composition for the phase CrS, a density of 4·091 g.cm.$^{-3}$ is calculated from our unit-cell dimensions; a composition of $CrS_{1.00}$ would lead to 4·139 g.cm.$^{-3}$. The interatomic distances in CrS are:

Cr–2 S	2·429 Å	Cr–2 Cr	3·044 Å
Cr–2 S	2·437 Å	Cr–4 Cr	3·522 Å
Cr–2 S	2·878 Å	Cr–2 Cr	3·826 Å
	S–12 S	3·357–3·994 Å	

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* $NiCr_2S_4$ was found to be isotypic with Cr_3S_4 with $a = 5.94$ Å, $b = 3.42$ Å, $c = 11.14$ Å; $\beta = 91.3°$.
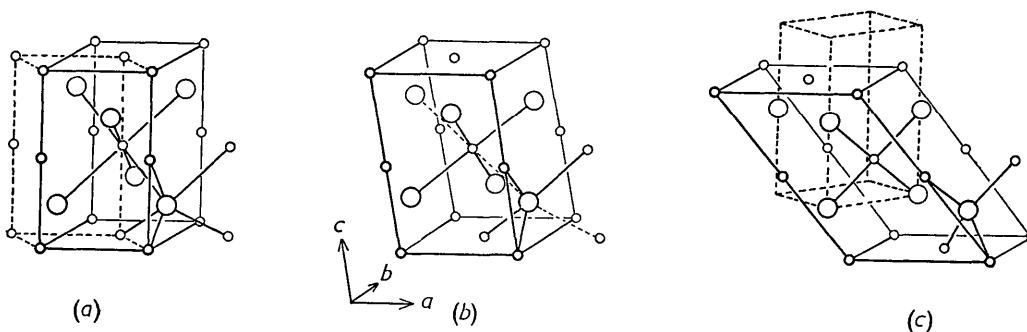
Fig. 5. Relation of the CrS structure to the NiAs- and PtS-structure types. Metal atoms are represented by small circles, anions by larger circles; in each diagram the environments of one metal atom and of one anion are marked. (a) The ideal NiAs structure. The metals are octahedrally surrounded by six anions, the anions by six metals in a trigonal prism. The conventional trigonal unit cell is indicated by broken lines. (b) The structure of CrS, intermediate between the NiAs and PtS types. Cr is surrounded by four S in a rectangle, while two more S at larger distances (broken lines) complete an elongated octahedron. The S environment may be regarded either as a slanting trigonal prism or as a distorted tetrahedron. (c) The structure of PtS. Here the metals are surrounded by a rectangle of S, while S has four metal neighbours forming a (somewhat distorted) tetrahedron. The conventional tetragonal unit cell is indicated by broken lines.

The structure of CrS is sketched in Fig. 5(b). Cr is surrounded by a tetragonal bipyramid of S (for $y_S = 0.321$ the distances to the basal S atoms would be exactly equal), S is surrounded by Cr in a configuration intermediate between a trigonal prism and a tetrahedron. The structure of CrS can perhaps best be described as intermediate between the NiAs and the PtS structure types (see Fig. 5). CrS is formally isotypic with CuO (Tunell, Posnjak & Ksanda, 1935), but the shapes of the unit cells are so different that it seems justified to regard the structure of CrS as a new type.

9. Discussion

Leaving CrS aside for the moment, the structures found for the chromium sulphides are intermediate between the NiAs and Cd(OH)$_2$ types. They are closely related to each other, so the system Cr–S superficially resembles a berthollide system. At the same time Bertaut's (1953) prediction that ionic compounds are ordered, appears to be right (except probably in the case of 'Cr$_7$S$_8$').

Nevertheless, the ionic picture of chromium sulphides certainly is too simple. From a purely electrostatical point of view structures based on a cubic anion packing (with the metals in the octahedral holes) are more favourable, since in structures related to the NiAs type rather short metal–metal contacts occur in the direction of the trigonal axis. These contacts are close enough for corresponding to bond distances. The fact that structures related to the NiAs type are known only for compounds of the transition elements indicates that intermetallic bonds actually are present and are even essential for the stability of theses structures. So our picture of the bond character in chromium sulphides comprises the presence of both ionic Cr–S bonds and metallic Cr–Cr bonds.

If it is assumed that all anions in the unit cell are chemically equivalent—which seems quite plausible—

then the following structures intermediate between the NiAs and Cd(OH)$_2$ types are geometrically possible:

I. Vacancies in metal lattice randomly distributed; such 'disordered structures' have been found, for example, for Fe$_7$S$_8$ above 340° C., Fe$_{0.90}$S below 190° C. (Grønvold & Haraldsen, 1952; Lotgering, 1956a). The diffraction pattern is that of a NiAs-type structure.

II. Vacancies confined to every second metal layer, but randomly distributed within these layers. Such a 'partly disordered structure' was found, for example, for 'Cr$_7$S$_8$'. The diffraction pattern is that of a Cd(OH)$_2$-type structure.

There is no obvious reason why the symmetry of alloys with type I or type II metal distributions should be lower than trigonal.

III. Vacancies in metal lattice confined to every second layer and ordered within the layers. In order to maintain the chemical equivalence of the anions, these 'ordered structures' can preserve trigonal symmetry only for the compositions MX_2 (Cd(OH)$_2$ type), M_2X_3, M_5X_6 and MX (NiAs type, see below). All compounds with other compositions must have lower symmetries, e.g. Fe$_7$S$_8$ (Bertaut, 1953) and Cr$_3$S$_4$.

The chromium sulphides exactly fit the above scheme, with the exception of CrS, for which compound a NiAs-type structure might be expected. Actually structures of this type have very rarely—if ever—been established at room temperature. The NiAs structure seems to have a typical high-temperature-phase character. At lower temperatures the NiAs type seems to be avoided by one of the following means:

1. When the ratio $R_X:R_M$ is small: disordering of the X lattice, e.g. in NbS (Schönberg, 1954), structures of the WC type.

2. When $R_X : R_M$ is of medium size: deformation of the structure by (a) lowering of the symmetry (e.g. CrS, structures of MnP type); (b) formation of super structures (e.g. FeS; Bertaut, 1954); (c) formation of new structure types (e.g. NiS); (d) elongation of the unit cell in the c direction (e.g. TiS; Schönberg, 1954).

3. When $R_X : R_M$ is large: chemical disproportionation; 'MX' is in reality a mixture of $M + M_{1-x}X$, e.g. $Rh_{1-x}Bi$ (Jdanov, 1954), $Co_{1-x}Te$ (Haraldsen, Grønvold & Hurlen, 1956), $Cr_{1-x}Te$ (own measurements). In these alloys $c:a$ is far below the ideal value.

At low temperatures alloys with structures related to the NiAs type will be either ferromagnetic or anti-ferromagnetic. The ferromagnetic alloys possess—at a given temperature—either an axis of easy magnetization parallel to the trigonal axis—e.g. 'MnBi' at room temperature (Guillaud, 1943), $Cr_{1-x}Te$ at room temperature (own measurements)—or a plane of easy magnetization perpendicular to this axis, e.g. 'MnBi' below 85° K.

For a picture of antiferromagnetism we divide the metal lattice into two sublattices. Two simple ways of performing this are:

(i) One sublattice consists of the odd-numbered metal layers *perpendicular* to the trigonal axis, the other of the even-numbered metal layers.

(ii) Sublattices *parallel* to the trigonal axis; one sublattice consists of the odd-numbered, the other of the even-numbered metal layers.

Model (i) will give rise to antiferromagnetism in type I structures and in MX compounds, but ferrimagnetism (= uncompensated antiferromagnetism) will result in type III structures (except MX compounds) and in all type II structures. Model (ii)—which from a magnetic point of view does not possess trigonal symmetry—will give rise to (compensated) antiferromagnetism in all trigonal structures intermediate between the NiAs and Cd(OH)$_2$ types, in Cr_3S_4, Fe_3Se_4 and Fe_7Se_8, but to ferrimagnetism in Fe_7Se_8 (Okazaki & Hirakawa, 1956).

The foregoing shows that a substance may pass from a ferrimagnetic into an antiferromagnetic state in two ways:

(a) A transition from a type II or type III into a type I structure; such a transitions is an order-disorder transition involving atomic rearrangement and therefore the high-temperature state can be 'frozen in' (Lotgering's (1956a) model for $Fe_{0.90}S$).

(b) A rearrangement of the spin order from model (i) to model (ii). No atomic rearrangement is involved and so such a transition cannot be frozen in. This might be a description of the behaviour of Cr_5S_6.

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